Cleaner Production Practices

A

Introduction

In this section you will find descriptions of cleaner production strategies in several industries. The intention is to give students the opportunity to look more in detail at how cleaner production concepts are, in reality, being used in a number of areas. Some of the strategies are, in addition, covered by a case study in the latter part of the book.

The sources are documents produced by authorities with responsibility for environmentally acceptable and improved industrial production. The European Integrated Pollution Prevention and Control Bureau (EIPPCB) of the EU, UNEP, and the US Environmental Protection Agency (EPA) are the most important agencies that have taken responsibility for this development.

The documents in this section have been shortened to a very abbreviated form. Only parts relevant for cleaner production strategies are included. In the original documents there is also extensive information about, for example, technology, environmental impacts, and relevant legal documents. The original documents all have extensive documentation of cases in industry, as well as details of monitoring, costs for investments needed for technology developments, and often references to relevant regulations.

The students studying one of these branches may wish to go to the original documents for a deeper study. Several of these are found on the accompanying CD.

The BREF Documents of the EU

The European Union DG Environment and the Information Exchange Forum (IEF) have published a number of documents to more precisely define what are Best Available Techniques (BAT) as referred to in the IPPC Directive. The documents are called BREF (best available techniques reference documents) and in their preliminary form DRAFT. The IEF consists of representatives from Member States industry and environmental non-governmental organisations. Each sector of work is addressed by a specific Technical Working Group (TWG) established for the duration of the work.

BREFs and DRAFTs are large documents. The adopted BREFs in English, together with translations of parts of them into all Member State languages, have been published on a CD by the Office for Official Publications of the European Communities. The CD is titled *Reference Documents on Best Available Techniques (Council Directive 96/61/EC): First edition (multilingual),* ISBN 92-894-3678-6, and can be ordered at: http://ec.europa.eu/environment/pubs/industry.htm

Or they can be downloaded as PDF-files at: http://www.epa.ie/Licensing/IPPCLicensing/BREFDocuments/

The following industries are included in the December 2006 BREF documents:

1. Chlor-Alkali Manufacturing industry.
2. Ferrous Metals Processing.
3. Intensive Rearing of Poultry and Pigs.
4. Large Volume Organic Chemical Industry.
5. Production of Iron and Steel.
6. General Principles of Monitoring.
7. Non Ferrous Metals Industries.
8. Pulp and Paper Industry.
9. Mineral Oil and Gas Refineries.
10. Tanning of Hides and Skins.
11. Textiles Industry.
12. Common Wastewater and Waste Gas Treatment/ Management Systems in the Chemical Sector.
13. Smitheries and foundries industry.
14. Surface Treatment using Organic Solvents.
15. Large Volume Inorganic Chemicals, Ammonia, Acids and Fertilisers Industries.
16. Emissions from Storage.
17. Food, Drink and Milk Industry.
18. Surface Treatment of Metals and Plastics.
19. Waste Treatments Industries.
20. Economics and Cross-Media Effects.
21. Manufacture of Organic Fine Chemicals.
22. Large Volume Inorganic Chemicals – Solid & Others Industry.
23. Ceramic Manufacturing Industry.
24. Production of Polymers.
25. Slaughterhouses and Animal By-Products Industries.
26. Production of Speciality Inorganic Chemicals.
27. Waste Incineration.
28. Cement and Lime Manufacturing Industries.
29. Industrial Cooling Systems.
30. Glass Manufacturing Industry.
31. Surface Treatment using Organic Solvents.
32. Waste Treatments Industries.

The Best Management Practices Documents of US EPA

The Best Management Practices for Pollution Prevention published by the US EPA Office of Research and Development is another source of documentation of cleaner production strategies. They can be downloaded as PDF-files at: http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/

The industries covered include the following branches:

1. Agricultural Chemical, Pesticide and Fertiliser Industry (2000).
2. Agricultural Crop Production Industry (2000).

3. Agricultural Livestock Production Industry (2000).
4. Aerospace Industry (1998).
5. Air Transportation Industry (1997).
6. Dry Cleaning Industry (1995).
7. Electronics and Computer Industry (1995).
8. Fossil Fuel Electric Power Generation Industry (1997).
9. Ground Transportation Industry (1997).
10. Health care Industry (2005).
11. Inorganic Chemical Industry (1995).
12. Iron and Steel Industry (1995).
13. Lumber and Wood Products Industry (1995).
14. Metal Casting Industry (1997).
15. Metal Fabrication Industry (1995).
16. Metal Mining Industry (1995).
17. Motor Vehicle Assembly Industry (1995).
18. Nonferrous Metals Industry (1995).
19. Non-Fuel, Non-Metal Mining Industry (1995).
20. Oil and Gas Extraction Industry (1999).
21. Organic Chemical Industry 2nd Edition (2002).
22. Petroleum Refining Industry (1995).
23. Pharmaceutical Industry (1997).
24. Plastic Resins and Man-made Fibres Industry (1997).
25. Printing Industry (1995).
26. Pulp and Paper Industry, 2nd Edition (2002).
27. Rubber and Plastics Industry, 2nd Edition (2005).
28. Shipbuilding and Repair Industry (1997).
29. Stone, Clay, Glass and Concrete Industry (1995).
30. Textiles Industry (1997).
31. Transportation Equipment Cleaning Industry (1995).
32. Water Transportation Industry (1997).
33. Wood Furniture and Fixtures Industry (1995).

The so-called Sector Notebook Project of the US EPA Office of Compliance adds to this series of documents, although it heavily relies on the first series.

UNEP Documents

UNEP has a series of documents, mostly referring to best practices in the agricultural sector, called Industry Sector Guides for Cleaner Production Assessment. At present they cover:

1. Dairy Processing.
2. Fish Processing.
3. Meat Processing.

The documents can be downloaded as PDF-files at:
http://www.agrifood-forum.net/publications/guide/

They are more concerned with introducing good practices in developing countries and contain many examples from such countries.

Descriptions

1. Dairy

The dairy industry processes milk and milk products at dairy processing plants. The life cycle of milk and milk products commences with the production of fresh cow's milk on dairy farms. The upstream process of fresh milk production on dairy farms and the downstream processes of distribution and post-consumer packaging management are not covered. The processing of milk to produce dairy products is, however, a significant contributor to the overall environmental load produced over the life cycle of milk production and consumption. Therefore the application of cleaner production in this phase of the life cycle is important. As in many food-processing industries, the key environmental issues associated with dairy processing (all covered in Section 1) are:

- High consumption of water.
- Generation of high-strength effluent streams.
- Consumption of energy.
- Generation of by-products.

2. Pulp and Paper

The pulp and paper industry converts wood or recycled fibre into pulp and primary forms of paper. *Pulp mills* separate the fibres of wood or from other materials, such as rags, linters, wastepaper, and straw in order to create pulp. *Paper mills* primarily are engaged in manufacturing paper from wood pulp and other fibre pulp, and may also manufacture converted paper products. The pulp and paper industry is an important component of the global manufacturing industry in both economic and environmental terms. In the northern Baltic Sea region, pulp and paper manufacture is responsible for a large part of regional economic activity.

Pulp and paper manufacturing can have potentially serious impacts on the environment and health of both human and wider ecosystems. Environmental problems include high consumption of water, high energy use, pollution of water streams by fibres and chlorinated organics from bleaching chemicals.

Many of the classical problems have been solved today in ways that well illustrate the power of cleaner production approaches. Emissions, however, continue to present toxicity problems. These facts emphasise the need to pursue closed loop strategies. Additionally, the effects of mill process changes on workers and local communities have rarely been factored into the mainstream debate on best routes forward. Decisions on how to make an ecologically responsible pulp mill must take these issues into account.

Pulp and paper is handled both in Section 2 and in Case Study 5.

3. Textile

The textile industry is comprised of a diverse, fragmented group of establishments that produce and/or process textile-related products (fibre, yarn, fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establishments receive and prepare fibres; transform fibres into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and furnish these materials at various stages of production.

The process of converting raw fibres into furnished apparel and non-apparel textile products is complex; thus, most textile mills specialise. Little overlap occurs between hitting and weaving, or among production of man made, cotton, and wool fabrics.

The classic environmental issues in these sectors include high water consumption, chemical pollution of water streams from dyeing and other wet operations. The work environment issues have also been high on the agenda.

The processes used, cleaner production practices and opportunities in the textile industry are described in more detail in Section 3. Also, Case Study 1 describes a factory for yarn production.

4. Glass

The glass industry in the European Union is very diverse. Products range from intricate hand-made lead crystal goblets to huge volumes of float glass produced for the building and automotive industries. Manufacturing techniques vary from small electrically heated furnaces in the ceramic fibre sector to cross-fired regenerative furnaces in the flat glass sector, producing up to 700 tonnes per day. Container glass production is the largest sector representing around 60% of the total glass production.

Glass manufacturing occurs in glass furnaces with temperatures up to 1650°C or 2000°C in the flame. A main environmental aspect of glass manufacturing is thus energy use, especially fossil fuel use. Another is the air emissions of NO_X, arising from the oxidation of atmospheric nitrogen at temperatures above 1300°C. Several cleaner production programmes address the issue of reducing NO_X emissions. The use of recycled glass, so-called cullet, has become very important. Use of cullet requires less energy, causes fewer emissions to air, and reduces waste. Both internal cullet and external recycled glass are important today. Cullet use in container glass production varies from <20% to >90%, with an EU average of 48%.

Glass manufacturing and its cleaner production practices and opportunities are described in Section 4. Several of the points in this section are of general relevance, such as energy saving and reduction of NO_X emissions.

5. Chlor-Alkali

Elemental chlorine gas is produced in the chlor-alkali process, the electrolysis of sodium chloride solution. Chlorine in turn is used for the production of plastics, notably PVC (polyvinylchloride), and e.g. chlorinated organic solvents. The EU production of chlorine is more than 9 million tonnes per year. As chlorine and sodium hydroxide are produced in fixed proportions there is a corresponding production of NaOH.

Chlorine production is environmentally problematic. The main technology, the mercury cell process, has been a significant source of mercury pollution of air, water, and wastes. The alternative, the diaphragm electrolysis method, is also environmentally problematic since the asbestos from diaphragms pollutes both the surroundings and the work place. There has thus been a strong pressure to change the technology. In Japan, where the industry was pressed to find alternatives in the aftermath of the Minamata Bay disaster, membrane cell electrolysis was developed in the 1970s. Today all chlor-alkali plants in Japan have converted to membrane cell technology. The first European membrane plant opened in 1983 at Akzo in Rotterdam. Still 50 plants in Europe use the mercury cell method using an estimated total of 12,000 tonnes of metallic mercury. Most likely these plants will be forced to change technology by regulation as soon as practicable, and no later than 2010.

Section 5 on the chlor-alkali production describes how to make this technology shift, but also some other main difficulties in chlor-alkali processes, such as the huge demand for electricity and hazards in handling the chlorine gas and caustic soda produced. In all these areas Cleaner Production approaches have been essential. The technique is also treated in Chapter 12.

6. Cement

Cement and concrete (a mixture of cement, aggregates, sand and water) are basic materials for the building and construction industry. Cement production therefore tracks the overall economic situation closely.

Cement is produced from clinker, produced in a large rotating oven, called kiln, at high temperatures. The raw material used is calcium carbonate. The carbonate loses carbon dioxide to air in the calcination reaction at about 900°C to leave calcium oxide, lime, behind. This in turn reacts at high temperature (typically 1400-1500°C) with silica, alumina, and ferrous oxide to form the clinker. The clinker is then ground or milled together with gypsum and other additives to produce cement.

The cement industry is a main emitter of the greenhouse gas carbon dioxide, both because of its high energy use and the calcination reaction. The emission of CO_2 is estimated at 900 to 1,000 kg/tonne of clinker, related to a specific heat demand of approximately 3,500 to 5,000 MJ/tonne of clinker. Approximately 60% originates in the calcination process and the remaining 40% in fuel combustion. Mostly fossils are used as fuels. However, almost any organic compound can be used and clinker production has been fuelled by e.g. old tyres, and has been used for destruction of hazardous waste.

Cleaner production programmes in this sector described in Section 6 are not trivial. Emissions of CO_2 have been progressively reduced by about 30% in the last 25 years mainly by more fuel-efficient kiln processes. But how to reduce CO_2 emissions from calcinations? One way is to reduce the amount of clinker in cement. A case study on environmental management at Kunda Tsement in Estonia is described in Case Study 1, Book 4 in this series.

1 – Dairy Industry

1. Background

Milk Products and the Environment

The dairy industry is processing milk and milk products at dairy processing plants. The life cycle of milk and milk products commences with the production of fresh cow's milk on dairy farms. Milk is then processed to produce pasteurised and homogenised market milk, butter, cheese, yogurt, custard and dairy desserts etc. It may also be preserved for a longer shelf life in the form of long-life (UHT), condensed, evaporated or powdered milk products. The various products are packaged into consumer portions and distributed to retail outlets.

For fresh dairy products, refrigerated storage is required throughout the life of the products to maintain eating appeal and prevent microbiological spoilage. Following use by the consumer, packaging is either discarded or recycled.

Here the upstream process of fresh milk production on dairy farms and the downstream processes of distribution and post-consumer packaging management are not covered. But it is known that the processing of milk to produce dairy products is a significant contributor to the overall environmental load produced over the life cycle of milk production and consumption. Therefore the application of Cleaner Production in this phase of the life cycle is important.

As in many food processing industries, the key environmental issues associated with dairy processing are:

- High consumption of water.
- Generation of high-strength effluent streams.
- Consumption of energy.
- Generation of by-products.

For some sites, noise and odour may also be concerns.

Dairy Processing Industries

Dairy processing occurs world-wide; however the structure of the industry varies from country to country. In less developed countries, milk is generally sold directly to the public, but in major milk producing countries most milk is sold on a wholesale basis. In Ireland and Australia, for example, many of the large-scale processors are owned by the farmers as co-operatives, while in the United States individual contracts are agreed between farmers and processors.

Dairy processing industries in the major dairy producing countries have undergone rationalisation, with a trend towards fewer but larger plants operated by fewer people. In the United States, Europe, Australia and New Zealand most dairy processing plants are today quite large. Plants producing market milk and products with short shelf life, such as yogurts, creams and soft cheeses, tend to be located on the fringe of urban centres close to consumer markets. Plants manufacturing items with longer shelf life, such as butter, milk powders, cheese and whey powders, tend to be located in rural areas closer to the milk supply. The general tendency world-wide, is towards large processing plants specialising in a limited range of products.

In eastern Europe, due to the former supply-driven concept of the market, it is still very common for 'city' processing plants to be large multi-product plants producing a wide range of products.

The general trend towards large processing plants has provided companies with the opportunity to acquire bigger, more automated and more efficient equipment. This technological development has, however, tended to increase environmental loads in some areas due to the requirement for long-distance distribution. Basic dairy processes have changed little in the past decade. Specialised processes such as ultrafiltration (UF), and modern drying processes, have increased the opportunity for the recovery of milk solids that were formerly discharged. In addition, all processes have become much more energy efficient and the use of electronic control systems has allowed improved processing effectiveness and cost savings.

The Sources

This text is extracted from a document on Cleaner Production measures in the dairy industry included in a series of Industrial Sector Guides published by the United Nations Environment Programme UNEP Division of Technology, Industry and Economics (UNEP DTIE) and the Danish Environmental Protection Agency.

http://www.agrifood-forum.net/publications/guide/

2. Dairy Processing

Milk Production

The processes taking place at a typical milk plant include:

- Receipt and filtration/clarification of the raw milk.
- Separation of all or part of the milk fat (for standardisation of market milk, production of cream and butter and other fat-based products, and production of milk powders).
- Pasteurisation.
- Homogenisation (if required).
- Deodorisation (if required).
- Further product-specific processing.
- Packaging and storage, including cold storage for perishable products.
- Distribution of final products.

Figure 1.1 is a flow diagram outlining the basic steps in the production of whole milk, semi-skimmed milk and skimmed milk, cream, butter and buttermilk. In such plants, yogurts and other cultured products may also be produced from whole milk and skimmed milk.

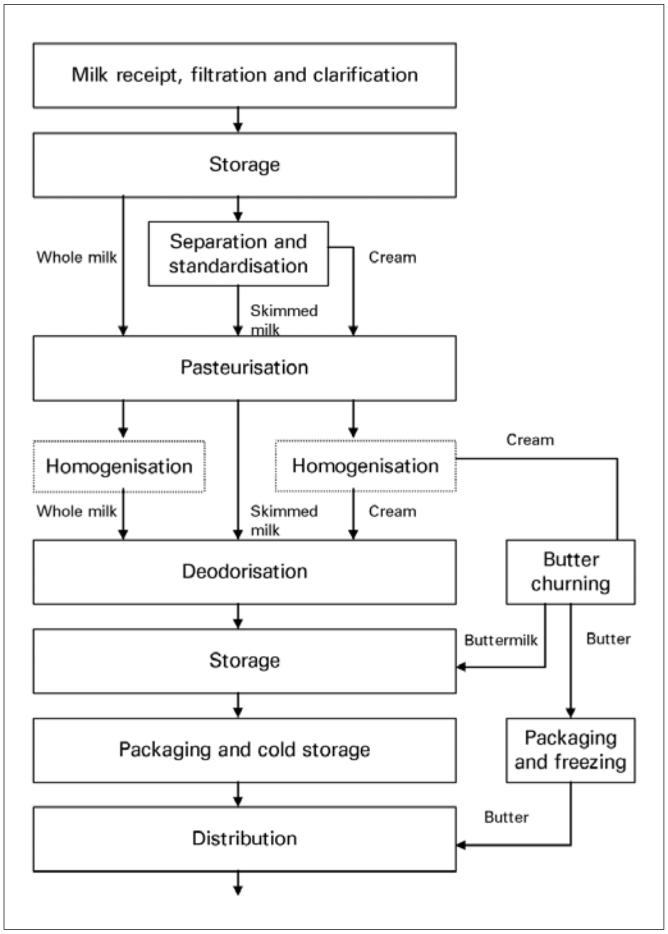


Figure 1.1 *Flow diagram for processes occurring at a typical milk plant.*

Butter Production

The butter-making process, whether by batch or continuous methods, consists of the following steps:

- Preparation of the cream.
- Destabilisation and breakdown of the fat and water emulsion.
- Aggregation and concentration of the fat particles.
- Formation of a stable emulsion.
- Packaging and storage.
- Distribution.

Figure 1.2 is a flow diagram outlining the basic processing system for a butter-making plant. The initial steps, (filtration/clarification, separation and pasteurisation of the milk) are the

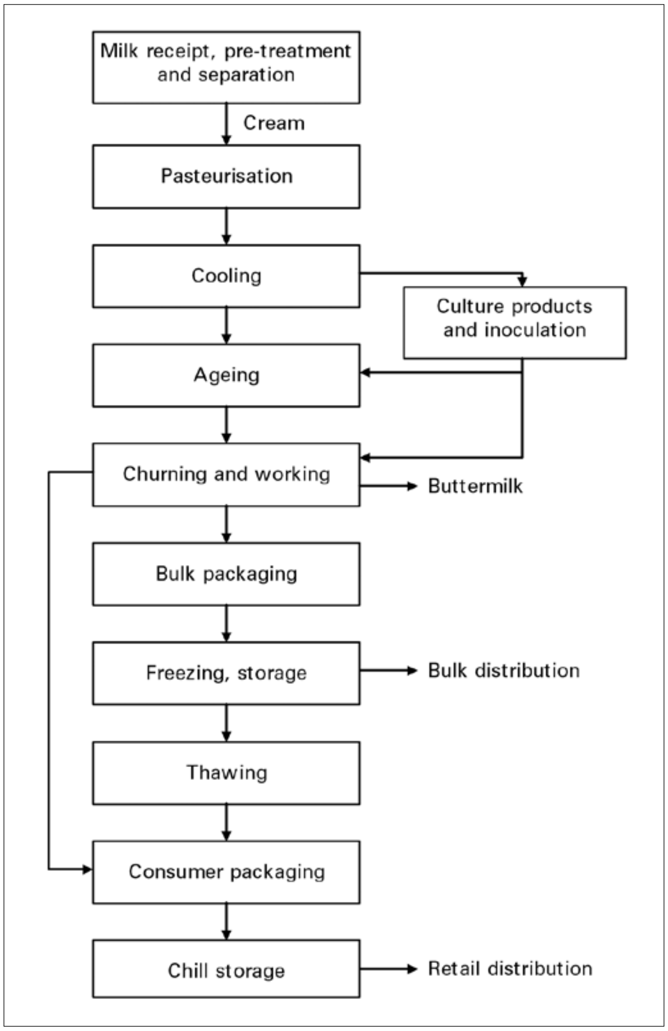


Figure 1.2 *Flow diagram for a typical butter-making plant.*

same as described in the previous section. Milk destined for butter making must not be homogenised, because the cream must remain in a separate phase.

After separation, cream to be used for butter making is heat-treated and cooled under conditions that facilitate good whipping and churning. It may then be ripened with a microbiological culture that increases the content of diacetyl, the compound responsible for the flavour of butter. Alternatively, culture inoculation may take place during churning.

Butter which is flavour-enhanced using this process is termed lactic, ripened or cultured butter. This process is very common in continental European countries. Although the product is claimed to have a superior flavour, the storage life is limited. Butter made without the addition of a culture is called sweet cream butter. Most butter made in the English-speaking world is of this nature.

Cheese Production

Virtually all cheese is made by coagulating milk protein (casein) in a manner that traps milk solids and milk fat into a curd matrix. This curd matrix is then consolidated to express the liquid fraction, cheese whey. Cheese whey contains those milk solids which are not held in the curd mass, in particular most of the milk sugar (lactose) and a number of soluble proteins.

Figure 1.3 outlines the basic processes in a cheese-making plant. All cheese-making processes involve some or all of these steps.

3. Cleaner Production Opportunities

General

Dairy processing typically consumes large quantities of water and energy and discharges significant loads of organic matter in the effluent stream. For this reason, Cleaner Production opportunities focus on reducing the consumption of resources (water and energy), increasing production yields and reducing the volume and organic load of effluent discharges.

At the larger production scales, dairy processing has become an extremely automated process and resource efficiency relies, to a large extent, on the efficiency of plant and equipment, the control systems that are used to operate them and the technologies used to recover resources. As a result many Cleaner Production opportunities lie in the selection, design and efficient operation of process equipment. Operator practices also have an impact on plant performance, for example in the areas of milk delivery, plant maintenance and cleaning operations. Therefore there are also opportunities in the areas of housekeeping, work procedures, maintenance regimes and resource handling.

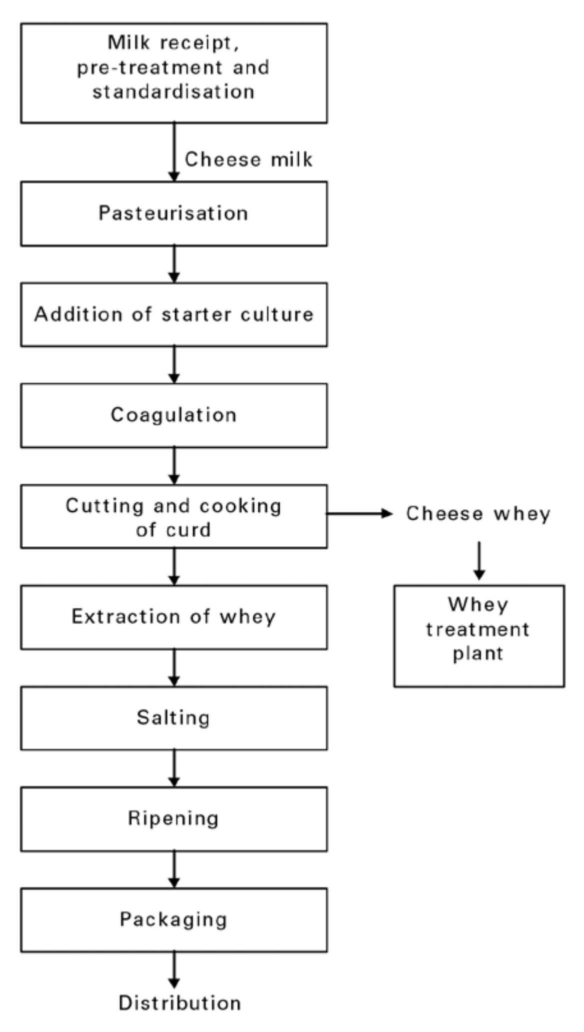


Figure 1.3 *Flow diagram for a typical cheese plant.*

Good Housekeeping

Many food processors that undertake Cleaner Production projects find that significant environmental improvement and cost savings can be derived from simple modification to housekeeping procedures and maintenance programmes. They are generic ideas that apply to the dairy manufacturing process as a whole. A checklist of general housekeeping ideas is the following:

- Keep work areas tidy and uncluttered to avoid accidents.
- Maintain good inventory control to avoid waste of raw ingredients.
- Ensure that employees are aware of the environmental aspects of the company’s operations and their personal responsibilities.
- Train staff in good cleaning practices.

- Schedule regular maintenance activities to avoid breakdowns.
- Optimise and standardise equipment settings for each shift.
- Identify and mark all valves and equipment settings to reduce the risk that they will be set incorrectly by inexperienced staff.
- Improve start-up and shut-down procedures.
- Segregate waste for reuse and recycling.
- Install drip pans or trays to collect drips and spills.

Water

Water is used extensively in dairy processing, so water saving measures are very common Cleaner Production opportunities in this industry. The first step is to analyse water use patterns carefully, by installing water meters and regularly recording water consumption. Water consumption data should be collected during production hours, especially during periods of cleaning. Some data should also be collected outside normal working hours to identify leaks and other areas of unnecessary wastage.

The next step is to undertake a survey of all process area and ancillary operations to identify wasteful practices. Examples might be hoses left running when not in use, CIP cleaning processes using more water than necessary, etc. Installing automatic shut-off equipment and restricters could prevent such wasteful practices. Automatic control of water use is preferable to relying on operators to manually turn water off.

Once wasteful practices have been addressed, water use for essential process functions can be investigated. It can be difficult to establish the minimum consumption rate necessary to maintain process operations and food hygiene standards. The optimum rate can be determined only by investigating each process in detail and undertaking trials. Such investigations should be carried out collaboratively by production managers, food quality and safety representatives and operations staff.

When an optimum usage rate been agreed upon, measures should be taken to set the supply at the specified rate and remove manual control. Once water use for essential operations has been optimised, water reuse can be considered. Wastewaters that are only slightly contaminated could be used in other areas. For example, final rinse waters could be used as the initial rinses for subsequent cleaning activities, or evaporator condensate could be reused as cooling water or as boiler feed water. Wastewater reuse should not compromise product quality and hygiene, and reuse systems should be carefully installed so that reused wastewater lines cannot be mistaken for fresh water lines, and each case should be approved by the food safety officer.

A checklist of water saving ideas follows:

- Use continuous rather than batch processes to reduce the frequency of cleaning.
- Use automated cleaning-in-place (CIP) systems for cleaning to control and optimise water use.
- Install fixtures that restrict or control the flow of water for manual cleaning processes.
- Use high pressure rather than high volume for cleaning surfaces.
- Reuse relatively clean wastewaters (such as those from final rinses) for other cleaning steps or in non-critical applications.
- Recirculate water used in non-critical applications.
- Install meters on high-use equipment to monitor consumption.
- Pre-soak floors and equipment to loosen dirt before the final clean.
- Use compressed air instead of water where appropriate.
- Report and fix leaks promptly.

Box 1.1 Reduction of Water Consumption for Cleaning at an Estonian Dairy Processing Plant

At an Estonian dairy processing plant, open-ended rubber hoses were used to clean delivery trucks. Operators used their fingers at the discharge end of the hose to produce a spray, resulting in ineffective use of water. Furthermore, the hoses were not equipped with any shut-off valve, and the water was often left running.

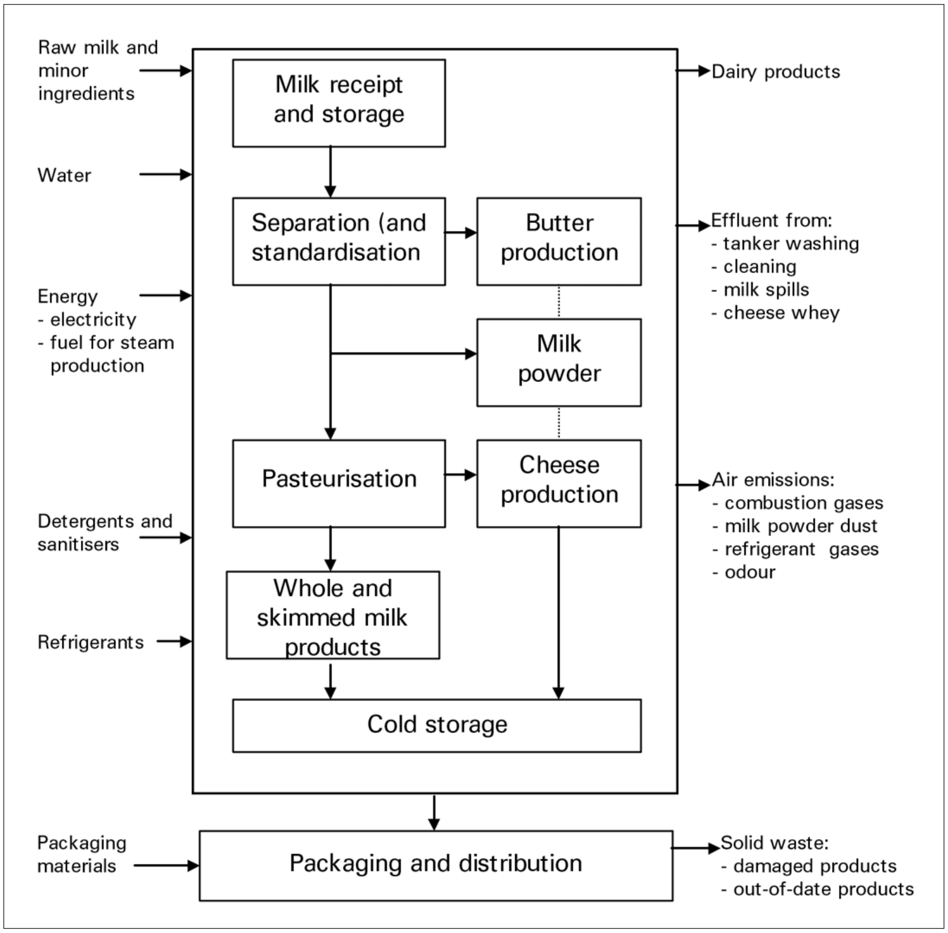
The operators found that they could reduce water consumption by installing high-pressure systems for cleaning the trucks, the production area and other equipment. Open-ended hoses were also equipped with trigger nozzles. The cost of this equipment was USD 6,450 and the saving in water charges was USD 10,400 per year; a pay back period of less than 8 months. Water consumption has been reduced by 30,000 m^3/year.

Reducing Effluent Pollution Loads

Effluent Cleaner Production efforts in relation to effluent generation should focus on reducing the pollutant load of the effluent. The volume of effluent generated is also an important issue. However this aspect is linked closely to water consumption. Therefore efforts to reduce water consumption will also result in reduced effluent generation.

Opportunities for reducing the pollutant load of dairy plant effluent focus on avoiding the loss of raw materials and prod-

Figure 1.4 *Inputs and outputs from milk receipt and storage vessels.*



ucts to the effluent stream. This means avoiding spills, capturing materials before they enter drains and limiting the extent to which water comes into contact with product residue. Improvements to cleaning practices are therefore an area where the most gains can be made.

A checklist of ideas for reducing pollutant loads in effluents:

- Ensure that vessels and pipes are drained completely and using pigs and plugs to remove product residue before cleaning.
- Use level controls and automatic shut-off systems to avoid spills from vessels and tanker emptying.
- Collect spills of solid materials (cheese curd and powders) for reprocessing or use as stock feed.
- Fit drains with screens and/or traps to prevent solid materials entering the effluent system.
- Install in-line optical sensors and diverters to distinguish between product and water and minimise losses of both.
- Install and maintain level controls and automatic shut-off systems on tanks to avoid overfilling.
- Use dry cleaning techniques where possible, by scraping vessels before cleaning or pre-cleaning with air guns.
- Use starch plugs or pigs to recover product from pipes before internally cleaning tanks.

Energy

Energy is an area where substantial savings can be made almost immediately with no capital investment, through simple housekeeping and plant optimisation efforts. Substantial saving are possible through improved housekeeping and the fine tuning of existing processes and additional savings are possible through the use of more energy-efficient equipment and heat recovery systems.

In addition to reducing a plant's demand for energy, there are opportunities for using more environmentally benign sources of energy. Opportunities include replacing fuel oil or coal with cleaner fuels, such as natural gas or biomass, purchasing electricity produced from renewable sources, or cogeneration of electricity and heat on site. For some plants it may also be feasible to recover methane from the anaerobic digestion of high strength effluent streams to supplement fuel supplies.

A checklist of energy saving ideas:

- Implement switch-off programs and installing sensors to turn off or power-down lights and equipment when not in use.
- Improve insulation on heating or cooling systems and pipe work.
- Favour more energy-efficient equipment
- Improve maintenance to optimise energy efficiency of equipment.
- Maintain optimal combustion efficiencies on steam and hot water boilers.
- Eliminate steam leaks.
- Capture low-grade energy for use elsewhere in the operation.

Receipt and Storage of Milk

Raw milk is generally received at processing plants in milk tankers. Some smaller plants may also receive milk in 25–50 L aluminium or steel cans or, in some less developed countries, in plastic barrels. Depending on the structure and traditions of the primary production sector, milk may be collected directly from the farms or from central collection facilities. Farmers producing only small amounts of milk normally deliver their milk to central collection facilities.

At the central collection facilities, operators measure the quantity of milk and the fat content. The milk is then filtered and/or clarified using centrifuges to remove dirt particles as well as udder and blood cells. The milk is then cooled using a plate cooler and pumped to insulated or chilled storage vessels, where it is stored until required for production.

Empty tankers are cleaned in a wash bay ready for the next trip. They are first rinsed internally with cold water and then cleaned with the aid of detergents or a caustic solution. To avoid build-up of milk scale, it is then necessary to rinse the inside of the tank with a nitric acid wash. Tankers may also be washed on the outside with a cold water spray. Until required for processing, milk is stored in bulk milk vats or in insulated vessels or vessels fitted with water jackets. Figure 1.4 is a flow diagram showing the inputs and outputs for this process.

Water is consumed for rinsing the tanker and cleaning and sanitising the transfer lines and storage vessels. The resulting effluent from rinsing and cleaning can contain milk spilt when tanker hoses are disconnected. This would contribute to the organic load of the effluent stream.

Table 1.1 provides indicative figures for the pollution loads generated from the receipt of milk at a number of plants. Table 1.2 provides indicative figures for the pollution loads generated from the washing of tankers. Solid waste is generated from milk clarification and consists mostly of dirt, cells from the cows' udders, blood corpuscles and bacteria. If this is discharged into the effluent stream, high organic loads and associated downstream problems can result.

Cleaner Production opportunities in this area focus on reducing the amount of milk that is lost to the effluent stream and reducing the amount of water used for cleaning. Ways of achieving this include:

- Avoiding milk spillage when disconnecting pipes and hoses.
- Ensuring that vessels and hoses are drained before disconnection.
- Providing appropriate facilities to collect spills.
- Identifying and marking all pipeline to avoid wrong connections that would result in unwanted mixing of products.
- Installing pipes with a slight gradient to make them self-draining.
- Equipping tanks with level controls to prevent overflow.
- Making certain that solid discharges from the centrifugal separator are collected for proper disposal and not discharged to the sewer.
- Using 'cleaning-in-place' (CIP) systems for internal cleaning of tankers and milk storage vessels, thus improving the effectiveness of cleaning and sterilisation and reducing detergent consumption.
- Improving cleaning regimes and training staff.
- Installing trigger nozzles on hoses for cleaning.
- Reusing final rinse waters for the initial rinses in CIP operations.
- Collecting wastewaters from initial rinses and returning them to the dairy farm for watering cattle.

Main product	Wastewater (m^3/tonne milk)	COD (kg/tonne milk)	Fat (kg/tonne milk)
Butter plant	0.07–0.10	0.1–0.3	0.01–0.02
Market milk plant	0.03–0.09	0.1–0.4	0.01–0.04
Cheese plant	0.16–0.23	0.4–0.7	0.006–0.03
Havarti cheese plant	0.60–1.00	1.4–2.1	0.2–0.3

Table 1.1 *Indicative pollution loads from the milk receival area.*

Main product	Wastewater (m^3/tonne milk)	COD (kg/tonne milk)	Fat (kg/tonne milk)
Market milk plant	0.08–0.14	0.2–0.3	0.04–0.08
Havarti cheese plant	0.09–0.14	0.15–0.40	0.08–0.24

Table 1.2 *Indicative pollution loads from the washing of tankers.*

2 – Pulp and Paper Industry

1. The Pulp and Paper Industrial History

In the 1800s, there was a shift away from using cotton rags to make paper. Instead, industrialisation helped wood become the most important source of fibre. The switch from a scarce fibre supply to a plentiful one opened up a vast, renewable, low cost source of fibre raw material, making large-scale paper production possible. Since that time, first mechanical and then chemical methods have been developed to produce pulp from wood.

The pulp and paper industry converts wood or recycled fibre into pulp and primary forms of paper. *Pulp mills* separate the fibres of wood or from other materials, such as rags, linters, wastepaper, and straw in order to create pulp. *Paper mills* primarily are engaged in manufacturing paper from wood pulp and other fibre pulp, and may also manufacture converted paper products. Other companies in the paper and allied products industry use the products of the pulp and paper industry to manufacture specialised products including paper board boxes, writing paper, and sanitary paper.

The Sources

Mazgaj, M., Yaramenka, K., Malovana, O., Cherre, E., Ibraimova, L. *Cleaner Production Measures for Pulp and Paper Industry*. Project report. Section of Industrial Ecology, Royal Institute of Technology, Sweden, 2006.

Miljöinfo från Skogsindustrierna. Skogsindustrierna, 1995.

Brännland, R. *Miljöskydd i cellulosatekniken.* Dept. of Pulp and Paper Technology, Royal Institute of Technology, Sweden, 1994.

Morin, R. (Environmental Manager, SCA Graphics Sundsvall AB.) A lecture in *Cleaner Production*, at the Royal Institute of Technology, Sweden, 2006.

Kraft Pulp Mill Compliance Assessment Guide. US EPA, May 1999.

Profile of the Pulp and Paper Industry. EPA Office of Compliance Sector Notebook Project, 1995.

See also *Case Study 5* on Pulp and Paper Production.

The manufacture of wood pulp is the single most important method for chemically converting wood into useful products, and as such is a highly important component of the global manufacturing industry in both economic and environmental terms. In certain regions, pulp and paper manufacture is a dominant industry and is responsible for a large portion of regional economic activity.

At the same time, pulp and paper manufacture can have potentially serious impacts on environmental quality and hence the health of both human and wider ecosystems.

Environmental Concerns

The presence of resin acids and other unidentified constituents continue to present toxicity problems for all kraft mills, regardless of bleaching chemicals. Ecosystems close to pulp mills which meet relatively tough existing environmental regulations continue to experience significantly reduced diversity in the plants and animals able to live near them. These facts emphasise the need to pursue closed loop strategies.

Additionally, the effects of mill process changes on workers and local communities have rarely been factored into the mainstream debate on best routes forward. Exposure to bleaching chemicals, process gasses, emissions from water treatment ponds, and bacteria and fungi on wood chips and sludge all directly impact the health and safety of the people working in the mill and the people who live near by. Decisions on how to make an ecologically responsible pulp mill must take these issues into account.

For mass-balance, environmental impact evaluation and cleaner production measures identification, the production process (in a life-cycle perspective) can be divided into 7 subprocesses:

1. Raw materials processes.
2. Wood-yard.
3. Fibre line.
4. Chemical recovery.
5. Bleaching.
6. Paper production.
7. Products and recycling.

2. Main Process Technologies

Pulp Production

The objective of the paper production technology is to separate cellulose fibres from the wood structure. The free fibres in the pulp are then the main raw material for paper production. Pulping processes can be of different types that determine what chemicals and amounts of water and energy used in the processes and, consequently, the environmental impacts of production.

Possible types of pulp production are Kraft (68%), mechanical (22%), semi-chemical (4%), sulphite (4%) and dissolving (2%).

Mechanical pulping is a process that uses mechanical force to separate fibres from the wood structure. *Ground wood pulping* was the first type of mechanical pulping process developed in Germany in the 1840s. In this process, wood is mechanically ground against large sandstone cylinders. The pulp is then screened to remove large pieces such as knots, etc. Next, the pulp is washed and bleached for use in paper making. One of the main things to note here is that this kind of pulp still contains lignin (essentially the glue that holds the cellulose fibres together), which means that its strength and brightness are low compared to pulp made from other processes. On the other hand the pulp yield is about 90% (defined as the amount of wood fibres produced per amount of wood raw material used).

Refiner mechanical pulping was introduced in the 1960s. In this process, wood chips pass between disks rotating in reverse directions to separate the fibres. The most common refiner pulping methods are Thermo-mechanical pulping (TMP) and Chemo-thermo-mechanical pulping (CTMP). In these processes, the wood is chopped into chips and then preheated with steam to about 120°C before mechanical force is applied in a disc refiner. In the CTMP process the wood chips are impregnated with sodium sulphite (Na_2SO_3). CTMP produces a pulp that is stronger and somewhat more light-coloured than TMP pulp. Thermo-mechanical pulp is mainly used in the production of newsprint as it is relatively cheap to produce and delivers adequate strength for this end-use. CTMP gives a pulp that has many usage areas, e.g. printing and writing paper and tissue paper.

Chemical pulping, as its name suggests, uses chemical rather than mechanical means of separating the cellulose fibres from each other by removing the lignin, leaving behind the fibre used in paper making. Here, the wood chips are "cooked" in a chemical solution, which dissolves lignin and other impurities.

Since chemical pulping removes lignin and other impurities, it produces a strong, bright pulp that is suited for the production of grades that require these properties, such as fine writing paper.

The first type of chemical pulping developed was *soda pulping*. This process used caustic soda as the chemical solution and was developed in England in the 1850s.

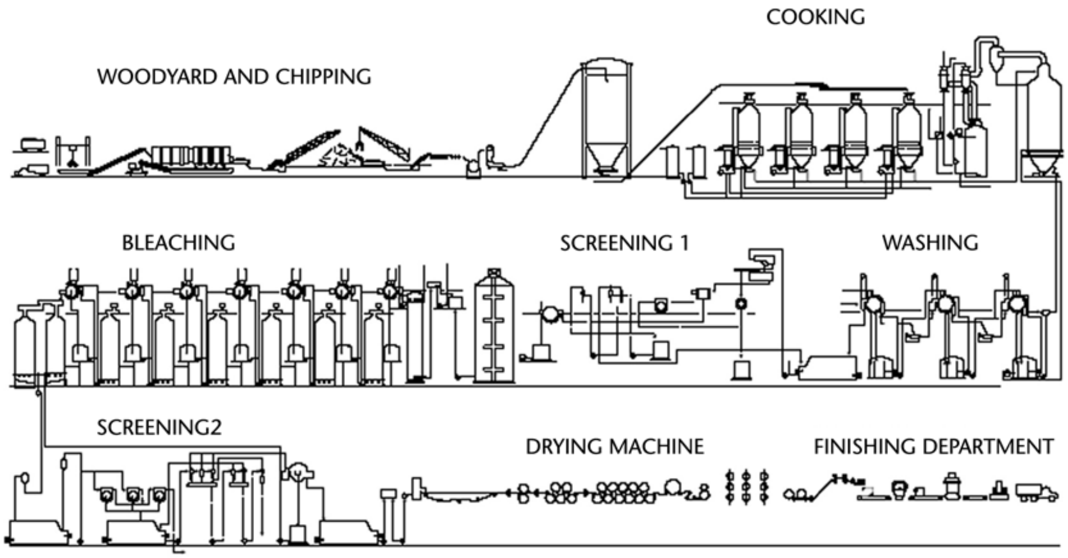


Figure 2.1 *Simplified flow diagram of an integrated pulp and paper mill (chemical pulping, bleaching and paper production) [EPA, 1995].*

A few years later in 1867, *sulphite pulping* was introduced. This process uses calcium, sodium, magnesium or ammonia salts of sulphurous acid as the chemical solution for dissolving lignin.

Sulphate or Kraft Pulping

Sulphate or Kraft pulping was invented in Germany in 1884 and remains the dominating technology today. It produces pulp with much higher strength compared to sulphite pulping. Note that "kraft" means strong in several European languages, including German and Swedish and both Germany and Sweden have long paper industry traditions. Kraft pulping can also use a wider variety of wood species than the sulphite pulping process as it is more effective at removing impurities like resins.

In the kraft pulping process, wood chips are "cooked" in a digester in a solution of sodium hydroxide and sodium sulphide called white liquor. In Kraft pulping the pulp yield is less than 50%.

A bonus of Kraft pulping is that the chemicals can be recycled and re-used in the mill. Another is that kraft fibre is exceptionally strong.

The fact that kraft pulping is the dominant pulping process in the world is the reason why we concentrate on this type of pulping when describing sub-processes within the industry.

Sulphate pulping starts in the *wood yard*: bark and dirt is removed from the wood logs (dry or wet *debarking*), reduced to chip fragments in chippers (*chipping*) and screened for separating fines and oversize chips (*screening*). During *digestion* chips are cooked in a chemical solution called *white liquor*. Batch digesters were developed first and this concept was further developed to create a continuous digester process. Both batch and continuous digesters are used in modern mills today.

In the batch process, the chips are cooked in the white liquor in a digester for several hours under pressure and at high temperature. Following the cooking stage, the chips are then blown into a blow pit which helps to break apart the fibre bundles.

In the continuous process, the chips are first steamed before being continuously fed into the top of the digester. The chips are impregnated with white liquor and cooked as they move downwards through each stage of the digester. The brown stock *washing* is done in several countercurrent stages in the lower half of the digester. The filtrate from this washing is called *black liquor* which is sent to the chemical recovery system. Then knots, bark, shives and other contaminants are removed from the pulp by *screening*. Before the pulp is sent to the bleaching stage (where required), an *oxygen delignification* stage usually is included as the final stage of the cooking section of the process. This process involves treating the pulp with oxygen to further oxidise and dissolve the remaining lignin in the pulp. It is designed to lower the "*kappa number*" of the pulp, which is a measure of its remaining lignin concentration. After the digester a typical coniferous pulp has a kappa number of between 20 and 30, which has a rather dark brown colour. The oxygen delignification stage reduces the kappa number to 10-12. During further *oxygen delignification* approximately half of the remaining lignin can be removed.

Bleaching

Bleaching is needed to remove colour associated with remaining residual lignin. Bleached kraft pulp is mainly used for printing and writing grades, while unbleached kraft pulp is used in the production of packaging grades. The three general approaches to bleaching are:

1. Elemental Chlorine Bleaching.
2. Elemental Chlorine Free Bleaching (ECF).
3. Totally Chlorine Free (TCF) bleaching.

The bleaching chemicals are *injected* into the pulp and the mixture is *washed* with water. This process is repeated several times and generates large volumes of liquid waste. Additionally, vents from the bleaching tanks emit hazardous air pollutants including chloroform, methanol, formaldehyde, and methyl-ethyl-ketone.

Depending on the bleaching chemicals used, the wastewater streams from the bleaching process may contain chlorine compounds and organics. The mixture of chemicals may result in the formation of a number of toxic chemicals (such as dioxins, furans and chlorinated organics). Although this effluent is generally released to a wastewater treatment plant, the chemicals named above simply "pass through" the plant (i.e. the treatment plant does not significantly reduce the concentrations of these pollutants) and accumulate in the rivers, lakes and oceans to which the treatment plant discharges.

Commonly used bleaching chemicals are elemental chlorine (C), sodium hypochlorite (H), chlorine dioxide (D), oxygen (O), ozone (Z) and hydrogen peroxide (P). In ozone and hydrogen peroxide bleaching it is necessary to stabilise the bleaching chemicals by removing metals from the pulp with a complexing agent (Q) such EDTA or DTPA. The E extraction stage uses sodium hydroxide to extract water insoluble chlorinated lignin and other coloured compounds from the pulp.

The bleaching process generally consists of a series of stages utilising alternating acidic and alkaline bleaching agents. Figure 2.2 shows some examples of typical bleaching sequences.

The Process Flowsheet

The process flowsheet of the kraft process is designed to recover the cooking chemicals and heat. In the recovery line, spent cooking liquor and the pulp wash water are combined to form a weak black liquor which is concentrated through *evaporation* from 16% to 60-80% solids in a multiple-effect evaporator system. The strong black liquor is then incinerated in a *recovery boiler*. Combustion of the organics dissolved in the black liquor provides heat for generating process steam. The carbon dioxide formed in the combustion reacts with part of the sodium in the black liquor to sodium carbonate (Na_2CO_3) and the sulphur content is converted to sodium sulphate (Na_2SO_4). The sulphate is converted to sodium sulphide (Na_2S) by reduction with carbon present in the melted slag at the bottom of the furnace.

The smelt is dissolved in water to form *green liquor*, which is transferred to a causticizing tank where quicklime (calcium oxide) is added to precipitate the carbonate content in the green liquor as calcium carbonate and instead produce the sodium hydroxide needed to convert the solution back to white liquor for return to the digester system. The precipitate from the causticizing tank is calcined in a lime kiln to regenerate quicklime.

Production of paper starts with *stock preparation* where various grades of pulp are mixed in a *mixing chest* to obtain the desired properties, *refined* to increase the strength of the paper, *screened* and *cleaned*. After that, different dyes, defoamers, fillers and retention agents are added (*filling*) and the consistency is adjusted with the addition of water ("white water") before the pulp suspension enters the head box of the paper machine.

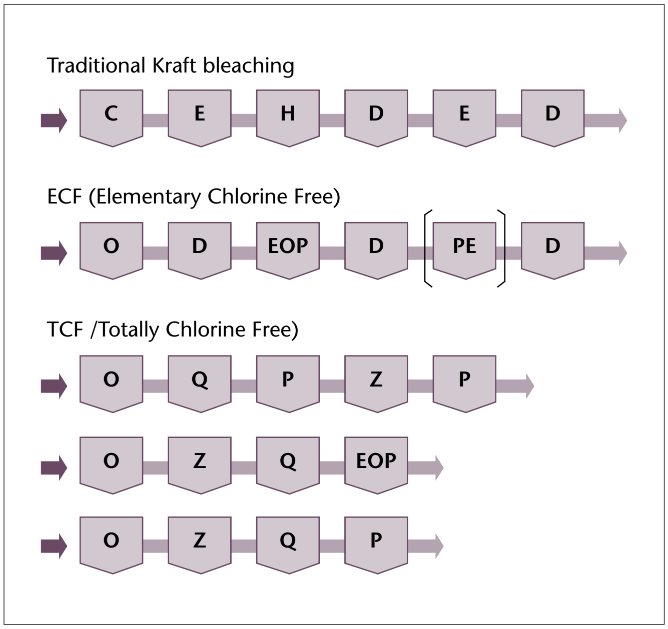


Figure 2.2 *Examples of bleaching sequences [adapted from Miljö-info från Skogsindustrierna, 1995].*

In the paper machine the fibre suspension is introduced to the wire net, where water is drained assisted with rolls, foils, and vacuum boxes (*dewatering*). It is further dewatered by *pressing* (up to a solid content of around 50%), and *drying* (to about 95% solids content).

Examples of *finishing operations* are sizing, coating, dyeing, and calendering. It includes not only the processes that take place at the factory itself, but also those of raw materials and products, such as transportation and final disposal. This life-cycle approach can be useful to define cleaner production measures as they can probably involve product modification or raw materials substitution.

3. The Most Important Cleaner Production Measures

The following CP measures are the most important in pulp and paper industry:

- *Chlorine-free production* – decreasing wastewater and air emissions toxicity. Almost without exception, the literature indicates that oxygen based bleaching sequences have also a superior efficiency over chlorine dioxide based sequences in this area. Even when combined with potential increased energy consumption in some oxygen based configurations, these mill designs are the most energy efficient available. Oxygen based kraft pulp show no appreciable shortcomings in quality relative to chlorine dioxide bleached products whereas oxygen based bleaching chemicals present the least immediate and long term hazards for workers and the general public.
- *Co-production* – recovering by-products from main production residue (decreasing solid wastes and wastewater amount and decreasing recourse consumption by creating a type of industrial symbiosis).
- *Closed loop operations* – decreasing discharges and saving water and resource consumption.
- *Chemicals recovery* – decreasing recourse consumption, wastewater amount and accident risks connected with chemicals transportation.
- Increasing the amount of *product recycling after use* (decreasing recourse and energy consumption and solid wastes to landfill).
- *Effective waste management* – segregating waste streams, waste separation prior to disposal for further recycling;

increasing recycled wastes within a company (chips, pulp, paper); producing energy from wastes; training employees in hazardous waste regulations.
- *Reduction of water consumption* – monitoring and analysing water consumption; reducing or elimination freshwater use where possible (wood-yard, brown stock washing, screening, causticizing system); replacing pump seals with mechanical seals; choosing less water-demanding process types (e.g. dry debarking).
- *Energy conservation* – choosing less energy-demanding process types (e.g. dry debarking); generating company's own power (e.g. from wastes or steam); improving the efficiency of high energy consumption equipment; steam meters provision; using "clean" fuels.
- *Effective wastewater treatment* – avoiding excessive treatment chemicals; conducting chemical analyses; comparing analytical results with compliance levels on a daily basis; recycling a part of the treated effluent back into the process.
- *Equipment maintenance* – effective belts for drainage, filtration, pressing etc.; design for decreasing discharges.
- *Effective air pollution prevention* – removing hazardous substances from the air by effective gas collection and gas treatment systems.
- *Increasing processes efficiency* – choosing more effective process types (e.g. kraft pulping instead of soda pulping).
- *Safe product and raw material handling and storage* – training employees to keep accurate records of chemicals used; keeping minimum supply of chemicals needed; labelling areas with keeping hazardous substances.
- *Reducing employees' hazards* – eye protection and noise reduction measures; spill collection systems; training employees on safety handling spills and spill reporting.

Thus, an *ideal paper mill* from cleaner production point of view is a chlorine-free and zero-discharge one, with minimised quantity and toxicity of air pollution and solid wastes. It is seen that closed loops represent the most effective approach to save both energy and resource consumption and at the same way to decrease all kind of wastes production. Such an approach is developed in the form of paper recycling, different types of substances reuse during production processes, co-production and chemicals recovery; nonetheless, it still provides opportunities to improve the processes. *Future research* can develop more sustainable reuse options for kraft pulping solid wastes, as well as pulping methods that result in purified by-products that can serve as feedstock for other manufacturing processes.

4. The Raw Materials

Wood

Raw materials for the pulp and paper production processes start with the forestry or chemical industry, which is followed by transport to the place of use and storage.

Important cleaner production measures include:

- Maintaining *moisture content* of the raw materials constant all year around.
- Keeping *chemical inventory to a minimum* (only as much as needed for current production) and buying small containers of infrequently used materials.
- *Labelling* storage area for hazardous substances.
- Providing *spill containment and collection systems* during storage.
- *Genetically modifying* forest trees.

Pulp and paper industries exploit biological raw materials, which are synthesised, modified and degraded in nature by microbes using a vast array of specific enzymes. Even though the pulp and paper industries have traditionally relied on mechanical and chemical processes, the potential for biotechnology is significant. Today, there is an increasing interest in biotechnology in order to develop environmentally compatible processes, to lower the energy consumption in mechanical pulping procedures and to develop new tools for improving the quality and the performance of the products.

Lignin is the main wood component that must be effectively removed from the pulp in order to guarantee high brightness of the subsequent paper products. The biochemistry and molecular biology of lignin biosynthesis are currently well understood, so it has been possible to use genetic engineering to modify lignin content and/or composition in poplars.

For example, suppression of the final enzyme in the biosynthesis of lignin monomers results in lignin with altered structure. Suppression of an enzyme involved in syringyl (S) lignin synthesis, results in dramatic reduction in S lignin content.

Kraft pulping of the transgenic tree trunks showed that these genetic modifications had improved characteristics, allowing easier delignification, using smaller amount of chemicals, while yielding more high-quality pulp.

Owing to the genetic modification savings in energy and pollutant chemicals were also achieved, thus leading to an environmentally more sustainable process.

The Wood-yard

Raw materials for the pulp and paper production processes start with the forestry or chemical industry, which is followed by transport to the place of use and storage.

Important cleaner production measures include:

- Maintaining *moisture content* of the raw materials constant all year around.
- Keeping *chemical inventory to a minimum* (only as much as needed for current production) and buying small containers of infrequently used materials.
- *Labelling* storage area for hazardous substances.
- Providing *spill containment and collection systems* during storage.

Wood-yard process includes debarking, slashing, chipping of wood logs and then screening of wood chips/secondary fibres (some pulp mills purchase chips and skip this step). The process is designed to supply a homogenous pulping feedstock.

The bark is usually either stripped mechanically or hydraulically with high powered water jets in order to prevent contamination of pulping operations. Hydraulic debarking methods may require a drying step before burning the bark. Usually, hydraulically removed bark is collected in a water flume, dewatered, and pressed before burning. Treatment of wastewater from this process is difficult and costly, whereas in dry debarking methods the removed bark can be channelled directly into a furnace.

Wet debarking produces 3-20 m³ wastewater/t processed material containing 15-50 kg suspended solids/t and 5-10 kg BOD_5/t and consumes about 20 kWh energy/t. Dry debarking will give 0-5 m³ wastewater/t processed material containing 0-10 kg suspended solids/t and 0-3 kg BOD_5/t and consumes about 20 kWh energy/t.

Important cleaner production measures include:

- Pulp *mills integrated with lumbering facilities*: acceptable lumber wood is removed during debarking; residual or waste wood from lumber processing is returned to the chipping process; in-house lumbering rejects can be a significant source of wood furnish.
- *Avoiding hydraulic debarking* – saving energy and water consumption, reducing wastewater amount.
- *Reusing leachate water*.
- *Co-production from bark*: mulch, ground cover, charcoal.
- *Burning bark* from debarking and small chips from chipping for energy production (depends on the moisture content).

Chemicals Recovery

Chemical recovery serves several important functions in a modern pulp mill: it removes water from the weak black liquor in evaporators and concentrators to enable incineration of the black liquor; it selectively removes organic contaminants from the water to allow for reuse in the pulp mill; it incinerates the concentrated black liquor in the recovery boiler; it recovers heat from the incineration process for steam generation and it dissolves the produced chemicals in water for future processing for pulping liquor generation.

Kraft pulping is a closed loop process in which the chemicals used to make pulp are recycled and reused in a digester. The recovery boiler is crucial to the process. It serves three critical functions in this process. Firstly it makes use of chemical energy in the organic portion of the liquor, to generate steam for the mill, secondly, it plays a major part in the sulphate process as a chemical reactor, and thirdly it destroys the dissolved organic matter and thus eliminates an environmental discharge. The black liquor recovery boiler functions as both a steam boiler and chemical reactor. It generates steam from the energy liberated during combustion of the organic constituents of black liquor, while chemicals from pulp digesting, such as sulphur and sodium, are recovered as smelt.

Important cleaner production measures include:

- Use of *new technologies* (Combined Heat and Power generation (CHP), heat transfer, heat exchange).
- Improvements of the *technical parameters of the recovery boiler* or furnace (geometrical shape etc.).
- *Use of light gas strippers and gas separation systems* which will remove hazardous and foul smelling pollution from the air and increase work place safety.
- *Deaerator tanks ahead of the boilers* to help reduce the intake of freshwater.
- Air emissions control devices.
- Providing *spill containment and collection systems*.

Use of Recycled Paper

After the production stage the product is transported to the place of distribution and use; after use it becomes either solid waste (and disposed to landfill or burnt) or can be considered as secondary resource for production.

Important cleaner production measures include:

- *Increasing recycling rates.* Recycling reduces energy consumption, decreases combustion and landfill emissions, and decreases the amount of carbon dioxide in the atmosphere. When paper products are reduced or recycled, trees that would otherwise be harvested are left standing. These living trees absorb carbon dioxide, a greenhouse gas. This process also saves money since recycling fibre is cheaper than harvesting and processing virgin fibre.
- Possibility for *easy packaging recycling*.
- Using *"green" fuel for transportation*.

Almost any kind of paper (newspaper, cardboard, packaging, postal mail, wrapping paper, catalogues) can be recycled. The use of recovered paper for new paper production substitutes the wood fibre and extends the life cycle. This is described as "the urban forest" as opposed to "the natural forest". The wood fibre, depending on quality can be reused four to six times in process of forming new paper. The recycling of paper is a perfect example of the paper industry's sustainable use of resources.

The Recycling Process

In Europe an average of 56% of used paper is recovered. The recycling process includes following stages:

Sorting: not all paper can be recovered. There are paper products that cannot be either collected or recycled. The portion of such paper products, which consist, for example, of cigarette papers, wallpaper, tissue papers and archives, is estimated to be about 19% of the total paper consumption. Sorting is the first stage of conversion of waste paper into the new one. Waste paper is divided into categories (newsprint, computer paper, magazines). The part that is suitable is shipped to further processing.

Dissolving: in this stage of paper recovery stickies and dioxins are eliminated. Paper is soaked and broken in giant washers and treated with chemicals. Stickers – sticky contaminants such as tapes or plastics covers – reduce paper quality and cause paper machines downtime. To eliminate sticky contaminants paper fibres should be grounded to particles size of <0,5 mm. Then the paper is extracted with CO_2 in 60°C and 34.5 MPa. Extraction efficiency for stickers removal is 55-75%. Another problem is presence of small quantities of dioxins and other chlorinated organic compounds. Kraft pulp may contain small but detectable levels of dioxins and related compounds, especially if their bleaching process used elemental chlorine. To eliminate dioxins recycled paper also is grounded to particles size of <0,5 mm. CO_2 solvent extraction conditions are 71°C and 34,5 MPa. Dioxin extraction efficiency is up to 95%.

De-inking: it is one of the key operations performed in recycling paper. The heat used in laser printing makes ink hard to remove because it deposits ink on the fibres. Traditional deinking processes rely on chemical and mechanical actions to remove ink from fibres and include several dispersion, flotation and washing steps. They thus reduce fibre strength, which must be compensated for with the addition of fortifying chemicals. A new technology, based on the electric field has been developed. The reactor comprises an anode and a cathode. Applying the direct current field to a reactor full of fibre slurry attracts the ink particles away from the fibres and causes the ink to coagulate. The massed particles float to the surface of the slurry with some help from gas bubbles generated by the electric field. The coagulated ink is then skimmed off the top of the slurry using rotation scoops, continuous conveyors. The current also helps remove dust particles from the fibre and creates oxygen in the reactor, both actions improve fibre brightness and whiteness.

Mixing: finally, the wet, shredded waste paper is blended with another material (wood pulp, chemicals) according to the type of end product is desired. Paper cannot be recycled indefinitely. Each time it is recycled, its quality degrades slightly because the fibres become more and more broken. At some point recycled paper has to be mixed in with virgin material, and eventually after repeated uses, it ends up in a landfill or and incinerator.

The paper making process itself is pretty much the same whether one uses virgin materials, recycled materials, or a mixture of the two.

Internet Resources

EIA Renewables

http://www.eia.doe.gov/cneaf/solar.renewables/at_a_glance/wood/woodenfa-03a.htm

EUROPA – Forest-based industries

http://europa.eu.int/comm/enterprise/forest_based/pulp_en.html

Reach for Unbleached Foundation – Human Health

http://www.rfu.org/cacw/pollutionhealth.htm

Paperonline

http://www.paperonline.org/

EIA Forest Products Industry Analysis Brief – MECS 1998

http://www.eia.doe.gov/emeu/mecs/iab98/forest/sources.html

Energy Conservation in the Pulp and Paper Industry

http://www.caddet.org/reports/display.php?id=995/

Environmental Impact assessment and environmental auditing in the pulp and paper industry, FAO Forestry Paper 129, 1996

http://www.fao.org/docrep/005/V9933E/V9933E00.htm

Vu Tuong Anh CLEANER PRODUCTION AUDIT IN THE PULP AND PAPER INDUSTRY: A CASE STUDY IN VIETNAM – Thesis submitted in partial fulfilment of the requirement for the degree of Master of Science

http://www.faculty.ait.ac.th/visu/Data/AIT-Thesis/Master%20Thesis%20final/Tuong%20pdf%2096.pdf

Gouvernement du Canada

http://www.biostrategy.gc.ca/english/view.asp?x=540&mid=50

Pulp and Paper Industry EPA Office of Compliance Sector Notebook Project Profile of the Pulp and Paper Industry 2nd Edition November 2002

http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/pulppasn.pdf

Reach for Unbleached Foundation – Sludge from Pulp and Paper Mills

http://www.rfu.org/cacw/pollutionSludge1.htm

The Irish Scientist

http://www.irishscientist.ie/2002/contents.asp?contentxml=02p153b.xml&contentxsl=is02pages.xsl

Damage Caused by the Paper Industry

http://www.cwac.net/paper_industry/

Inland Paper board and Packaging, Rome Liner board Mill Energy Assessment

http://www1.eere.energy.gov/industry/bestpractices/pdfs/inlandpaper.pdf

De-inking Recycled Paper: A brighter future thanks to Georgia Tech de-inking research

http://gtresearchnews.gatech.edu/reshor/deink.html

3 – Textile Industry

1. Introduction

Industrial Processes in the Textile Industry

The textile industry is comprised of a diverse, fragmented group of establishments that produce and or process textile-related products (fibre, yarn, fabric) for further processing into apparel, home furnishings, and industrial goods. Textile establishments receive and prepare fibres; transform fibres into yarn, thread, or webbing; convert the yarn into fabric or related products; and dye and furnish these materials at various stages of production.

The process of converting raw fibres into furnished apparel and non-apparel textile products is complex; thus, most textile mills specialise. Little overlap occurs between hitting and weaving, or among production of man-made, cotton, and wool fabrics. The processes consists of:

1. Yarn formation.
2. Fabric formation.
3. Wet processing.
4. Fabrication.

These stages are highlighted in the process flow chart shown in Figure 3.1.

Material Use

The twentieth century has seen the development of the fist man-made fibres (rayon was first produced in 1910). Although natural fibres (wool, cotton, silk, and linen) are still used extensively today, they are more expensive and are often mixed with man-made fibres such as polyester, the most widely used synthetic fibre.

Man-made fibres include 1) cellulosic fibres, such as rayon and acetate, which are created by reacting chemicals with wood pulp; and 2) synthetic fibres, such as polyester and nylon, which are synthesised from organic chemicals. Since man-made fibres are synthesised from organic chemicals, yarn formation of man-made fibres does not involve the extensive cleaning and combing procedures associated with natural fibres. Man-made fibres, both synthetic and cellulosic, are manufactured using spinning processes that simulate or resemble the manufacture of silk.

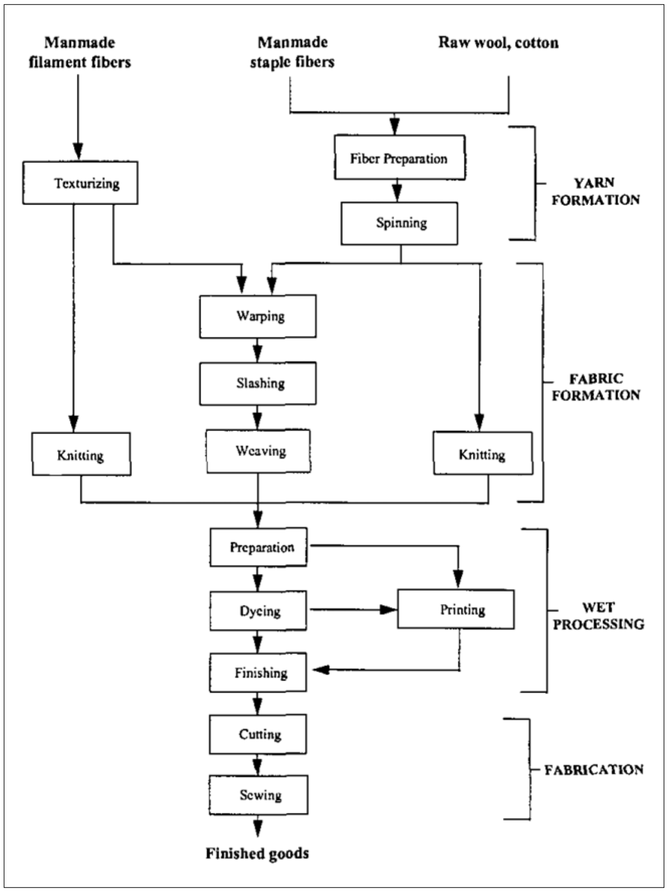


Figure 3.1 *Typical textile processing flow chart [US EPA, 1997].*

The Sources

Sector Notebook Project: Profile of the Textile Industry. US EPA, Office of Compliance, 1997.
http://www.epa.gov/compliance/resources/publications/assistance/sectors/notebooks/textilsn.pdf

Best Management Practices for Pollution Prevention in the Textile Industry. US EPA, Office of Research and Development, 1995.

Additional references are cited in the text.

2. Industrial Processes

Yarn Formation

Textile fibres are converted into yarn by grouping and twisting operations used to bind them together. Although most textile fibres are processed using spinning operations, the processes vary depending on whether the fibres are natural or man-made. Natural fibres, known as staple when harvested, include animal and plant fibres, such as cotton and wool. These fibres must go through a series of preparation steps before they can be spun into yarn, including opening, blending, carding, combing, and drafting. Man-made fibres may be processed into yarn or staple-length fibres so that they can be spun. Filament yarn may be used directly or following further shaping and texturising.

Yarn formation can be performed once textile fibres are uniform and have cohesive surfaces. Natural fibres are first cleaned to remove impurities and are then subjected to a series of brushing and drawing steps designed to soften and align the fibres.

Tufts of fibre are conveyed by air stream to a *carding machine*, which transports the fibres over a belt equipped with wire needles. A series of rotating brushes on top of the belt causes the fibres to tease out and align into thin, parallel sheets. Several card slivers are fed to the *combing machine* and removed as a finer, cleaner, and more aligned comb sliver. Slivers are then combined into a continuous, rope-like strand and fed to a machine known as a *drawing frame*. The drawing frame contains several sets of rollers that rotate at successively faster speeds. As the slivers pass through, they are further drawn out and lengthened, to the point where they may be five to six times as long as they were originally. *Drafting* then uses a frame to stretch the yarn further and winds it onto a rotating spindle.

The fibres are now spun together into either spun yarns or filament yarns. Filament yarns are made from continuous strands of man-made fibre (e.g. not staple length fibres). Spun yarns are composed of overlapping staple length fibres that are bound together by twist. Filament yarns may be used directly to make fabric or further twisted to the desired consistency.

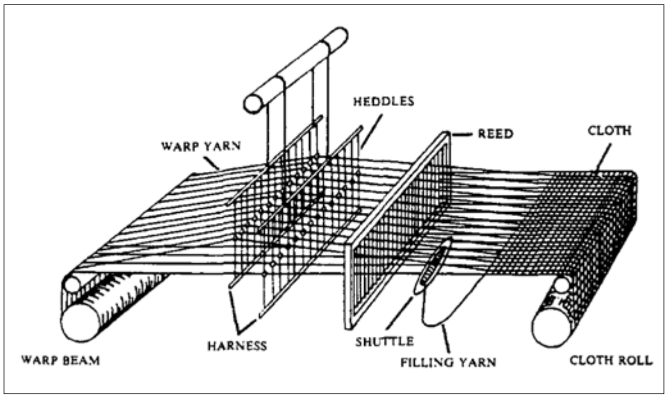


Figure 3.2 *Typical shuttle loom [I.B. Wingate, Fairchild's Dictionary of Textiles, Fairchild Publications, 1979].*

Man-made *fibre spinning* is the process of forming fibres by forcing a liquid through a small opening beyond which the extruded liquid solidifies to form a continuous filament. Following spinning, the man-made fibres are drawn, or stretched, to align the polymer molecules and strengthen the filament. Man-made filaments may then be texturised or otherwise treated to simulate physical characteristics of spun natural fibres.

Fabric Formation

The major methods for fabric manufacture are weaving and knitting. *Weaving*, or interlacing yarns, is the most common process used to create fabrics. Weaving mills classified as broad woven mills consume the largest portion of textile fibre and produce the raw textile material from which most textile products are made.

Weaving is performed on modern looms, which contain similar parts and perform similar operations to simple hand-operated looms. Fabrics are formed from weaving by interlacing one set of yarns with another set oriented crosswise. The warp yarns are then unwound and passed through a sue solution (sizing klashing) before being wound onto a warp beam in a process known as beaming.

Shedding is the raising of the warp yarns to form a shed through which the filing yarn, carried by the shuttle, can be inserted. The shed is the vertical space between the raised and un-raised warp yarns.

The filling yarn is wound onto a quill, which in turn is mounted in the shuttle. As the shuttle moves back and forth across the shed, it weaves an edge. Conventional shuttle looms can operate at speeds of about 150 to 160 picks per minute. With each weaving operation, the newly constructed fabric must be wound on a cloth beam.

Knitted fabrics may be constructed by using hooked needles to interlock one or more sets of yarns through a set of loops. Tufting is a process used to create carpets, blankets, and upholstery. Tufting is done by inserting additional yarns into a ground fabric of desired weight and yarn content to create a fabric.

Wet Processing

Woven and knit fabrics cannot be processed into apparel and other finished goods until the fabrics have passed through several water-intensive wet processing stages. Wet processing enhances the appearance, durability, and serviceability of fabrics by converting un-dyed and unfinished goods, known as gray or greige (pronounced gri[zh]) goods, into finished consumers' goods. Also collectively known as finishing, wet process-

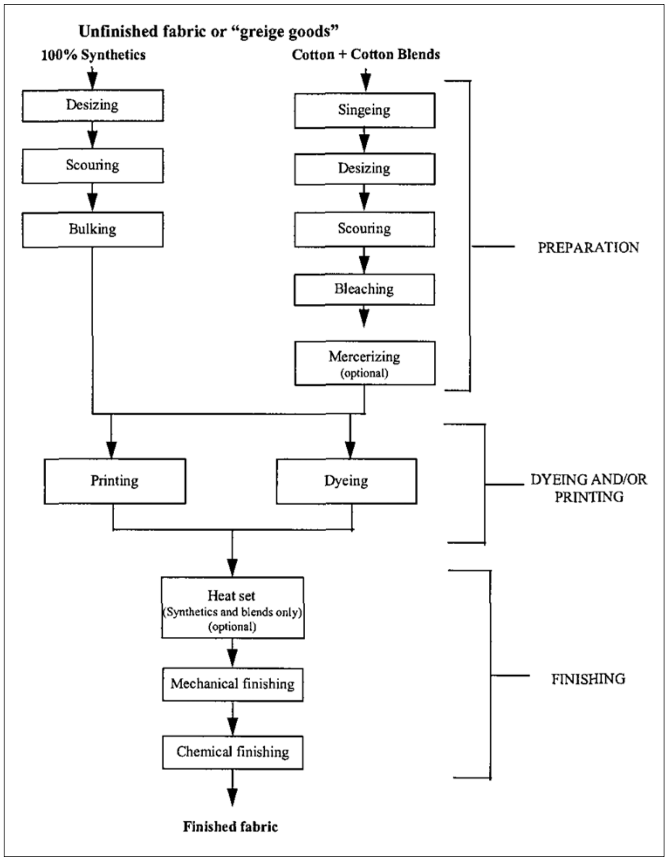


Figure 3.3 *Typical wet processing steps for fabrics [ATMI, Textiles: America's First Industry, 1997].*

ing has been broken down into four stages: fabric preparation, dyeing, printing, and finishing. In terms of waste generation and environmental impacts, wet processing is the most significant textile operation.

Much of the waste generated from the industry is produced during the wet processing stages; Relatively large volumes of wastewater are generated, containing a wide range of contaminants that must be treated prior to disposal. Significant quantities of energy are spent heating and cooling chemical baths and drying fabrics and yarns [Snowden-Swan, 1995].

Fabric Preparation

Most fabric that is dyed, printed, or finished must first be prepared. In preparation, the mill removes natural impurities or processing chemicals that interfere with dyeing, printing, and finishing. If fabrics contained no contamination upon arrival for wet processing, preparation processes would be unnecessary, eliminating about half the pollution outputs from wet processing and a significant amount of wastewater. The primary pollutants from preparation is wastewater containing alkalinity, BOD, COD, and relatively small amounts of other contaminants such as metals and surfactants.

If a fabric is to have a smooth finish, *singeing* is essential. Singeing is a dry process used on woven goods that removes fibres protruding from yarns or fabrics. These are burned off by passing the fibres over a flame or heated copperplates.

Desizing is an important preparation step used to remove size materials applied prior to weaving. Man-made fibres are generally sized with water-soluble sizes that are easily removed by a hot-water wash or in the scouring process. Natural fibres such as cotton are most often sized with water-insoluble starches or mixtures of starch and other materials. Enzymes are used to break these starches into water-soluble sugars, which are then removed by washing before the cloth is scoured.

Scouring is a cleaning process that removes impurities from fibres, yarns, or cloth through washing. Alkaline solutions are typically used for scouring; however, in some cases solvent solutions may also be used. Scouring uses alkali, typically sodium hydroxide, to break down natural oils and surfactants and to emulsify and suspend remaining impurities in the scouring bath.

Bleaching is a chemical process that eliminates unwanted coloured matter from fibres, yarns, or cloth. Bleaching decolorises coloured impurities that are not removed by scouring and prepares the cloth for types of chemicals are used as bleaching agents. The most common bleaching agents include hydrogen peroxide, sodium hypochlorite, sodium chlorite, and sulphur dioxide gas.

Mercerisation is a continuous chemical process used for cotton and cottoned polyester goods to increase dye ability, lustre, and appearance. This process, which is carried out at room temperature, causes the flat, twisted ribbon-like cotton fibre to swell into a round shape and to contract in length. During mercerising, the fabric is passed through a cold 15 to 20% solution of caustic soda and then stretched out on a tenter frame where hot-water sprays remove most of the caustic solution.

Dyeing and Printing

Dyeing operations are used at various stages of production to add colour and intricacy to textiles and increase product value. Most dyeing is performed either by the finishing division of vertically integrated textile companies, or by specialty dye houses. Dyes used by the textile industry are largely synthetic; typically derived from coal tar and petroleum-based intermediates. Dyes are sold as powders, granules, pastes, and liquid dispersions, with concentrations of active ingredients ranging typically from 20 to 80%.

Dyeing can be performed using continuous or batch processes. In batch dyeing, a certain amount of textile substrate, usually 100 to 1,000 kilograms, is loaded into a dyeing machine and treated with a solution containing the dye. The dye molecules attach to the fibres over a period of minutes to hours. Auxiliary chemicals and controlled dye bath conditions, mainly temperature, accelerate and optimise the action. The dye is fixed in the fibre using heat and/or chemicals, and the tinted textile substrate is washed to remove unfixed dyes and chemicals.

Fabrics are often printed with colour and patterns. Of the numerous printing techniques, the most common is rotary screen. Other methods used include direct, discharge, resist, flat screen and roller printing. Pigments used in most printing operations do not require washing steps and generate little waste [Snowden-Swan, 1995]. Compared to dyes, pigments are typically insoluble and have no affinity for the fibres. Resin binders are typically used to attach pigments to substrates. Solvents are used as vehicles for transporting the pigment and resin mixture to the substrate. The solvents then evaporate leaving a hard opaque coating.

Finishing

Finishing encompasses chemical or mechanical treatments performed on fibre, yarn, or fabric to improve appearance, texture, or performance. Mechanical finishes can involve brushing, ironing or other physical treatments used to increase the lustre and feel of textiles. Application of chemical finishes to textiles can impart a variety of properties ranging from decreasing static adherence to increasing flame resistance. The most common chemical finishes are those that ease fabric care, such as the permanent-press, soil-release, and stain resistant finishes. Chemical finishes are usually followed by drying, curing, and cooling steps. Application of chemical finishing is often done in conjunction with mechanical finishing steps.

Mechanical and Chemical Treatments

Heat setting is a dry process used to stabilise and impart textural properties to synthetic fabrics and fabrics containing high concentrations of synthetics. When man-made fibres are heat set, the cloth maintains its shape and size in subsequent finishing operations and is stabilised in the form in which it is held during heat setting. Brushing and napping decrease the lustre of fabrics by roughening or raising the fibre surface and change the feel or texture of the fabric. Calendering or ironing can be used to reduce surface friction between individual fibres, thereby softening the fabric structure and increasing its sheen. Lustre can be added to yarns by flattening or smoothing the surfaces under pressure. This can be achieved by beating the fabric surface or passing the fabric between calendering rolls. Shearing removes surface fibres bypassing the fabric over a cutting blade. Compacting compresses the fabric structure to reduce stresses in the fabric.

Optical finishes added to either brighten or delustre the textile. Absorbent and soil release finishes alter surface tension and other properties to increase water absorbency or improve soil release. Softeners and abrasion-resistant finishers are added to improve feel or to increase the ability of the textile to resist abrasion and tearing. Physical stabilisation and crease-resistant finishes may include formaldehyde-based resin finishes, stabilise cellulosic fibres to laundering and shrinkage, imparting permanent press properties to fabrics.

Fabrication

Finished cloth is fabricated into a variety of apparel and household and industrial products. The simpler of these products, such as bags, sheets, towels, blankets, and draperies, often are produced by the textile mills themselves. Apparel and more complex house wares are usually fabricated by the cutting trades. Before cutting, fabrics must be carefully laid out. Accuracy in cutting the lay fabric is important since any defects created at this point may be carried through other operations and end up in the final product. For simple household and industrial products, sewing is relatively straightforward. The product may then be pressed to flatten the fabric and create crisp edges.

3. Environmental Impacts

Management of Chemicals in the Production Process

USA 1997 data indicate that about 57% of the toxic wastes were managed on-site through recycling, energy recovery, or treatment. About 11% of the wastes were managed off site. The remaining portion of toxic chemical wastes (about 33%) were released to the environment through direct discharges to air, land, water, and underground injection, or were disposed off-site.

The releases and transfers are dominated by large volumes of solvents which are used extensively in coating textile materials with plastic and other synthetic materials. The top three chemicals released by volume are methyl-ethyl-ketone (MEK), toluene, and methanol. These three account for about 64% of the industry's total releases.

Wastewater

Wastewater is, by far, the largest waste stream for the textile industry. Large volume wastes include wash water from preparation and continuous dyeing, alkaline waste from preparation, and batch dye waste containing large amounts of salt, acid, or alkali. Primary sources of biological oxygen demand (BOD) include waste chemicals or batch dumps, starch sizing agents, knitting oils, and degradable surfactants. Wet processing operations, including preparation, dyeing, and finishing, generate the majority of textile wastewater.

Types of wastewater include cleaning water, process water, non-contact cooling water, and storm water. The amount of water used varies widely in the industry depending on the specific processes operated at the mill, the equipment used, and the prevailing management philosophy regarding water use. Because of the wide variety of process steps, textile wastewater typically contains a complex mixture of chemicals.

Desizing, or the process of removing size chemicals from textiles, is one of the industry's largest sources of wastewater pollutants. In this process, large quantities of size chemicals used in weaving processes are typically discarded. More than 90% of the size used by the U.S. textile industry, or 90,000 tons, is disposed of in the effluent stream. The remaining 10% is recycled [EPA, 1996]. Desizing processes often contribute up to 50% of the BOD load in wastewater from wet processing.

Dyeing operations generate a large portion of the industry's total wastewater. The primary source is spent dye bath and wash water, typically containing by-products, residual dye, and auxiliary chemicals. Additional pollutants include cleaning solvents, such as oxalic acid. Of the 700,000 tons of dyes produced annually worldwide, about 10 to 15% of the dye is disposed of in effluent from dyeing operations [Snowden-Swan, 1995]. The average wastewater generation from a dyeing facility is estimated at between one and 8 thousand m³ per day. Dyeing and rinsing processes for disperse dyeing generate about 150 litres of wastewater per kg of product [Snowden-Swan, 1995].

Table 3.1 Typical BOD Loads from Preparation Processes.
PVA=polyvinyl alcohol; CMC=carboxy methyl cellulose;
1 pound= 450 g. [US EPA, 1995].

Process	Pounds of BOD per 1,000 Pounds of Production
Singeing	0
Desizing	
starch	67
starch, mixed size	20
PVA or CMC	0
Scouring	40-50
Bleaching	
peroxide	3-4
Hypochlorite	8
Mercerising	15
Heat setting	0

Many textile mills have few or no metals in their effluent. Dyes may contain metals such as zinc, nickel, chromium, and cobalt. In most dyes, metals are simply impurities generated during dye manufacture.

Salts in textile-dyeing wastewater is a potential problem area. Salt is used mostly to assist the exhaustion of ionic dyes, particularly anionic dyes, such as direct and fibre reactive dyes on cotton. Typical cotton batch dyeing operations use 20% to 80% of the weight of goods dyed, and the usual salt concentration in such wastewater is 2,000 ppm to 3,000 ppm. According to one study, a moderate-sized mill that dyed about 200 tonnes per week of cotton knit fabrics produced well over 25 tonnes of salts and a pH of over 10.

Emission to Air

The textile industry is a relatively minor source of air pollutants, but does emit a wide variety of chemicals in small amounts. Acetic acid and formaldehyde are two major emissions as well as solvent vapours. Nitrogen and sulphur oxides are emitted from boilers, and formaldehyde, acids, softeners, and other volatile compounds emissions from resin finishing and drying operations. Carriers and solvents may be emitted during dyeing operations.

Solid waste

Typical efficiency for using fabric averages from 72 to 94%. Cutting room solid waste generates a high volume of fabric scrap. This can be reduced by increasing fabric utilisation efficiency in cutting and sewing. Fabrication solid waste from carpets amounts to about 2% of an annual 900 million square yards of production (a value of $100 million). Although a large portion of cutting waste goes to landfill, some innovative programmes being implemented to recycle this material. Some facilities collect cotton lint for resale. Cotton trash, leaves, and stems collected during the yarn formation have been sold to farmers as animal feed.

4. Cleaner Production Opportunities

Most of the pollution prevention activities in the textile industry have focused on reducing chemical use, reusing process water, and reducing all solid waste forms – pallets, cardboard, etc. This section describes some of the pollution prevention opportunities for textile facilities. Much of the following section is based upon *Best Management Practices for Pollution Prevention in the Textile Industry* by the U.S. EPA Office of Research and Development.

The best way to reduce pollution is to prevent it in the first place. Some companies have creatively implemented pollution prevention techniques that improve efficiency and increase profits while at the same time minimising environmental impacts. This can be done in many ways such as reducing material inputs, re-engineering processes to reuse by-products, improving management practices, and employing substitution of toxic chemicals.

Management of Raw Materials

Raw material quality control programmes can be implemented by establishing specific and appropriate purchasing, packaging, and inventory control policies to prevent the ordering and use of untested materials. Textile companies can work with suppliers and develop purchasing codes that commit companies to using less-polluting raw materials. Facilities can also work with vendors to set acceptable guidelines for the purity and content of chemicals, like chemical specialities, which are typically of unknown composition to the textile mill.

Mills in the United Kingdom adopted *purchasing policies* as a way to reduce pollution. Researchers determined that 70% of woollen mills in the United Kingdom emitted pentachlorophenol (PCP), a harmful agricultural residue in wool, from their finishing plants. A study determined that it originated in the incoming greige goods. By specifying in company purchasing policies that they would not accept PCP-containing greige goods, the presence of PCP in wastewater decreased by 50%.

At its Monroe, North Carolina facility Bloomsburg Mills uses dye carrier chemicals, such as tetrachloroethylene, biphenyl, and trichlorobenzene, to promote level dyeing. In an effort to reduce regulatory burdens reporting, Bloomsburg Mills discussed with vendors the elimination of these chemicals. The company substituted a dye carrier containing methyl naphthalene with non-photochemically reactive solvents. This subsequently reduced the release of hazardous air pollutants by 91%.

Pre-screening raw materials can be used to determine interactions with processes, substrates, and other chemicals, as well as environmental effects, proper handling, and emergency procedures for chemicals. This can enable the early detection of mislabelled drums and changes in the formulation of a chemical specialty, and reduce the occurrence of costly production mistakes stemming from untested chemicals being processed. Protocol for incoming chemical quality control may consist of:

- Marking the date the container was opened.
- Checking pH, viscosity, density, conductivity, and colour.
- Comparing data with previous history and vendor's standard values.
- Entering data on a control chart for display.
- Maintaining records; and reviewing data with the vendor.

A committee at a facility in Lumberton, North Carolina pre-screened raw material (dyes and chemicals) to ensure that offensive smelling, toxic, and other objectionable material use were minimised in the production facility. In the event that raw materials with undesirable properties had to be used due to lack of alternatives, these raw materials were identified to all workers before use. This process entailed no capital costs. Benefits, such as the ability to dispose of waste treatment sludge since they did not contain toxics or metals, were realised.

Facilities can work with vendors to ensure that *packages* can be returned without being cleaned on site. Off site cleaning transfers chemical wastes back to the production facility, which may be better able to handle wastes. Chemical specialities should be purchased in returnable, reusable containers. Purchase of chemicals in bulk containers and intermediate bulk containers eliminates waste packing materials, and reduces spillage, handling costs, and worker exposure to chemicals.

At its Monroe, North Carolina facility, Bloomsburg Mills eliminated the disposal of 50 drums to the landfill each week by receiving and storing process chemicals in reusable totes and plastic drums. Amital began purchasing dyes and chemicals in intermediate bulk containers (IBCs) or in bulk. Drum disposal decreased by 69 per week, or about 3,500 annually. Pallet disposal decreased by 40 per week, or 2,000 annually.

Chemical Substitution

Since textile manufacturing is a chemically intensive process, a primary focus for pollution prevention should be on substituting less-polluting chemicals for textile process chemicals. Chemical substitution can eliminate chemical waste and the need for costly pollution control equipment. Opportunities for chemical substitution vary substantially among mills because of differences in environmental conditions, process conditions, product, and raw materials.

By *replacing solvents*, facilities can reduce waste, reduce costs associated with treatment systems, and increase worker safety. This is one of the best methods to prevent pollution. Some textile chemicals that can be substituted include desizing agents, dyes, and auxiliaries. For instance, replacing enzymes with hydrogen peroxide to desize starch can be cost-effective.

Improved fixation reactives can be used to reduce unreacted and degraded dye in spent bath and improve the reuse potential of wash water. High-temperature reactives can also be used in dyeing for simultaneous application of disperse and reactive dyes. This reduces energy use and eliminates the caustic bath required after disperse dyeing. Finally, auxiliaries, such as phosphates, can be substituted with acetic acid and EDTA to reduce phosphorus load in wastewater. New washing agents can also be used to increase wash efficiency, decrease water consumption, and improve fastness of reactives [Snowden-Swan, 1995].

Bloomsburg Mills substituted a solvent containing isopropanol and heptane as a suitable spot-washing alternative for trichloroethane, a hazardous air pollutant. Cleveland Mills Company reduced formaldehyde emission to the air by 84% by switching to low-shade change resins in the production process. Formaldehyde emissions at the mill dropped from 3,500 to 580 pounds per year. One textile facility found that they could replace 100 parts sodium sulphide with 65 parts alkaline solution containing 50% reducing sugars plus 25 parts caustic soda. As a result, sulphide levels dropped substantially to below 2 ppm [Snowden-Swan, 1995].

Waste can be reduced by replacing chemicals in some processes with mechanical or other *non-chemical treatment*. Instead, some textile mills add chemicals to counteract harmful side effects of other chemicals. In many cases, offending chemicals should be adjusted, substituted, or removed from a process, rather than adding chemicals to offset undesired side effects of other chemicals.

JP Stevens and Company, Inc. substituted chemical biocides, used in disinfecting air washers and cooling towers, with the use of ultraviolet light. During a 6-month test period, results showed improved worker safety, reduced discharge of biocides to the sanitary sewer, reduced chemical inventory and handling, improved work place air quality, and reduced pH and foaming problems in wastewater. The facility also showed enhanced air washer performance and more consistent control of work place air quality. The UV system operated with no required maintenance or repairs during the test. Based on chemical savings, the pay back is expected to be 11 to 18 months.

Process Modification

Process changes that optimise reactions and raw materials use can be used to prevent pollution. Modifications may include improved process control systems or changes in chemical application methods.

Mills have been moving towards *reduced bath ratio dyeing*. Bath ratio is defined as the weight of goods (or fabric) divided by the weight of the bath. Some chemicals, such as salt and lubricants, act on the dye bath, whereas others, such as dyes and softeners, act on the fabric. In each case, these chemicals are factored into either the weight of the bath or the weight of the fabric. Low bath ratio dyeing can save energy and reduce chemical use, because energy and chemical use depend on bath volume. At its Lumberton, North Carolina facility, Alamac Knits upgraded jet dyeing machinery to low-liquor-ratio machines with shorter cycles. This modification resulted in a decrease of between 60 and 70% of consumption of dye chemicals.

Table 3.2 *Example of costs and savings for dye bath reuse [US EPA, 1995].*

Description of Cost/Savings	Value ($)
Total Costs	
Lab and support equipment	9,000
Machine modifications, tanks, pumps, pipes	15,000-25,000
Annual Operating Costs	1,000-2,000
Total Savings (Annual)	
Dyes and chemicals	15,000
Water	750
Sewer	750
Energy	4,500

Use of *pad batch (cold) dyeing* for cotton, rayon, and blends conserves energy, water, dyes and chemicals, labour, and floor space. Pad batch dyeing methods do not require salt or chemical specialities, so this method can be a good way for facilities to reduce waste and save money. While pad batch dyeing is a cost-effective way for facilities to apply reactive dyes to cotton and rayon, this method may not achieve the desired initial fabric properties for all cottons. Pad batch dyeing is also not appropriate for dyeing synthetic fabrics. Salt consumption can be reduced from as much as 100% of weight of goods to zero. Water consumption for pad batch dyeing with beam wash-off is only 10% of the amount used to dye fabrics using beck methods, or 10 litres per kg of dyed fabric. Energy consumption can be reduced from about 20,000 BTUs per kg of dyed fabric for beck methods to under 4,000 BTUs per kg for pad batch methods with beam washing. In addition, labour costs and chemical use can be reduced up to 80% as compared to atmospheric beck methods.

Counter current washing decreases wastewater from preparation processes. Counter current washing is simple, easy to implement, and relatively inexpensive. Counter current washing is a technique to reuse the least contaminated water from the final wash for the next-to-last wash and so on until the water reaches the first wash stage. Wash water from the first stage is discharged. Counter current washing equipment can be retrofitted to any multi stage continuous washing operation, whether it is installed for different fabrics or for dyeing, printing, or reparation operations. Flow optimisation is usually a good pollution prevention activity to run in conjunction with counter current washing. Bloomsburg Mills uses counter current washing to conserve water during the scouring process.

The cleaner wash water enters the exit wash unit and counter flows back toward the dirtier units.

It is possible to reduce waste and increase production efficiency by *optimising process conditions*, such as temperature and time. Also, the processes themselves can be modified to increase efficiency. An American Corporation improved dyeing exhaustion by extending the length of time fabrics were dyed by 15 minutes. Results showed about a 60% drop in BOD and chemical oxygen demand (COD), a 20% drop in fats, oils, and grease, and a 98% drop in ammonia-nitrogen. This resulted in a saving of $35,000 annually.

A possibility to reduce waste and increase production efficiency is to *combine operations*. For instance, combined scouring and bleaching can save energy and water. Cold pad-batch methods can be used at room temperature for long desizing, scouring, and bleaching cycles.

Recovery, recycling, and reuse can be effective tools for minimising pollutant releases to the environment. By recovering solvents and raw materials, textile mills can reduce raw materials costs and can reduce pollution with little modification of existing processes. Water is widely used in the industry for processes ranging from dyeing to preparation and finishing. Raw materials, such as un-exhausted dyestuff and additives, can also be recycled.

Dye bath reuse is the process of analysing, replenishing, and reusing exhausted hot dye baths to dye further batches of material. Although not applicable to all processes, in some processes, dye bath reuse can reduce pollution concentrations and effluent volume and generally requires a smaller capital cost than pre-treatment plant construction. It also saves on the costs of dyes, chemicals, and energy. Dye bath reuse principles can also be applied to bleach baths. Depending on the machine, types of fabrics, and range of shades, after a couple of years, dye bath reuse could save companies about $21,000 per year for each machine. Amital saved a large amount of money by reusing dye baths and non-contact cooling water. The facility reduced its water consumption from 1,280 to 400 m³ per day and simultaneously increased production from 12 to 20 batches per day. Additionally, energy consumption for heating dye bath decreased substantially. The investment saved the company about $13,000 a month and paid for itself 30 days after implementation [Snowden-Swan, 1995].

Table 3.3 *Typical water savings using counter current washing [US EPA, 1995].*

Number of washing steps	Water savings (%)
2	50
3	67
4	75
5	80

Wet processing consumes a large amount of water from rinsing of textiles. *A yarn finishing company* drastically reduced wastewater pollution, soda (Na_2CO_3), and caustic consumption by implementing recycling. The new process involved reusing the rinse bath three times following mercerising rather than dumping the bath water after each use. The spent rinse water was then processed in an evaporator and concentrated caustic was reused in mercerising. The facility reduced suspended solids by 80%, COD by 55%, and neutralising soda in the wastewater by 70%.

Equipment Modification

An additional method to reduce waste is to modify, retrofit, or replace equipment. Some facilities are switching to computer-controlled dyeing systems, which analyse the process continuously and respond more quickly and accurately than manually controlled systems. In many cases, modifying equipment can provide source reduction by reducing the ratio of water and chemicals to textile goods.

The use of *automated process control equipment* has had a significant effect on the textile industry. Chemical dosing systems can be optimised to deliver the right amount of the right chemical at just the right time. These systems improve the efficiency and reliability of chemical reactions in the dye bath, ensuring more consistent and reproducible results. In addition, these systems reduce the tendency to overuse environmentally harmful chemicals, which may pass through treatment systems un-reacted or may react to produce undesirable by-products. Dosing systems can also reduce handling losses and equipment cleanup. Automated dosing systems are commercially available and are being adopted throughout the textile industry.

Amital, which produces acrylic yarn, implemented computer technology to automate dye bath flow and temperature in a new facility. This enabled the facility to precisely control the addition of auxiliary chemicals, such as retarders and levelling agents. Bloomsburg Mills upgraded instrumentation and process controls for the dyeing process from manual to computer control. The controlled time of the wash after dyeing has reduced water usage by 28% and fuel heat consumption per yard produced by 15.9%.

Continuous horizontal washers can conserve energy and water. Horizontal washers work for woven fabrics in a narrow weight range. These washers operate by spraying clean wash water on the top half pass of fabric as it makes a series of horizontal traverses upward in the machine.

Many textile companies use *continuous knit bleaching ranges* to reduce water consumption. These ranges consume less water, energy, and chemicals than batch preparation knitting equipment.

Companies can improve production efficiency and maintain low operating costs by incorporating *pollution prevention codes* into their management procedures. These codes can include a written commitment by senior management to ongoing waste reduction at each of the company's facilities and to include pollution prevention objectives in research and new facility design. Establishing training and incentive programmes and improving record keeping are other ways that companies can prevent pollution without changing industrial processes.

In dyeing operations, start ups, stop offs, and colour changes often result in losses of substrate, potential off-quality work, and chemically intensive cleaning of machines and facilities. *Scheduling dyeing operations to minimise machine cleaning* can have a considerable effect on pollution prevention. Changes required by scheduling activities generate significant amounts of waste for the textile mill. Machine cleaning is a significant contributor to waste load for textile facilities. A well planned dyeing schedule may reduce the number, of machine cleanings required and the pollution that results from start ups, stop offs, and colour changes.

Modifying *equipment cleaning practices* may reduce wastewater discharges and reduce solvent use. Substituting cleaning solvents with less toxic solvents can reduce hazardous waste generation and can simplify treatment of wastewater.

Good inventory management can reduce waste by using materials efficiently and reducing the likelihood of accidental releases of stored material. Although it may seem simplistic, housekeeping and work habits of chemical mixers can account for 10 to 50% of a mill's total effluent load in BOD, COD, metals, and organic solvents. Improvements in housekeeping generally cost little or nothing and improve employee morale, work place safety, and product quality.

Companies should establish safety procedures for receiving, storing, and mixing chemicals, and implement *workers training programmes*. These programmes should inform workers of the environmental impacts of chemicals and identify those most harmful to the environment.

References

Snowden-Swan, L. J. Pollution Prevention in the Textile Industries, in *Industrial Pollution Prevention Handbook*, Freeman, H. M. (Ed.), McGraw-Hill, 1995.

4 – Glass Industry

1. Glass Production

The Products and the Industry

The glass industry in the European Union is extremely diverse, both in the products made and the manufacturing techniques employed. Products range from intricate hand-made lead crystal goblets to huge volumes of float glass produced for the construction and automotive industries. Manufacturing techniques vary from small electrically heated furnaces in the ceramic fibre sector to cross-fired regenerative furnaces in the flat glass sector, producing up to 700 tonnes per day.

The total production of the glass industry within the EU in 1996 was estimated at 29 million tonnes, excluding ceramic fibres and frits (Table 4.1).

Container glass production is the largest sector representing around 60% of the total glass production. The sector covers the production of glass packaging i.e. bottles and jars. In 1997 the sector produced over 17.3 million tonnes of glass products from the 295 larger furnaces operating in the EU. The beverage sector accounts for approximately 75% of the total tonnage of glass packaging containers. The main competition is from alternative packaging materials steel, aluminium, cardboard composites and plastics. A significant development within the sector has been the increased use of recycled glass. The average rate of utilisation of post consumer waste within the EU container glass sector is approximately 50% of total raw material input, with some installations utilising up to 90% waste glass.

The diversity of the glass industry results in the use of a wide range of raw materials. A main environmental issue is the control of dust from the handling of fine materials. The main raw materials for melting are glass forming materials (e.g. silica sand, cullet), intermediate/modifying materials (e.g. soda ash, limestone, feldspar) and colouring/decoloring agents (e.g. iron chromite, iron oxide).

Table 4.1 *Approximate sector based breakdown of glass industry production (excluding ceramic fibre and frit sectors).*

Sector	% of Total EU Production (1996)
Container Glass	60
Flat Glass	22
Continuous Filament Glass Fibre	1.8
Domestic Glass	3.6
Special Glass	5.8
Mineral Wool	6.8

The Sources

The text is a summary of the IPPC (European Commission Integrated Pollution Prevention and Control) *Reference Document on Best Available Techniques in the Glass Manufacturing Industry,* December 2001.

The most widely used classification of glass type is by chemical composition, which gives rise to four main groupings:

1. Soda lime glass.
2. Lead crystal glass and crystal glass.
3. Borosilicate glass.
4. Special glasses.

The first three of these categories account for over 95% of all glass produced. The thousands of special glass formulations produced mainly in small amounts account for the remaining 5%. With very few exceptions most glasses are silicate based, the main component of which is silicon dioxide (SiO_2). Stone wool is an exception to this classification of glass types in that the typical chemical composition does not fit into any of these categories.

The vast majority of industrially produced glasses have very similar compositions and are collectively called soda-lime glasses. A typical soda-lime glass is composed of 71-75% silicon dioxide (SiO_2 derived mainly from sand), 12-16% sodium oxide ("soda" Na_2O from soda ash – Na_2CO_3), 10-15% calcium oxide ("lime" CaO from limestone – $CaCO_3$) and low levels of other components designed to impart specific properties to the glass. It is obvious that glass manufacturing leads to important CO_2 emissions.

Historical Origins

Glassy materials do occur naturally, for example, obsidian is often found in volcanic areas and has a composition comparable to man-made glass. This material, which consists mainly of silicon dioxide, and sodium and calcium compounds, was used by early man to make arrowheads, spearheads and knives.

It is thought that glass making originated in Egypt and Mesopotamia, but developed later and independently in China, Greece and the Northern Tyrol. Ancient glass manufacture is believed to be linked with the production of ceramics or bronze, where it could have originated as a by-product. Glass manufacturing in Europe developed further in the Middle Ages, and Venice became the European centre of glass art. In the 14th century, glass workshops were set up all over the continent and at the same time the manufacture of flat glass for glazing developed in France.

Drinking glasses and bottles were main products. For centuries, window glass was blown with a glass-blowing pipe into large cylindrical bodies, cut up and ironed flat while still hot. Only limited glass quantities could be handled and the window glass was very small.

In the 18th century, some factories were already producing more than 1 million bottles per year (around 3 tonnes/day), by manual mouth-blown techniques. During the industrial revolution of the 19th century, technical progress accelerated: furnaces were heated with coal instead of wood; the first automatic machines were used; and blowing was done using compressed air in metallic moulds. At the end of the 19th century, the continuous furnace was invented by Friedrich Siemens, allowing large-scale continuous production and the use of machinery.

Two important steps were taken in the 20th century: The full mechanisation of bottle manufacture with the introduction of the first automatic IS (individual section) machine around 1920, and the invention of the float process for flat glass in 1962. Today, the production of an IS machine can be above 500 bottles/minute and the production of float can be up to 900 t/d.

2. The Technologies

Glass Melting Technologies and Energy Use

Melting, the combination of the individual raw materials at high temperature to form a molten glass, is the central phase in the production of glass. The melting process is a complex combination of chemical reactions and physical processes, and melting can be divided into several stages: heating; primary melting; fining and homogenisation; and conditioning. Glass making is a very energy intensive activity and the choice of energy source, heating technique and heat recovery method are central to the design of the furnace. The same choices are also some of the most important factors affecting the environmental performance and energy efficiency of the melting operation. The three main energy sources for glass making are natural gas, fuel oil and electricity.

The ovens used were originally not energy saving, but today several energy efficient ovens are in common use.

Regenerative furnaces utilise regenerative heat recovery systems. Burners are usually positioned in or below combustion air/waste gas ports. The heat in the waste gases is used to preheat air prior to combustion, by passing the waste gases through a chamber containing refractory material, which absorbs the heat. The furnace only fires on one side at a time. After about twenty minutes, the firing is reversed and the combustion air is passed through the chamber previously heated

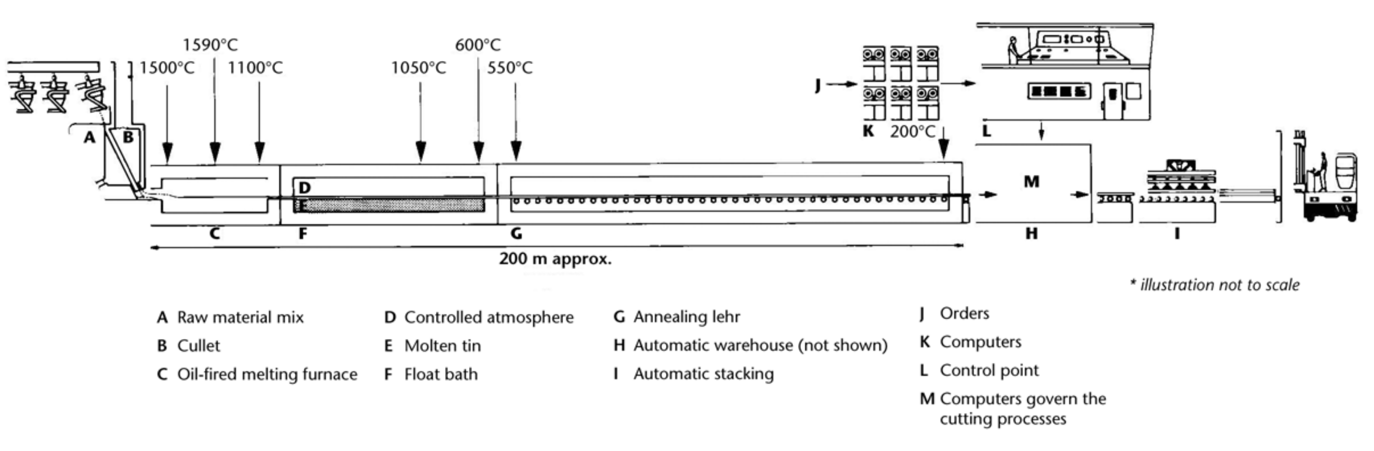


Figure 4.1 *The float glass process.*

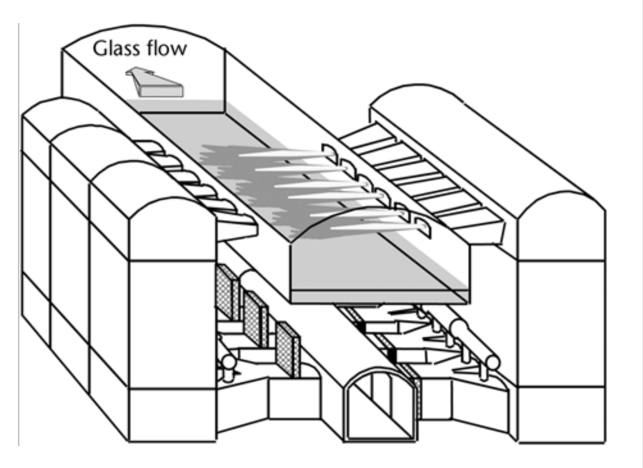


Figure 4.2 *A cross-fired regenerative furnace.*

by the waste gases. Preheat temperatures up to 1400°C may be attained leading to very high thermal efficiencies.

Recuperative furnaces utilise heat exchangers (termed recuperators) for heat recovery, with continuous preheat of combustion air by the waste gases. Air preheat temperatures are limited to around 800°C for metallic recuperators. The specific melting capacity (per unit of melter area) of recuperative furnaces is around 30% lower than for a regenerative furnace. The burners are located along each side of the furnace, transverse to the flow of glass, and fire continuously from both sides. This type of furnace is primarily used where high flexibility of operation is required with minimum initial capital outlay, particularly where the scale of operation is too small to make the use of regenerators economically viable.

Oxy-fuel firing involves the replacement of the combustion air with oxygen (>90% purity). The elimination of the majority of the nitrogen from the combustion atmosphere reduces the volume of the waste gases by about two thirds. Therefore, furnace energy savings are possible because it is not necessary to heat the atmospheric nitrogen to the temperature of the flames. The formation of thermal NO_x is also greatly reduced. In general, oxy-fuel furnaces have the same basic design as unit melters, with multiple lateral burners and a single waste gas exhaust port. However, furnaces designed for oxygen combustion do not utilise heat recovery systems to pre-heat the oxygen supply to the burners.

Electric furnaces consist of a refractory lined box supported by a steel frame, with electrodes inserted either from the side, the top or more usually the bottom of the furnace. Energy for melting is provided by resistive heating as the current passes through the molten glass. The technique is commonly applied in small furnaces particularly for special glass. There is an upper size limit to the economic viability of electric furnaces, which depends on the cost of electricity compared with fossil fuels. The replacement of fossil fuels in the furnace eliminates the formation of combustion products.

Combined fossil fuel and electric melting can take two forms: predominantly fossil fuel firing with electric boost; or predominantly electrical heating with a fossil fuel support. Electric boosting is a method of adding extra heat to a glass furnace by passing an electric current through electrodes in the bottom of the tank. A less common technique is the use of gas or oil as a support fuel for a principally electrically heated furnace.

Process Inputs and Outputs

The core process inputs can be divided into four main categories:

1. Raw materials (those materials which form part of the product).
2. Energy (fuels and electricity).
3. Water.
4. Ancillary materials (processing aids, cleaning materials, water treatment chemicals, etc).

Glass industry raw materials are largely solid inorganic compounds, either naturally occurring minerals or man-made products. The glass industry as a whole is not a major consumer of water, the main uses being cooling, cleaning and batch humidification. Glass making is an energy intensive process and therefore fuels can form a significant input to the processes.

The core process outputs can be divided into five main categories:

1. Product.
2. Emissions to air.
3. Liquid waste streams.
4. Solid process residue.
5. Energy.

All of the sectors within the glass industry involve the use of powdered, granular or dusty raw materials. The storage and handling of these materials represents a significant potential for dust emissions. The major environmental challenges for the glass industry are emissions to air and energy consumption. Glass making is a high temperature, energy intensive activity, resulting in the emission of products of combustion and the high temperature oxidation of atmospheric nitrogen; i.e. sulphur dioxide, carbon dioxide, and oxides of nitrogen. Furnace emissions also contain dust and lower levels of metals. It is estimated that in 1997 the glass industry emissions to air amounted to around of 0.7% of total EU emissions of these substances. Total energy consumption by the glass industry was approximately 265 PJ.

The emissions from downstream activities can vary greatly between the different sectors. Although there are similarities in the melting techniques used in many sectors the downstream activities tend to be specific. Emissions to air can arise from: coating application and/or drying; secondary processing (e.g. cutting, polishing, etc); and from some product forming operations (e.g. mineral wool, and ceramic fibre). In general, emissions to the water environment are relatively low and there are few major issues that are specific to the glass industry.

A characteristic of most of the sectors is that the great majority of internally generated glass waste is recycled back to the furnace. The main exceptions to this are the continuous filament sector, the ceramic fibre sector and producers of quality sensitive products in the special glass and domestic glass sectors. The mineral wool and frits sectors show a wide variation in the amount of waste recycled to the furnace ranging from nothing to 100% for some stone wool plants.

3. Cleaner Technologies Options

Primary Techniques

A glass furnace is a very dynamic environment and any changes to the chemistry or operating conditions can have consequent effects within the melting process and on emissions. A low level of emission from material carry over is achieved by maintaining a level of moisture in the raw materials and by controlling the batch blanket coverage, particle size, gas velocity and burner positioning. The most important factors affecting volatilisation are temperature, water vapour content in the furnace atmosphere, and the velocities of the gases at the surface of the melt.

Sodium chloride can be a significant factor in emissions of dust and chlorides. It is used in some special glasses as a refining agent, but is more usually present as a low level impurity in soda ash made by the Solvay process. Pressure from the Glass Industry has led soda ash producers to lower NaCl levels significantly in recent years (now generally around 1 kg/tonne).

The emission levels achievable using primary techniques are difficult to quantify, because of the wide range of factors that can affect the results and the wide variation in furnace types and glass formulations. Average mass emissions are around 0.4 kg/tonne of glass melted, and the majority of the emission concentrations fall into the range of 100-300 mg/m³. In general, for other compositions the optimisation of primary techniques could be expected to reduce emissions by 10-30%.

Melting Technique Selection

The choice of melting technique depends on many factors but particularly the required capacity, the glass formulation, fuel prices, and existing infrastructure. The choice is one of the most important economic and technical decisions made for a new plant or for a furnace rebuild. From an environmental perspective, melting techniques that are inherently less polluting or can be controlled by primary means are generally preferred to those that rely on secondary abatement.

Regenerative furnaces are generally more energy efficient than other conventional fossil fuel fired furnaces due to the more efficient combustion air preheating system. The low energy use per tonne of glass melted leads to reductions in many of the pollutants associated with combustion. However, the high preheat temperatures favour higher NO_x formation. Recuperative furnaces are less energy efficient than regenerative furnaces, but still recover a substantial amount of heat via the recuperator system. Further improvements in energy efficiency are possible using further techniques, e.g. electric boost, waste heat boilers, gas preheating, and batch/cullet preheating.

Materials Handling

The diversity of the Glass Industry results in the use of a wide range of raw materials. The majority of these materials are solid inorganic compounds, either naturally occurring minerals or man-made products. They vary from very coarse materi-

Table 4.2 *Theoretical energy requirements for melting common glass formulations.*

Parameter	**Type of glass**		
	Soda-Lime (Flat/Container Glass)	Borosilicate (8% B_2O_3)	Crystal Glass (19% PbO)
	Energy requirement (GJ/tonnes)		
Heat of reaction	0.49	0.41	0.40
Enthalpy of glass	1.89	1.70	1.69
Enthalpy of gases emitted	0.30	0.14	0.16
Theoretical energy requirement	2.68	2.25	2.25

als to finely divided powders. Liquids and, to a lesser extent, gases are also used within most sectors. There are very few issues regarding emissions to air from materials handling that are specific to the Glass Industry. Bulk powder materials are usually stored in silos, and emissions can be minimised by using enclosed silos, which are vented to suitable dust abatement equipment such as fabric filters. Where practicable collected material can be returned to the silo or recycled to the furnace.

4. Techniques for Controlling Emissions to Air

Particulate Matter – Dust – and Metals

The nature of the dust (particulate matter) emission from glass furnaces varies for different processes, but depends mainly on the furnace design and operation, and on the glass composition. The three main sources of dust from melting are:

- Batch material carry over.
- Volatilisation and reaction of substances from batch materials and the glass melt.
- Metals impurities in the fuels.

The main sources of metals are impurities in raw materials, metals in raw materials/additives used to impart specific properties (e.g. lead oxides, and colorants/decolorants), cullet and fuel. External cullet is an important source of metal contamination particularly for lead (in some cases >400 ppm) but also for other metals for example, mercury contamination can occur if cullet contains mercury vapour light tubes.

There are three main approaches to controlling emissions of metals either within the dust or as gaseous components.

1. Raw material selection to minimise contamination and where practicable to use alternative additives. Raw material selection includes cullet sourcing and sorting.
2. Dust abatement techniques, particularly bag filter systems and electrostatic precipitators. Where emissions contain significant metal concentrations high efficiency dust abatement systems can generally reduce emissions to less than 5 mg/Nm³.
3. Gaseous metal emissions (e.g. selenium) can be substantially reduced by the use of dry or semi-dry scrubbing techniques in combination with dust abatement. In some instances, and particularly in Germany, a major factor in the driving force for the installation of dust abatement combined with dry or semi-dry scrubbing has been the reduction of metal emissions.

The collection of particulate emissions use most importantly electrostatic precipitators and bag filters. The electrostatic precipitator (EP) consists of a series of high voltage discharge electrodes and corresponding collector electrodes. Particles are charged and subsequently separated from the gas stream under the influence of the electric field. EPs are very effective in collecting dust in the range 0.1 μm to 10 μm, and overall collection efficiency can be 95-99%. Actual performance varies depending mainly on waste gas characteristics and EP design.

In practice the collected dust can be recycled in most cases and depending on the sorbent chosen the material can replace a portion of the other raw materials particularly sodium sulphate (and where appropriate fluoride and lead containing materials). Problems could occur in the Container Glass Sector where the sulphate requirements for a reduced glass, especially with high cullet levels, are very low. This could limit the potential for recycling dust especially if high sulphur fuel oil is used, and a portion of the collected dust would have to be disposed of off-site.

Oxides of Nitrogen, NO_X

Due to the high temperatures in glass furnaces (up to 1650°C and 2000°C in the flame) the major source of NO_X is thermally generated NO_X, arising from the oxidation of nitrogen in the combustion atmosphere at temperatures above 1300°C. The main sources of the nitrogen are combustion air, atomising air (in oil fired furnaces), and air leakage into the furnace. The predominant species is NO (90-95%) formed by the reaction $N_2 + O_2 \rightarrow 2NO$. Levels of NO_2 are very low, and most NO_2 detected in the emissions results from atmospheric oxidation of NO. The conditions in the furnace are such that nitrous oxide (N_2O) is not detected in the emissions.

The main factors influencing NO_X formation are, flame temperature, oxygen content in the reaction zone and the residence time in the high temperature zone of the flame. The primary control measures for NO_X seek to generate those conditions least favourable for NO_X formation, i.e. to avoid the simultaneous presence of nitrogen and oxygen at high temperature. The flame temperature can be reduced by reducing the combustion air preheat temperature. For example, the combustion air temperatures in recuperative furnaces are significantly lower than in regenerative furnaces, resulting in lower flame temperatures and lower NO_X concentrations. If the fuel and air/oxygen are injected at the same place in the burner, a flame is produced with a hot oxidising primary zone close to the port and a cooler secondary zone further away. The majority of the NO_X is produced in the hottest zone. Therefore, by reducing the proportion of either the air or the fuel injected at the burner the maximum temperature and the NO_X formation are reduced. The remaining fuel or air is added later in the combustion zone. Emission reductions of up to 35% can be achieved using this technique.

Special furnace designs have been developed which reduce NO$_x$ emissions, e.g. the low-NO$_x$ melter. These designs have been very successful but there are certain process constraints that limit their applicability. The FENIX process is a combustion optimisation package based on primary measures, that is tailored for a specific furnace. Results of 510 mg/Nm^3 and around 1.1 kg/tonne of melt have been reported. Oxy-fuel firing involves the replacement of the combustion air with oxygen. The elimination of the majority of the nitrogen from the combustion atmosphere reduces the volume of the waste gases by about two thirds. Therefore, energy savings are possible because it is not necessary to heat the atmospheric nitrogen to the temperature of the flames.

Nitrates are used in glass manufacture as oxidising agents and also as fining agents. By far the most common nitrate used is sodium nitrate, but in some special glass applications potassium or barium nitrate are also used. Although sodium nitrate acts as a fining agent, its primary use is as an oxidising agent, and in most applications sodium sulphate would be the preferred fining agent. During the melting process the nitrates dissociate to form NO, NO$_2$, N$_2$, and O$_2$. The O$_2$ is used to oxidise the melt (particularly iron Fe^{2+} to Fe^{3+}) to give a very clear glass, and to oxidise any organic components of the batch materials.

Oxides of Sulphur, SO$_x$

The main techniques for controlling SO$_x$ emissions are fuel selection, batch formulation and acid gas scrubbing. In oil fired processes the main source of SO$_x$ is the oxidation of sulphur in the fuel. In conventional glass making, sulphates are the main source of SO$_x$ emissions from batch materials. Sulphates are the most widely used fining agents and are also important oxidising agents. In most modern glass furnaces the levels of batch sulphates have been reduced to the minimum practicable levels, which vary depending on the glass type. With closed loop filter dust recycling, the SO$_x$ emission levels observed today, are generally in the range of 200-800 mg/Nm^3 for natural gas firing and 800-1600 mg/Nm^3 with 1% S fuel oil. The majority of installed SO$_x$ scrubbing systems operate with dry lime scrubbing at a temperature of around 400°C, which is the waste gas temperature obtained from an efficient regenerative type furnace. At these temperatures, an SO$_x$ reduction of around 50% can be achieved. An improved SO$_x$ reduction rate can be reached at temperatures around 200°C and with a humid atmosphere but this involves further considerations.

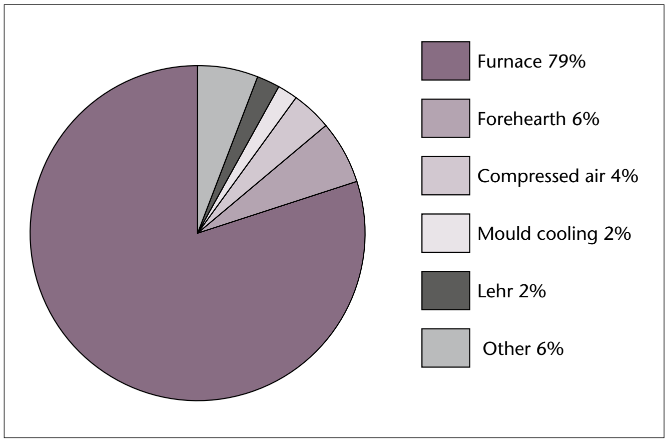


Figure 4.3 *Energy usage in a typical container glass plant.*

The most obvious way to reduce SO$_x$ emissions is to reduce the sulphur content of the fuel. The use of natural gas is increasing within the industry. For example, almost all fossil fuel fired glass wool furnaces, most continuous filament glass fibre furnaces, and around 50% of all container furnaces are fired on natural gas. The general experience within the industry is that conversion to natural gas results in higher NO$_x$ emissions, 25-40%, although with increased experience the differential is narrowing.

Oxides of Carbon

Oxides of carbon include carbon dioxide (CO$_2$) and carbon monoxide (CO). Carbon monoxide arises as a product of incomplete combustion and is rarely emitted from Glass Industry installations at a level to cause environmental concern. Significant levels are encountered in stone wool cupolas, but most plants are fitted with an afterburner to oxidise the emissions before release. Carbon dioxide arises from the combustion of fossil fuels or other organic materials, and from the decomposition of carbonate batch materials. Carbonates such as soda ash and limestone are the main sources of alkali metal oxides and alkali earth metal oxides in glass making. The only real alternative sources of these oxides are post consumer waste and process waste. That is cullet for glass processes, and process wastes, recycled product and slag (stone wool only) for mineral wool.

5. Energy Saving

Melting Technique and Furnace Design

The energy necessary for melting glass accounts for over 75% of the total energy requirements of glass manufacture. The cost of energy for melting is one of the largest operational costs for glass installations and there is a significant incentive for operators to reduce energy use. The choice of melting technique can have a great effect on the energy efficiency. The choice is largely determined by a range of economic considerations. The main factor is the desired production rate and the associated capital and operating costs over the life of the furnace. An important aspect of the operating costs is the energy usage, and in general the operator will choose the most energy efficient design possible.

In conventional fossil fuel fired furnaces the main difference in furnace design is whether the heat recovery system is based on regenerators or a recuperator. One of the main factors in the choice is the furnace size. Regenerative furnaces achieve a higher preheat temperature for the combustion gases, up to 1400°C compared with 800°C for recuperative furnaces, resulting in better melting efficiencies. The generally larger size of the regenerative furnaces also makes them more energy efficient than the smaller recuperative furnaces. This is because structural losses are inversely proportional to the furnace size, the main reason being the change in surface area to volume ratio. A modern regenerative container furnace will have an overall thermal efficiency of around 50%, with waste gas losses around 20%, and structural losses making up the vast majority of the remainder. The thermal efficiency of a recuperative furnace without heat recovery will be closer to 20%.

The energy recovered by regenerators may be maximised by increasing the quantity of refractory bricks employed. In practice, these may be organised in enlarged regenerator chambers or in separate but connected structures, giving the term multi-pass regenerators. The maximum theoretical efficiency of a regenerator is 80% because the mass of waste gases from a furnace exceeds that of the incoming combustion air and the heat capacity of exhaust gases exceeds that of the combustion air. In practical terms the efficiency will be limited by cost, and structural losses become more significant as the size of the regenerators increases. It is difficult to conceive a cost effective regenerator design with an efficiency greater than 70-75%.

Combustion Control and Fuel Choice

In recent decades the predominant fuel for glass making has been fuel oil, although the popularity of natural gas is increasing. Natural gas firing results in lower SO_X emissions but generally gives rise to higher NO_X emissions. This is because the natural gas flame is less radiant and has generally resulted in higher energy consumption, approximately 7-8%. However, as experience of gas firing increases performance levels progressively approaching those associated with oil firing can be achieved. Natural gas has a higher ratio of hydrogen to carbon and its use reduces overall emissions of CO_2 by up to 25% for a given pull rate. The developments in low NO_X burner systems have also resulted in energy savings. By reducing the amount of combustion air to close to stoichiometric levels, less energy is lost in the waste gas. The improvements made to the combustion system, the heat transfer systems and general process control during developments intended for NO_X reduction, have in many cases also led to improvements in furnace operation and efficiency.

Use of Recycled Glass, Cullets

The use of cullet, that is recycled glass, in a glass furnace can significantly reduce the energy consumption and its use is generally applicable to all types of furnace i.e. fossil fuel fired, oxy-fuel fired and electrically heated furnaces. Most sectors of the glass industry routinely recycle all internal cullet. The main exceptions are continuous filament glass fibre (where it is not considered possible due to quality constraints) and stone wool and frit production (where cullet as such is not produced). The base internal cullet level in the batch will usually be in the range of 10 to 25%. Cullet has a lower melting energy requirement than the constituent raw materials because endothermic chemical reactions associated with glass formation have been completed and its mass is 20% lower than the equivalent batch materials. Therefore, increasing the cullet level in the batch has the potential to save energy, as a general rule each 10% of extra cullet results in a 2.5-3.0% reduction in furnace energy consumption. The use of cullet generally results in significant cost savings as a result of the reduction in both energy and raw material requirements.

Distinction should be made between internal cullet (recycled glass from the production line) and external cullet (recycled glass from consumer or external industrial sources). The composition of external cullet is less well defined and this limits its application. High final product quality requirements can restrict the amount of foreign cullet a manufacturer can use. However, the Container Glass Sector is uniquely placed to take advantage of using significant quantities of foreign cullet from bottle recycling schemes. At the time of writing, except where special schemes are established, the significant use of external cullet is restricted to the Container Glass Sector and some areas of the Mineral Wool Sector. Glass sectors with higher quality demands or low availability of external cullet (e.g. flat glass) may try to contract large consumers to recycle the waste glass they generate.

Cullet use in container glass production varies from <20% to >90%, with an EU average in the region of 48%. Recycling rates vary widely between Member States depending on the material schemes for post-consumer glass collection. High quality container glass products have lower cullet levels than standard products.

In the Domestic Glass Sector, quality considerations generally prevent the use of external cullet in the process. Internal cullet usage is limited by the availability of cullet at the correct quality and composition. The average amounts of internal cullet used are 25% for soda-lime products, and 35% for lead crystal.

In addition to the substantial energy savings possible with cullet usage, there are a number of other important associated environmental benefits. In terms of furnace operation high cullet levels can also give other benefits such as low particulate emissions. Cullet is easier than batch to pre-heat. Emissions of CO_2, SO_X, NO_X and dust are greatly reduced due to reduced fuel usage and lower furnace temperatures. Emissions of other volatile substances may also be lower due to the reduced temperatures. The increased cullet usage reduces these raw material derived emissions and reduces the consumption of virgin raw materials.

Waste Heat Boiler

The principle of this technique is to pass waste gases directly through an appropriate tube boiler to generate steam. The steam may be used for heating purposes (space heating and heating of fuel oil storage and piping) or, via a suitable steam motor or turbine to drive electricity generation equipment or plant items such as air compressors or IS machine ventilator fans. Incoming gases from regenerators/recuperators are usually in the temperature range from 600°C to 300°C. The outlet temperature determines the available recoverable heat, which is limited to approximately 200°C due to the risk of condensation in the boiler and to ensure correct stack operation. Boiler tubes exposed to furnace waste gases can become coated with condensed materials (e.g. sodium sulphate, depending on the composition) and must be periodically cleaned to maintain recovery efficiency (less important for boilers operating downstream of dust removal devices). In situ cleaning may be carried out automatically by steam, by mechanical means, or by periodic maintenance.

Batch and Cullet Preheating

Batch and cullet is normally introduced cold into the furnace, but by using the residual heat of the waste gases to preheat the batch and cullet, significant energy savings can be possible. This only applies to fossil fuel fired glass furnaces. In the stone wool industry, predominantly cupola furnaces are used, which have a design that preheats the raw materials intrinsically.

Direct preheating involves direct contact between the flue gas and the raw material (cullet and batch) in a cross-counter flow. The waste gases are supplied to the preheater from the waste gas duct behind the regenerator. They pass through the cavities in the preheater, thereby coming into direct contact with the raw material. The outlet temperature of the cullet is up to 400ºC. The system incorporates a bypass that allows furnace operation to continue when preheater use is either inappropriate or impossible.

Indirect preheating is in principle a cross-counter flow, plate heat exchanger, in which the material is heated indirectly. Depending on the throughput, the material will normally be heated up from ambient temperature to approximately 300°C. The waste gases flow horizontally through the individual modules and will be cooled down by approximately 270°C-300°C.

These techniques have a number of environmental effects. In general, the energy savings have been between 10 to 20%, NO_X emission have been reduced, and emission of acidic compounds have been reduced to between 50% and 90%.

5 – Chlor-Alkali Manufacturing Industry

1. The Chlor-Alkali Industry

Industrial and Economical Development of the Chlor-Alkali Sector

The electrolytic production of chlorine from sodium chloride solution (brine), the chlor-alkali process, was introduced on an industrial scale around 1890, both with the diaphragm cell and the mercury cell process. The membrane cell process was not developed until 1970. Currently, 95% of world chlorine production is obtained by the chlor-alkali process.

Since the 1940s world chlorine production has risen enormously, on the back of the burgeoning demand for plastics, notably polyvinylchloride (PVC) and polyurethanes, the production of chloroaromatics such as chlorobenzene, solvents containing chlorinated hydrocarbons, and inorganic chlorine compounds. In 1995 it was about 44 million tonnes, EU accounting for about 24% of that capacity. After a fall at the beginning of the 1990s, production in western Europe now seems to be stabilised at around 9 millions tonnes per year (9.2 million tonnes in 1999).

The chlor-alkali process is one of the largest consumers of electrical energy. The chlorine production of a country is an indicator of the state of development of its chemical industry. The total value of western European chlor-alkali sector in 1995 production is 3 billion euros and the turnover generated by chlor-alkali related products amounted to some 230 billion euros, that is about 60% of the turnover of the west European chemical industry. Euro Chlor estimates that there are 46,000 employees involved in the direct production of chlorine in the EU. When chlorine derivatives and chlorine-dependent industry are included the number of employees is approximately two million.

The Sources

The text is a summary of the IPPC (European Commission Integrated Pollution Prevention and Control) *Reference Document on Best Available Techniques in the Chlor-Alkali Manufacturing Industry,* December 2001.

Technologies In Use

The main technologies applied for chlor-alkali production are mercury, diaphragm and membrane cell electrolysis, mainly using sodium chloride as feed or to a lesser extent using potassium chloride for the production of potassium hydroxide.

The co-production of chlorine and sodium hydroxide in fixed proportions – 1.128 tonnes of caustic (as 100% NaOH) per tonne chlorine produced – has always been a problem for the chlor-alkali industry. Both products are used for very different end uses with differing market dynamics and it is only by rare chance that demand for the two coincides. Depending on which demand is dominant, either can be regarded as a by-product and the price varies dramatically accordingly.

Chlorine itself is difficult to transport long distances; however it can be, and is, readily exported as ethylene-di-chloride (EDC), a precursor for PVC. Caustic soda is a globally traded commodity. Hydrogen is also a co-product (28 kg for 1 tonne of chlorine). Hydrogen is generally used on-site as a combustible or sent as a fuel to other companies. It can also be used on integrated sites for certain applications in particular because of its high purity: synthesis of ammonia, methanol, hydrochloric acid, hydrogen peroxide, etc.

Environmental Relevance of the Chlor-Alkali Industry

Inputs and pollutant outputs from the chlor-alkali industry are quite specific to the cell technology used, the purity of the incoming salt and the specifications of the products. Because of the huge amount of electricity needed in the process, energy can be considered as a raw material.

Historical mercury and PCDD/F (dibenzodioxin and dibenzofuran) contamination of land and waterways from mercury and diaphragm chlor-alkali plants is a big environmental problem at some sites. For many years, the mercury cell has been a significant source of environmental pollution, because some mercury is lost from the process to air, water, products and wastes. Inorganic mercury can be metabolised to form highly toxic methyl mercury by anaerobic bacteria, and this organic mercury is bioaccumulated in the food chain.

In the 1950s a chemical plant producing acetaldehyde discharged a spent catalyst containing organic mercury into Minamata Bay, Japan. A number of people (mostly fishermen) became seriously ill and some were disabled. This event was at the origin of environmental regulations in Japan and caused changes into mercury free technologies in some industrial sectors.

The chlor-alkali industry was the largest domestic user of mercury in 1989-90 in the USA and this could be expected to be the same in Europe. According to Euro Chlor, the total mercury emission to air, water and products from chlor-alkali plants in western Europe was 9.5 tonnes in 1998, ranging between 0.2-3.0 g Hg/tonne of chlorine capacity at the individual plants. Decision 90/3 of 14 June 1990 of the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPARCOM) recommends that existing mercury cell chlor-alkali plants should be phased out as soon as practicable, and no later than 2010.

As regards the diaphragm technology, due to the potential exposure of employees to asbestos and releases to the environment, the use of good practices is needed and some efforts are being made to replace the asbestos with other diaphragm material.

2. Processes and Techniques

The Basic Processes

Industrial chlor-alkali production, consisting of electrolysis of molten sodium salts (Figure 5.1), depends on three basic processes, the diaphragm cell, the mercury cell, and the membrane cell process. Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode.

At the anode, chloride ions are oxidised and chlorine (Cl_2) is formed. At the cathode in the mercury process a sodium/mercury amalgam is formed. Later hydrogen (H_2) and hydroxide ions (OH^-) are formed as sodium in the amalgam reacts with water in the denuder. In membrane and diaphragm cells, water decomposes to form hydrogen (H_2) and hydroxide ions (OH^-) at the cathode.

The *anode* reaction for all processes is:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

The *cathode* reaction is:

$$2Na^+(aq) + 2H_2O + 2e^- \rightarrow H_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

The *overall* reaction is:

$$2Na^+(aq) + 2Cl^-(aq) + 2H_2O \rightarrow 2Na^+(aq) + 2OH^-(aq) + Cl_2(g) + H_2(g)$$

The operation of a chlor-alkali plant is dependent on the availability of huge quantities of direct-current (DC) electric power, which is usually obtained from a high voltage source

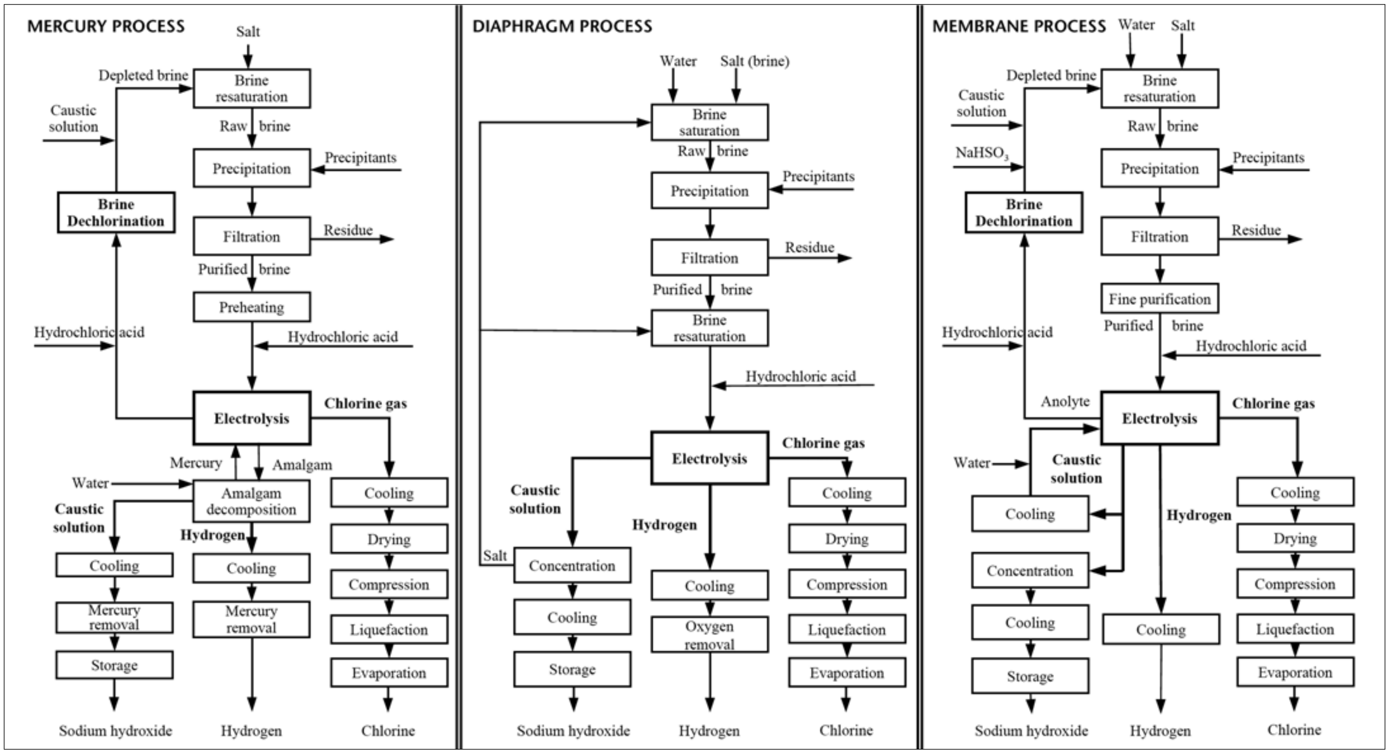


Figure 5.1 *Flow diagram of the three main chlor-alkali processes.*

of alternating current (AC). The lower voltage required for an electrolyser circuit is produced by a series of step-down transformers. Silicon diode rectifiers convert the alternative current electricity to direct current for electrolysis. The voltage is increased with increasing distance between the anode and the cathode. On the other hand, a close distance means a higher frequency of short-circuiting in the amalgam cell.

The Mercury Cell Process

The mercury cell process involves two "cells". In the primary electrolyser, the brine cell, purified and saturated brine, 25% sodium chloride, flows through an elongated, slightly inclined trough. In the bottom of this trough a shallow film of mercury (Hg) flows along with the brine. Closely spaced above the cathode, an anode assembly is suspended (see Figure 12.1a).

Electric current decomposes the brine passing through the narrow space between the electrodes, liberating chlorine gas at the anode and metallic sodium at the cathode. The chlorine gas accumulates above the anode and is discharged to the purification process. At the surface of the mercury cathode, the sodium forms a liquid amalgam (0.2-0.4% Na by weight) which flows to a separate reactor, called the decomposer or denuder, where it reacts with water in the presence of a graphite catalyst to form sodium hydroxide and hydrogen gas. The sodium-free mercury is fed back into the electrolyser and reused. The brine anolyte leaving the cell is saturated with chlorine and must be dechlorinated before being returned to the dissolvers.

The mercury process has the advantage over diaphragm and membrane cells that it produces a chlorine gas with nearly no oxygen, and a 50% caustic soda solution. However, mercury cells operate at a higher voltage than diaphragm and membrane cells and, therefore, use more energy (caustic soda concentration excluded). The process also requires a pure brine solution with little or no metal contaminants to avoid the risk of explosion through hydrogen generation in the cell. The amalgam process inherently gives rise to environmental releases of mercury.

The Diaphragm Cell Process

In the diaphragm process all reactions take place within one cell and the cell effluent contains both salt and caustic soda. A diaphragm is employed to separate the chlorine liberated at the anode, and the hydrogen and caustic soda produced directly at the cathode. Without the diaphragm to isolate them, the hydrogen and chlorine would spontaneously ignite and the caustic soda and chlorine would react to form sodium hypochlorite (NaClO) and sodium chlorate ($NaClO_3$). The diaphragm is usually made of asbestos. The saturated brine percolates through the diaphragm into the cathode chamber, where it is decomposed to approximately 50% of its original concentration. Heating caused by passage of current through the diaphragm cell raises the operating temperature of the electrolyte to 80-99ºC. The cell liquor containing ca. 11% caustic soda and 18% sodium chloride is evaporated to 50% NaOH by weight at which point all of the salt precipitates out.

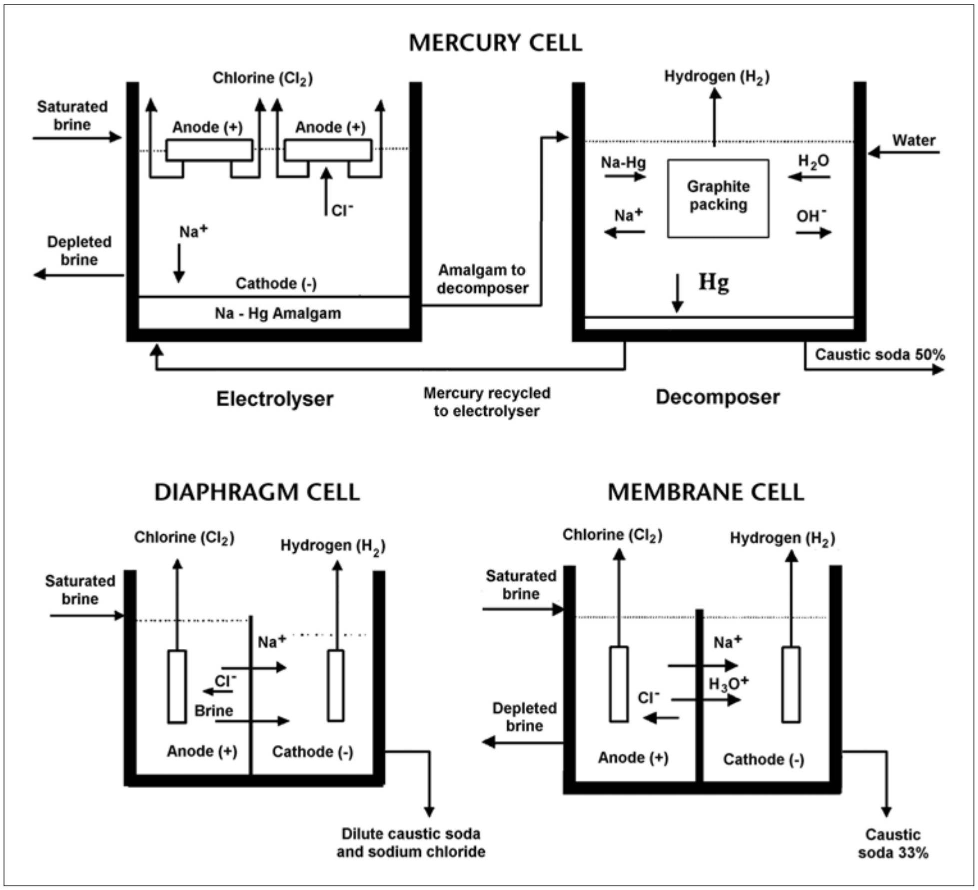


Figure 5.2 *Simplified scheme of chlorine electrolysis cells.*

Diaphragm cells have the advantage of operating at a lower voltage than mercury cells and operating with less pure brine than required by membrane cells. A disadvantage is that asbestos diaphragms inherently gives rise to environmental releases of asbestos. At the beginning the diaphragms were made of asbestos only and were rapidly clogged by calcium and magnesium ions coming from the brine. Beginning in the early 1970s, asbestos diaphragms began to be replaced by diaphragms containing 75% asbestos and 25% of fibrous fluorocarbon polymer polytetrafluoroethylene (PTFE) of high chemical resistance.

In western Europe electrolytic cell anodes were made of graphite until the late 1960s, when anodes of titanium coated with ruthenium oxide (RuO_2) and titanium oxide (TiO_2) were developed. The use of RuO_2 and TiO_2 coated metal anodes reduces energy consumption by about 10% and their life expectancy is higher. When graphite anodes were used, the diaphragm became inoperable after 90-100 days due to plugging of the diaphragm by particles of graphite. Nowadays, all plants in the European Union use metal anodes and the lifetime of the diaphragm is over one year.

The Membrane Cell Process

In this process, the anode and cathode are separated by a water-impermeable ion-conducting membrane. Brine solution flows through the anode compartment where chloride ions are oxidised to chlorine gas, while the sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution. Water added to the catholyte circuit is hydrolysed, releasing hydrogen gas and hydroxide ions, forming caustic soda typically at 32-35%. The solution is recirculated before it is discharged from the cell. The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment; therefore, the caustic soda solution produced does not contain salt as in the diaphragm cell process. Depleted brine is discharged from the anode compartment and re-saturated with salt.

The cathode material used in membrane cells is either stainless steel or nickel. The cathodes are often coated with a catalyst that is more stable than the substrate and that increases surface area and reduces over-voltage. The anodes used are metal. The membranes used in the chlor-alkali industry are commonly made of perfluorinated polymers and generally reinforced with PTFE fibres to improve the membrane mechanical strength.

Membrane cells have the advantage of producing a very pure caustic soda solution and of using less electricity than the other 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 caustic soda produced may need to be evaporated (using steam) to increase concentration to 50%, and the chlorine gas produced may need to be processed to remove oxygen. Furthermore, the brine entering a membrane cell must be of a very high purity, which often requires costly additional purification steps prior to electrolysis.

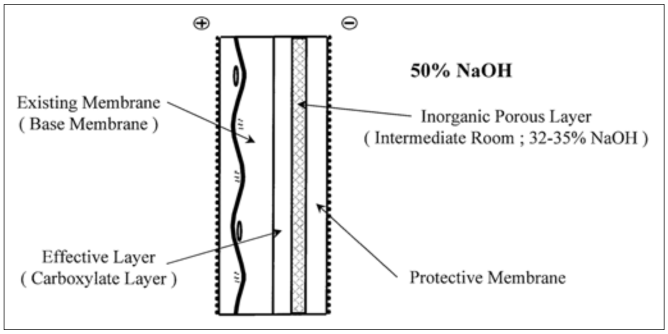


Figure 5.3 *Structure of Fx-50 membrane producing 50% caustic soda.*

The membrane electrolysis process uses ion exchange membranes. Asahi Glass (Flemion) installed the first industrial membrane plant in Japan in 1975 due to the pressure of Japanese environmental regulations and Japan was the first country to install the membrane process on a massive scale in the mid-1980s. Today, it is the most promising and fast-developing technique for the production of chlor-alkali and it will undoubtedly replace the other two techniques in time. Since 1987 practically 100% of the new chlor-alkali plants world-wide apply the membrane process. The replacement of existing mercury and diaphragm cell capacity with membrane cells is taking place at a much slower rate because of the long lifetime of the former and because of the high capital costs of replacement.

Auxiliary Processes

Apart from the cells, which remain the heart of the chlorine production line, there are other processing steps or equipment, common to amalgam, diaphragm and membrane technologies. These are:

- Salt unloading and storage.
- Brine purification and re-saturation.
- Chlorine processing.
- Caustic processing.
- Hydrogen processing.

The brine purification process consists of a primary system for mercury and diaphragm technologies and an additional secondary system for membrane technology. This operation is needed to avoid any undesirable components (sulphate anions, cations of Ca, Mg, Ba and metals) that can affect the electrolytic process.

Apart from sulphates and hardness ions, the brine may contain ammonium ions or organic nitrogen which are converted to nitrogen trichloride in the electrolytic cell. If concentrated in liquid form in downstream processes, NCl_3 may explode with disastrous results. Chlorination at a pH higher than 8.5 or hypochlorite treatment of the brine is capable of destroying a large proportion of the ammonium salt impurity.

Mercury and membrane systems usually operate with brine recirculation and re-saturation. Some diaphragm cell lines have a once-through brine circuit, whilst others employ brine saturation using the salt recovered from the caustic evaporators.

Chlorine and Caustic Soda Production, Storage and Handling

The products of the chlor-alkali process, chlorine and caustic soda, are both very reactive, toxic and corrosive and requires special precautions.

The chlorine mostly goes through a series of processes for cooling, cleaning, drying, compression and liquefaction before it can be used, although partly it is used as a dry gas, and very occasionally directly from the electrolysers. In the primary cooling process, the total volume of gas to be handled is reduced and a large amount of moisture is condensed.

Chlorine from the cooling system is more or less saturated with water vapour. Drying is accomplished in countercurrent sulphuric acid contact towers which reduce the moisture content to less than 20 ppm. After drying, chlorine gas might be scrubbed with liquid chlorine or treated with ultra-violet irradiation to reduce levels of nitrogen trichloride and then it may be compressed in a variety of compressors. Because of heat build-up from compression, multistage units with coolers between stages are usually necessary. The chosen liquefaction pressure and temperature chosen influence the choice of cooling media and the safety precautions necessary to operate safely.

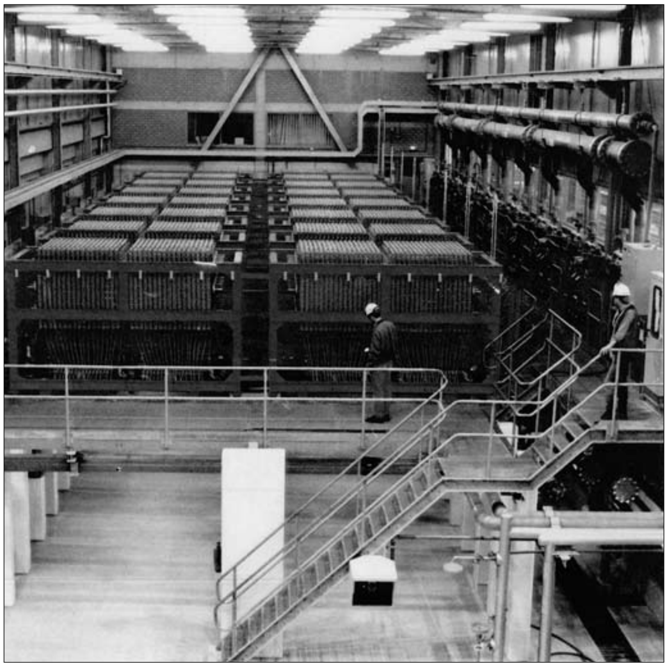


Figure 5.4 *View of a membrane cell room equipped with bipolar electrolysers.*

The caustic soda produced is normally pumped through a cooler, then through a mercury removal system (for the mercury process) and then to the intermediate and final storage sections. Because of its highly reactive and corrosive properties, caustic soda requires resistant construction materials for handling and storage. The solutions also require steam or electrical heating where temperatures can fall below the upper freezing point.

3. Environmental Impacts

Overall Consumption and Emission Levels of All Cell Plants

Inputs and pollutant outputs of the chlor-alkali industry are quite specific to the cell technology used but also depend on the specifications of the products (O_2 or CO_2 content, for example), the purity of the incoming salt and the geographical location of the plant. The inputs are primarily salt and water as feedstock; acids and chemical precipitants used to remove impurities in the input brine or output chlorine/caustic soda; cooling agents (CFCs, HCFCs, HFCs, ammonia, etc.) for liquefying and purifying the chlorine gas produced. The chlor-alkali process needs huge amounts of electricity and electrical energy is a major input. The main pollutant outputs which are common to all three electrolytic processes are chlorine gas emissions, spent acids, cooling agents, impurities removed from the input salt or brine.

The amalgam technology emits mercury through air, water, wastes and in the products. At present some 12,000 tonnes of mercury are contained in mercury cells in the EU. When the plants are converted or shut down, this mercury has the potential to be released into the global environment. Currently, there is no European Union policy or legislation on how to deal with this huge amount of pure mercury. In 2007 a proposal to outlaw export of Hg is developed by the EU Commission and prepares for long-term storage.

The main issue with the diaphragm technology is asbestos. Both the potential exposure of employees to asbestos and releases of asbestos to the environment are of concern. Historical mercury and PCDD/F (dibenzodioxin and dibenzofuran) contamination of land and waterways from mercury and diaphragm chlor-alkali plants is a big environmental problem at some sites. The contamination is due to fallout of mercury and historical disposal of graphite sludges, from the use of graphite anodes, and other wastes on and around the plant sites.

The membrane cell process has inherent ecological advantages over the two older processes, as it does not use mercury or asbestos, and it is the most energy efficient process. Despite these advantages, the change of technology to membrane cells has been slow in western Europe because most existing chlorine plants were installed in the 1970s with a plant life of 40-60 years and there has been no need for new production capacity. Nor has there been a legislative drive to change technology.

Inputs for the Production

Water is used in the process for preparation of the brine, for maintaining the water balance in the reaction to form NaOH in the membrane and mercury cells. Apart from the water needed for cooling, generally 2-2.5 m³ of water is consumed per tonne of chlorine produced for plants using a brine recirculation process. For waste brine processes, about 10 m³ of water per tonne of chlorine produced is required.

Energy is used both as electricity and as heat. About half of the energy expended is converted into the enthalpy of the products. The rest is converted into heat transferred to the air in the building and the products, which have to be cooled. The heat is partly recirculated through preheating of the brine. Surplus heat might also be used for heating surrounding buildings or for the concentration of caustic soda. Insulation of the cells and salt dissolvers reduces the need for ventilation of the cell room and increases the amount of heat transferable. The hydrogen produced in chlor-alkali plants can be used as a raw material in the synthesis of chemicals or as a fuel.

The total energy use associated with Best Available Technique (BAT) for producing chlorine gas and 50% caustic soda is less than 3,000 kWh (AC) per tonne of chlorine when chlorine liquefaction is excluded and less than 3,200 kWh (AC) per tonne of chlorine when chlorine liquefaction and evaporation are included. For a plant with an annual capacity of 150,000 tonnes of chlorine this approaches 500 GWh.

Chlorine, Mercury and Asbestos Emissions

Because chlorine is a hazardous gas, leakage from electrolytic cells should be avoided. However, small amounts of chlorine might be emitted through leakage and handling of the cell covers. Chlorine detectors are used for immediate indication of any significant leakage. Chlorine concentration in the electrolysis hall can be below odour detection level if the cells are operated in a slight vacuum. Estimated emissions vary from close to zero to 16 g chlorine per tonne of chlorine produced.

The total mercury emission to air, water and products from chlor-alkali plants in western Europe was 9.5 tonnes in 1998, ranging from 0.2-3.0 g Hg/tonne of chlorine capacity at the individual plants.

The majority of mercury losses occur, however, in the various process wastes. For 1997, OSPARCOM reported 31 tonnes of mercury in solid wastes not recycled. Mercury in solids disposal plant-by-plant were in the range of 0-84 g Hg/tonne chlorine capacity in 1998, as reported by Euro Chlor. Euro Chlor reports 27 g in 1977, 8 g in 1987 and around 2 g in 1997 mercury per tonne chlorine. The industry moved in the 1990s to membrane cell process. The first European membrane plant opened in 1983 at Akzo in Rotterdam.

Mercury-contaminated waste water streams are collected from all sources and generally treated in a waste-water treatment plant. The mercury level in chlorine is negligible, i.e. less than 0.001 g/tonne. Hydrogen and caustic soda from amalgam chlor-alkali plants contain a certain amount of mercury, and purification is needed before the products are sold.

Asbestos emissions from the baking furnace were calculated as being about 5 g per year, corresponding to an emission of 0.036 mg of asbestos per tonne of chlorine capacity in a plant of 140,000 tonnes annual chlorine capacity. Asbestos is considered to be carcinogenic and enter the human body by either inhalation or ingestion. At the end of the lifetime of an asbestos diaphragm, the asbestos is removed from the cathode can by means of high pressure water-jet cleaning. Asbestos is collected with the rinsing water and can be discharged. A filter press can be installed to remove asbestos from the rinsing water. Reported emissions give values of under or equal to 30 mg/l.

Solid Wastes

Solid wastes in the diaphragm process consist of wastes generated during brine purification and scrapped cell parts, including cell covers, piping and used diaphragms. The asbestos diaphragms in modern diaphragm chlor-alkali plants have a lifetime of approximately one year. Reported figures are in the range of 0.09 to 0.2 kg solid residue per tonne of chlorine capacity (13.5-30 tonnes of asbestos per year, with a chlorine capacity of 150,000 tonnes). 0.1 kg per tonne chlorine capacity is the medium average reported by the industry. Discarded cell parts are either landfilled on-site or sent off-site for disposal, depending on the legislation of the country.

Chlorinated Hydrocarbons

Chlorinated hydrocarbons ($C_XCl_YH_Z$) are formed in a reaction between organic contaminants in the electrolyser and free oxidants. Examples of chlorinated hydrocarbons found in the effluent of chlor-alkali plants are chloroform (CCl_3H), dichloromethane (CCl_2H_2), carbon tetrachloride (CCl_4), tetrachloroethylene (C_2Cl_4). The emissions of chlorinated hydrocarbons from chlor-alkali plants have decreased significantly after the switch from graphite to metal anodes. The releases of chlorinated hydrocarbons is normally low but can be higher for plants that destroy the produced bleach in the chlorine destruction unit and discharge the remaining liquid. Discharges to water measured as extractable organic halogens (EOX), were in the range of 0.03-1.16 g/tonne chlorine capacity, where the higher figure is reported from a plant with bleach destruction.

Safety Aspects of Chlor-Alkali Plants

Safety aspects are of much concern in the chlor-alkali industry. Production, loading, storage and transportation of chlorine require compliance with certain provisions designed to minimise the possibility of incidents giving rise to danger to operators, the public or the plant. A general policy for the prevention of and response to industrial accidents is usually based on the prevention principle (e.g. Annex IV to IPPC Directive), i.e. the plant is constructed and operated in such a way as to prevent any uncontrolled development and to reduce the consequences of accidents.

In the European Union the SEVESO Directive (82/501/EEC), regulates control of major industrial hazards. The “SEVESO II” Directive (96/82/EC) represents a fundamental revision of the Directive. Storage and processes using chlorine are part of the scope of the Directive starting from 10 tonnes, along with hydrogen starting from 5 tonnes, while the alkali solutions are not covered.

4. Cleaner Production Opportunities

Safety Measures

In hazard and risk assessment studies, the design of chlor-alkali installations and equipment and the operating and maintenance routines are examined in detail to reduce the risks for people and the environment at source as much as possible. The most important substance to consider is chlorine. Preventative measures are the most important, although corrective and emergency measures are also of importance. General measures related to safety are mainly linked to reliable and efficient safety management systems based on:

- Training of personnel including basic knowledge of chlorine properties, correct operating practice, emergency procedures.
- Identification and evaluation of major hazards including written information for personnel about safety measures in normal and abnormal conditions.
- Instructions for safe operation including permanent monitoring of the installations under the responsibility of a designated person, good compliance with safety parameters defined in the safety report, including periodic inspection and control of materials specified according to safety hazards, and maintenance programmes for the installations.
- Planning for emergencies and recording of accidents and near-misses.

The safety management systems should be completed with appropriate technical measures, such as high quality preventive and protective systems, enhanced leak detection and leak isolation, and good protection of employees and temporary workers on the site with appropriate and well maintained equipment.

On-Site Re-Concentration of Spent Sulphuric Acid

Concentrated sulphuric acid (92-98%) is used to dry chlorine. Up to 20 kg of acid is consumed per tonne chlorine produced. The spent acid usually becomes a waste product or one that requires reprocessing. The spent acid can be used to control pH in process and waste water streams or to destroy surplus hypochlorite. It can be returned to an acid producer for re-concentration or sold to any user who can accept this quality of acid. Sulphuric acid can also be re-concentrated on-site in closed loop evaporators which reduces the consumption to 0.1 kg of acid per tonne of chlorine produced. The spent sulphuric acid is concentrated to 92-98% by indirect heating with steam. Materials used must be highly corrosion-resistant to avoid corrosion problems, in particular if the feed acid is polluted. Main achievements leads to significant reduction in sulphuric acid consumption.

Treatment of Wastewater Containing Free Oxidants, Including Bleach Destruction

The chlor-alkali industry potentially discharges waste water containing free oxidants such as Cl_2, Br_2, hypochlorite (OCl^-), hypobromite (OBr^-) and NH_XBr_Y. The free oxidants can be destroyed by chemical reduction, by catalytic reduction or by thermal decomposition. It is also possible to recover the chlorine by acidification of the waste hypochlorite stream. This would seem especially attractive to large chlorine plants when considerable amounts of spent acid are available (spent sulphuric acid from chlorine drying). If the quantities are low, the hypochlorite produced can be recycled in the cell brine at low pH.

Carbon Tetrachloride-Free Chlorine Liquefaction and Purification

Although outlawed, carbon tetrachloride is still used at some locations for removal of nitrogen trichloride (NCl_3) and for absorption of tail gas. However, other alternatives which do not use CCl_4 are available and applicable to existing plants. First of all, if chlorine can be used directly without liquefaction it may not be necessary to remove the NCl_3. A preventative measure to avoid the accumulation of NCl_3 is to specify low ammonium ion concentration in purchased salt (for example vacuum salt without addition of ferrocyanides to avoid caking). Another is to purify the brine to remove ammonium ions (for example by chlorination at a pH higher than 8.5 or hypochlorite treatment of the brine). Available techniques for NCl_3 destruction, not using CCl_4, include adsorption with activated carbon filters, ultraviolet light, and high metal temperatures, particularly of copper base alloys at temperatures of 80-100°C, to decompose NCl_3.

Mercury Emission Abatement

Although mercury emissions have been greatly reduced, it is understood from comparing performances of applied abatement techniques that improvements are still possible. Good housekeeping based on motivated staff is of great importance for the reduction of air emissions. Monitoring of possible leakages and recovery of mercury is important to react as quickly as possible to avoid mercury evaporation. Continuous monitoring of mercury concentration in the cell room, removal of mercury spillage and immediate intervention at leakage (aided by appropriate housekeeping and continuous monitoring) and immediate isolation of Hg in closed vessels are important measures.

After treatment, mercury can be recovered and reused. Recuperation of mercury is possible from caustic treatment sludges, hydrogen and waste gas treatment when using chemical processes, water treatment sludges, the mercury distillation unit, the area for handling mercury-contaminated parts (for example, when changing the decomposer graphite). In most cases, the mercury-containing solid residue that result from treatment need stabilisation before being disposed of. Stabilisation serves to transform metallic mercury to a less soluble, more stable chemical state in order to reduce the risk of leaching from the final disposal site in the short and long term. In many cases, mercury is treated with sulphur or sulphur compounds to transform it to mercury sulphide or with selenium to mercury selenide. This can also be combined with physical stabilisation, for example in cement-based materials.

For final disposal, the residue can be sent to a waste landfill (hazardous or non-hazardous, depending on mercury content), to deep rock storage (now implemented in Sweden) or to salt mines.

Conversion of Mercury Cell Plants to Membrane Technology

The conversion of mercury cell plants to membrane technology has the advantage of avoiding any future losses of mercury to the environment and reduces the energy consumption. At the Borregaard plant in Sarpsborg (Norway) recently installed membrane cells have resulted in electrical energy savings of 30% per tonne of 100% NaOH. According to Euro Chlor an estimated typical electrical energy saving after conversion is 15% and the total energy saving about 10%.

Table 5.1 *Comparison of typical energy use by the mercury, diaphragm and membrane cell chlor-alkali technologies, assuming production of 50% caustic soda and before liquefaction of chlorine.*

Parameter	Amalgam Technology	Asbestos/ Diaphragm Technology	Membrane Technology
Theoretical voltage (V)	3.15	2.19	2.19
Current density (kA/m^2)	8-13	0.9-2.6	3-5
Cell voltage (V)	3.9-4.2	2.9-3.5	3-3.6
Caustic strength (% by weight)	50	12	33
Electrical energy use (alternating current) (ACkWh/t Cl_2)	3,360 at 10 kA/m^2	2,720 at 1.7 kA/m^2	2,650 at 5 kA/m^2
Electrical energy use by other electrical equipment (pumps, compressors, etc) (ACkWh/t Cl_2)	200	250	140
Total energy use (ACkWh/t Cl_2)	**3,560**	**2,970**	**2,790**
Energy use by steam to concentrate caustic to 50% (ACkWh/t Cl_2)	0	610	180
Adjusted total energy use (ACkWh/t Cl_2)	**3,560**	**3,580**	**2,970**

To realise the conversion most membrane cell operators have either built a brand new "green field" plant or expanded production capacity with a new plant alongside their mercury facilities. Some have completely converted their existing plant, but there are also examples of partial conversion. The saving of space makes it theoretically possible to install up to four times more capacity with membrane technology in an existing building, but a clean space is needed for the membrane cells.

The main changes include the following measures: For the brine system the main concern is the purity of the brine feed to the existing cell room system. The design and operation of the electrolysers are essentially different and no old parts can be reused. Reuse of the rectifiers of the power supply depends on the type of membrane cell configuration and power requirements. While mercury cell technology produces 50% caustic soda membrane cells require a recirculating system with associated heat exchange and dilution and produce 33% caustic soda. If more concentrated caustic soda is needed, an evaporator system is also necessary. The reuse of existing process piping is not appropriate when converting to a membrane process, as the physical location is often very different from that required by membrane electrolysers.

Box 5.1 Data from the Conversion of the Borregaard Chlor-Alkali Plant to Membrane Technology

Context of old production units
- Cell room built in 1949: 3 floors, 122 cells.
- Mercury air emissions: 1.4 g/tonne chlorine capacity.
- Mercury water emissions (water ion exchange process): 0.25 g/tonne chlorine capacity.

Driving force for conversion
- Demand from the Norwegian authorities to switch to a mercury-free process.
- Demand for higher production of sodium hydroxide and wish to lower operating costs.

The conversion
- Decision made to convert: autumn 1995.
- Conversion carried out: autumn 1997.
- Shutdown time: 7 weeks.

Characteristics of new plant
- 40000 tonnes Cl_2 capacity/year at 4.35 kA/m^2.
- Supplier: Asahi Glass Co. Ltd. Japan.
- Engineering: Krebs-Swiss.
- Electrolyser: AZEC-B1 bipolar, 4 electrolysers, each 75 cells.
- Membrane area: 2.88 m^2 per cell.
- Membrane: Flemion 893.

Reused equipment
- Rectifiers.
- Hydrogen treatment and HCl production units.
- Chlorine liquefaction section and compression.

New equipment
- Cell room for electrolysers: The existing building was considered old and mercury-contaminated.
- Electrolysis section.
- Brine circuit: brine filtration unit, ion exchange unit, brine dechlorination unit.
- Sodium hydroxide concentration unit and evaporation system.
- Chlorine gas drying unit and chlorine gas absorption unit.
- Power supply and wiring (excluding rectifiers).
- Pumps, instruments and piping.

Cost of conversion
- Total cost of conversion was about 210 million NOK (26.6 million euros October 1997) corresponding to about 665 euros/tonne chlorine capacity. This figure includes 2.4 million euros for the clean-up of the old plant and the storage of mercury-contaminated waste but excludes the cleanup of soil pollution.

Economic benefits
- Electricity: 30% reduced per tonne 100% NaOH.
- Personnel: 25% reduced.
- Some mercury sold for batteries, instruments and to mercury chlor-alkali plants.
- Return on investment: 5 years (depending on the caustic market).

Decommissioning
- No cleaning-up of mercury-contaminated soil.
- Monitoring of mercury emission to air from old cell room.
- Construction of a sealed disposal facility for mercury-contaminated wastes: 1800 ^{m3}, 3 special membranes with sand filter seals between. The bunker is ventilated and the vented air led through a carbon filter. The majority of the wastes (about 55%) was mercury contaminated process equipment (steel and rubber lined steel).
- 95 tonnes of mercury drained from the cells.

Abatement of Asbestos Emissions in Diaphragm Cell Plants

In its various formulations, the polymer modified asbestos (PMA) diaphragm, containing a minimum of 75% of chrysotile asbestos mixed with PTFE fibres, is the most common diaphragm in use today. The major potential sources of air emissions are during diaphragm deposition, treatment of operating cells with asbestos slurry and the disposal of spent asbestos. Contaminated water also needs to be collected and recycled as far as possible. Laboratory tests using asbestos-free diaphragms began in the mid-1980s, following the increasing pressure to reduce the use and emissions of asbestos. Suitable alternatives have been developed at industrial scale with the objective of bringing the new asbestos-free diaphragm technology to the same commercial level as the polymer modified asbestos (PMA) diaphragms.

Changing from Diaphragm Cells to Membrane Technology

Conversion of a diaphragm plant to membrane technology can be an attractive choice because of removal of the hazardous asbestos, the high energy efficiency, and the pure 33% caustic produced directly from the cells. This is especially the case when there is a need for high purity 50% caustic, due to the reduced costs of evaporation and the higher caustic quality of the membrane technology. A conversion to asbestos-free diaphragms requires substantially less change in the existing cell room than a conversion to membranes, and thus a lower capital investment. A comparison of the manufacturing costs is dependent on steam costs and the required caustic quality.

The important changes to an existing plant when converting from diaphragm cells to membrane technology include additional brine purification, including hardness removal ion exchange techniques; additional brine dechlorination to protect the ion exchange resin, by adding primary and secondary dechlorination and possibly re-saturation to the brine recirculation loop; inclusion of a cell room caustic soda recirculation system; and change of electrolysers and details of the cell room system.

Hydrogen Usage

Hydrogen should be used as a chemical or as fuel in order to conserve resources.

Heat Usage

Heat produced in the electrolysis should be used in several of the processes in the plant, including the production of steam, heating caustic soda for concentration and heating buildings.

High Performance Membranes

New high-performance membranes are now commercially available to equip electrolysers. There are high-performance membranes for use in narrow and zero gap electrolysers (low cell voltage, reduced energy use) for the production of chlorine and 30-35% caustic soda. They are all reinforced composite membranes, having sulphonate and carboxylate polymer layers. In the design of a membrane electrolyser using standard membranes, minimising the voltage drop through the electrolyte gap is accomplished by reducing the gap.

New Cathode Designs

A number of new promising techniques are being developed with energy savings as the main driving force. An interesting example is a specific development of activated cathode technology, the pre-cathode concept. Oxygen depolarised cathodes in membrane cells have the potential to save around 500-600 kWh/tonne of chlorine produced (an approximate 15% reduction) and are now being tested at the industrial scale. At least one supplier is developing a membrane that can produce high concentration (50%) caustic soda and believes that it could be available at an acceptable cost within a few years. The life time of the diaphragm has also been found to be improved by introduction of the pre-cathode.

The utilisation of oxygen depolarised cathodes (ODCs) in the chlor-alkali electrolysis is an integration of the fuel cell process into the membrane electrolysis cell: the cathode half cell reduces oxygen instead of producing hydrogen. This lowers the cell voltage by about 1 volt and means a substantial energy saving, as predicted from the theory. The ODC is a gas diffusion electrode which separates caustic from the oxygen side, from where the gas diffuses into the porous electrode structure to the catalyst centres and reacts with the cathodic water to produce OH^- ions. All other functions are the same as in the normal membrane electrolysis. An energy gain of about 500-600 kWh/t chlorine produced was achieved.

6 – Cement Manufacturing Industry

1. The Cement Industry

Cement Production

Cement is a basic material for building and civil engineering construction. Output from the cement industry is directly related to the state of the construction business in general and therefore tracks the overall economic situation closely. The production of cement in the EU-12 in 1995 was 172 million tonnes.

In Europe the use of cement and concrete (a mixture of cement, aggregates, sand and water) in large civic works can be traced back to antiquity. Portland cement, the most widely used cement in concrete construction, was patented in 1824. In 1995 there were 252 installations producing cement clinker and finished cement in the EU-15 and a total of 437 kilns. In recent years typical kiln size has come to be around 3000 tonnes clinker/day.

There is generally little import and export of cement, mainly as a result of the high cost of road transport. Road deliveries of cement generally do not exceed distances of 150 km. Consequently, the rate of consumption equals the rate of production for many EU member states, with the exception of Greece and Denmark. Their export accounts for approximately 50% of their cement production.

Technologies

Cement is a finely ground, non-metallic, inorganic powder when mixed with water forms a paste that sets and hardens. This hydraulic hardening is primarily due to the formation of calcium silicate hydrates formed by mixing water and the cement components.

The Sources

The text is a summary of the IPPC (European Commission Integrated Pollution Prevention and Control) *Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries,* December 2001.

See also Case Study 1 on Kunda Cement in Book 4 of this series.

Naturally occurring calcareous deposits such as limestone, marl or chalk provide the source for calcium carbonate. Silica, iron oxide and alumina are found in various ores and minerals, such as sand, shale, clay and iron ore. Power station ash, blast furnace slag, and other process residue can also be used as partial replacements for the natural raw materials. To produce 1 tonne of clinker the typical average consumption of raw materials in the EU is 1.57 tonnes. Most of the balance is lost from the process as carbon dioxide emission to air in the calcination reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

The cement industry is thus main emitter of the greenhouse gas carbon dioxide, both because of its large energy use and the calcination reaction. About 5% of global CO_2 emissions is due to cement production.

In 1994 Europe's cement industry produced 44%, Portland-composite cement 43%, Portland cement while Blastfurnace, Pozzolanic and other cements accounted for the rest. 78% of the production relied on dry process kilns, the rest is accounted for by semi-dry, semi-wet process and wet process kilns. The choice of manufacturing process is primarily motivated by the nature of the available raw materials.

The cement industry is an energy intensive industry with energy typically accounting for 30-40% of production costs. Various fuels can be used to provide the heat required for the process. The most commonly used fuels were pet coke (39%) and coal (36%) followed by different types of waste (10%), fuel oil (7%), lignite (6%) and gas (2%) (1995 statistics).

The emissions from cement plants which cause greatest concern are nitrogen oxides (NO_X), sulphur dioxide (SO_2) and dust. Other emissions to be considered are carbon monoxides (CO), volatile organic compounds (VOCs), polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), metals, and noise.

2. Production Technologies

The Basic Processes

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate ($CaCO_3$) at about 900°C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO_2); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1400-1500°C) with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the clinker. The clinker is then ground or milled together with gypsum and other additives to produce cement.

There are four main process routes for the manufacture of cement; the dry, semi-dry, semi-wet and wet processes:

In the *dry process*, the raw materials are ground and dried to raw meal in the form of a flowable powder. The dry raw meal is fed to the preheater or precalciner kiln or, more rarely, to a long dry kiln.

In the *semi-dry process* dry raw meal is pelletised with water and fed into a grate preheater before the kiln or to a long kiln equipped with crosses.

In the *semi-wet process* the slurry is first dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate preheater or directly to a filter cake drier for raw meal production.

In the *wet process*, the raw materials (often with high moisture content) are ground in water to form a pumpable slurry. The slurry is either fed directly into the kiln or first to a slurry drier.

Figure 6.1 shows an overview of a dry process precalciner route.

The choice of process is to a large extent determined by the state of the raw materials (dry or wet). A large part of world clinker production is still based on wet processes. However, in Europe, more than 75% of production is based on dry processes thanks to the availability of dry raw materials. Wet processes are more energy consuming. All processes have the following sub-processes in common:

- Winning of raw materials.
- Raw materials storage and preparation.
- Fuels storage and preparation.
- Clinker burning.
- Cement grinding and storage.
- Packing and dispatch.

Raw Materials

Naturally occurring calcareous deposits such as limestone, marl or chalk provide the source for calcium carbonate. Silica, iron oxide and alumina are found in various ores and minerals, such as sand, shale, clay and iron ore. Power station ash, blast furnace slag, and other process residue can also be used as partial replacements for the natural raw materials as can fly ash,

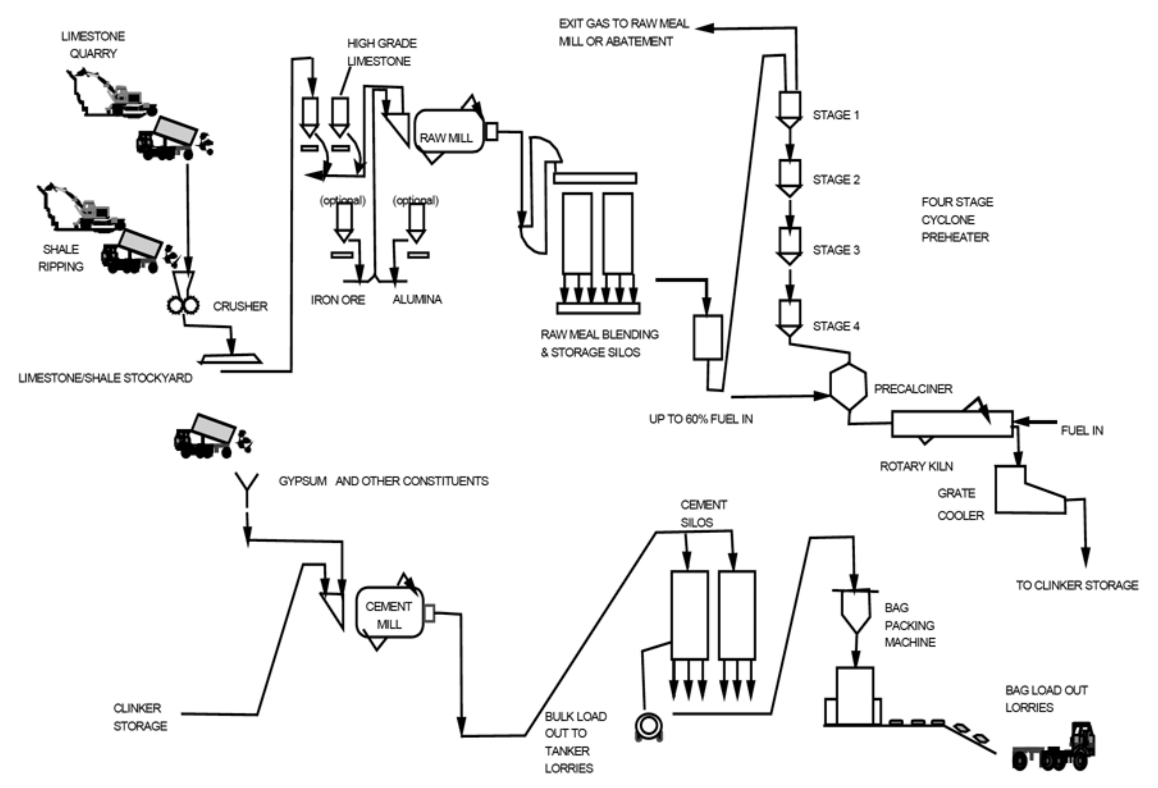


Figure 6.1 *A typical precalciner dry process.*

blast furnace slag, silica fume, iron slag, paper sludge, pyrite ash and phosphogypsum (from flue gas desulphurisation and phosphoric acid production).

The natural raw materials are most often obtained from open surface quarries, by rock drilling, blasting, excavation, hauling and crushing. In most cases the quarry is close to the plant. Preparation of the raw material is of great importance to the subsequent kiln system both in getting the chemistry of the raw feed right and in ensuring that the feed is sufficiently fine.

The raw materials are ground and mixed together to form a homogeneous blend with the required chemical composition. For dry and semi-dry kiln systems, the raw material components are ground and dried to a fine powder, making use mainly of the kiln exhaust gases and/or cooler exhaust air. The fineness and particle size distribution of the product leaving a raw grinding system is of great importance for the subsequent burning process.

Fuels

Three different types of fuels are mainly used in cement kiln firing; in decreasing order of importance these are pulverised coal and pet coke; (heavy) fuel oil; and natural gas. The main ash constituents of these fuels, silica and alumina compounds, combine with the raw materials to become part of the clinker.

The high temperatures and long residence times in the kiln system destroys completely all organic substances, which makes a wide variety of alternative fuel options possible, in particular different types of wastes. Wastes, that are fed through the main burner, will be decomposed in the primary burning zone, at temperatures up to 2000°C. The types of waste most frequently used as fuels in Europe today are used tyres, waste oils, sewage sludge, rubber, waste woods, plastics, paper waste, paper sludge, and spent solvents.

In order to keep heat losses at minimum, cement kilns are operated at lowest reasonable excess oxygen levels. This requires highly uniform and reliable fuel metering allowing easy and complete combustion. This is possible with all liquid and gaseous fuels. For pulverised solid fuels, good design of hoppers, conveyors and feeders is essential. Solid fuel preparation (crushing, grinding and drying) is usually carried out on site.

Clinker Burning

This part of the process is the most important in terms of emissions and of product quality and cost. In clinker burning, the raw meal is fed to the rotary kiln system where it is dried, preheated, calcined and sintered to produce cement clinker. The clinker is cooled with air and then stored. In the clinker burning process it is essential to maintain kiln charge temperatures of between 1400 to 1500°C and gas temperatures of about 2000°C. The clinker needs to be burned under oxidising conditions, why an excess of air is required in the sintering zone. Since the rotary kiln was introduced around 1895 it has become the central part of all modern clinker producing installations.

The first rotary kilns were long wet kilns, where the whole heat consuming thermal process takes place in the kiln itself. The introduction of the dry process allowed drying, preheating and calcination to take place in a stationary installation rather than in the rotary kiln.

The rotary kiln consists of a steel tube with a length to diameter ratio of between 10:1 and 38:1. The tube is supported by two to seven (or more) support stations, has an inclination of 2.5 to 4.5% and a drive rotates the kiln about its axis at 0.5 to 4.5 revolutions per minute. The combination of the tube's slope and rotation causes material to be transported slowly along it. In order to withstand the very high peak temperatures the entire rotary kiln is lined with heat resistant bricks (refractories). All long and some short kilns are equipped with internals (chains, crosses, lifters) to improve heat transfer.

The fuel introduced via the main burner produces the main flame with flame temperatures around 2000°C. For process-optimisation the flame has to be adjustable within certain limits. In a modern indirectly fired burner, the flame is shaped

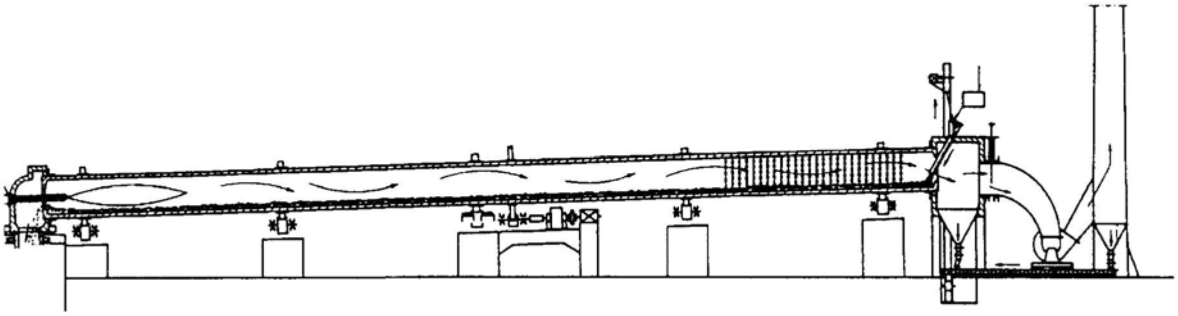
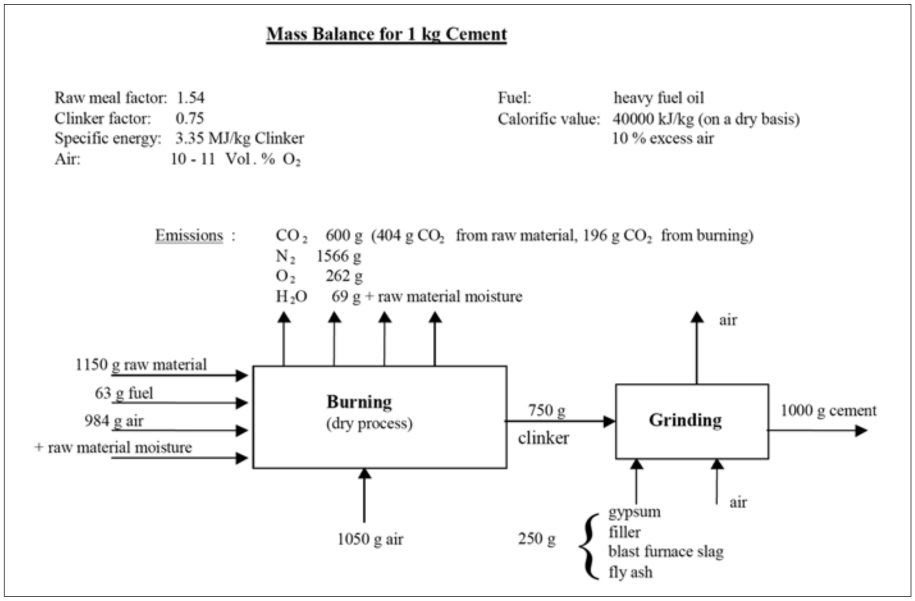


Figure 6.2 *Long wet rotary kiln with chains.*

Figure 6.3 *Mass balance for the production of 1 kg cement.*



and adjusted by the primary air (10-15% of total combustion air).

The largest long kilns have a length-to-diameter ratio of 38:1 and can be more than 200 m long. These huge units produce around 3600 tonnes/day using the wet process (Belgium, US, former Soviet Union). Long dry kilns were developed in the US based on batch type dry homogenising systems for raw material preparation. Because of the high fuel consumption only a few have been installed in Europe.

Grate preheater technology, better known as the Lepol kiln, was invented in 1928. It represented the first approach to letting part of the clinkering process take place in a stationary installation outside the kiln. This allowed the rotary kiln to become shorter and reduced the heat losses and increased energy efficiency. The rotary kiln exhaust gas enters the preheater with a temperature of 1000-1100°C. As it flows through the layer of material in the hot gas chamber the exhaust gas cools down to 250-300°C, and leaves the drying chamber at 90-150°C.

The invention of the suspension preheater in the early 1930s was a significant development. Preheating and even partial calcination of the dry raw meal takes place by maintaining the meal in suspension with hot gas from the rotary kiln. The considerably larger contact surface allows almost complete heat exchange, at least theoretically.

The four-stage cyclone preheater kiln system was standard technology in the 1970s when many plants were built in the 1000 to 3000 tonnes/day range. The exhaust gas, which has a temperature of around 330°C is normally used for raw material drying. Almost all four-stage suspension preheaters operate with rotary kilns with three supports.

The precalcination technique has been available to the cement industry since about 1970. In this procedure the heat input is divided between two points. Primary fuel combustion occurs in the kiln burning zone. Secondary burning takes place in a special combustion chamber between the rotary kiln and the preheater. In this chamber up to 60% of the total fuel can be burnt in a typical precalciner kiln. This energy is basically used to calcine the raw meal, which is almost completely calcined when it enters the kiln.

Clinker Coolers

The clinker cooler is an integral part of the kiln system and has a decisive influence on performance and economy. The cooler has two tasks: to recover as much heat as possible from the hot (1450°C) clinker so as to return it to the process; and to reduce the clinker temperature to a level suitable for the equipment downstream. Heat is recovered by preheating the air used for combustion in main and secondary firing as close to the thermodynamic limit as possible. However, this is hindered by high temperatures, the extreme abrasiveness of the clinker and its wide granulometric range. Rapid cooling fixes the mineralogical composition of the clinker to improve the grindability and optimise cement reactivity.

There are two main types of coolers, rotary and grate. The tube cooler uses the same principle as the rotary kiln, but for reversed heat exchange. Arranged at the outlet of the kiln, often in reverse configuration, i.e. underneath the kiln, a second rotary tube with its own drive is installed. Cooling in grate coolers is achieved by passing a current of air upwards through a layer of clinker lying on an air-permeable grate. Introduction and development of modern technology reciprocating grate coolers started around 1983. The design was a step closer to optimum heat exchange and also more compact coolers using less cooling air and smaller dedusting systems.

Cement Grinding and Storage

Clinker and other cement components are stored in silos or in closed sheds until further processed. Portland cement is produced by intergrinding cement clinker and sulphates such as gypsum and anhydrite. In blended cements (composite cements)

Table 6.1 Consumption of raw materials in cement production.
A typical cement plant has an annual production of about 1 Mt (1 million tonnes) clinker.

Materials (dry basis)	per tonne clinker	per tonne cement	per Mt clinker
Limestone, clay, shale, marl, other	1.57 t	1.27 t	1,568,000 t
Gypsum, anhydrite	-	0.05 t	61,000 t
Mineral additions	-	0.14 t	172,000 t

there are other constituents, such as granulated blast furnace slag, natural or artificial pozzolanas, limestone, or inert fillers.

Grinding plants may be at separate locations from clinker production plants. Commonly used finish grinding systems are tube mill, closed circuit, vertical roller mill, and roller press. The crushed material leaving the mill is transported to a separator, the oversize fraction being returned to the mill. Mineral additions are usually ground together with the clinker and gypsum. The particle size distribution of the product leaving the cement grinding system is of great importance for the cement quality. The ready product is stored in silos until shipped.

3. Consumption and Emission Levels

Consumption of Raw Materials and Energy

For cement on average, energy costs in the form of fuel and electricity represent 50% of the total production cost. 80% of this is used in the burning process. The chemical reaction takes in a modern process about 60% of the burning energy use and becomes part of the product. The theoretical energy use for the burning process (chemical reactions) is about 1700 to 1800 MJ/tonne clinker. Total burning energy requirement is in MJ/tonne clinker about 3000 for dry process, multi-stage cyclone preheater and precalciner kilns, 3100-4200 for dry process rotary kilns equipped with cyclone preheaters, 3300-4500 for semi-dry/semi-wet processes (Lepol-kiln), up to 5000 for dry process long kilns, and 5000-6000 for wet process long kilns.

Electrical energy represents approximately 20% of the overall energy requirement or 90-130 kWh/tonne cement. The main use is for the mills for finish grinding and raw grinding and the exhaust fans from kiln/raw mill and cement mill, which together account for more than 80% of electrical energy usage.

Emissions

The main environmental issues associated with cement production are emissions to air and energy use. Waste water discharge is usually limited to surface run off and cooling water only and causes no substantial contribution to water pollution. The storage and handling of fuels is a potential source of contamination of soil and ground water.

The releases to air from the kiln system derive from the physical and chemical reactions of the raw materials and the combustion of fuels. The main constituents are nitrogen from the combustion air; CO_2 from calcination and combustion of fuel; water vapour from the combustion process and from the raw materials; and excess oxygen.

In all kiln systems the solid material moves counter currently to the hot combustion gases. This counter current flow acts as a built-in circulating fluidised bed. Thus many components that result from the combustion of the fuel or from the transformation of the raw material remain in the gas phase only until they are absorbed by, or condensed on, the raw material flowing counter currently.

Typical kiln exhaust gas volumes expressed as m³/tonne of clinker (dry gas, 101.3 kPa, 273°K) are between 1700 and 2500 for all types of kilns. There are also releases of particulates from all milling operations i.e. raw materials, solid fuel and product. There is potential for the release of particulates from outside storage of raw materials and solid fuels as well as from materials transport systems, including cement product loading.

Oxides of Nitrogen

Nitrogen oxides (NO_X) are of major significance with respect to air pollution from cement manufacturing plants. NO_X emission measurements revealed a mean value of 2.1 g NO_2/kg of clinker, which corresponds to 1050 mg NO_2/m³. The mean values varied from 371–964 mg NO_X/m³. NO and NO_2 are the dominant nitrogen oxides in cement kiln exhaust gases (NO >90% of the nitrogen oxides).

There are two main sources for production of NO_X:

- Thermal NO_X when part of the nitrogen in the combustion air reacts with oxygen to form oxides of nitrogen in the kiln burning zone, where it is hot enough, above 1200°C. The reaction increases with temperature and oxygen content (air excess factor). Hard-to-burn mixes which require hotter burning zones will tend to generate more thermal NO_X than kilns with easier-burning mixes.
- Fuel NO_X when nitrogen chemically bound in the fuel either form N_2 gas, or react with oxygen in the air to form various oxides of nitrogen. In a precalciner the prevailing temperature of 850-950°C is too low to form significant thermal NO_X, but fuel NO_X will occur.

Sulphur Dioxide

Sulphur dioxide emissions from cement plants are primarily determined by the content of the volatile sulphur in the raw materials. Kilns that use raw materials with little or no volatile sulphur have little problems with SO_2 emissions.

Dust

Traditionally the emission of dust, particularly from kiln stacks, has been the main environmental concern in cement manufacture. The main sources of dust are kilns, raw mills, clinker coolers and cement mills. In all these processes large volumes of gases are flowing through dusty materials. The design and reliability of modern electrostatic precipitators and bag filters reduce dust emissions to levels, often below 10 mg/m³, where they cease to be significant.

Carbon Dioxides CO_2

The emission of CO_2 is estimated at 900 to 1000 kg/tonne clinker, related to a specific heat demand of approximately 3500 to 5000 MJ/tonne clinker, but also depending on fuel type. Mineral additions reduce CO_2 emission as counted per tonnes of cement. Approximately 60% originates in the calcination process and the remaining 40% is related to fuel combustion. As an example, a specific heat demand of 3000 MJ/tonne of clinker and the use of hard coal with a calorific value of 30 MJ/kg and a carbon content of 88% results in a CO_2 emission of 0.32 tonne per tonne of clinker, when regarding fuel part only. Using natural gas instead reduces this level by approximately 25%. Emissions of combustion CO_2 have been progressively reduced about 30% in the last 25 years mainly by more fuel efficient kiln processes.

Other Emissions

The emission of *carbon monoxide CO* is related to the content of organic matter in the raw material, but may also result from poor combustion when control of the solid fuel feed is suboptimal. Depending on the raw material deposit, between 1.5 and 6 g of organic carbon per kg clinker are brought into the process with the natural raw material. Control of CO levels is critical in cement kilns when EPs are used for particulate abatement. If the level of CO in the EP rises (typically to 0.5% by volume) then the electrical system is tripped (switched off) to eliminate the risk of explosion. This leads to unabated particulate releases from the kiln. CO trips can be caused by unsteady state operation of the combustion system.

In combustion processes in general, the occurrence of *volatile organic compounds* is often associated with incomplete combustion and CO formation. In cement kilns, the emission will be low under normal steady-state conditions, due to the large residence time of the gases in the kiln, the high temperature and the excess oxygen conditions. Concentrations may increase during start-up or upset conditions.

Any chlorine input in the presence of organic material may potentially cause the formation of *polychlorinated dibenzodioxins (PCDDs)* and *polychlorinated dibenzofurans (PCDFs)* in the combustion processes. Their formation is known to oc-

Table 6.2 *Emission ranges data from European cement kilns.*

Parameter	mg/Nm³	kg/tonne clinker	tonnes/year
NO_x (as NO_2)	<200–3000	<0.4-6	400-6000
SO_2	<10–3500	<0.02-7	<20-7000
Dust	5–200	0.01-0.4	10-400
CO	500–2000	1-4	1000-4000
CO_2	400-520 g/Nm³	800-1040	0.8-1.04 million
TOC	5-500	0.01–1	10-1000
HF	<0.4-5	<0.8-10 g/t	<0.8-10
HCl	<1-25	<2-50 g/t	<2-50
PCDD/F	<0.1-0.5 ng/Nm³	<200-1000 ng/t	<0.2-1 g/year
Metals:			
∑ (Hg, Cd, Tl)	0.01-0.3 (mainly Hg)	20-600 mg/t	20-600 kg/year
∑ (As, Co, Ni, Se, Te)	0.001-0.1	2-200 mg/t	2-200 kg/year
∑ (Sb, Pb, Cr, Cu, Mn, V, Sn, Zn)	0.005-0.3	10-600 mg/t	10-600 kg/year

Note: Mass figures are based on 2000 m³/tonne clinker and 1 million tonnes clinker/year. Emission ranges are one-year averages and are indicative values based on various measurement techniques. O_2-content is normally 10%.

cur by *de novo* synthesis within the temperature window of cooling from 450 to 200°C. Thus it is important that as the gases are leaving the kiln system they should be cooled rapidly through this range. Emissions of PCDDs and PCDFs is generally low during steady kiln conditions.

Raw materials and fuels will always contain *metals*, but concentrations vary widely from one location to another. In particular, the use of coal and waste fuels may increase the input of metals into the process. The behaviour of the metals in the burning process depends on their volatility. Nonvolatile metal compounds remain within the process and exit the kiln as part of the cement clinker composition. Semi-volatile metal compounds are partly taken into the gas phase at sintering temperatures to condense on the raw material in cooler parts of the kiln system. Thallium and mercury and their compounds are particularly easily volatilised and to a lesser extent so are cadmium, lead, selenium and their compounds. The dusts from the production of cement contain small amounts of compounds of metals.

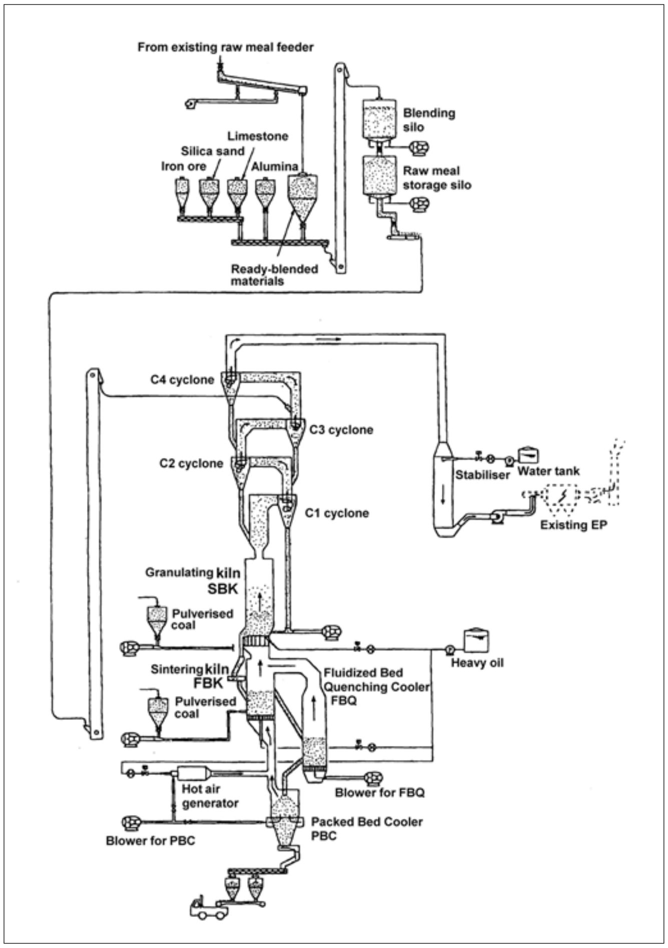


Figure 6.4 *Fluidised bed cement kiln.*

Waste

Waste produced during clinker production consists basically of unwanted rocks, which are removed from the raw materials during the preparation of the raw meal, and kiln dust removed from the by-pass flow and the stack, which is not recycled.

4. Technology Development and Cleaner Production Opportunities

Reducing Material Input

The environmental impact of cement manufacturing is largely caused by clinker production. In Europe the average clinker content in cement is 80-85%. Many manufacturers work to further lower the clinker content, e.g. by adding fillers, such as sand, slag, limestone, fly-ash and pozzolana, in the grinding step. One reported technique claims to exchange 50% of the clinker with maintained product quality/performance and without increased production cost. Cement standards define some types of cement with less than 20% clinker, the balance being made of blast furnace slag.

Recycling of collected dust to the production processes lowers the total consumption of raw materials. This recycling may take place directly into the kiln or kiln feed or by blending with finished cement products.

The use of suitable wastes as raw materials can reduce the input of natural resources, but should always be done with satisfactory control on the substances introduced to the kiln process. Cement production offers one possibility to burn hazardous waste, that otherwise is a problem.

Careful selection and control of substances entering the kiln can reduce emissions. For example, limiting the sulphur content of both raw materials and fuels can reduce releases of SO_2. The same is valid for raw materials and fuels containing other substances, for example nitrogen, metals and organic compounds.

Selection of Process

The selected process will affect the releases of all pollutants, and will also have a significant effect on the energy use. For new plants and major upgrades a dry process kiln with multistage preheating and precalcination is today state of the art. The wet process kilns operating in Europe are generally expected to convert to the dry process when renewed, and so are semi-dry and semi-wet processes. Thus kiln systems with 5 cyclone preheater stages and precalciner are considered standard technology for new plants. Such a configuration will use 2900-3200 MJ/tonne clinker. Reduced energy input in other kiln systems requires short dry process kiln with multi stage preheating and precalcination. The application of the latest generation of clinker coolers and recovering waste heat as far as possible, utilising it for drying and preheating processes, are examples of methods which cut primary energy consumption.

Any kiln system should be run under optimal conditions. Optimisation includes homogenising the raw material, ensuring uniform coal dosing and improving the cooler's operation. To ensure that the feed rate of solid fuel is steady with minimal peaks, it is essential with good designs of hopper, transport conveyor and feeder. Optimisation can include many elements ranging from instruction/training of the kiln operators up to installation of new equipment such as dosing systems, homogenisation silos, preblending beds and new clinker coolers. Reduction of emissions, such as NO_X, SO_2 and dust, are secondary effects of the optimisation of the clinker burning process.

Fluidised Bed Technology

A technology using fluidised bed cement kiln system is a project subsidised by the Ministry of International Trade and Industry in Japan since 1986. A 200 tonnes clinker/day large scale pilot plant was constructed in the end of 1995.

The suspension preheater is a conventional 4-stage cyclone preheater which preheats and calcines the raw meal. The granulating kiln is granulating the raw meal into granules of about 1.5-2.5 mm diameter at a temperature of 1300°C. In the sintering kiln the sintering of the granules is completed at a temperature of 1400°C. The fluidised bed quenching cooler quickly cools the cement clinker from 1400 to 1000°C. Finally, the cement clinker is cooled down to about 100°C in the packed bed cooler.

The cement clinker produced in the fluidised bed kiln are of the same or better quality as the clinker from a commercial plant. The NO_X emission is 115-190 mg/m³ when heavy oil is used and 440-515 mg/m³ when pulverised coal is used as fuel. According to a feasibility study of a 3000 tonne clinker/day plant the heat use can be reduced by 10-12% compared with a suspension preheater rotary kiln with grate cooler. It is therefore expected that the CO_2 emission can be reduced by 10-12%.

The final target of the technical development of the fluidised bed cement kiln system based in the feasibility study on a 3000 tonne clinker/day plant is: reduction of heat use by 10-12%; reduction of CO_2 emission by 10-12%; a NO_X emission level of 380 mg/m³ or less; current SO_X emission levels; reduction of the construction cost by 30%; reduction of the installation area by 30%.

Techniques for Controlling NO_X Emissions

Reduced emissions of NO_X is achieved by reduced flame and burning temperatures and the consumption of fuel, as well as by zones with a reducing atmosphere in the kiln system. Control of oxygen content (excess air) is critical to NO_X control. Generally the lower the oxygen content (excess air) at for instance a cement kiln back end, the less NO_X is produced. NO_X reductions of up to 30% have been reported.

Table 6.3 *Overview of techniques for controlling NO_X.*

Technique	Kiln systems applicability	Reduction efficiency	Reported emissions		Reported costs [3]	
			mg/m³ [1]	kg/tonne [2]	investment	operating
Flame cooling	All	0-50%	400-	0.8-	0.0 -0.2	0.0-0.5
Low-NO_x burner	All	0-30%			0.15-0.8	0
Staged combustion	Precalciner	10-50%	<500-1000	<1.0-2.0	0.1-2	0
	Preheater				1-4	0
Mid-kiln firing	Long	20-40%	No info.	-	0.8-1.7	No info.
Mineralised clinker	All	10-15%	No info.	-	No info.	No info.
SNCR	Preheater and Precalciner	10-85%	200-800	0.4-1.6	0.5-1.5	0.3-0.5
SCR – data from pilot plants only	Possibly all	85-95%	100-200	0.2-0.4	ca. 2.5 [4]	0.2-0.4 [4]
					3.5-4.5 [5]	No info. [5]

1) Normally referring to daily averages, dry gas, 273 K, 101.3 kPa and 10% O_2.

2) Kg/tonne clinker: based on 2000 m³/tonne of clinker.

3) Investment cost in 106 euros and operating cost in euros/tonne of clinker, normally referring to a kiln capacity of 3000 tonne clinker/day and initial emission up to 2000 mg NO_X/m³.

4) Costs estimated by Ökopol for a full scale installation (kiln capacities from 1000 to 5000 tonne clinker/day and initial emissions from 1300 to 2000 mg NO_X/m³), operating costs ca. 25% lower than for SNCR.

5) Costs estimated by Cembureau for a full scale installation.

Flame cooling. Addition of water to the fuel or directly to the flame reduces the temperature and increases the concentration of hydroxyl radicals. This can have a positive effect on NO_X reduction in the burning zone. Reduction efficiency from 0-50% has been reported.

Designs of *low-NO_X burners* vary in detail but essentially the coal and air are injected into the kiln through concentric tubes. The primary air proportion is reduced to some 6-10% of that required for stoichiometric combustion (typically 20-25% in traditional burners). The net effect of this burner design is to produce very early ignition, especially of the volatile compounds in the fuel, in an oxygen-deficient atmosphere. NO_X reductions of up to 30% are achievable in successful installations.

Selective catalytic reduction (SCR) reduces NO and NO_2 to N_2 with the help of NH_3 and a catalyst at a temperature range of about 300-400°C. This technology is widely used for NO_X abatement in other industries (coal-fired power stations, waste incinerators). Large NO_X emission reductions are potentially achievable by SCR high dust systems (85-95%). As the catalysts remove hydrocarbons as well, SCR will in general also reduce VOC and PCDD/Fs.

Selective non-catalytic reduction (SNCR) involves injecting NH_2X compounds into the exhaust gas to reduce NO to N_2. The reaction has an optimum in a temperature window of about 800 to 1000°C; sufficient retention time must be provided for the injected agents to react with NO. The right temperature window is easy to obtain in suspension preheater kilns, precalciner kilns and possibly in some Lepol kilns. The most common NH_2X agent is about 25% ammonia in water. The achievable NO_X emission level can in the best of cases be less than 200 mg/m³ if the initial level is not higher than about 1000-1300 mg/m³ (80-85% reduction), although the majority of installations are today operated to achieve an emission level of 500-800 mg/m³ (10-50% reduction). The first full scale plant with SNCR technology has been in operation in Germany in the end of 1999. Two Swedish plants, dry process cyclone preheater/precalciner kilns, installed SNCR in 1996/97. A reduction of 80-85% has been achieved at both kilns. The driving force for these plants to invest in high-performing SNCR installations was the Swedish policy to reduce NO_X emissions.

Staged combustion is applied at cement kilns supplied with several combustion stages. This technique is mostly carried out with specially designed precalciners. The first combustion stage takes place in the rotary kiln under optimum conditions for the clinker burning process. The second combustion stage is a burner at the kiln inlet, which produces a reducing atmosphere that decomposes a portion of the nitrogen oxides generated in the sintering zone. The high temperature in this zone is particularly favourable for the reaction which reconverts the NO_X to elementary nitrogen. Some modern well optimised plants achieve emission levels below 500 mg NO_X/Nm³ with multi-staged combustion.

The addition of mineralisers, e.g. calcium fluoride, to the raw material to adjust the clinker quality allows the sintering zone temperature to be reduced, which leads to less NO_X formation. The NO_X reduction might be between 10 and 15%, but reductions of up to 50% has been reported.

Techniques for Controlling SO_2 Emissions

The first step with respect to SO_2 control is to consider primary process optimisation measures, including the smoothing of kiln operation, choice of oxygen concentration and choice of raw materials and fuels. Increasing the oxygen content in long kilns is decreasing the SO_2 level and increasing the NO_X level. A balance to protect the environment should be sought by optimising $NO_X/SO_2/CO$ by adjusting the back end oxygen content. SO_2 reductions of up to 50% have been reported. The *addition of absorbents* such as slaked lime ($Ca(OH)_2$), quicklime (CaO) or activated fly ash with high CaO content to the exhaust gas of the kiln can absorb some of the SO_2. The SO_2 will react with the lime to $CaSO_3$ and $CaSO_4$, which becomes incorporated into the clinker. SO_2 reductions of 60 to 80% can be achieved by absorbent injection in suspension preheater kiln systems.

To reduce very high SO_2 emissions (more than 1500 mg/Nm³) a separate scrubber is required. One type of *dry scrubber* uses a venturi reactor column to produce a fluidised bed consisting of a blend of slaked lime and raw meal. The intensive contact between gas and absorbent, the long residence time and the low temperature allow efficient absorption of SO_2. The gas leaving the venturi is loaded with absorbent which is collected in an electrostatic precipitator. An SO_2 reduction of 90% may be achieved, that corresponds to a clean gas content of 300 mg SO_2/m³ when the initial SO_2 concentration is 3000 mg/m³. A dry scrubber will also reduce emissions of HCl and HF.

The *wet scrubber* is the most commonly used technique for flue gas desulphurisation in coal fired power plants. The SO_X is absorbed by a liquid/slurry sprayed in a spray tower or is bubbled through the liquid/slurry. The absorbent can be calcium carbonate, hydroxide or oxide. The wet scrubbers currently in use in the European cement industry are all spray towers. The slurry is sprayed in counter current to the exhaust gas and collected in a recycle tank at the bottom of the scrubber where the formed sulphite is oxidised with air to sulphate and forms calcium sulphate dihydrate. The dihydrate is separated and used as gypsum in cement milling and the water is returned to the scrubber. The SO_2 reduction achieved can be more than 90%.

Pollutants such as SO_2, organic compounds, metals, NH_3, NH_4 compounds, HCl, HF and residual dust (after an EP or fabric filter) may be removed from the exhaust gases by adsorption on *activated carbon*. If NH_3 is present, or added, the filter will remove NO_X as well.

Techniques for Controlling Dust Emissions

The three main point sources of dust emissions from cement plants are kiln systems, clinker coolers and cement mills. Various dedusting devices have been used in the past for these three duties but nowadays only electrostatic precipitators (EPs), or fabric filters are standard. Both types have a very high dedusting efficiency during normal operation. A disadvantage of fabric filters is that used filter bags are waste and have to be disposed of according to national regulations. Dust releases from handling and storage of materials and the crushing and grinding of raw materials and fuels, called fugitive dust, can also be significant.

Electrostatic precipitators generate an electrostatic field across the path of particulate matter in the air stream. The particles become negatively charged and migrate towards positively charged collection plates. The collection plates are rapped or vibrated periodically, so the material falls into collection hoppers below. EPs are able to operate under conditions of high temperatures, up to approximately 400°C, and high humidity. Under best conditions EPs can reduce levels down to 5-15 mg/m³ as monthly average.

The basic principle of *fabric filtration* is to use a fabric membrane which is permeable to gas but which will retain the dust. Initially, dust is deposited both on the surface fibres and within the depth of the fabric, but as the surface layer builds up the dust itself becomes the dominating filter medium. Gas for treatment can flow either from the inside of the bag outwards or vice versa. The use of modern fabric filters can reduce dust emissions to below 5 mg/m³. Besides dust, the fabric filter also removes substances that adsorb to the dust particles, such as dioxins and metals if present.

Fugitive emission sources mainly arise from storage and handling of raw materials, fuels and clinker and from vehicle traffic at the manufacturing site. Proper and complete maintenance of the installation always has the indirect result of reducing fugitive dust by reducing air leakage and spillage points. Outdoor storage piles of dusty materials should be avoided. Point sources of dust can be controlled by a water spray injection system. Areas used by lorries should be paved when possible, clean and watered, especially during dry weather.

Case Studies

B

Case Study 1

Vernitas Textile Company Ltd
Lithuania

Vernitas Textile Company – From Environmental Disaster to Environmental Recognition

1. Introduction

Vernitas Textile Company in Marijampole

Marijampole is a town in the southwest of Lithuania, on the Sesupe river in the Marijampole region with a population of 52,100. After World War II Marijampole developed as an industrial city, specialising in manufacturing equipment for the food industry, automotive parts, furniture, building and textiles. In Soviet times there were two major textile companies in Marijampole, but only Vernitas managed to survive.

Vernitas produces yarn based on polyacryl nitrile (PAN) acrylic fibre, which is imported. The technology consists only of mechanical processing except for the initial step where a part of the PAN fibre is processed with steam. The technology is old, but as new types of PAN fibres with improved hygienic and other properties becomes available, PAN yarns are becoming much better. Also there is some market demand for mixed yarns, and Vernitas is now introducing yarns where PAN is mixed with natural fibres.

Vernitas has a capacity of producing 6,000 tons of yarn per year, but has been through a period with much smaller sales. In the last few years the situation is improving through the opening of new markets, and today approximately 70% of the production is exported to European countries.

In the last few years the management has been very enthusiastic about cleaner production (CP) measures. Energy consumption and the environmental issues are given full attention. The project described here was not the first CP project in the company. The previous projects were very successful, and the management became interested in new CP projects. The company has implemented most of the identified improvement solutions, and continues to investigate new improvement measures.

The Cleaner Production Project

The Energy and Cleaner Technology Project of Vernitas was carried out by APINI (at Kaunas University of Technology, Lithuania), CIPAI (Kaunas, Lithuania), and COWI (Denmark); it was supported by the Danish Environmental Protection Agency (DEPA). The project consisted of an energy and cleaner technology audit, resulting in a number of proposed measures for energy savings and reduction of other environmental impacts. The project was carried out in 2002, and the proposed measures were implemented in the following years.

A “top-down” investigation was carried out in the company. The company was viewed as a “black box” and all inputs and outputs of energy and mass of this box, primarily through measurements and emission factors, were analysed. The company was analysed on three levels:

1. Main data for black box overview of the entire company.
2. Main process data enabling a distribution of the energy consumption and the environmental impacts on main processes (building a “layer cake”).

3. Detailed data and measurements for one or two specific processes.

In the initial phase of data collection, the focus was on levels 1 and 2. Later level 3 data were collected/measured for the 2-3 focus areas, which were selected for detailed investigation.

2. Processes to be Audited

The Yarn Production Process

Yarn Preparation. This process consists of the following subprocesses:

- Stretch-breaking.
- Re-breaking.
- Intersecting.
- Finishing.

The main issues here were the ventilation and the working environment. The air was extracted from the ceiling and floor. The suction was poor however. As a result there was a great deal of dust in the air, on the ceiling and walls and on the vents. PAN dust can cause irritation and health problems. But air conditions were continually monitored and, according to the company, the working environment regulations were complied with. The air was humidified to 60% for quality reasons. There was considerable noise from the machines.

Spinning. This spinning was done in 100 spinning machines with 336 elements on each machine. Air was supplied onto the reels of the machines to maintain quality. The process was divided into 10 sections, separated by a half wall to ensure that the different coloured yarns were kept apart. The main issues here were again the ventilation and the working environment. Similar observations were made as in yarn preparation, although the dust content in the air did not appear to be so high. The noise level was higher here than in the yarn preparation process.

Twisting. This process consisted of rewinding onto other reels and double twisting. The main issues here were again the ventilation and the working environment. Similar observations were made as in yarn preparation, although the dust content in the air did not appear to be so high. Air was extracted directly from the machines. Most of the humidifiers were not working. The noise level was high.

Shrinking. The yarn was heated by steam via steam chambers. Because the steam had insufficient pressure to reach the required heat, electric heat was added to increase the temperature. The main issues here were again the ventilation and the working environment. Similar observations were made as in yarn preparation although the dust content in the air did not appear to be so high. Air was extracted directly from the machines.

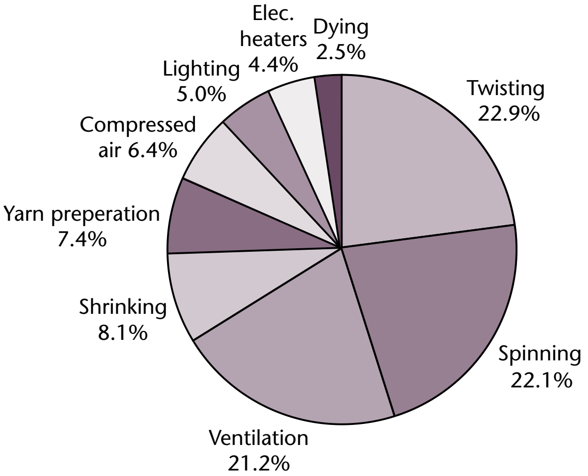


Figure 1.1 *Distribution of the electricity consumption among processes and auxiliary equipment.*

Cleaning for all four processes was carried out with compressed air.

Dyeing

This process was only three years old, using a relatively new technology. The yarns were weighed in order to calculate the correct amount and mixture of dye. The dye mixture consisted of the dye, yarn softeners and retardants. Three main dyes were used:

- Cation dye for polyacryl nitrile.
- Reactive dye for wool.
- Reactive dye for cotton.

The empty dye containers were either returned to the supplier or sold. Dye residue from tapping was stored in open buckets. Insufficient waste had accumulated for it to be sent away for disposal.

The yarns were lifted by winch into a chamber, and dyes and water added. The yarns were then washed in the same chamber. The number of washes depended on the colour. Fresh water was added each time. No water was recycled.

After the final wash, the yarns were lifted out and placed on the floor to dry. Water was drained through holes in the floor to wastewater pipes. This initial drying reduced the energy needed to dry the yarns in the drying chamber.

Final drying took place in a second chamber by hot air from a steam coil. The hot water gathered from this process was collected in a water basin and reused once the temperature had fallen sufficiently. Air from the dyeing process was emitted directly outside.

The water used in the processes was chemically treated, filtered in two tanks, and softened in two other tanks. The water was then stored in large basins. The wastewater was led through a series of sedimentation basins. The water from the last basin was led directly out to the sewerage without any further treatment. No sediment had been removed from the basins in the three years the dyeing process had been operating.

The company measured water consumption and wastewater effluents for this process. This environmental aspect was the main issue in this process.

3. Energy Auditing

Energy Data

An energy balance was established to create a basis for selecting the action areas for detailed investigation. The method was to gather overall actual energy consumption data for year 2000. The registered consumption was:

- Electricity: 11,577 MWh.
- Hot water: 1,756 MWh.
- Steam: 4,073 MWh.

The total heat consumption was thus 5,829 MWh.

Further detailed equipment data (type, fluid flow, pressure head, operation hours etc.) was collected for all power consumers with an electric motor larger than 5 kW. We also collected detailed data on heat consumption in processes and for heat and ventilation.

Finally a memo with the results of the energy mapping was prepared to be approved by Vernitas.

Electric Energy Balances

The result of the mapping of the electricity consumers and their consumption is shown in Table 1.1. The total calculated electricity use added up to 11,878 MWh, which is approx. 300 MWh (≈2.5%) more than actually consumed. The relative data presented in the above figure shows that the major electricity consumption was related to the processes in which a total of 67% of the electricity was consumed and 76% of the total power capacity installed.

The distribution of the electricity consumption by type of equipment is shown in Table 1.2. The main part (69%) of the installed motor capacity was installed on special textile machines in the company and only 25% is installed on so-called service equipment such as fans, pumps and compressors.

The situation is almost the same when it comes to the actual electricity consumption where again the numerous special textile machines and electric heaters accounted for approx.

Table 1.2 *Electricity consumption by type of equipment.*

Equipment	Motor		Electricity consumption	
	kW	%	MWh/ year	%
Machines	5,390	69	7,189	61
Fans	1,500	19	2,717	23
Pumps	110	1	100	1
Compressors	414	5	756	6
Elect. heaters	231	3	520	4
Lighting	204	3	596	5

Table 1.1 *Electricity consumers and consumption at Vernitas, year 2000.*

Process	Motor (kW)	Average load (%)	Operating hours (hours/year)	Electricity consumption (MWh/year)
Yarn preparation	743	64	1850	879
Spinning	1950	77	1750	2,625
Twisting	2377	59	1925	2,717
Shrinking	320	100+	2500	968
Dyeing	360	90	5300	300
Ventilation	1250	72	2700-3700	2,517
Compressed air	414	≈75	2800-4500	756
Electric heaters	231	90	2500	520
Lighting	204	100	≈2920	596
Total plant	7,849	-	-	11,878

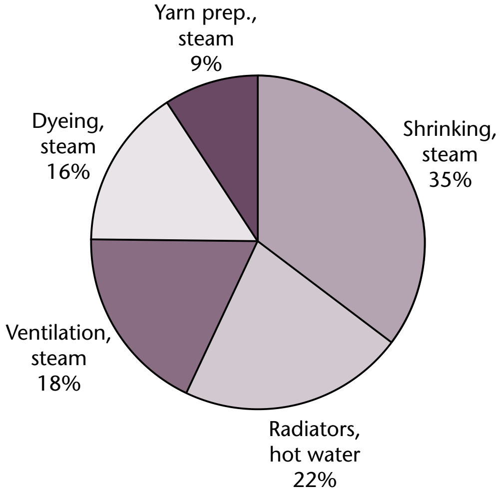


Figure 1.2 *Distribution of the heat consumption at Vernitas, year 2000.*

65% of the total consumption and service equipment accounts for approx. 30%. The remaining 5% was used for lighting.

Possibilities for Energy Efficiency Improvements

The mapping of the electricity consumers and their use showed that 61% of the consumption was related to operation of the numerous textile machines installed at the company and that another 4% was related to electric process heating (T>180ºC) installed in the shrinking machines. In total 65% of the electricity consumption (≈7,500 MWh/year) was related to consumers that were very difficult to optimise as this would require replacement of highly costly textile machines.

This left 35% of the electricity consumption (≈4,100 MWh/year) related to operation of service equipment and lighting, which was of interest in terms of optimisations. In this situation we chose to focus the efforts to identify relevant electricity savings by an analysis of the operation of fans for ventilation of the production halls (≈2000 MWh/year) and the operation of the air compressors (750 MWh/year).

Lighting was left out as a potential for electricity savings as the cost of replacing all the existing fittings was considered too high compared to possible savings.

Heat energy balance

The results of mapping the heat energy consumers and their consumption are shown in Table 1.3.

The total heat consumption based on steam and hot water added up to 5,475 MWh per year. The total actual measured heat consumption was approx. 5,800 MWh. The distribution of the heat consumption is shown in Table 1.3 and Figure 1.2 for the main heat consuming departments and utility systems. The results proved that 60% of the heat consumption was process heat and 40% heating of ventilation air and premises (radiators).

Possibilities for Heat Efficiency Improvements

In 2001, Vernitas installed three new boilers in the company's heating substation, two steam boilers and one hot water boiler. However, the operation of the steam system was not exactly energy efficient as no condensate at all was returned to the boiler station. This does not appear from the above presentation of the mapped heat consumption. Some of the steam was in fact used as steam for injection, which means that the condensate was polluted by effluents from the textiles. But in the heating substation condensate from the steam used to heat water for the ventilation system was actually wasted to the sewer. Water had to be added to cool the sewer water as the allowed temperature limit of sewage was max. 40°C.

We thus chose to focus the efforts of identifying heat savings by analysing how to optimise the operation of this particular heating process and the use of condensate. Furthermore, we looked into the possibilities for heat recovery from the air compressors and the use of steam condensate from the heating processes in the dyeing department as feed water in the dyeing processes.

Table 1.3 *Heat consumers and consumption at Vernitas, year 2000.*

Process	Heat capacity (kW)	Average load (%)	Operating hours (hours/year)	Heat consumption (MWh/year)
Yarn preparation, steam	385	70	1850	500
Shrinking, steam	770	100	2500	1925
Dyeing, steam	1700	25	2000	850
Hot water radiators	1000	50	2400	1,200
Hot water ventilation heating	770	55	2400	1,000
Total plant	4,625	-	-	5,475

4. Energy Saving Possibilities

Optimisation of the Humidification System

The humidification system at Vernitas was used to keep the necessary humidity in the production areas and to keep the dust and fibre content in the air as low as possible. The humidification system was a Russian-made pressure-fed system, using water under pressure (1.0 bar g) and compressed air (2.0 bar g) to atomise the water in a fine spray. The principal construction of such a system is shown in Figure 1.3.

The possibility of saving energy is related to a replacement of the existing spraying nozzles with new ones with a lower consumption of both water and compressed air.

Of the 316 nozzles installed at Vernitas, 66% or approx. 208 nozzles were used during the project. The savings after replacing them was estimated to be about 1.37 mill Nm³/year. This amount of compressed air equals 52% of the 3 bar air production.

The energy saving related to this amount of compressed air was found to be approx. 120,000 kWh/year with a cost of 23,200 LTL (approx. 6000 euros) per year. The reduced operation time of the air compressors meant an additional saving on the maintenance cost of approx. 3,900 LTL/year. The total savings thus amounted to approx. 27,000 LTL (7,000 euros) per year.

The cost of 208 new nozzles was 83,200 LTL. With an estimated cost of automation and design works of 20,000 LTL the total calculated investment amounted to 103,200 LTL. (26,000 euros). Pay back time = 3.8 years.

Modernisation of the Heating Substation

The heating substation prepared hot water (80-90°C) for heating the air in the conditioning system using heat exchangers. The nominal (designed) capacity of this system was 1 MW. Normally, this system operated at a 50% load, i.e. 500 kW (≈800 kg steam per hour) and the hot water was cooled to approx. 60°C in the air conditioning heat exchangers and then returned to the heating substation.

This hot water system was heated by steam in two tubular “steam – water” heat exchangers. These heat exchangers were old and close to being worn out, bound to be replaced in the near future. The main problem in the system was that all condensate (T≈95°C) was discharged to the sewer instead of being returned to the boiler. Moreover, in order to fulfill temperature requirements to the sewage (T<40°C), cold water was added to the sewage. Finally, the condensate wasted had to be replaced by adding the same amount of softened water to the steam system.

This was a substantial waste of energy and water, as the condensate could easily be returned to the steam system via the deaerator. Based on 2,400 hours of operation per year the savings potential by returning the condensate was as follows: heat: 160,000 kWh; water: 5,000 m³/year. The value of these savings was calculated based on the cost of natural gas and a reduced amount of sewage. With a heat price of 0.085 LTL/kWh, a discharge fee on sewage of 2.54 LTL/m³, a water price of 0.07 LTL/m³ and a price of softening feed water of approx. 0.30 LTL/m³ the total savings were estimated to be 27,000 LTL (7,000 euros) per year.

The cost of new heat exchangers, valves etc. was 105,000 LTL and with an estimated cost of automation and design work of 35,000 LTL, the total investment amounted to 140,000 LTL (35,000 euros). Pay back time was thus 5.2 years. However, the equipment of the heating substation was in very poor condition and probably due to be rehabilitated in the near future. For this reason a more realistic comparison would be between the investments and pay back time of rehabilitation of the heating station using the same principles as at present, and rehabilitation using the improved technology and principles mentioned above.

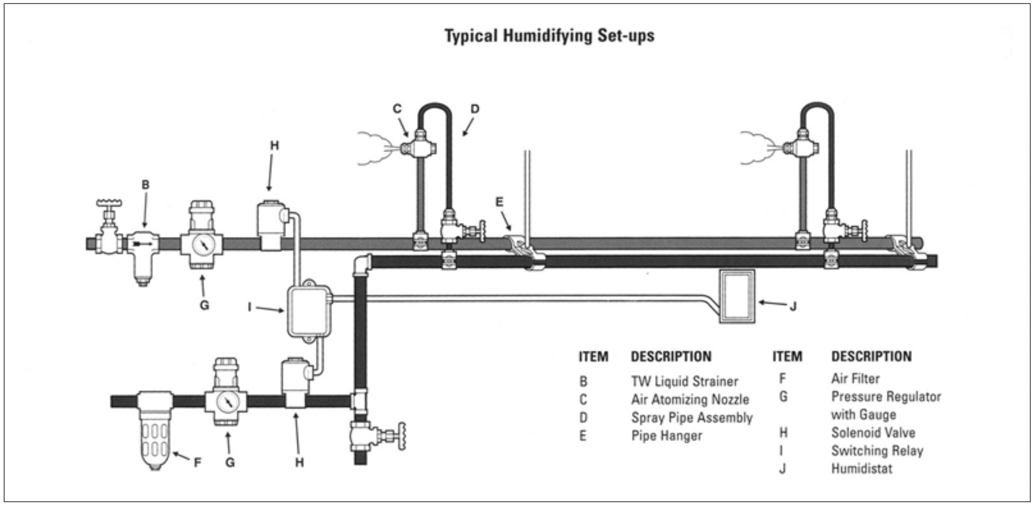


Figure 1.3 *Pressure fed humidification system.*

Installation of Variable Frequency Drives on Fans

The ventilation and air conditioning system consisted of 9 air supply fans and 9 exhaust fans. Of these 18 fans only 3 were equipped with variable frequency drives (VFD). The remaining 15 units operated at constant speed and the airflow was controlled with dampers.

Installation of VFDs would result in significantly better energy efficiency of the fans at part load (50-90%), which was approx. 75% of the operation time. The results showed that installation of variable speed drives on the 15 fans in the ventilation and air conditioning system would lead to yearly electricity savings of 551,300 kWh. This was equal to approx. 26% of the electricity consumption on these fans. In general the pay back time of the VFDs was estimated as 1.6-3.0 years.

Heat Recovery in the Compressed Air System

After a complete change of air compressors, the company has today three modern screw compressors (1x3 and 2x6 bar) supplying compressed air to the various users in the processes.

All three air compressors are air-cooled and the hot cooling air from the two compressors is exhausted to a technical floor above the engine room and the hot cooling air from the one compressor is exhausted back into to the engine room. At full load the total effect of the heat cooled off amounts to 223 kW.

In principle the waste heat from the compressors is already used for heating purposes but neither the technical floor nor the engine room needs to be heated by the hot cooling air. Therefore, analyses have been made in order to find a better use of this heat.

The most obvious place to direct the heat has been found to be a new raw material storage facility, which is to be erected right next to the engine room.

The energy savings related to directing the hot cooling air from the air compressors to the new storage are based on a heating demand throughout the heating season, which is approx. 28 weeks/year during late fall, winter and early spring.

With 10 average daily operation hours at Vernitas and operation 6 days a week, the total number of hours in which the air compressors are operating close to full load is approx. 60 hours per week.

The remaining hours (when production is shut down) the air compressors may be switched on, but as all machines and the humidification system are shut down, the compressor load will be very low and the potential for heat recovery is close to zero.

Therefore, during the 28 weeks of heating season the total number of operation hours in which heat can be recovered from the air compressors amounts to approx. 1,700 hours. With an average compressor load of 80% the potential for heat recovery amounts to 303,300 kWh/year. Possible savings are 25,800 LTL (about 6,500 euros) per year. With the suggested investment the pay back time of this waste heat recovery system would be approx. 2.0 years.

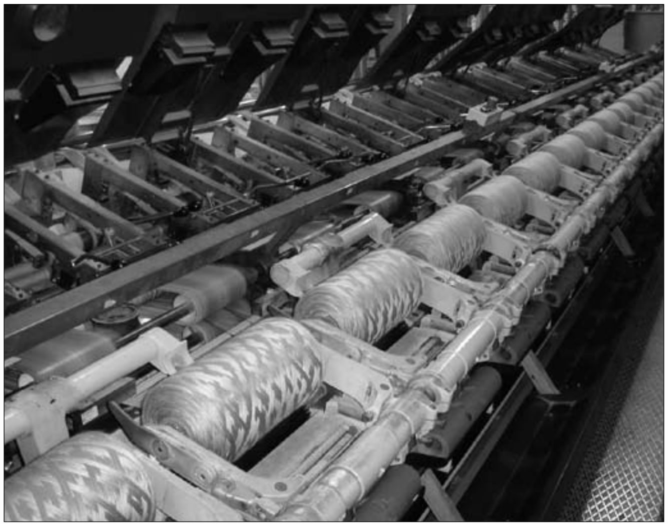


Figure 1.4 *The spinning machines.*

Recycling of Condensate in the Dyeing Department

In the dyeing department steam was used to heat water for dye mixtures, for rinsing of the yarn after dyeing and to heat drying air. The steam condensate (T≈97°C) from these processes is discharged directly to the sewage – thus a lot of heat is wasted.

The potential for heat recovery in the dyeing processes, depends on the direct use of steam condensate as make-up water in the processes. Based on the production data from 2001 the consumption of water (not including dyeing of wool) was 26,600 m^3 and steam 2,160 MWh (≈3,300 tons).

Of the total water consumption approx. 24,600 m^3/h (≈92%) was needed as warm process water at 50°C. Heating 24,600 m^3/h from 8°C to 50°C required approx. 1200 MWh. Today, the water is heated to approx. 35°C by waste heat from cooling of drying air. Thus 770 MWh of the 1200 MWh is covered by heat recovery. This leaves 430 MWh to be covered by steam (660 tons) or by using the steam condensate as make-up water (added back to the process).

The substitution of softened water with steam condensate (T≈97°C) and the reduced steam consumption due to the heat recovery contributes to the recycling of steam condensate. The result is a temperature rise of the warm process water from 35°C to 45°C. The heat recovery would then be approx. 290 MWh/year (≈490 tons of steam) and the heat demand would drop to 140 MWh/year or 170 tons/year of steam. The amount of condensate to be recycled would amount to 2,810 tons/year.

Moreover, chemicals for preparing 2,810 m³ of softened water will be saved and 2,810 m³ of sewage will be saved. The value of these 3 types of savings is:

- Heat: 24,700 LTL/year.
- Chemicals: 800 LTL/year.
- Sewage: 7,100 LTL/year.

The total savings amount to: 32,600 LTL (8,000 euros) per year. Investment analysis of this measure has not been performed as this project was just evaluated in the final stages of the project very close to the deadline. However, the equipment needed to carry out this project was considered to be quite simple (piping, tank, deaeration equipment, valves, filters and a pump) and as a consequence the investment would also be limited, max. 50,000 LTL. The pay back time was thus estimated to be in the order of 1.5 years.

5. Chemicals Use and Water and Wastewater Management

The Possibilities

In the initial analyses it was decided that the most important environmental aspect at the company is the environmental impacts of the dyeing department. This led to the following cleaner technology measures:

1. Reduction and substitution of chemicals used in the dyeing processes.
2. Treatment of wastewater from the dyeing department.
3. Possibility of recycling wastewater from the dyeing department.
4. Recycling of cooling water from spinning machines.

Minimisation/Optimisation of the Use of Chemicals

In general the overall analyses for minimisation/optimisation of chemicals were performed according to the following steps, recommended by the BREF document for the textile industry [IPPC, 2001]:

1. Investigating the use of the chemicals.
2. Investigating the possibilities of omitting the use of the chemicals.
3. Investigating the possibilities of reducing the use of chemicals (this step should not be considered if the chemicals are assessed to be hazardous, unless substitution is not possible).
4. Investigating the possibilities of replacing the chemicals with alternatives that have less negative impacts on the environment.

Especially step 2 and 3 demanded very detailed knowledge about the specific processes in the company. Therefore the staff and the department manager were involved. The dyeing department used (in the year 2000) a total of about 160 different chemicals in a total quantity of 26,419 kg.

Both the number and the total quantity of chemicals can be critical. The number can be critical because the more different chemicals there are, the more difficult it is to control and minimise the potential risk of each different chemical. The total quantity of chemicals can be critical, because the larger the quantity of hazardous chemicals used, the larger the risk of environmental pollution.

While investigating the use of chemicals at the company, a serious lack of safety data sheets was found. Therefore it was not possible to get an overall assessment of the environmental hazards of these chemicals, and an adequate list of chemicals to be replaced could not be made.

Today Vernitas is not able to reach the limit values for zinc in the effluents from the dyeing department. The local authorities thus have suggested that the company should invest in a wastewater treatment plant. But it seems cheaper and more environmental friendly to find the source of the zinc emission in the effluent. Zinc, which is a chemical ingredient of several dyes, is a heavy metal. Other heavy metals are also common in pigments. Heavy metals are environmentally hazardous. Some are environmentally toxic and all of them are bioaccumulative. That means that the concentration of the heavy metal will increase in the food chain.

By investigating the existing safety data sheets at the company we found that several types of pigments contained heavy metals. The company contacted the suppliers of dyes in Germany to ask what they would propose to reduce especially the zinc emission, but also emission of other heavy metals in the effluent from the dyeing department. The suppliers commented that zinc derivatives traditionally play an important role, as counter-ions, in the formulation of all standard cationic dyes for PAN. But the companies had identified this as a possible ecological problem and addressed the issue, by developing cationic dyes based on Zinc- free formulations. The investigation led to a serious cooperative effort with the chemical suppliers, which so far have enabled Vernitas to substitute part of the dyes with more environmentally friendly ones.

Wastewater Treatment and Reuse

The purpose of this investigation was to reduce the consumption of process water and the quantity of wastewater discharged to the municipal wastewater treatment plant.

The quantity of wastewater from the company was approximately 40,500 m³ per year. The existing wastewater treatment plant of the company consisted of six tanks in series, with overflow between the tanks. The performance of the treatment plant was assessed very low on the basis of measurements of influent and effluent parameters of the plant. After treatment, the company discharged the "treated" wastewater directly to the municipal wastewater treatment plant. The quality of this "treated" wastewater was very low. In particular there were e.g. no equalisation tanks for balancing the inlet flow to the treatment plant. The content of Zn in the treated wastewater was, as mentioned, above municipal limits.

The discharge of wastewater from the company to the municipal wastewater treatment plant can be reduced (both by quantity and degree of pollution) by separating the wastewater into two types: Wastewater for discharge and Wastewater for reuse.

Wastewater for discharge was wastewater from the dyeing process together with the first washing/rinsing step. This wastewater was characterised by high salinity, high content of heavy metals, high content of organic matter, high content of dye residual, and pH≥10. The wastewater from the dyeing processes can be treated by activated carbon or through either aerobic or anaerobic biological treatment.

Wastewater for reuse was wastewater from the second and further rinsing steps, which could reused after membrane filtration (nanofiltration or reverse osmosis). This wastewater was generally characterised by low concentrations of salt, heavy metals, organic matter, dye residual and neutral pH. The quantities of the two types of wastewater are given in Table 1.4. After consulting experts for wastewater treatment, it was concluded that the treatment plant could be designed as shown in Figure 1.5. The recommended treatments require that the wastewater is distributed into two lines. This could be done with the aid of automatic valves to distribute the wastewater according to the actual process step.

Table 1.4 *Quantity of wastewater produced at the company after the recommended separation of the quantity of wastewater for reuse, wastewater for discharge and total wastewater production.*

	Wastewater production			
	m^3/h	m^3/d	m^3/ month	m^3/ year
Wastewater for reuse	2.0	50	1,100	13,000
Wastewater for discharge	4.2	100	2,300	27,500
Total wastewater	6.2	150	3,400	40,500

Treatment of Wastewater for Reuse

The possibility of using membrane filtration to treat wastewater from the rinsing steps was analysed. Membrane filtration is widely used in dairies, for biotechnology applications and for treatment of water and wastewater. The technology has been used in the textile industry for many years for cleaning of wastewater (mix of wastewater and separated wastewater streams). However, membrane filtration has not been used or tested for cationic dyes.

The surface properties of a membrane are similar to the surface properties of a textile material. Therefore cationic dyes might adsorb directly to the generally used membranes, which would result in clogging of the membrane. This means that the membrane would have to be cleaned, which might be difficult with common techniques, or replaced. Nevertheless one of the leading membrane manufacturers en-

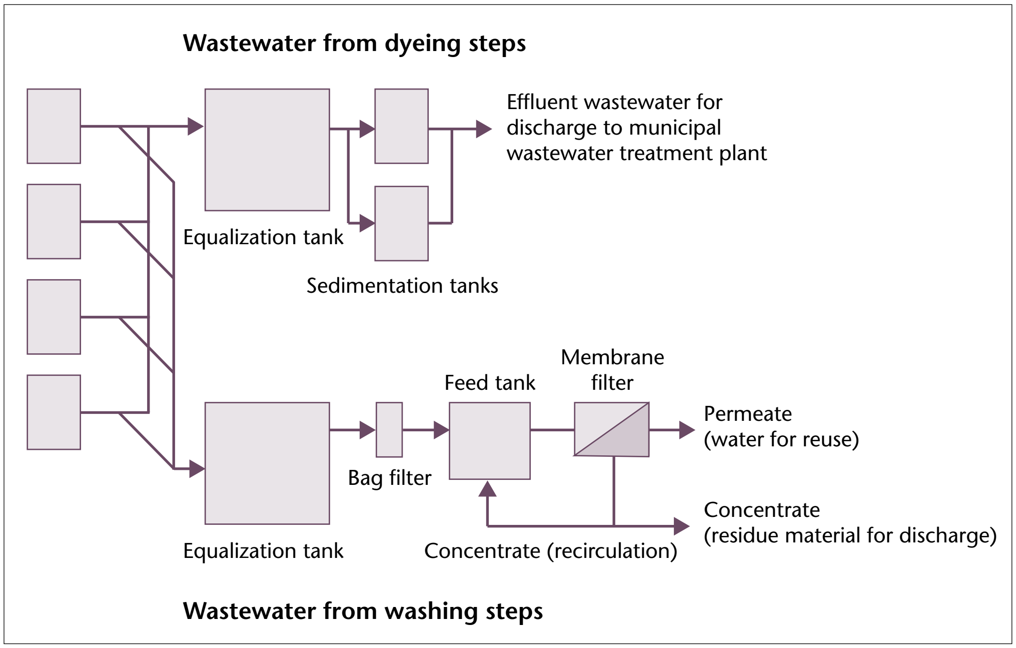


Figure 1.5 *Flow diagram of the proposed wastewater treatment plant at Vernitas.*

sured the company that it would be able to design a membrane for filtration of cationic dyes, even if it is not on the market.

The membrane manufacturer reckons that it is most likely that the membrane filtration system would consist of a nanofiltration membrane followed by reverse osmosis with internal recirculation. This configuration has been used for treatment of wastewater from textile industries. The principle of a membrane filtration system with internal recirculation is shown in Figure 1.6.

Treatment of Wastewater for Discharge

We proposed that the wastewater from the dyeing processes should be treated in the existing treatment plant before discharge to the municipal wastewater treatment plant. The wastewater treatment plant should be extended with an equalisation tank (Figure 1.5) with a volume of approximately 50 m³ for balancing the wastewater flow. Further, it is suggested that the sedimentation tanks be coupled in parallel and not in series as today. Hereby the load on each tank would be reduced and a better performance would be achieved.

The system should also consist of a bag filter with a cut-off value of approximately 10 μm for removal of fibres and other larger particles in the wastewater. For better operation conditions under maintenance, an installation of two parallel bag filters should be considered. The technical advantages of the membrane filtration system with internal recirculation are:

- Possibility of optimising the membrane pressure.
- Small risk of biofouling.
- Possibility of continuous operation.
- Low energy consumption.
- Easy cooling and heating of the system.

The possibility of varying pressure and flow is important. The feed pump delivers the quantity required at a pressure corresponding to the pressure at the concentrate outlet, while the recirculation pump gives the difference pressure and cross flow necessary for minimising the risk for membrane biofouling. The installation of reverse osmosis gives the possibility for removal of salt from the wastewater, which would make a desalination plant unnecessary. The concentrate residual (approximately 1% of the treated wastewater) from the membrane system can be treated in the municipal wastewater treatment plant or in an anaerobic digester.

A new treatment plant will save the company for approximately LVL 50,000 per year. With an investment of LVL 875,000 the project is today not feasible from an economic point of view. But as the costs of process water and discharge of wastewater are expected to increase significantly in the future, we recommended the company to reconsider this project at a later stage.

Because of the poor economy for membrane filtration the following solution was proposed instead:

- Separate the wastewater in the types 1 and 2.
- Bypass the type 2 wastewater.
- Improve the treatment of type 1 by installing an equalisation tank and coupling the sedimentation tanks in parallel.

Reuse of Cooling Water from Spinning Machines

The first process in the PAN yarns production is the stretch breaking process. PAN tops are stretched in 10 stretch breaking machines "SEYDEL". The technological process requires that stretching shafts be cooled. Shafts were cooled with water from their own well (before the year 2001, the production water from the municipal water supplier was used). Because this water is used only for cooling of shafts, it is not polluted and is discharged to the rain (run off) sewerage.

One stretch-breaking machine uses 2 m³/hour of cooling water. The total use of cooling water is 20 m³/hour, assuming that the number of working days is 150, and Vernitas works 8 hours (one shift). Total use of water is about: 24,000 m³ per year (the management provided a figure of 24,090 m³/year). The supplied water temperature is about 9°C or lower, and the outgoing water temperature is about 21°C. Necessary water pressure is about 2.5 atmospheres. At present the company pays 0.07 LVL/m³ (as taxes) for water from a well (not including cost of water pumping from the well and well maintenance). Water discharge to the rain sewerage is free of charge.

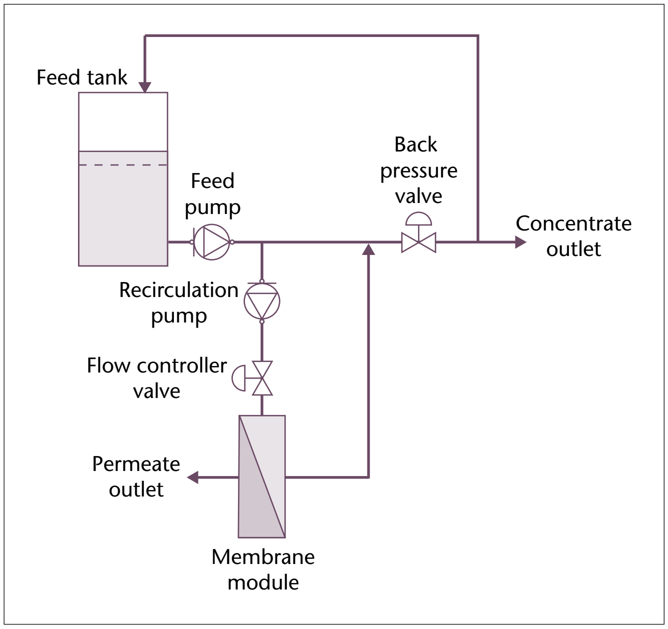


Figure 1.6 *Membrane filtration with internal recirculation.*

The engineers of the company have tried to construct a cooling water recycling system by connecting indoor water capacities. The experiment was unsuccessful because the water temperature drop was not sufficient.

In the initial stage of the investigation it was decided to use another outside underground water reservoir with a capacity of 1000 m³. The reservoir was previously used for storing fire protection water. The large volume of the reservoir and a distance of some 200 m to this capacity should ensure the necessary temperature drop.

According to the company calculations the installation cost for the above project of recycling water is 400 m zinced pipes; two pumps, one of 7.5 kW with a capacity of 50 m³/h and a reserve pump of 10 kW with a capacity of 70 m³/h (the second to be used in case of an emergency). The company already had the two required pumps, thus the cost of these is set to zero.

The company decided to implement this proposal immediately, using its own resources. The construction work took approximately two weeks and was carried out by two workers. The calculated pay back period was 1.67 years. The above calculation does not include the electricity for the pump for water recycling. The reason is that the saved cost of water pumping from the well is not included either and the two costs are estimated to be equal.

Contacts

Company

JSC Vernitas
Vladas Danilovas, *Technical Director*
Stoties g. 16, LT-68108 Marijampole, Lithuania
Tel: +370-343 73533
Fax: +370-343 70680
E-mail: info@vernitas.lt
http://www.vernitas.lt

Author

Tomas Pivoras
APINI, Institute of Environmental Engineering
Kaunas University of Technology
K. Donelaicio 20-307, LT-3000 Kaunas, Lithuania
Tel: +370-7-224-655
Fax: +370-7-209-372
E-mail: ppc.kaunas@apini.ktu.lt
E-mail: tomas.pivoras@ktu.lt

References

IPPC (Integrated Pollution Prevention and Control). BREF Reference Document on Best Available Techniques for the Textiles Industry, 2003.
http://eippcb.jrc.es/

U.S. EPA (U.S. Environmental Protection Agency). Manual – Best Management Practices for Pollution Prevention in the Textile Industry, 1996.
http://www.p2pays.org/ref/02/01099.htm

Case Study 2

Klaipėdos Baldai

Lithuania

Klaipėdos Baldai Furniture Manufacturing

1. Furniture Manufacturing

Furniture Industry in Lithuania

The furniture industry is a rapidly developing and dynamic sector in Lithuania with a growth rate of about 20-25% in recent years. In 2004 a total of 738 registered companies were selling for a total of 373.3 million euros. The companies were mostly small: 1-20 employees (35%), 20-99, (50%) and over 100 employees (15%). The largest producers are also the largest exporters, exporting some 60-80% of their production.

Klaipėdos baldai is the largest furniture manufacturer in Lithuania, with more than 600 employees. The product range of the company includes around 500 types of separate furniture units: bedroom, office, children room furniture and a large variety of different products for export. The company uses different thickness chipboard, covered with natural beech, oak, ash, cherry and other kind of veneer or synthetic foils, laminates.

Like elsewhere in Lithuania, furniture sales increased mainly due to export, which is related to the successful introduction of working Quality and Environment Management Systems. In 2004 Klaipėdos baldai was awarded the National Prize of Quality, and its furniture collection ANDA was recognised as the best product of the year in Lithuania.

The main partner of Klaipėdos baldai AB is Joint Stock Company Klaipėdos baldu prekyba. The Company trades in furniture in Lithuania, the CIS countries, Latvia and Estonia. Foreign partners include SODIM in Belgium and IKEA in Sweden.

The Production

There are many different grades and styles of furniture. Three grades of furniture often are described by the industry as high end, medium end, and low end. Generally, high-end furniture is made of solid wood and wood veneers and has the wood grain showing through the finish. The finishing process includes multiple finishing steps and is labour intensive. Low-end furniture, on the other hand, is often made of medium density fibreboard (MDF) with some plastic components and some natural wood. Also, the pieces often have either a coloured or printed wood grain finish, and the finishing process is less labour intensive. Medium-end furniture may be made of some combination of MDF and solid wood and may or may not show the natural wood grain.

Environmental Certification

Environmental issues are of great strategic importance to Klaipėdos baldai. Environmental work is performed with a focus on long-term sustainability. The Environmental Policy is in conformity with the objectives and strategic programme of environmentally friendly manufacturing.

Klaipėdos baldai was the first certified company in Lithuanian furniture industry receiving ISO 9001 quality certificate in 1998 and ISO 14001 in 1999. This was not only the first EMS certificate in Lithuanian furniture industry, but also a totally new phenomenon in Lithuanian economy. Until then, not many Lithuanian businessmen cared about the responsible use of natural resources and the impact of their activities on the environment. Klaipėdos baldai, while expanding its production volumes, pays more and more attention towards solutions of environmental problems, and today works with long-term environmental protection planning.

Cleaner Production Project Development

The Cleaner Production (CP) programme was performed in the company with a goal to improve the quality of the environment through eliminating, preventing, and/or reducing all waste generated by manufacturing prior to off-site recycling, treatment, or disposal. To effectively accomplish this, the programme included an ongoing, comprehensive assessment of the operations at the facility. As the CP activity would lower costs, the company expected to be able to improve its competitiveness through the programme. The company set up the following goals:

- Protect human health and environmental quality.
- Reduce operating costs.
- Improve employee morale and participation.
- Enhance the company's image in the community.
- Assist in compliance with environmental laws.

Most environmental problems are linked to economic development, and business conditions are becoming more and more complicated due to the increasing environmental concerns. Therefore, the practical application of sustainable development principles in the company is becoming an important aspect of business competition. On the other hand, sustainable development opens new business opportunities, e.g. development of more environmentally friendly products and processes. Additionally, the application of preventive environmental management measures helps to:

- Increase productivity.
- Reduce the use of natural resources and the associated costs.
- Reduce costs for waste management and pollution control and related risks.

In total it amounts to the improvement of environmental, economic and social performance, thus providing for competitive advantages.

2. Environmental and Sustainability Policies

Employee Participation and Social Responsibility

Employees are likely to feel better when they believe that management is committed to providing a safe work environment and the company is acting as a responsible member of the community. By participating in pollution prevention activities, employees have an opportunity to be part of a ”team,” and interact positively with co-workers and management. Helping to implement and maintain a pollution prevention programme will normally increase each employee's sense of commitment to the company goals. This positive atmosphere helps to retain a competitive work force and to attract high-quality new employees.

The quality of the environment has become an issue of critical importance to society. Klaipėdos baldai's policy and practices for controlling waste increasingly influence the attitudes of the local community at large to become more positive. The company creates environmentally compatible products and avoids excessive use of material and energy resources. Therefore its image is enhanced both in the community and with potential customers and consumers.

The company's CP plan included standard operating procedures that comply with environmental laws and regulations. By following the plan, the company increases its chances of avoiding violations and associated penalties.

Environmental Improvements

The investment policy of the company is not simply assigned for the increase of manufacturing output, but for the reduction of the impact on environment as well. Therefore, the company installed modern and environmentally friendly heating and ventilating equipment and fire protection measures. Important environmental improvement measures were implemented also:

1. Centralised waste collection and sorting.
2. Modernisation of the ventilation system.
3. Implementation of rain water treatment equipment.
4. Modernisation of the boiler house.
5. Hermetization of windows and insulation of walls in production departments and administration.
6. Implementation of new modern technologies, which increased performance of ventilators, reduced the wood dust emission sources by 6 (11 instead of 17); and reduced electrical and heat energy consumption by 30%.

Protect Human Health and Environmental Quality, Air Quality and Emissions

Typical harmful pollutants that can be reduced significantly by pollution prevention techniques include:

- Air emissions, including solvent fumes, fine particulates, and carbon monoxide.
- Land disposal, including ash from incineration, waste solvents, and debris.

- Water disposal, including wastewater contaminated with solvents and other toxic materials.

Volatile organic compounds (VOC) typically make up a significant amount of the solvents used in wood finishing. Many VOCs are damaging to the central nervous system. Long-term exposure may result in behavioural effects. Some VOCs are suspected carcinogens.

The health and safety of employees is threatened by poor ventilation, mishandling of chemicals, and a lack of proper safety equipment. An informative employee training programme is an important way to reduce accidents. Reducing the amount of chemical materials and wastes at a facility is also beneficial, because it reduces the amount of space required for storage and the potential for accidental spills. Furthermore, hazardous waste transportation requirements may be reduced if the volume of pollution is minimised.

Reduce Operating Costs

Cost savings are particularly noticeable when the costs resulting from the treatment, storage, or disposal of wastes are allocated to the production unit, product, or service that produces the waste. Materials costs, or the costs of purchasing materials, can be reduced by adopting production and packaging procedures that consume less resources. This approach uses resources more efficiently and reduces the quantity and toxicity of waste generated.

As wastes are reduced, the percentage of raw materials converted to finished products increases. This results in a proportional decrease in materials costs. Waste management and disposal costs may be reduced when less waste is produced. Required procedures for proper handling of the waste at the facility – in addition to specific treatment, disposal, and transportation methods – are typically labour-intensive and very costly. These requirements and their associated costs are expected to increase. People examine production processes from

Table 2.1 *Typical furniture manufacturing and refinishing operations: materials used and hazardous wastes that might be generated.*

Process/ Operation	Materials Used	Typical Material Ingredients	General Types of Waste Generated
Wood Cleaning and Wax Removal	Petroleum distillates, white spirits	Petroleum distillates, mineral spirits	Ignitable wastes Toxic wastes Solvent wastes
Refinishing/ Stripping	Paint removers, varnish removers, enamel removers, shellac removers, paint solvents, turpentine	Acetone, toluene, petroleum distillates, methanol, methylene chloride, alcohols, ketones, oxygenated solvents	Ignitable wastes Toxic wastes Paint wastes Solvent wastes
Staining	Stains	Mineral spirits, alcohol, pigments	Ignitable wastes Toxic wastes Solvent wastes
Painting	Enamels, lacquers, epoxies, alkyds, acrylics	Toluene, pigments, titanium dioxide, epoxy-ester resins, aromatic hydrocarbons, glycol ether, halogenated hydrocarbons, vinyl acetate acrylic	Ignitable wastes Toxic wastes Paint wastes Solvent wastes
Finishing	Varnish, shellac, polyurethane, lacquers, wood treatments, polish	Denatured alcohols, resins, shellac, petroleum distillates, toluene di-isocyanate	Ignitable wastes Toxic wastes Spent solvents Solvent still bottoms
Brush Cleaning and Spray Gun Cleaning	Paint thinners, enamel reducers, varnish removers, shellac removers, white spirits	Acetone, toluene, petroleum distillates, methanol, methylene chloride, isopropanol, mineral spirits, alcohols	Ignitable wastes Toxic wastes Spent solvents Solvent still bottoms
Maintenance	Antifreeze, spent solvent from parts washers, batteries, spent fluorescent lamps, used computer/electronic equipment		Toxic wastes Solid wastes Spent solvents

a fresh perspective; they find opportunities for increasing efficiency that might not otherwise have been noticed.

Production scheduling, material handling, inventory control, and equipment maintenance are all areas in which facilities can work to reduce the production of waste of all types, thereby controlling the costs of production. Energy costs will decrease as the facility implements pollution prevention measures in various production lines. In addition, by thoroughly assessing how operations interact, companies can reduce the energy used to operate the overall facility.

3. The Air Cleaning System

The Air Cleaning System Review

Klaipėdos baldai had two production departments with a total of 12,355 m² of floor area. The work caused considerable dust emission, which created a bad atmosphere for the workers. Also the areas surrounding the factory were badly polluted, mostly by saw dust. Klaipėda Municipality passed a resolution requesting that the company reduce the emissions. Also according ISO 14001 air pollution was established as a significant aspect that should be solved.

The air cleaning system, called cyclones, used in the company (Figure 2.1) was quite inefficient. The polluted air from the production departments using the cyclone system was treated only up to 70-90%. Therefore it was not possible to return the air to the department and a lot of heat, especially in cold season, was wasted.

Figure 2.1 *Sleeve filters air-cleaning system AAGAARD. Produced in Denmark, in 2001.*

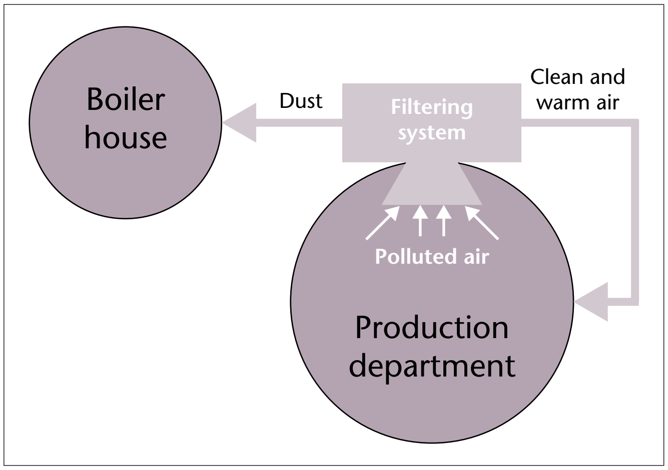


Figure 2.2 *CP project scheme.*

The main findings from the review found that:

- The dust cleaning system was very ineffective, and could not meet environmental requirements.
- There was significant heat and electrical energy losses due to very low performance of the ventilators.
- High noise level.

The CP project aimed to:

1. Reduce saw dust air pollution.
2. Reduce electrical and heat energy consumption.
3. Improve work conditions by regulation of intake and take-out air streams.
4. Reduce noise level.
5. Reduce the general pollution background in the region.

The Installation of a New Ventilation System

In 1998-1999 the company introduced new modern technologies to reduce dust emission sources. New ventilators were installed in the place of the removed old ventilators. For air extraction the old pipe channel system was still be used but for the cleaned returned air a new pipeline system was installed.

The company decided to replace the cyclone system, with a dust extraction and filter system, which allowed clean warm air to return to the working area (Figure 2.2).

The new filtering system consisted of 6 filtering sections with 288 filter bags with a special quick assembly sleeve. Polluted air from the production departments through a special system was transported to the filters. After cleaning, it returned to the production area and was distributed through air channels. Due to the fast speed the air temperature of the returned clean air was only 2-3°C lower than the incoming air.

The system was designed for continuous operation (24 hours). Cleaning of the filters was automatic and could be performed during operation or during stops by means of regeneration fans (1.1 kW), which rinsed the filter bags by blowing a reverse airflow through the bags. The filter hopper was automatically emptied by means of a chain conveyor, which fed the chips to the end of a rotary valve. The chain conveyor was running on bearings and sliding forward on anti-static slide rails.

The company installed a capacity of 45,000 m³/h with three fans and machine groups connected to the filter. The fans were placed outside the building.

The cleaning process, dust transportation, system start and stop as well as safety functions were controlled automatically.

Energy Savings – Recirculation of Warm Air

Also winter/summer valves were installed. They provided the possibility of not returning the cleaned air in summer time. The modular construction of the filtering system provided the company with the possibility of expanding the system according to needs (this type of filter can be supplied to handle up to 250,000 m³/h).

The body of the filtering system is made from galvanised tin, and the filter bags from special anti-static polyester fabric. The collected dust is transported to the company's boiler house by screw conveyor and used as fuel.

The recirculation of clean warm air significantly reduced the energy losses and emissions to the outside air from the company's boiler house. The effective new ventilators of the air cleaning system reduced the electric energy consumption. The installed ventilators had an extremely low noise level. Extra noise reduction, typically 15-20 dB (A), was achieved by building the fan into a sound box. The sound box, which has forced cooling air circulation, was made of galvanised, weather resistant steel sheets and was thus suitable for outdoor use.

Table 2.2 *Environmental results of the CP project.*

Energy consumption Reduction (kWh)	
Electric energy	1,098,452
Heat energy	1,377,600
Reduction of pollution (t/year)	
Atmospheric pollution reduction	2152.6
Wood dust	6.24
Ashes	1.072
SO_x	9.22
CO	6.15
NO_x	0.856
CO_2	2129.06

Table 2.3 *Economical savings.*

Kind of cost reductions	euros
Electric energy savings	54,868
Heat energy savings	35,336
Environmental taxes	310
Annual production costs	90,514

Results – Environmental and Economic Benefits

A summary of the environmental benefits of the new system (Table 2.2) included electric energy savings of some 1,000,000 kWh, heat energy savings of 1,377,600 kWh. The reduction of dust was reduced with more than 2,000 tons per year, pollutants with some 25 tons per year, and carbon dioxide with 2,000 tons per year.

The economic savings from the new ventilation system (Table 2.3) was the results of diminished energy costs and reduced fines for air emissions. A total of 90,514 euros reduced costs is then compared to the investments, which were 228,700 euros. The pay back period was thus 2.53 years.

4. Modernisation of the Boiler House

Review of Local Energy Production

The heat energy to all production facilities at Klaipėdos baldai was generated at a boiler house located in the territory of the company. The capacity of the boiler house was 1.3 MW, but the efficiency only 43.8%, thus very low. Approximately 30% of energy was consumed to operate the boiler itself (mainly for the air supply to the combustion). The fuel was supplied to the boiler house by pneumatic transport, which used a significant amount of electric energy.

The wood waste from the production was used as fuel for heat energy production. Annually 3,754 tons (thin wood waste – 2,628 t/year, nubbly wood waste – 1,126 t/year) of furniture wood waste was available at Klaipėdos baldai.

Emissions from the boiler house exceeded stated CO and NO_x maximum levels by 1.7 and 2 times respectively. The environmental fees for the emissions during 2001 were in total of 1,671 euros. This was mainly due to the insufficient control of the combustion process.

Analysis of the boiler house facilities revealed:

- High losses of heat due to the imperfect construction and worn-out conditions.
- High consumption of electric energy (draught and blowing ventilation, pneumatic transportation of fuel).
- Incomplete combustion resulting in higher emissions (burning process was regulated manually).

After a rapid increase of production the heat energy generation for the company became insufficient. As a result, considerations concerning investments for the constructions of the new boiler house were started. For its own purposes the company would need 4,000 MWh of heat energy. The price would be 12.2 euros per MWh. All together it would make 48,600 euros per year. If the same amount of energy would be purchased from the municipal supplier, the price would be 30.1 euros per MWh and in total would make 75,200 euros. The economic benefit of the locally produced energy would thus be 26,600 euros per year, as compared to the municipally supplied heat energy. This was the strong argument for Klaipėdos baldai to start implementing the CP project "Modernisation of the boiler house".

The New Boiler House

The environmental and economic audit led to the proposal that the old boiler house should be modernised. The main aims of the project was to:

- Decrease ambient air pollution.
- Decrease consumption of electric energy.
- Improve working conditions.
- Improve the environmental situation in the surroundings.

A new boiler house building was erected, and two boilers installed with effects of 1.1 and 2.8 MW, that is 3 times increased capacity, to provide sufficient heat energy, to be used in three production departments and storage facilities.

A new fully automated control system with distribution box, control panel (incl. O_2-regulator, alarm system etc.) was installed. The control system ensured optimal burning through monitoring the oxygen concentration in the emitted smoke and fuel supply processes. The emissions to the atmosphere were thus significantly reduced.

The water system included circulation pumps (120 m³/h), a water treatment system with a capacity of 0.5 m³/h chemical treatment. The chemical water preparation is performed using automatic filtering.

The old boiler was dismantled and sold as scrap. The building of the boiler house was demolished as it was not economical to renovate it, either from environmental and technical, or an economic point of view.

Savings and Profit

The economic benefits of the new boiler house were considerable. The savings were in the following categories:

Savings of electric energy. The operation of the new boiler house facilities required less electric energy as compare to the facilities in the old boiler house. In this respect electric energy consumption was reduced by 79,000 kWh, which made up 4,580 euros of savings per year.

Savings of water. The new installations in the boiler house reduced the consumption of water used for heating by 3,000 m³, which made 2,259 euros of savings per year.

Savings for operation and maintenance. Expenditures for operation and maintenance were reduced from 39,901 to 11,400 euros compared to the old boiler house and made up 28,501 euros per year.

Savings of heat energy. Expenditures for heat energy production in the new boiler house, compared to the old one, were reduced from 172,498 to 83,410 euros, i.e. the savings were 89,088 euros per year.

Table 2.4 *The annual net savings and profitability after implementation of CP project for the boiler house.*

Category of costs	Costs before CP project (euros)	Costs after CP project (euros)	Annual net savings and profit (euros)
Consumption of electric energy	12,488	8,004	4,580
Consumption of water	4,344	2,085	2,259
Operation & maintenance	39,901	11,400	28,501
Heat energy production	172,498 *	83,410	89,088
Environmental fee	1,671	219	1,452
Total net savings			**125,880**
Profit from sold heat energy	39,968	79,935	39,967
INCOMES			**165,847**

** The overall heat energy costs consisted of energy produced by company (48,656 euros) and energy bought from municipal suppliers during the heating season (123,842 euros).*

Reduced environmental fees. Lower emission exhausts of NO_X, CO and solids have reduced environmental fees by 1,452 euros per year.

Profit from the sold heat energy. At the same time the innovations at the boiler house opened the possibilities of Klaipėdos baldai selling energy to the other companies. For the needs of the company, the boiler house was operating 7 months per year. The remaining 5 months' surplus energy was sold to neighbouring companies. Heat energy production made up 600 MWh per month. It means that every year 3,000 MWh of heat energy could be sold to other companies, at a price of 13.3 euros per MWh. The incomes were thus projected to be 39,900 euros.

The investments for the new boiler house and installations were estimated 374,246 euros. The annual net savings and profit after installation of the boiler house gave to Klaipėdos baldai 165,847 euros in income. Thus, the pay backs of investment were 3 years and the return rate was 31.5%.

Contacts

Company

Klaipėdos baldai AB
Joniškės str. 21, LT-91267 Klaipėda, Lithuania
Tel: + 370-46-31 39 35
Fax: + 370-46-31 39 51
E-mail: info@kbaldai.lt
http://www.klaipedos-baldai.lt

Authors

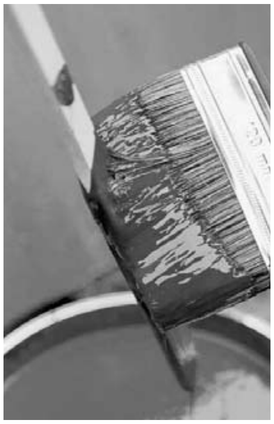
Žaneta Stasiškienė and Tomas Pivoras

Contact address

Assoc. Prof. Dr. Žaneta Stasiškienė
APINI, Institute of Environmental Engineering
Kaunas University of Technology
K. Donelaicio str. 20 - 312, LT-3000, Kaunas, Lithuania
Tel: +370-37-30 07 63
Fax: +370-37-20 93 72
E-mail: zastas@ktu.lt

Case Study 3

Greenchem Programme
Sweden



Greenchem Programme – Wax Esters as Wood Coating Material

1. Background

Green Chemistry and the Greenchem Project

One of the largest challenges to chemical technology is to reduce the dependency on fossil resources. The chemical industry is therefore exploring ways to use renewable resources to replace crude oil and improve sustainability. The use of renewable biological resources instead of oil will not only decrease oil dependency, but also decrease carbon dioxide emissions and reduce the emission of other pollutants connected to the use of oil.

Another important concern of green chemistry is to increase the efficiency of chemical transformations and use less energy. The case to be described shows that the use of enzymatic catalysis, often discussed as *bioprocesses*, instead of conventional inorganic catalysis, allows more energy-efficient production. This is still a topic for research but the number of industry-scale bioprocesses in operation started to increase during the last decade. Most of today's commercial enzymatic processes possess a variety of positive features, such as high productivity, high product concentrations, and a lack of undesirable by-products.

The research programme *Speciality Chemicals from Renewable Resources – Greenchem* is a Swedish interdisciplinary research programme at Lund University concerned with the development and application of biocatalysts for the production of fine chemical products from renewable raw materials. The programme includes research activities within both biotechnology and environmental systems analysis and involves cooperation with several industrial partners. Consumer and industrial desire for more environmentally benign paints and coatings is growing rapidly. The production of wax esters to be described here has been developed within the *Greenchem* programme.

Biological Materials for Industrial Purposes – Waxes

Waxes, or wax esters, are esters of long-chain carboxylic acids and long-chain alcohols. In nature one may find them as protective coatings on fruits, for example on apples, or as the material in beehives. As biological substances they are non-hazardous compounds with good biodegradability. The waxes have attracted the industry since they have a number of potential applications. One of them is to serve as ingredients in coatings for wooden surfaces.

Wax esters can be made from renewable resources, such as vegetable oils. High atom economy can be achieved as one molecule of water is the only side-product in the key production step, the condensation of the carboxylic acid and the alcohol. As biological material there are a number of potential enzymatic processes which may be used for their production. Here a lipase was used.

Conventional Industrial Production of Wax Esters

The conventional technology for the production of wax esters is based on the reaction of the alcohol and the carboxylic acid at temperatures above 150°C in the presence of a strong alkaline or acid as catalyst. The reaction is unselective and the waste and catalyst residue need to be removed in post-reaction purification.

In the conventional method neutralisation of the acid, steam treatment for distillation, and both deodorising and bleaching are needed. In post-reaction the product has to be dried. During the post-reaction stages there is a loss in product yield of up to five percent. Finally, the amount of raw materials required is larger than in enzymatic catalysis, since the process is less selective and some of the raw material will turn into by-products. The amount of waste, such as solvents, bleaching residue and by-products generated in conventional chemical production, is up to five times as high as in enzymatic production.

The Green Process

It is clear that there is much to be gained from an enzymatic production of wax esters. The enzymatic production of wax esters is more environmentally friendly than the conventional one. The energy required is much smaller and the yield is larger. The lesser amount of refining needed also results in higher yield.

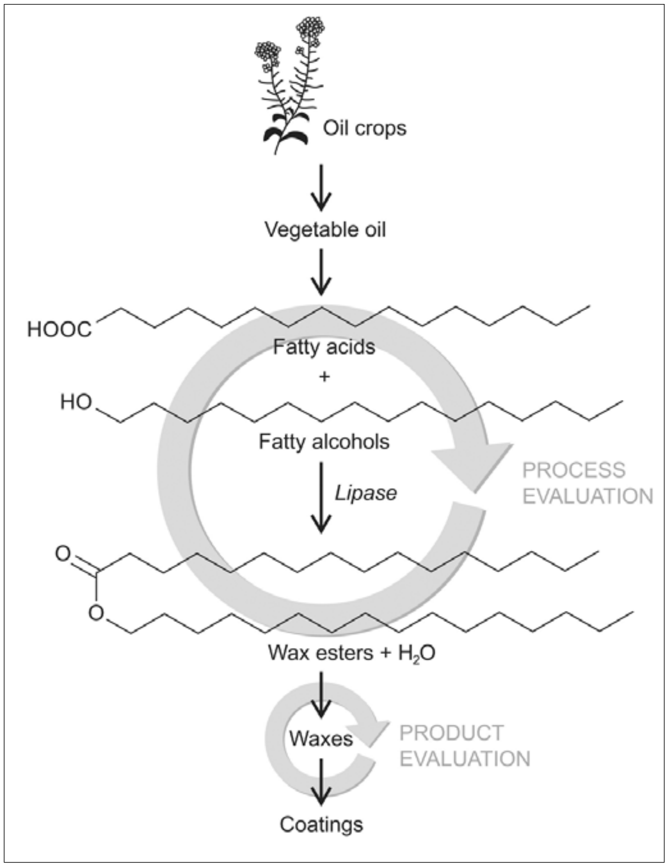


Figure 3.1 *Illustration of wax production from renewable resources.*

Table 3.1 *Molecular formulae of the synthesised wax esters.*

Cetyl palmitate	$H_3C(CH_2)_{15}OOC(CH_2)_{14}CH_3$
Behenyl behenate	$H_3C(CH_2)_{21}OOC(CH_2)_{20}CH_3$
Dibehenyl adipate	$H_3C(CH_2)_{21}OOC(CH_2)_4COO(CH_2)_{21}CH_3$
Dibehenyl sebacate	$H_3C(CH_2)_{21}OOC(CH_2)_8COO(CH_2)_{21}CH_3$

The challenge was thus to develop an attractive, green process for the enzymatic production of wax esters. Key points to address were the evaluation of possibilities for use of a solvent-free process and of finding methods for achieving sufficiently high conversion levels to allow the product to be used with only a minimum of purification.

From an economic point of view, the process had to be efficient enough to prevent the enzyme costs from becoming prohibitive. To this end, a process methodology was developed, which allowed four different wax esters to be produced enzymatically in a litre-scale reactor. Their properties as wood coating waxes were investigated by the industrial partners that participated.

2. Production

Wax Esters

The alcohols used were cetyl alcohol with 16 carbon atoms in the chain and behenyl alcohol with 22 carbon atoms in the chain. The carboxylic acids used were palmitic acid with 16 carbon atoms and behenic acid with 22 carbon atoms as well as adipic acid (1, 6-hexanedioic acid) and sebacic acid (1, 10-decanedioic acid).

Four wax esters were prepared. These were (Table 3.1) two monoesters, cetyl palmitate and behenyl behenate, and two diesters, dibehenyl adipate and dibehenyl sebacate. The numbers of carbon atoms in these compounds were thus 32, or 44 for the monoesters and 50 and 54 for the diesters.

The production of an ester amounts to the joining of the acid and alcohol in a so-called condensation reaction. It is clear that the atom yield in these reactions were very large since the only atoms lost as by-products are those of water during the condensation of the acid and alcohol.

Choice of Enzymatic Processes

The enzyme chosen was a lipase. The enzyme in the cell normally catalyses the hydrolysis of an ester, that is, the splitting of the ester bond. Here such a reaction was run backwards. This is possible as the water is removed, the equilibrium will be pushed towards the ester rather than the alcohol and acid. Of course, the energy required for the synthesis of the bond needs to be available.

The enzyme used, available commercially from Novozymes A/S in Denmark, was lipase B extracted from the yeast *Candida antarctica*. The enzyme was immobilised to a solid carrier and thus could be filtrated off after the reaction and used over again. The enzyme was quite stable. It survived low pH and rather high temperature up to 80°C, without being destroyed.

Choice of Solvents

Choice of the solvent to be used in a process is a key issue from a green chemistry perspective. Super critical carbon dioxide and ionic liquids are often referred to as *green solvents*, but use of a solvent-free process is the most attractive alternative. Solvent-free enzymatic esterification processes were a natural choice in the present study.

Removal of Water

The esterification reaction, which results in esters and water, is reversible. Thus to achieve a high yield, one of the products, water, needed to be removed. The reaction mixture should therefore contain as little water as possible.

Most enzymes need a certain amount of water in order to work. In such cases, water removal at a fixed water activity (relative humidity) is better than extensive drying. There are several methods to control the water activity of the reaction mixture. A practical way of controlling the water activity in a reactor is to measure it continuously with a sensor and to adjust it to a set value by passing air (or nitrogen) through the reaction mixture. Dry air is used to remove water from the reactor and humid air to add it. This can be carried out on a small or a large scale. If needed, the water activity can also be set at different values for separate stages of the reaction. A further advantage of this approach is that the gas bubbles produced improve the mixing in the reactor so that stirring can be reduced or even be avoided entirely, lowering the energy consumption. In this study only passing dry air for removal of water was used.

Several other possible means of water removal, such as vacuum evaporation, pervaporation, addition of cation-exchange resins, use of molecular sieves and azeotropic distillation, were not used.

Choice of Temperature

The reaction temperatures were chosen so that all the substrates (monoester synthesis) or a major part of them (diester synthesis) were in liquid form. An increase in temperature leads to an increase in reaction rates, but also to an increase in enzyme inactivation rates as well as an increase of the energy consumption. In the temperatures used, the enzyme could be filtered from the product and reused approximately 5–6 times altogether according to another study.

It has been shown earlier that between 65 and 75°C the reaction rate for isopropyl palmitate synthesis increases with increasing temperature. The optimal working temperature for the immobilised enzyme was 70–80°C according to the supplier. The initial reaction rates for the monoesters were approximately twice as high as those for the di-esters, dibehenyl adipate and dibehenyl sebacate. This might possibly be due to the fact that, at the reaction temperature employed, the di-acids were not completely melted or dissolved initially. As the reactions proceeded, they dissolved, the reaction mixtures then becoming clear.

3. Results

Reaction Equipment

A batch-wise process was used: all ingredients were added to one reaction vessel from which they were recovered after the reaction. In the beginning a solvent-free synthesis of cetyl palmitate was performed in a 25 ml round-bottomed flask. In the 25 ml-scale, removal of water occurred by simple evaporation to the surrounding air. This did not work on a larger scale.

Later on a one litre reactor containing a sensor for water activity measurement and equipment for the automatic adjust-

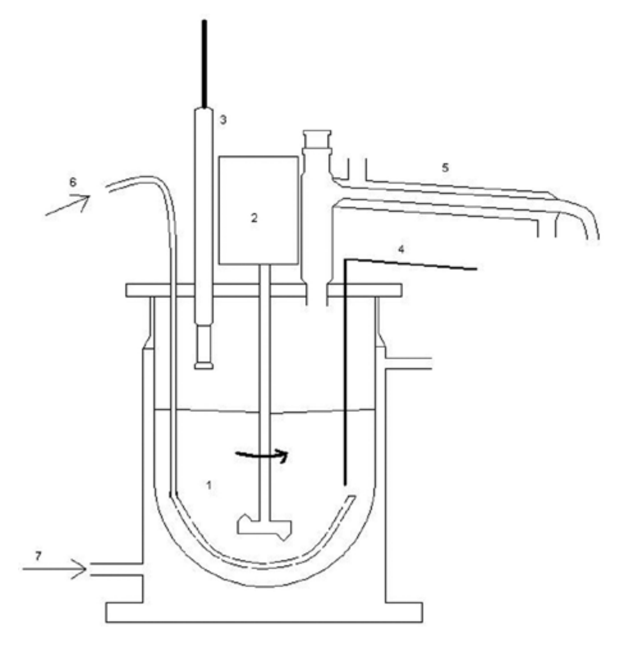


Figure 3.2 Litre scale reactor for enzymatic esterification.
1. Reaction liquid, 2. Stirrer, 3. Water activity sensor, 4. Thermometer, 5. Condenser, 6. Dry air inlet, 7. Heating medium, glycerol, inlet.

ment of water activity by use of dry or humid air was constructed (Figure 3.2).

Monitoring

Two different methods were used to monitor the reaction. The reaction was followed by gas chromatography and/or titration of the remaining acid. These methods produced similar results. Final samples were also analysed by titration of the hydroxyl groups.

Reaction

The small scale synthesis of cetyl palmitate was performed at 65°C in a three-necked round-bottomed flask. The larger scale synthesis of all four esters was performed using a one litre-scale reactor.

The alcohol and the acid were mixed in equimolar amounts and, when the substrates had been melted, the immobilised lipase, i.e. the enzyme, was added to start the reaction. During the reaction, water activity and temperature were measured in the air above the reaction liquid by a relative humidity sensor. The reaction mixture was analysed by gas chromatography and/or titration.

Yields

When the synthesis was performed in the litre-scale reactor with an equimolar mixture of the starting materials carboxylic acid and alcohol, without any deliberate water removal, only 65% conversion was obtained. When the water was removed during the process by a stream of dry air passing through the reactor all four esters were synthesised at high conversion, 95–99% (Table 3.2).

In most cases some conversion could be observed before addition of enzyme, which could be explained by spontaneous esterification during the drying of the substrates. Almost complete, 98%, conversion to cetyl palmitate was achieved when the reaction mixture was dried by use of dry air from the start.

The various reactions differed in initial reaction rate after the enzyme was added. The initial reaction rate was highest for cetyl palmitate, even though this reaction was run at a lower temperature than the others.

4. Industrial Scale Production

Design of the Industrial Scale

The large-scale enzymatic production of wax esters commercially is still under development, and there are only few companies utilising these reactions. In this study some calculations were made on the properties of large-scale synthesis of wax esters. We assumed a production of 25 tonnes annually.

The reactor system most similar to the reactor used in the laboratory-scale experiments described in the present study would be a batch reactor employing air stripping. There are certain differences between the laboratory- and the large-scale systems, however. In large-scale productions there is separate heating of the in going air and the reactor. We assumed drying by heated air from the surroundings rather than by dried air and heat exchange between the in- and outgoing air.

The calculations for industrial-scale production assumed a total of six reactor systems, using air-stripping or evaporation for water removal. Heating of the reactor was achieved by circulating hot water in a mantle around the reactor and/or by preheating the air used for water removal. Both batch and continuously stirred tank reactors were evaluated.

The calculations were based on suitable reactor volumes for an annual productivity of 25 tonnes, which were estimated to be 102 L for batch and 22 L for the continuous systems. For the reactor 20 mm of insulation was used and a heat exchanger was assumed for in- and outgoing air flows when applicable, with an efficiency of 83%. The efficiency of the air heating was assumed to be 90%. The ambient temperature was assumed to be 20°C in all cases.

Energy Requirements

The energy requirements for the large-scale production of 25 tonnes of wax esters were estimated, both for batch and for continuous reactor systems using two different types of water

Table 3.2 Concluding results from ester synthesis.
Conversion results from titration. The initial reaction rate is based on mmoles ester bonds formed.

Ester	Temperature (°C)	Initial reaction rate (mmole $\text{min}^{-1}\ \text{g}^{-1}$)	Melting point product (°C)	Final conversion of alcohol (%)	acid (%)
Cetyl palmitate	65-67	3.4	50-51	98	99
Behenyl behenate	85-88	2.9	69-73	99	98
Dibehenyl adipate	90-93	1.4	70-73	99	99
Dibehenyl sebacate	88-90	1.4	71-74	95	99

Table 3.3 *Comparison of the energy requirements for the best enzymatic method and for the conventional production method.*

Energy demand	Enzymatic (MJ/tonne)	Conventional (MJ/tonne)
Preheating	300	540
Heat losses from reactor	40	105
Air heating	55	n/a
Mixing and water removal	25	40
Heat demand for reactor	80	80
Total	500	765

removal systems: air-stripping or evaporation. In addition, estimates were made of the energy requirements of a conventional process. The results of the calculations on the best enzymatic and conventional alternatives are shown in detail in Table 3.3.

The energy requirements for the large-scale reactor systems vary between 500 and 1500 MJ/tonne. The various batch reactors were the most efficient. On the basis of calculations concerning the best enzymatic process (batch reactor), the conventional method had an estimated energy requirement of 765 MJ/tonne, which is one and a half times that of the enzymatic process. The preheating of the substrates is the most energy-consuming step in the process, representing 60% (300 MJ/tonne) of the total energy requirement for the enzymatic process.

For the conventional chemical process conducted at 150°C, the preheating step would require 70% (540 MJ tonne) of the total energy requirements, which is 80% greater than for the enzymatic process. Several post-production steps are needed for the conventional method, although these have not been included in the calculations. Previous calculations [Hills, 2003 show that the chemical method, due to the higher temperature and the post-reaction purification steps, has energy requirements up to two and a half times as high as for enzymatic production.

Measurements of the litre-scale synthesis of wax esters indicate energy requirements of 125–160 GJ/tonne of the product, depending on the wax ester involved. The large difference as compared with the calculations for large-scale production (two orders of magnitude, in fact) clearly demonstrates the need for adequate insulation and energy recirculation for an acceptable level of energy efficiency to be achieved in large-scale production.

Products

Products made with use of enzymatic reactions have a higher consumer appeal than those made using the conventional processes, due to the environmental benefits that result. The wax esters were emulsified in water using a surfactant, the emulsions being treated further to allow them to be used in industrial wood coating equipment.

The monoesters cetyl palmitate and behenyl behenate behaved well in the wood coating equipment and produced waxy surfaces on pine wood, whereas the di-esters formed precipitates in the coating equipment, making further evaluation of them impossible. Since the melting points of the di-esters were only slightly higher than the melting point of the behenyl behenate, it was probably some other property of the di-esters that caused this behaviour.

The monoesters produced surfaces with good resistance to water, almost as good as the existing product, Vaxoline (Table 3.4). (The commercial Vaxoline product contains an acrylate in combination with a wax emulsion: approximately 40% of the dry weight is acrylate and the rest is wax.) However, the resistance to fat achieved was relatively poor. In order to improve the fat resistance, it is likely that the size of the molecules needs to be increased. Work in this direction is continuing with polyesters. Additionally more additives may be needed to gain the desired properties. The wax esters produced in the study will be evaluated for other applications as well.

5. Conclusions

Green Chemistry

The reaction can be carried out catalytically, either using a chemical catalyst, such as a strong acid, or using an enzyme.

Table 3.4 *Evaluation of the use of wax esters as components in wood coatings, as performed by Akzo Nobel Industrial Coatings. Evaluation scale 1-5, 5 being the best, (n/a = not available).*

	Vaxoline	Cetyl palmitate	Behenyl behenate	Dibehenyl adipate	Dibehenyl sebacate
Performance in coating equipment	5	5	5	1	1
Water 16h	5	4	4	n/a	n/a
Fat 6h	5	2	3	n/a	n/a
Fat 24h	4	1	2	n/a	n/a

The enzymatic process presented in this work thus fulfils several of the twelve principles of green chemistry formulated by Anastas and Warner in 1998.

Evaluation

The enzymatic process consumed 34% less energy and generated less waste than chemical esterification using a strong acid as catalyst. Two of the esters worked well in the industrial wood coating equipment employed and produced surfaces resistant to water and somewhat less to fat stains.

Life cycle assessment (LCA) has been recognised as a tool for the environmental evaluation of new, green alternative processes. This involves quantifying the benefits these have compared to the traditional chemical processes. In an ordinary LCA, the total environmental impact is calculated for the complete life cycle of the product, from cradle-to-grave. Such LCAs include feed stock production and the manufacturing, use and final disposal of the product. In considering only the processes, a gate-to-gate perspective can be employed. This is relevant when the systems compared utilise the same raw material and the product they result in are the same. One important parameter of LCA is the input of energy, which is analysed here for the processes involved. A schematic diagram of the chemical and the enzymatic processes is shown in Figure 3.3.

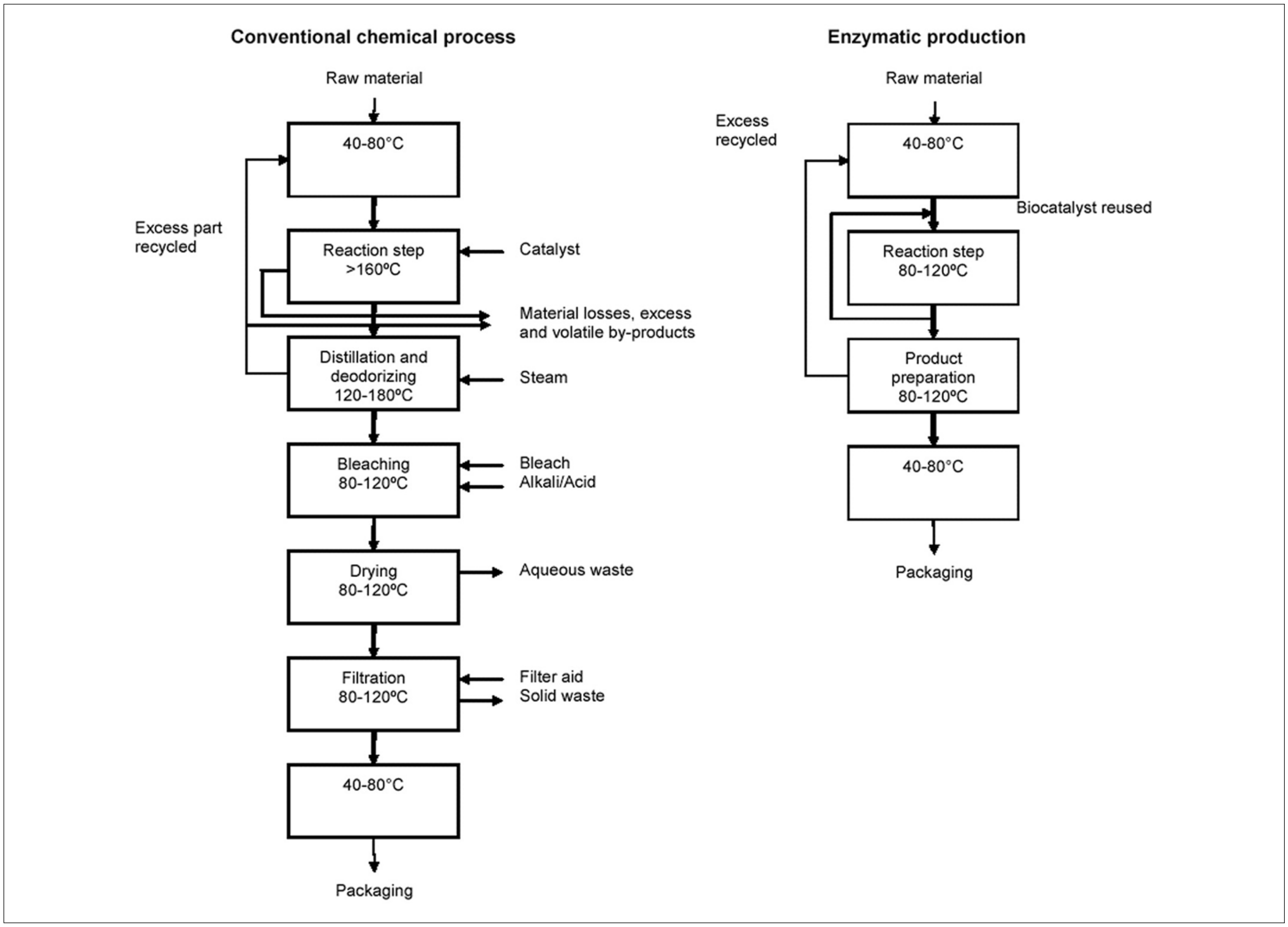


Figure 3.3 *Schematic diagrams of conventional chemical ester synthesis and the corresponding enzymatic process.*

Contacts

Companies

Akzo Nobel Industrial Coatings AB (Malmö, Sweden)
http://www.ic-akzonobel.com

IKEA of Sweden (Älmhult, Sweden)
http://www.ikea-group.ikea.com/corporate/

Authors

Anna E. V. Petersson *
Linda M. Gustafsson **
Mathias Nordblad *
Pål Börjesson **
Bo Mattiasson *
Patrick Adlercreutz *

* *Department of Biotechnology,*
Centre for Chemistry and Chemical Engineering,
Lund University
** *Environmental and Energy Systems Studies,*
Department of Technology and Society,
Lund University

Contact address

Greenchem Research Programme
Department of Biotechnology
Centre for Chemistry and Chemical Engineering,
Lund University,
P.O. Box 124, SE-221 00, Lund, Sweden.
E-mail: anna.petersson@biotek.lu.seb

Financing

The Foundation for Strategic Environmental Research (MISTRA).

References

Anastas, P. T. and Warner, J. C. *Green Chemistry: Theory and Practice*. Oxford University Press, 2000.

Derksen, J. T. P., Cuperus, F. P. and Kolster, P. Paints and Coatings from Renewable Resources, in *Industrial Crops and Products*, vol. 3, no. 4, pp. 225–236. Elsevier, 1995.

Hills, G. Industrial Use of Lipases to Produce Fatty Acid Esters, in *European Journal of Lipid Science and Technology*, vol. 105, no. 10, pp. 601–607. WILEY-VCH, 2003.

Petersson, A. E. V., Gustafsson, L. M., Nordblad, M., Börjesson, P., Mattiasson, B. and Adlercreutz, P. Wax Esters Produced by Solvent-Free Energy-Efficient Enzymatic Synthesis and their Applicability as Wood Coatings, in *Green Chemistry*, vol. 7, no. 12, pp. 837–843. Royal Society of Chemistry, 2005.

Schmid, A., Dordick, J. S., Hauer, B., Kiener, A., Wubbolts, M. and Witholt, B. Industrial Biocatalysis Today and Tomorrow, in *Nature*, vol. 409, no. 6817, pp. 258–268. Nature Publishing Group, 2001.

Straathof, A. J. J., Panke, S. and Schmid, A. The Production of Fine Chemicals by Biotransformations, in *Current Opinion in Biotechnology*, vol. 13, no. 6, pp. 548–556. Elsevier, 2002.

Thomas, S. M., DiCosimo, R. and Nagarajan, V. Biocatalysis: Applications and Potentials for the Chemical Industry, in *Trends in Biotechnology*, vol. 20, no. 6, pp. 238–242. Elsevier, 2002.

Case Study 4 **Meat Processing Industry**
Russia

Energy Management in a Meat Processing Company

1. The Background

The Company

The food processing company to be described here was created in 1992 on the basis of a large meat processing plant from 1933. For years it has been one of the more advanced meat processing industries in Russia.

At present the company occupies an area of 96 hectares. Its east-west extension is 1,150 m and the north-south 1,250 m. 380–500 m from the northern border of the industrial area there is a residential area. The sanitary-protective zone of the enterprise is 1,000 m.

There are several production units at the company. To the Meat Processing Plant No 1 (MPP-1) and No 4 (MPP-4), comes a Shop of Dry Broth (SDP) and a Factory of Medical Preparation (FMP). More than 500 different meat products, sausages and medical preparations are produced. The company has the capacity to manufacture more than 200 tonnes of sausages daily.

The company has its own heat power station, repair-mechanical department, compressor shop, automobile and railway transportation stations, construction shop, wastewater treatment station, trading office and factory shops.

Improvement of the Technology and Environmental Protection

During the last few years the company has replaced outdated equipment and technologies in the main production. At the same time technologies for improved environmental protection were also introduced. As a consequence the emissions of pollutants into air, wastewater to the urban sewage treatment plant, and the quantity of industrial solid waste have decreased substantially.

One of the basic environmental problems remaining unsolved is the relatively large consumption of energy. This constitutes a considerable and unjustified weakness of both the economy and the environmental impact.

Energy Production and the Cleaner Production Project

The Heat Power Station (HPS) of the company is a cogeneration station with combined generation of both heat and electric power. The heat and electricity are used for the entire plant and not easily divided between the individual processes or products.

At the power station fuel expenses are the largest part of the production costs. They are divided between heat (77%) and electric energy (23%).

The cost for heat during summer is 80 RUR/Gcal (RUR = Russian Roubles per Giga calories; 80 RUR = 2.3 euros; 1 Gcal = 1,160 kWh); during the cold winter season the cost increases by some 40% to 110 RUR/Gcal.

The work to reduce heat losses began within the framework of a Cleaner Production programme in 1999. A working group reviewed the production of electricity and heat in detail. The most important result was that the poor insulation of heat

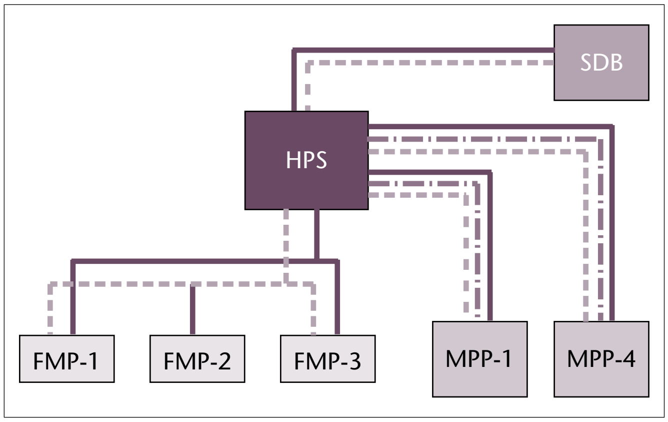


Figure 4.1 Scheme of Emergency Sites of Heat Pipelines. *FMP = Factory of Medical Preparations; MPP = Meat Processing Plant; SDB = Shop of Dry Broth; HPS = Head Power Station.*

pipelines caused heat losses exceeding the norm by 5–25%. The company thus decided to improve the thermal insulation of its heat pipelines.

The objectives of the thermal insulation improvements were to:

- Reduce the heat losses.
- Maintain the heat produced to the factory.
- Create safe conditions for the employees.

The project lifetime was 10 years. The period of project implementation was three months.

2. The Cleaner Production Project

The Heat Pipelines

The heat pipelines were transporting (Table 4.1):

- Steam at 3 atmosphere pressure and 265°C.
- Steam at 8 atmosphere pressures and 395°C.
- Hot water at 60°C for processes.
- Hot water for heating the rooms.

Steam at 3 atmospheres dominates and accounts for about 80% of the heat.

Pipelines in bad condition accounted for about 40% of the total length. It included the pipelines delivering heat to meat production plants 1 and 4, the Shop of Dry Broth and the Factory for Medical Preparation.

Table 4.1 *Distribution of heat consumption between production sites.*

Production	Steam, 8 atm (Gcal/year)	Steam, 3 atm (Gcal/year)	Hot water (Gcal/year)	Heating (Gcal/year)
Temperature	**395°C**	**265°C**	**60°C**	**varying**
MPP-1	892	11,685	862	633
MPP-4	328	8,686	1,034	380
FMP	–	27,273	1,018	1,052
SDB	2,831	–	4,511	284
Total:	4,051	47,644	3,368	2,349
Heat losses	203	2,382	842	587
Losses (%) above permitted	5	5	25	25

Table 4.2 *Diameters (mm) and lengths (meter) of the pipelines on the scheme.*

Diameter of a pipe (mm)	Length pipelines, 8 atm. vapour (m)	Length pipelines, 3 atm. vapour (m)	Length pipelines of hot water (m)
89	–	–	236
100	400	400	–
108	–	–	383
150	–	–	635
250	–	–	400
273	1,020	1,174	311
385	100	–	–
Total length (m)	1,520	1,574	1,965

The loss of a total of some 4,000 Gcal/year basically was occurring where the insulation of the pipelines was broken.

A diagram of the heat pipeline, where replacement of insulation is required, is given in Figure 4.1. Table 4.2 shows the size of the pipelines.

Properties of Thermal Insulation Materials

A study of modern thermal insulation materials was carried out. The properties of several of the most frequently used types of the materials are given at the Table 4.3.

The material need for the insulation of hot water/vapour pipelines is calculated from the required thickness of thermal insulation material. Most important is thermoconductivity and heat losses. The calculation for the "cylinders" of Rockwool is given as an example:

The *pipeline used for hot water at 60°C* needs 20 mm of insulation. The diameters and lengths of the pipelines to be insulated and the required volumes of insulation are as follows:

Diameter	Length	Thickness of insulation	Volume of insulation
89 mm	236 m	20	1.32 m^3
150 mm	635 m	20	5.98 m^3
250 mm	400 m	20	6.28 m^3
273 mm	311 m	20	8.00 m^3

The pipelines for steam at 3 atmosphere and 265°C was as follows:

Diameter	Length	Thickness of insulation	Volume of insulation
100 mm	400 m	30	3.76 m^3
273 mm	1,174 m	30	30.19 m^3

The pipelines for steam at 8 atmosphere and 395°C was as follows:

Diameter	Length	Thickness of insulation	Volume of insulation
100 mm	400 m	20	2.51 m^3
273 mm	1,020 m	30	26.23 m^3
385 mm	100 m	30	63.63 m^3

From the data it is concluded that about 4,500 m of pipelines should be insulated and a total of 91 m^3 of insulation material is required. When the same calculations were made for the other materials (Table 4.4) it was found that the same degree of insulation would require 418 m^3 of Mineral-wadding Stitched Mats or 412 m^3 Mineral-wadding Products with Goffered Structure.

Table 4.4 also shows the costs for various materials according to the prices of Russian suppliers.

Table 4.3 *The properties of thermal insulation materials (RUR = Russian Roubles).*

Material	Average density (kg/m^3)	Heat conductivity (Wt/m·K)	Temperature of application (°C)	Life expectancy (years)	Price (RUR/m^3)
Mineral-wadding cylinders Rockwool (TU 361180-85)	125	0.035	+40…+600 (incombustible)	5	1,050
Mineral-wadding stitched mats (GOST 21880-86 Sort 100)	120	0.057	+180…+450 (incombustible)	5	600
Mineral-wadding products with goffered structure (TU 36.16.22.8-86)	110	0.05	+60…+400 (incombustible)	5	700

Table 4.4 *The comparative characteristics of thermal insulation materials (RUR = Russian Roubles).*

Material	Average density (kg/m^3)	Heat conductivity (Wt/m·K)	Required volume (m^3)	Mass (kg)	Price (RUR/m^3)	Material costs (RUR)
Mineral-wadding cylinders Rockwool (TU 361180-85)	125	0.035	90.51	11,313.8	1,050	95,036
Mineral-wadding stitched mats (GOST 21880-86 Sort 100)	120	0.057	417.99	50,158.8	600	250,794
Mineral-wadding products with goffered structure (TU 36.16.22.8-86)	110	0.05	411.73	45,290.3	700	288,211

The comparative study thus showed that the most material-effective as well as cost-effective insulation material was provided by Rockwool.

The Outside Protective Layer

On the outside of the insulation is added an outside protective layer. To determine the material needed for the outside layer it was necessary to take into account the increased pipeline diameter due to the mineral-wadding cylinders of Rockwool. The radius of the pipeline was increased by the thickness of this layer. The needed amount of the insulation materials was calculated as shown in Table 4.5.

The comparison of three types of outside protective materials (Table 4.6) showed that the most cost-effective one was glass-fibre. Hence it is advisable to use a combination of mineral-wadding cylinders of Rockwool and an external coating of glass-fibre.

3. Conclusions of the Insulation Project

Calculation of Return of Investment

The investments necessary for thermal insulation change are given in Table 4.7. They include the material cost and the cost for installation. The price per installation of 1 m of thermal insulation was 20 RUR, and the length of the pipeline to be insulated was 5,089 m. The cost was thus:

$$20 \times 5{,}089 = 101{,}780 \text{ RUR}$$

The total cost for the investment was thus calculated to 864,547 RUR.

The annual savings due to reduced heat losses were estimated from the cost of 1 Gkal (100 RUR) and the saving of 4,014 Gkal/year which amounted to 401,400 RUR.

Then the pay back *(PB)* time is:

$$PB = I_0/B = 864{,}547/401{,}400 = 2.15 \text{ years.}$$

Net Present Value *(NPV)* of heat pipelines modernisation with the terms of service life of insulation of 10 years and nominal interest rate 10%:

$$NPV = B\,k - I_0$$

where k is the discount factor, k = 6.415.

$$NPV = 401{,}400 \times 6.415 - 864{,}547 = 1{,}710{,}434 \text{ RUR } (55{,}175 \text{ USD})$$

Table 4.5 *Calculation of the amount of outside insulation material needed.*

Diameters of pipes (m)	Vapour pipeline, 8 atm (m)	Vapour pipeline, 3 atm (m)	Hot water pipeline (m)	Outside protective layer (m^2)		
				Vapour pipeline 8 atm	Vapour pipeline 3 atm	Hot water pipeline
0.089	–	–	236	–	–	382.38
0.1	400	400	–	703.36	803.84	0
0.108	–	–	383	–	–	711.95
0.15	–	–	635	–	–	1,515.36
0.25	–	–	400	–	–	1,456.96
0.273	1,020	1,174	311	4,266.13	4,910.23	1,300.75
0.385	100	–	–	558.92	–	–
Total material consumption:				16,609.88 m^2		

Table 4.6 *The Properties of materials for an outside protective layer.*

Outside insulation material	Thick-ness (mm)	Life expectancy (year)	Density (m^3/kg)	Surface of material (m^2)	Price of material (RUR/m^2)	Cost (RUR)
Steel zinc-coated (GOST 14918-80)	0.55	10	7,800	16,610	66.25	1,100,405
Glass-fibre (TU 6-11-145-80)	0.4	8	186	16,610	25	415,247
Ruberoid (GOST 10923-83 Sort 420)	0.3	2	1,100	16,610	12	199,319

Table 4.7 *Costs of investments.*

Investment	Cost (RUR)
Documentation and design	3,000
Materials	709,131
Transportation and storage costs	12,282
Labour cost	101,780
Social taxes	38,954
Total (I_o):	**864,547**

Calculation of Natural Resources Consumption

The consumption of natural resources for the chosen combination of thermal insulation materials was calculated using the MIPS methods. Thus the MI factors obtained from the Wuppertal Institute were used to compare the natural resource use for some of the investments (Table 4.8). It is clear that the chosen solution of Rockwool insulation with a protective layer of glass-fibre is the best alternative for a minimum value of MIPS.

Conclusions

The results of the comparative analysis of various types of thermal insulation materials were determined both by means of traditional parameters of profitability and based on the MIPS concept.

The most effective type of thermal insulation is the combination of Mineral-wadding cylinders of Rockwool and outside protective layer of glass-fibre, TU 6-11-145-80.

The insulation of the worst parts of the heat pipelines required a significant investment (27,889 USD), their pay back time is 2.15 years, and for 10 years of operation it will yield a Net Present Value of 55,175 USD.

Contacts

Authors

Olga Sergienko and Sergey Esaulov

Contact address

Olga Sergienko
St. Petersburg State University
of Refrigeration and Food Technology
Lomonosova ulitsa, 9, 191002 St. Petersburg, Russia
Tel/Fax: +7-(812)-315 22 14
E-mail: OlgaSergienko@svs.ru

Internet Resources

The Wuppertal Institute

http://www.wupperinst.org/en/home/index.html

Table 4.8 *Material Input.*

Material	Required mass (kg)	MI-factor (kg/kg)	Natural resources (kg)
Thermal insulation material			
Mineral-wadding cylinders Rockwool (TU 361180-85)	22,627	4.7	106,349
Mineral-wadding stitched mats (GOST 21880-86. sort 100)	100,317	4.7	471,492
Mineral-wadding products with goffered structure (TU 36.16.22.8-86)	90,580	4.7	425,728
Outside protective layer *			
Steel zinc-coated (GOST 14918-80)	71,256	3.0 (iron-coated)	213,770
Glass-fibre (TU 6-11-145-80)	1,544	3.6 (polyester fibre)	5,560
Ruberoid (GOST 10923-83 Sort 420)	27,406	2.0 (linoleum)	27,406

** The outside insulation layer is calculated for mineral-wadding cylinders of Rockwool.*

Case Study 5

SCA Pulp and Paper mills
Sweden

Pulp and Paper Industry in Sweden – An Ideal Case for Cleaner Production

1. Pulp and Paper Production

Pulp and Paper in the Baltic Sea Region

Pulp and paper production is an important industrial branch in the Baltic Sea region. Of world production Sweden, Finland and Russia has about 4% each of pulp and 5% each of paper. Of world export Sweden has 11% of pulp and 12% of paper, only behind Canada and Finland. European Union countries constitute the most important market. Production approximately increased ten-fold during the 20th century. This development had its parallel in the increased production of wood raw material, especially spruce, from the large forests in the region.

Some of Europe's largest paper producers are located in Sweden. The merger of Swedish Stora with Finnish Enso in 1998 created a giant that is now the world's second-largest paper producer, specialising in publication and fine papers (in addition to packaging boards and wood products). Swedish producers have also taken the lead in other niches, aided by the country's strength in research and biotechnology coupled with high-tech chemical processes and supply of primary fibre from native slow-growth forests.

The Companies

Ranked third in Europe after Germany and Finland, Sweden's pulp and paper industry maintains a strong competitive edge. A decade-long round of restructuring has resulted in the global industry becoming highly concentrated in a few players and production plants. In Sweden, the six largest *pulp mills* account for almost 60% of national capacity, which in turn is close to the current annual production level of 11.4 million tons.

The largest pulp producers include Södra, Stora Enso and SCA (Svenska Cellulosa Aktiebolaget) with a number of plants in Sweden and abroad. Also, the development of the plants has gone from many smaller factories to a few very large plants. Concentration is almost as high in the paper sector, with the 12 largest *paper mills* (out of a total of 47) accounting for 65% of the national 11.5 million ton capacity.

Environmental Improvements

It is in connection with this development that a dramatic improvement in the environmental and technical performance of pulp and paper production has taken place. The dominating problems have been the emissions of fibres, BOD and COD, and chlorinated hydrocarbons. In Sweden these were at their worst in the mid 1960s. Since then a systematic effort for improvements has resulted in dramatic decreases in environmental impact and improved economic performance.

Research is still very active and important in the sector. As a result, pulp production is coming closer to the ideal of the "closed factory" or "zero emission factory", where nothing is emitted except the products. Secondly the energy efficiency is increasing to the extent that it is possible to sell lignin as a biofuel, as an additional product from the sector.

2. The Process Technologies

Sulphate or Kraft Pulping

The objective of the paper production technology is to separate cellulose fibres from the wood structure, kept together by lignin. The free fibres in the pulp are then the main raw material for paper production. *Sulphate or Kraft pulping*, dominating production today, produces pulp with high strength and can use a wide variety of wood species. The pulp yield is less than 50%, but the chemicals can be recycled and re-used in the mill. (See *Cleaner Production Practices* for further details.)

Bleaching

Bleaching is needed to remove colour associated with remaining residual lignin. Bleached kraft pulp is mainly used for printing and writing grades, while unbleached kraft pulp is used in the production of packaging grades. The bleaching chemicals are *injected* into the pulp and the mixture is *washed* with water. This process is repeated several times and generates large volumes of liquid waste. Additionally, vents from the bleaching tanks emit hazardous air pollutants including chloroform, methanol, formaldehyde, and methyl-ethyl-ketone.

The Recovery of Chemicals

The process flowsheet of the kraft process is designed to recover the cooking chemicals and heat. In the recovery line, spent cooking liquor and the pulp wash water are combined to form a weak black liquor which is concentrated through *evaporation* from 16% to 60-80% solids in a multiple-effect evaporator system. The strong black liquor is then incinerated in a *recovery boiler*. Combustion of the organics dissolved in the black liquor provides heat for generating process steam. The carbon dioxide formed in the combustion reacts with part of the sodium in the black liquor to sodium carbonate (Na_2CO_3) and the sulphur content is converted to sodium sulphate (Na_2SO_4). The sulphate is converted to sodium sulphide (Na_2S) by reduction with carbon present in the melted slag at the bottom of the furnace.

The smelt is dissolved in water to form *green liquor*, which is transferred to a causticizing tank where quicklime (calcium oxide) is added to precipitate the carbonate content in the green liquor as calcium carbonate and instead produce the sodium hydroxide needed to convert the solution back to white liquor for return to the digester system. The precipitate from the causticizing tank is calcined in a lime kiln to regenerate quicklime.

Production of Paper

Production of paper starts with *stock preparation* where various grades of pulp are mixed in a *mixing chest* to obtain the desired properties, *refined* to increase the strength of the paper, screened and cleaned. After that, different dyes, defoamers, fillers and retention agents are added (*filling*) and the consistency is adjusted with the addition of water ("white water") before the pulp suspension enters the head box of the paper machine.

In the paper machine the fibre suspension is introduced to the wire net, where water is drained assisted with rolls, foils, and vacuum boxes (*dewatering*). It is further dewatered by *pressing* (up to a solid content of around 50%), and *drying* (to about 95% solids content). Examples of *finishing operations* are sizing, coating, dyeing, and calendering.

3. Environmental Problems in Pulp and Paper Industry

Water Use

Pulp mills are – and were even more so in the past – big *water users*. The total requirement of raw water has through cleaner production measures been reduced from about 200-300 m³ per ton of pulp in 1970 to well below 50 m³/ton, in some mills even below 10 m³/ton. Their consumption of fresh water can seriously harm habitats near mills, reduce water levels necessary for fish, and change water temperature, a critical environmental factor for fish.

The level of wastewater treatment varies widely throughout the world depending on individual mill policy, company policy and state legislation. However there are a few general areas of concern that can be identified in a way outlined below. The most common organic pollutants in effluents are suspended solids (SS) e.g. lost cellulose fibre, dissolved organic compounds such as dissolved lignin compounds, carbohydrates, starch and hemi-cellulose (BOD/COD). Acidic compounds are predominantly natural resin acids.

From mills using elemental chlorine in their bleaching sequence, waste waters contain chlorinated organic products formed by elemental chlorine reacting with wood products to form chlorinated organics (AOX). Wastewater flow from a traditional pulp and paper mill constitutes 160-230 m³ per ton of paper.

Solid Waste

Paper production produces a large amount of *solid waste*. Firstly, during the debarking and chipping process, wood chips or fibres often become contaminated with dirt or sand when they fall from conveyors. That renders them unusable to make paper or as a fuel. Bark is also contaminated with sand and dirt. Secondly, within the recovery process, the paper fibres can be recycled only a limited number of times before they become too short or weak to be used for producing high quality paper. The broken, low- quality fibres are separated out to become waste sludge. All the inks, dyes, coatings, pigments, staples and "stickies" (tape, plastic films, etc.) are also washed off the recycled fibres to join the solid wastes.

Energy

The pulp and paper industry uses 84% of the *fuel energy* consumed by the forest products industry as a whole. It is one of the largest producers of greenhouse gas (GHG) emissions. Over the past few years, the pulp and paper industry has considerably reduced its GHG emissions by introducing energy conservation projects and by increasing its use of biomass as an energy source. A modern kraft pulp mill is essentially self-sufficient in energy. The only oil consumer is the causticing oven, where oil can in fact be replaced with bio-fuel.

A paper mill requires between 400 and 1000 kWh electricity/ton paper and 4-8 GJ heat/ton for drying in the paper machine. In an integrated pulp and paper mill this energy is provided from the recovery boiler.

Bleaching

Depending on the bleaching chemicals used, the wastewater streams from the bleaching process may contain chlorine compounds and organics. The mixture of chemicals may result in the formation of a number of toxic chemicals (such as dioxins, furans and chlorinated organics). Although this effluent is generally released to a wastewater treatment plant, the chemicals named above simply "pass through" the plant (i.e. the treatment plant does not significantly reduce the concentrations of these pollutants) and accumulate in the rivers, lakes and oceans to which the treatment plant discharges.

Emissions

Regulated wastes and emissions from the pulp and paper industry include liquid and solid wastes, air emissions, and wastewater.

Air emissions from chemical pulp mills are primarily made up of particulates, hydrogen sulphide, oxides of sulphur and oxides of nitrogen. Micro-pollutants include chloroform, dioxins and furans, other chlorinated and volatile organics. Emissions from kraft mills also contain reduced sulphur gases as methyl mercaptan, dimethyl sulphide and dimethyl disulphide which together with hydrogen.

Wastewater releases contain chlorinated phenolics, dioxins, furans and other chlorinated compounds, phosphates, small amounts of residual organics and suspended sediments.

Paper mills also produce non-hazardous *solid waste* such as sludge derived from their pulping and bleaching operations.

4. Cleaner Production Measures

Increasing Brown Stock Washing Efficiency

After cooking, the brownish pulp needs to be carefully washed. Any remaining cooking liquor will increase the chemical consumption in subsequent stages. It is also of the utmost importance to recover the cooking chemicals and the dissolved organic substances. The brown stock washing is done in several counter–current stages. The filtrate from this washing is the black liquor sent to the chemical recovery system. Efficient washing is critical to maximise return of cooking liquor to chemical recovery and to minimise carry over of cooking liquor (known as brown stock washing loss) into the bleach plant, because excess cooking liquor increases consumption of bleaching chemicals. The most common washing technology is rotary vacuum washing, carried out sequentially in two or four washing units. Other washing technologies include diffu-

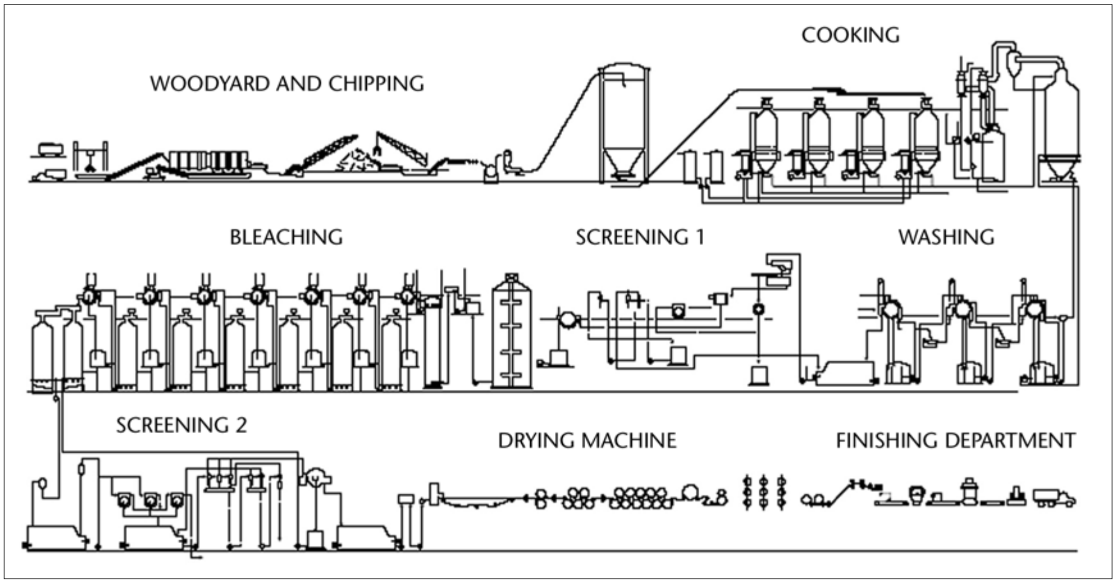


Figure 5.1 *Simplified flow diagram of an integrated pulp and paper mill (chemical pulping, bleaching and paper production) [U.S. EPA, Office of Compliance. Sector Notebook Project: Profile of the Pulp and Paper Industry, 1995].*

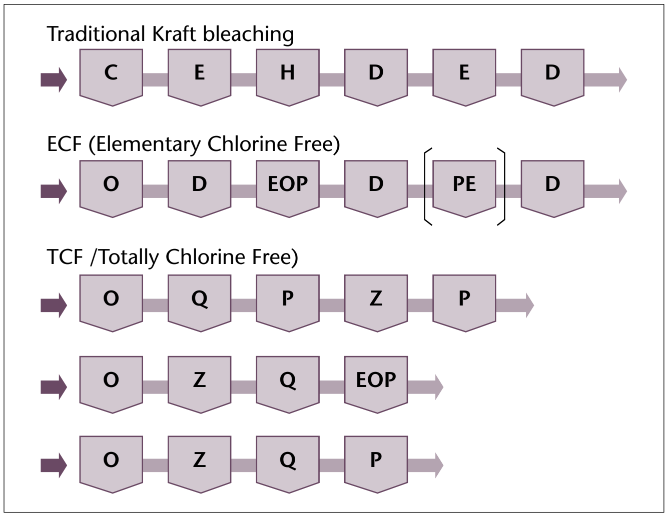


Figure 5.2 *Examples of bleaching sequences. Bleaching chemicals are elemental chlorine (C), sodium hypochlorite (H), chlorine dioxide (D), oxygen (O), ozone (Z) and hydrogen peroxide (P). Metals are removed with a complexing agent (Q) such EDTA or DTPA [adapted from Miljöinfo från Skogsindustrierna, 1995].*

sion washers, rotary pressure washers, horizontal belt filters, wash presses, and dilution/extraction washers.

Water Reuse from Evaporators

The evaporation plant is always one of the largest steam consumers in the mill. Black liquor from the cooking plant with a dry solids content of 14-18% is concentrated normally to 65-75% before burning in the recovery boiler. Modern evaporation plants can operate at about 80% solids content. To minimise primary steam consumption, multiple-effect evaporation, with five to seven effects in series is used.

Stripping of foul condensate from the effects is necessary for environmental reasons, and also if the condensate is reused (instead of fresh water) in the mill. The stripper column could be heat-integrated with the evaporation plant.

The evaporation demand normally lies in the range of 6-9 tonnes water/ADMT (air dry metric ton). Differences in heat demand between different mills with the same number of effects in series are largely due to differences in the solids content of the feed (weak black liquor). In the evaporation plant the weak black liquor, which comes from the washing department, is concentrated to as high a concentration as possible depending on the design of the plant.

Recycling of Material

In open screen rooms, wastewater from the screening process goes to wastewater treatment prior to discharge. In closed loop screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. Centrifugal cleaning (also known as liquid cyclone, hydro cyclone, or centricleaning) is used after screening to separate relatively dense contaminants such as sand and dirt from the fibre material.

Solid Waste Recycling

Rejects from the screening process are either repulped or disposed of as solid waste. Pulp screening, removes remaining oversized particles such as bark fragments, oversized chips, and uncooked chips. The selective screening philosophy addresses the removal of unwanted particles from the pulp. The optimal solution is reached by integrating screening into the modern fibre line process;

One way of *sludge utilisation* is by means of land-spreading; this method of sludge disposal is an area of concern, as sludge constituents are not well identified, the sludge in any given mill is highly variable, and the effects of the sludge components on land is not thoroughly researched. The major concerns are possible contamination of soils with heavy metals and organic micro-pollutants. Well-designed, independently monitored pilot projects of significant duration are necessary before this practise can become widespread.

Bleaching

Bleaching is defined as any process that chemically alters pulp to increase its brightness. Typically, 4-8% of pulp is lost due to bleaching agent reactions with the wood constituents cellulose and hemicellulose, but, these losses can be as high as 18%.

Important cleaner production measures include:

Avoid chlorine bleaching. Chemical pulp bleaching has undergone significant process changes since the beginning of the 1960s. At that time, nearly every chemical pulp mill that used bleaching incorporated elemental chlorine (Cl_2) into some of its processes. Initially some of the elemental chlorine bleaching stages were replaced by sodium hypochlorite (NaClO) and chlorine dioxide (ClO_2) Environmental concern has been a strong driving force for the development of new bleaching technologies as Elemental Chlorine Free (ECF) and Total Chlorine Free (TCF) bleaching technologies.

From an environmental point of view, the most important changes in bleaching technology has been the introduction of oxygen delignification and the use of 100% chlorine dioxide in the pre-bleaching stage. Since chlorine dioxide predominantly acts as an oxidant, the formation of chlorinated lignin, low molecular weight phenols and acids can be shown to strongly decrease. At the same time, the formation of chlorinated dioxins and dibenzofurans both in the product and in the effluent is reduced to levels around or below the detection limit.

Because of the different reaction mechanisms different types of bleaching chemicals are utilised in a bleaching sequence. Acid and alkaline stages are used to complement each other. Peroxide bleaching is relatively slow and requires long reaction times and therefore large reactor volumes or increased pulp consistency. Increased pressure makes higher reaction temperatures possible, resulting in a reduced reaction time or improved bleaching outcome. It is necessary to remove metal ions to avoid degradation of the hydrogen peroxide by using metal complexation agents (i.e. EDTA or DTPA) or acid washing. An advantage with peroxide compared with the other oxygen bleaching chemicals is that peroxide bleaching at optimal conditions brightens the residual lignin. A final solution has still not been achieved for either approach. Remaining tasks include:

- *Continuing research on biotechnological bleaching and electrochemical bleaching:* Research has to explore further these processes by synthesising improved mediators, by improving bleaching enzymes and optimising electrochemical processes for bleaching pulp. Ultimately this research may lead to novel, cost-effective, bleaching strategies that are environmentally benign.
- *Air emissions control devices.*
- Providing *spill containment and collection systems*.

Paper Production

Pulp in the stock is heated and mixed. Some different chemicals and fillers like alum, clay, and starch are added to the pulp stock for enhancement of certain paper properties. Next, the pulp suspension is evenly distributed over a travelling belt of fine wire screening, and carried to rolls. Part of the water contained in the pulp suspension passes through the screen with the assistance of vacuum boxes and pressing between rolls. The long fibres are laid down as a fibre layer on the wire net. The fibre layer is carried over to a system of pressing and heated rolls, dewatering the paper to a water content of around 50%. Then the paper is air dried in a steam-heated dryer section. After drying, the sheet may be surface treated and then finished. A considerable portion of the fine fibres and some fillers also pass through the screen wire with the water. Because of its colour, this wastewater is called “white water”. The main sources of waste from paper mills are beaters and paper machines.

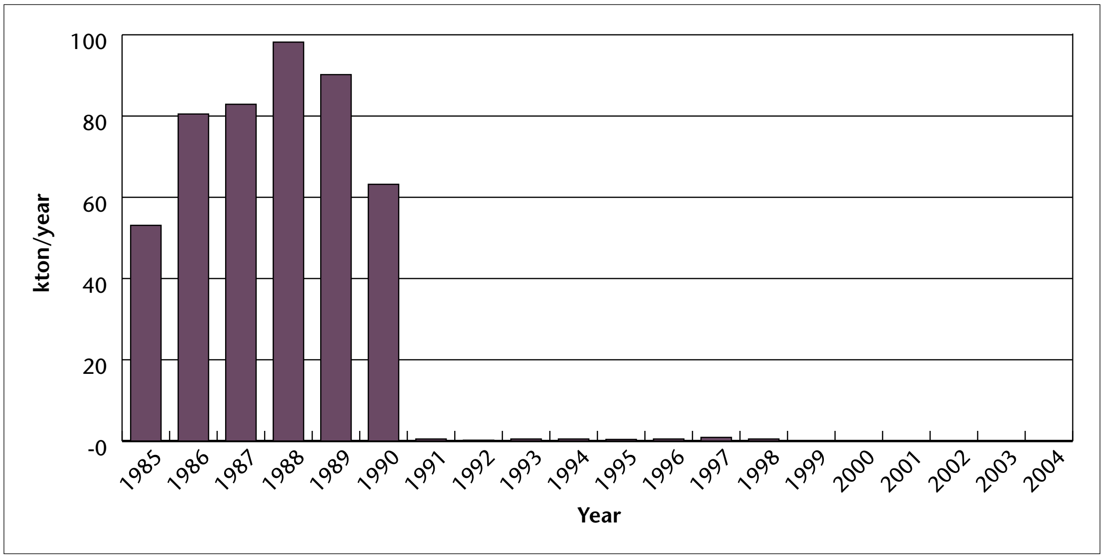


Figure 5.3 *Amount of organic waste sent to landfill from SCA Forest Products, Östrand pulp mill [Roine Morin, Environmental Manager of SCA Graphic Sundsvall AB].*

Important cleaner production measures include:

- *Cleaning the roll* in the paper machines to avoid a broken paper line. This action is an opportunity to improve housekeeping and will reduce the amount of breakage paper and, since it doesn’t need any process changes, can be easily implemented.
- *Adjustment of edge cutter* to reduce side trimming loss. This action concerns process control and can benefit to marginal reduction of pollution load by reduction of paper trimming loss and reduction of reprocessing of paper trimming.
- *Use of soft water as a boiler feed water.* It is also the change to better process control which can reduce pollution to the air by the way of reduced scaling of boiler tube and increased boiler efficiency and capacity; Recycling water evaporated from drying process by condensing.
- *Optimising the thermal effects on water* used in the paper machine and stock preparation area.
- Providing *disk save-all* for paper machine.
- *Repulping rejected paper* in a closed loop manner.

Decreased Water Discharges

The dramatic decrease of water use in the pulp production has also result in very much lower discharges in the waste-

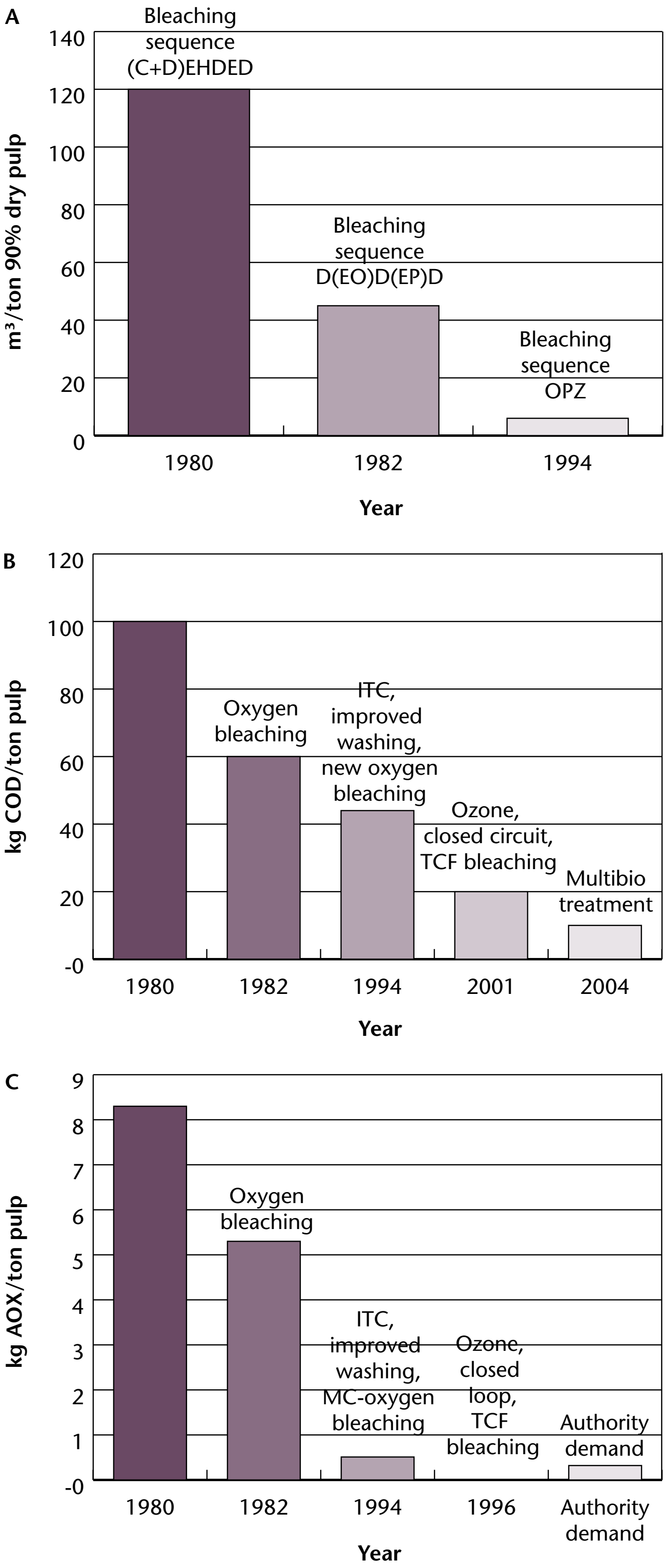


Figure 5.4 *A) Wastewater flows, total volume from SCA Forest Products, Östrand pulp mill. B) COD in the wastewater. C) AOX in the wastewater. Bleaching sequences are shown in Figure 5.2.*

water. This is illustrated in Figure 5.4A, the development of the wastewater flow from a modern pulp mill, the SCA Forest Products, Östrand Pulp mill in Sweden.

Likewise has the content of oxygen consuming material, mostly fibres, decreased due to sometimes rather simple measurers such as sieves, and much better technology. Figure 5.4B shows the development of emissions of COD since 1980 from the Östrand pulp mill. The reductions have been achieved through application of cleaner production measures and wastewater treatment.

Finally the changed technology for bleaching has resulted in much less use of chlorine and chlorine gas. As a result the emissions of chlorinated organic compounds have decreased considerably. Figure 5.4C shows the emissions of adsorbable (that is, those that are biologically problematic) organically bound halogens (mostly chlorine) called AOX, from SCA Forest Products, Östrand pulp mill. This is, from an environmental point of view, one of the most significant achievements in the pulp and paper industry.

Contacts

Company

SCA Graphic Sundsvall AB
Östrand Pulp Mill
Roine Morin, *Environmental Manager*
SE-861 81 TIMRÅ, Sweden
Tel: +46-(0)60-16 40 00
Fax: +46-(0)60-57 43 28
E-mail: roine.morin@sca.com
http://www.pulp.sca.com

Author

Lennart Nilson
Royal Institute of Technology
School of Energy and Environmental Technology,
Dept. of Industrial Ecology
SE-100 44 Stockholm, Sweden
Tel: +46-8-790 87 13
Fax: +46-8-790 50 34
E-mail: lennart@ket.kth.se
http://www.ima.kth.se

References

Mazgaj, M., Yaramenka, K., Malovana, O., Cherre, E. and Ibraimova, L. Project report, *Cleaner Production Measures for Pulp and Paper Industry*. Royal Institute of Technology, Section of Industrial Ecology, Sweden, 2006.

Case Study 6

Assa Abloy Metallurgic Industry
Sweden

Surface Treatment Processes in a Metallurgic Industry

1. Introduction

Intro

Surface treatment is a very common process in the manufacturing industry. There are also a large number of businesses that work solely with surface treatment. Some of these have very large installations, while others are small enterprises with only a few employees.

Quite another type of industry with substantial surface treatment activity is the electronics industry, in which copper coating and etching of printed circuit boards are important operations.

Surface treatment is a good example of how to combine cleaner production and end-of-pipe measures to reduce a serious emission problem in form of metal polluted wastewaters. In the concept of surface treatment we include a number of operations e.g. pickling, de-greasing, phosphatation, lacquering, chemical surface treatment, galvanic surface coating etc. Some of the environmental problems connected with surface treatment are in addition to emissions of metals, complexation agents as e.g. cyanides, acid and alkaline waste waters and solvents from de-greasing and painting operations.

Assa Abloy Metallurgic Industry

The examples described below are taken from the development of cleaner production methods at a plant for locks in Eskilstuna, Sweden. The plant belongs to Assa Abloy, an important metallurgic industry in the production of locks and security systems. Assa Abloy is the world's leading manufacturer and supplier of locking solutions. The Group has in all some 30,000 employees and annual sales of about 3 billion euros (2005). Number of employees was in 2005 29,500 in more that 150 companies operating in 40 countries. The company thus has a strong global presence and holds more than 10% of the world market. We thus have reason to believe that the achievements at the Eskilstuna plant will be used in many other places.

The plant and methods discussed below are also described on the film available on the accompanying CD.

2. The Technologies

Several Techniques

The surface of metal objects is important for the function, protection and appeal of the products. Thus great concern and much technology have developed to meet the need of surface treatment. The surfaces applied include metal surfaces, for example by chrome, copper or nickel; or they might be a paint or lacquer surface. The application of these surfaces can be made by dipping the product in a bath, by electro-coating with a galvanic method, or by spraying.

Dipping Techniques

This is used to apply a metal surface. The objects are suspended on a frame and dipped into a series of baths, all water solutions. The central part of this process, consists of dipping into of a bath, where the metal to be applied to the surface of the objects is dissolved as a salt in water.

- De-greasing and cleaning using a slightly alkaline bath with tensides.
- Rinsing to remove tensides etc.
- Bath to apply the surface coating. This may be an electrolytic process.
- First rinsing bath.
- Second rinsing bath.
- Possibly a third rinsing bath.

Spraying Techniques

In the classical spraying techniques the paint is dissolved in a solvent and sprayed on the object. The disadvantage of this method is that a substantial part of the paint is not used and that large amounts of solvents are disseminated in the surrounding and needs to be taken care of. Solvents used to be both health-wise and environmentally noxious. Nowadays more often less problematic solvents are used, e.g. alcohols, which are degraded in the environment and not as toxic.

A more modern type of spraying is using a powder to spray on the objects in a small space in which the unused powder can be recovered. No solvent is used. By a following heat treatment the powder melts on the surface of the object and creates the coating desired.

3. Environmental Concerns

Water Consumption

In the traditional method for rinsing, the treated objects were rinsed in a single bath. As the concentration of the treatment components, in particular the metals when a metal surface was applied, increased rapidly, this rinsing bath had to be renewed very often and large amounts of water were used in the process.

Wastewater Containing Metal

The large number of baths in the dipping techniques all give rise to a water solution to be discarded as wastewater, often with a considerable concentration of metals. Some of these are highly noxious, e.g. nickel is both allergenic and carcinogenic; copper as a heavy metal is not good for the environment, and chromium, especially compounds of chromium 6, are very noxious, again being both toxic and carcinogenic. The wastewater could thus not be left to a municipal sewage as it is. Wastewater treatment has thus been an important concern for the industry.

4. Wastewater Treatment Options

Precipitation of Metals

An end-of-pipe solution to the metal emission problem will result in a rather complicated cleaning process. Depending on the type of surface treatment, several treatment stages may be required.

The traditional method of dealing with wastewaters containing metals is to purify the water by chemical precipitation. The most common method is to precipitate the metals as hydroxides. It that case sodium hydroxide or, if the operation is large, lime (calcium oxide) is used, yielding a metal hydroxide precipitate according to the formula:

$$Me^{2+} + 2OH^{-} \longleftrightarrow Me(OH)_2\ (s)$$

Metals can also be precipitated as sulphides. Metal sulphides are less soluble than the hydroxides. Sulphide precipitation will give a better purification but the process will unfortunately also create problems of other kinds, e.g. risks for formation and release of hydrogen sulphide. There are chemicals available on the market that will produce metal sulphides, without the risk of hydrogen sulphide, but the costs for these chemicals are substantially higher than sodium hydroxide or lime.

A treatment unit for metal precipitation (Figure 6.1) normally consists of three parts. In the first stage the precipitation chemical is added under rapid mixing. The precipitate formed often consists of very small particles that are very difficult to separate by sedimentation. In order to get larger and more easily separated particles, special flocculation agents, e.g. a polyelectrolyte, are added in the second stage. This will cause the small particles to coagulate in larger flocks. These flocks are then separated in the third stage that usually is a sedimentation stage, often in form of a lamella sedimentation unit.

The chemical precipitation of metals is an equilibrium reaction. This means that there will always be a certain remaining concentration of dissolved metal in the purified wastewater. This remaining concentration is determined by the equilibrium equation.

An important factor for the separation efficiency is in fact the choice of pH for the precipitation. Different metals have maximum precipitation at different pH values. If a wastewater contains several different metals is will be impossible to achieve a maximum separation of all the metals. In fact it would require a multi stage precipitation process with different pH in each stage to achieve. This is however generally not economically justifiable. Usually a pH in the interval 9-10 is chosen.

The separation result is also determined by a number of other factors, making the precipitation process a rather complicated purification process. For instance, complexation agents counteract the metal precipitation, which makes it necessary to remove these before the precipitation stage. Further the surface treatment processes are often batch processes, so the purification stage will need a buffer tank in order to even out the flows.

A Second Stage of Wastewater Treatment – Polishing

In order to improve the separation result the chemical precipitation stage can be supplemented with a second purification stage, a so-called polishing stage. About half of the remaining metals in the purified water are bound as metal hydroxides, but these particles are too small to be separated in the sedimentation stage. By adding a filter stage, e.g. a sand filter, the separation can be improved.

Another option is to supplement the process with an ion exchange stage. With the ion exchanger a substantial part of the metal ions that were not precipitated can be separated.

Cleaning the Water of Other Substances

In the case of chromation the wastewater will contain chromium both as chromium (III) in the form of positive Cr^{3+} ions and as chromium (VI) in the form chromate (CrO_4^{2-}), a negative ion that cannot be separated by chemical precipitation. The purification unit has to be supplemented with a chromate reduction stage in which the Cr (VI) is reduced to Cr (III) with for example bisulphite.

If cyanides are used in the surface treatment process, these have to be removed from the wastewater before precipitation as well. Cyanide removal may be achieved either by chemical or electro-chemical oxidation. In chemical cyanide removal the water is treated with e.g. hypochlorite oxidising the cyanide to cyanate and then to carbon dioxide and nitrogen gas.

From the chemical precipitation process an environmentally hazardous metal hydroxide sludge is produced. This has to be de-watered as far as possible. This is normally done in a filter press in which a sludge with a solids content of about 30% can be achieved. The sludge has to be deposited in such a way that water is prevented from penetrating into the depository to leach the metals. According to EU regulations the landfill has to be designed as a so-called Class-1 landfill with very advanced sealing arrangements.

5. Cleaner Production Measures

Replace the Technology

One measure that is easily identified, but that in most cases actually is or at least is considered to be impossible, is to change to a completely different type of surface treatment that will completely avoid the emission problem in question. However, there are examples where this has been accomplished. For example, it has been feasible to, for environmental reasons, replace cadmium coating with other types of surface treatment. Nickel could be replaced by an alloy of copper, zinc and tin.

The use of chromium priming is another surface treatment process that, because of the environmental risks with chromium (VI), has been problematic and reduced substantially. Most often chromium (VI) is replaced by chromium (III).

Process integrating measures also include changing of raw materials and auxiliary chemicals used in a process. In order to avoid many of the problems that are connected with the use of cyanides, some companies are trying to convert to completely cyanide-free surface treatment methods.

Reducing Water Volumes Needed in the Process

In chemical or electro-chemical surface treatment processes the metal items to be treated are immersed in different process baths. Between the different treatment stages the items have to be thoroughly rinsed so that chemicals from one stage do not contaminate the next, impairing the quality of the product.

It is important to take measures to reduce the carry-over, that is, the amount of fluid film that the goods will attach to and carry with them from a bath. If this can be done the volume needed for rinsing will decrease and so will water consumption.

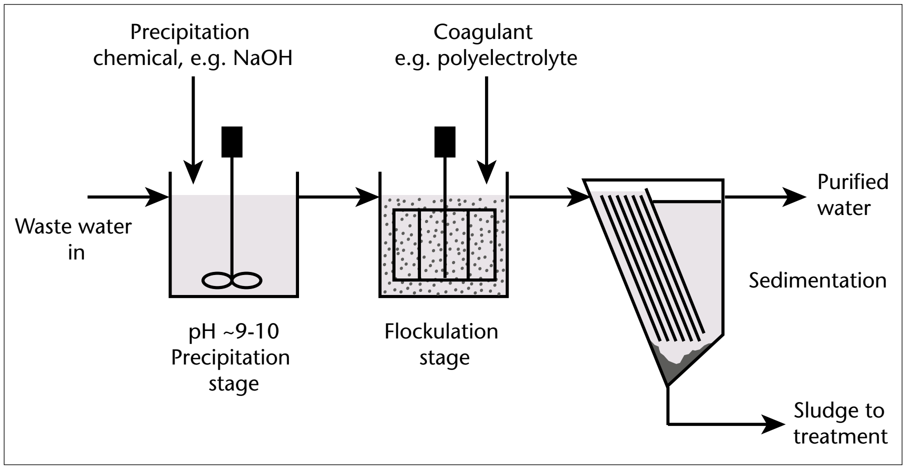


Figure 6.1 *Chemical metal precipitation.*

The size of the carry-over is affected by the following factors:

- *The viscosity of the process liquid.* A lower viscosity gives a thinner liquid film. The viscosity can be influenced by e.g. a temperature increase and the addition of a surfactant.
- *The shape of the goods and the way of mounting.* It is important that the items do not have pockets, in which liquid can be carried from one bath to another. By mounting the goods in a way that drainage is facilitated, the carry-over can be minimised.
- *Time for drainage.* It is necessary to allow sufficient time for the fluid film to drain from the items.
- *Recirculation of carry-over* with the aid of e.g. a wiper device or air blower.
- *The concentration of the bath.* By reducing the concentration of the bath as far a possible, the carry-over loss can be reduced.

Efficient Rinsing – Counter Current and Spray

A very efficient way of reducing the pollutant emissions with the wastewater from an industrial process is to reduce the water consumption in the process. The reason for this is that the concentration of pollutants will increase when the amount of water is reduced. And since a pollutant reduction stage such as a precipitation stage will render purified wastewater with a residual concentration that is independent of the concentration before the treatment stage, the total amount of pollutant emission will be reduced.

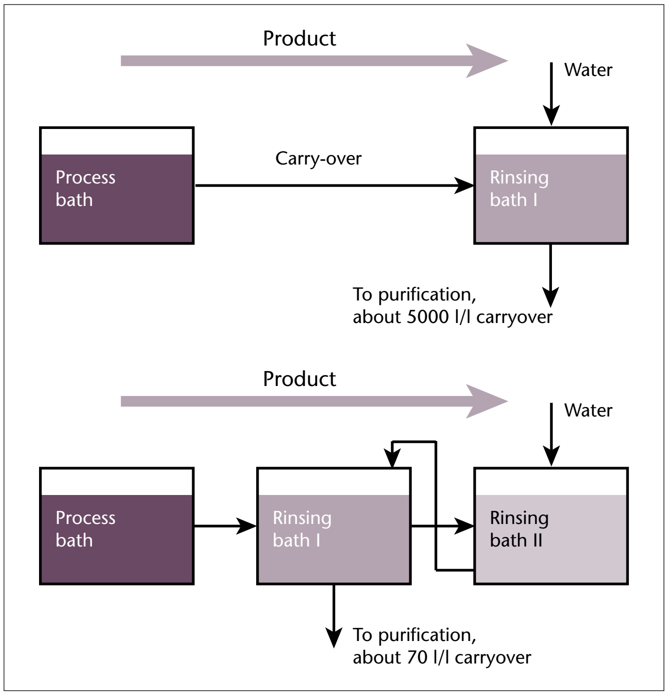


Figure 6.2 *Countercurrent rinsing.*

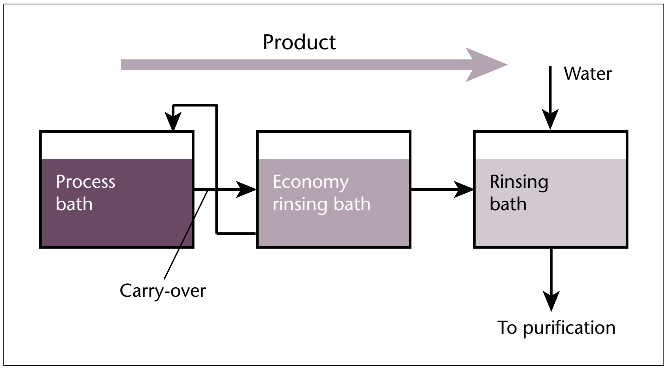


Figure 6.3 *Economy rinsing technique.*

There are a number of measures that may be taken in order to reduce the water consumption of a surface treatment process. Some options are:

In countercurrent rinsing the contaminated goods are rinsed in a first stage with the water from a preceding rinsing stage and the cleanest water is introduced in the last rinsing stage. The water for the different stages is led from one stage to the next in the opposite direction of the movement of the products, hence the name countercurrent rinsing (Figure 6.2).

Spray rinsing instead of rinsing in baths is a water conserving technique. One stage of spray rinsing corresponds in efficiency to about two stages of countercurrent bath rinsing.

Economy Rinsing
– Re-circulation of the Process Chemicals

The consumption of rinsing water can be drastically reduced by introducing a so-called economy rinsing stage, placed between the process bath and the regular rinsing stages (Figure 6.3). There is no water inflow to the economy rinsing stage, which in fact will eventually become a diluted process bath. The economy rinsing bath liquid is returned to the process stage to compensate for the loss of liquid because of the carry-over as well as because of evaporation losses. At the same time a large portion (60-90%) of the metals are recovered that otherwise would load the wastewater treatment unit.

With warm surface treatment processes the evaporation losses are considerable and here the economy rinsing technique is particularly advantageous. Some surface treatment plants even utilise shut-downs e.g. during week-ends to evaporate water to enable increased recirculation from the economy rinsing stage in order to increase the recovery of metals lost with the carry-over. Another option for increasing the recovery

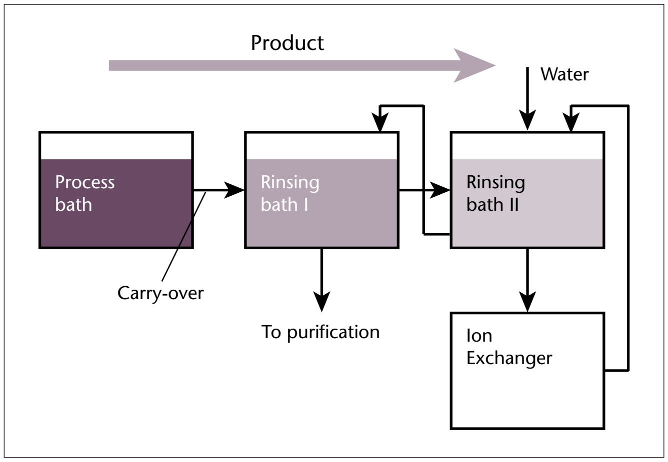


Figure 6.4 *Ion exchange as a kidney stage.*

from the economy rinsing stage is to concentrate the economy rinsing liquid before it is recirculated. This may be achieved by e.g. ion exchange, reversed osmosis or evaporation.

Process Integration – Re-circulation of Chemicals

Purity of the product is governed by the pollutant concentration in the last rinsing stage. The concentration in the last rinsing stage can be reduced either by increasing the influx of water to this stage or by cleaning the water in the last rinsing stage in a so-called kidney stage, e.g. an ion exchange unit. The ion exchange unit functions in fact like a kidney, purifying the water in the last rinsing stage allowing a considerable reduction of the amount of pure water needed to maintain a sufficiently low pollutant concentration in the rinsing stage (Figure 6.4).

The ion exchanges adsorbs the metals in the solution and thus removes and concentrates them. As the ion exchanges are eluted with NaOH (anionic exchanger) or HCl (cationic exchanger) the metals are recovered in a concentrated solution and can be re-circulated to the process.

Conclusion

The different measures accounted for above may be combined in several ways. This enables the almost total closing of the water cycle of some types of surface treatment processes. Especially warm surface treatment processes can be made practically wastewater free. Figure 6.5 shows an example of how different measures for process closing can affect water consumption and metal losses.

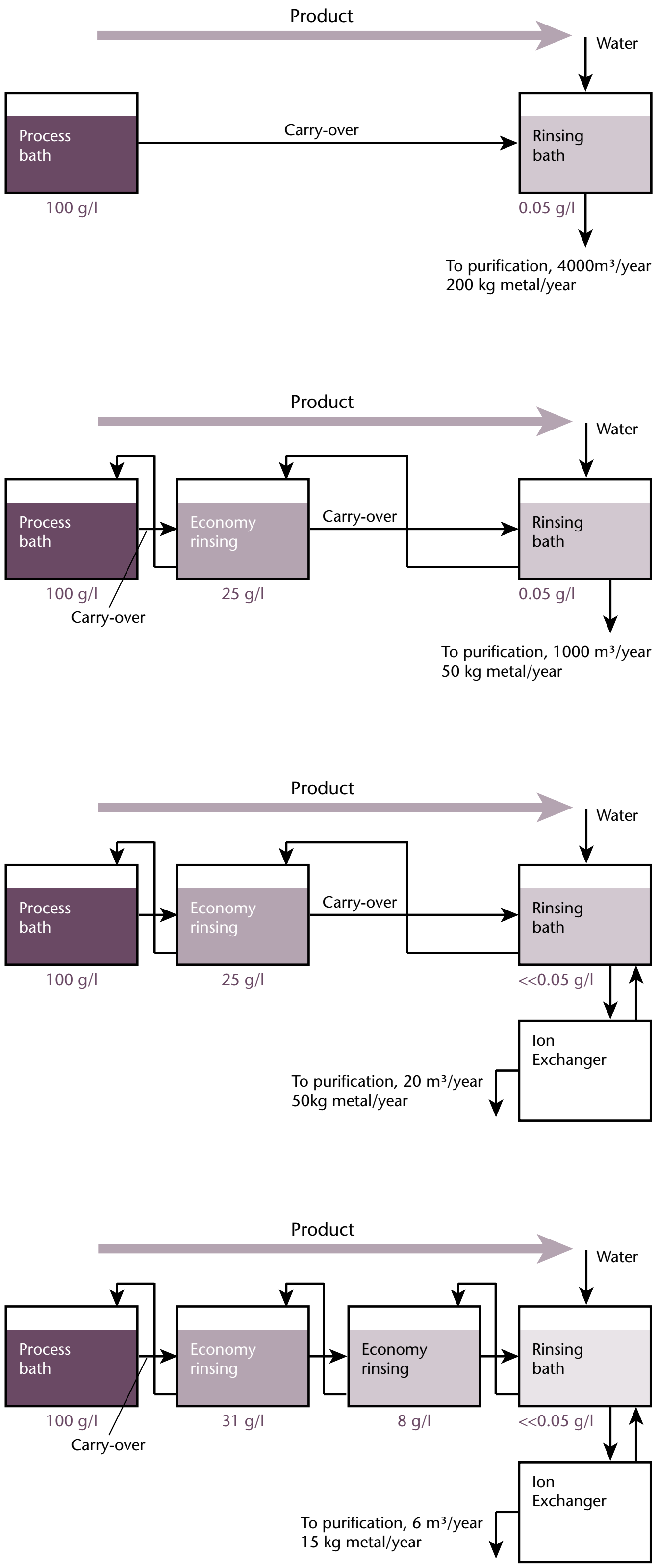


Figure 6.5 *Comparison between different alternatives for process integration of a surface treatment process.*

Contacts

Company

Assa Industri AB
Jarmo Lillsjö, *Process Engineer*
Box 371, 631 05 Eskilstuna, Sweden
Tel: +46-(0)16-17 70 00
Fax: +46-(0)16-17 70 18
E-mail: csg@assaindustri.se
http://www.assa.se

Author

Lennart Nilson
Royal Institute of Technology
School of Energy and Environmental Technology,
Dept. of Industrial Ecology
SE-100 44 Stockholm, Sweden
Tel: +46-8-790 87 13
Fax: +46-8-790 50 34
E-mail: lennart@ket.kth.se
http://www.ima.kth.se