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Water Reuse in Paper Mills - Measurements and Control Problems in Biological Treatment

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Measurements and Control Problems in Biological Treatment

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Licentiate Thesis

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Abstract

Paper manufacturing is a complex and multidisciplinary science due to the diversity of paper products, used raw materials and different production processes. Besides fibres different chemicals, water and energy are needed to produce paper. The use of fresh water has decreased significantly during the last decades and there are several reasons for this, such as: limited availability of fresh water, increased cost for effluent treatment and marketing benefits.

This decreased consumption has been made possible by the reuse of process water instead of fresh water. However, at a certain degree of closure different problems occur. Many of them are in some way related to the growth of microorganisms in the system. One method to solve the problems is to implement an internal kidney consisting of at least a biological treatment step. Since nutrients, such as nitrogen and phosphorous, normally are limited in the whitewater these have to be added in order to have an efficient biological treatment process. One major challenge is to operate the biological system with low concentrations of nutrients in the effluent otherwise the conditions in the whitewater system will be negatively affected. Consequently, there is a need for automatic control of the nutrient addition.

It is possible to control the flow of whitewater to the treatment process but not the actual concentrations of organic compounds in the whitewater, which therefore can be regarded as a process disturbance. An investigation was made at two different paper mills with different degrees of closure to determine the variation of chemical oxygen demand (COD) in the whitewater. The results showed that the whitewater concentration in an open mill could vary a lot whereas the conditions were more stable in a closed mill.

For the control there is a need for information about the process state and output from the system. In this case, for controlling a biological treatment of whitewater, different on-line instruments are needed. First of all, a market survey, limited to instruments for measurements of organic matter,

ammonium and orthophosphate, was conducted. The experiences gathered about use of on-line instruments at several of the Swedish municipal treatments plants were explored in a telephone survey. One interesting observation was that most on-line instruments were only used for monitoring. The number of instruments used for direct control was low but this number was increasing as new and better instruments are becoming available. As a conclusion of these two surveys, three different brands of instruments were deemed suitable for measurements in whitewater.

Computer simulation is an important tool for evaluation of different controllers but requires a mathematical model of the system. Laboratory experiments were initiated to determine important parameters for such a model. Both mesophilic and thermophilic treatment of recycled fibre whitewater with a fluidised anaerobic reactor and an aerobic suspended biofilm process resulted in high removal of COD of around 90%. The nutrient requirement for the anaerobic mesophilic reactor was determined to 19 mg N/g $COD_{reduced}$ and 2.5 mg P/g $COD_{reduced}$. For thermophilic degradation the requirement was determined to 24.5 mg N/g $COD_{reduced}$ and 4.4 mg P/g $COD_{reduced}$ for the anaerobic process and the corresponding values for the aerobic process were 37.1 mg N/g $COD_{reduced}$ and 5.5 mg P/g $COD_{reduced}$. A decrease of the added amount of nitrogen to 77% of what was originally consumed did not have any immediate effect on the COD reduction.

Pilot tests with the purpose to study both the stability of a biological treatment process and evaluate two different on-line instruments were conducted at a packaging board mill. The results demonstrated that the removal efficiency was not markedly affected from variations of the load to the combined anaerobic/aerobic treatment process and that both instruments failed to provide stable results. Experiences from other instruments have been gathered during the assembly of a complete system consisting of a pilot plant of a biological treatment process, on-line instruments and data-acquisition equipment.

It has been demonstrated that it is possible to use on-line instruments for measurements in whitewater to acquire information about the biological treatment process. This information could be used in several different ways for the control of the addition of nutrients. Different control structures are suggested ranging from feed forward of the organic load with corrective feedback of concentrations in the anaerobic effluent to more complex model-based control structures with automatic update of model parameters.

Acknowledgements

I would like to first express my gratitude towards Dr. Thomas Welander who gave me the opportunity to continue my education. He performed an inhuman effort when he, in a very short time, wrote the major part of the project application for the ClosedCycle project, which I have been working on. The ClosedCycle project is financially supported by the European Commission, which is gratefully acknowledged.

I am also very grateful for the support and encouragement throughout my project from my supervisor Prof. Gustaf Olsson and co-supervisor Assoc. Prof. Ulf Jeppsson. On numerous occasions I was very frustrated and felt rather lost. The feeling I had was the same feeling you would have if you were asked to put together a bicycle and your starting materials were some seeds for a rubber tree and pieces of iron ore. Although both of my supervisors are usually very busy people, they always had time to discuss the rubber tree and the iron ore and so with their help I managed to create the bicycle in the end.

As a graduate student I had the privilege of attending various courses and met a lot of nice fellow Ph.D. students, such as the people from the department of Water and Environmental Engineering. Special thanks go to Michael Ljunggren, who provided me with pictures and practical information about some of the processes used in wastewater treatment. Michael also shared my interest for training and so during breaks there was always some stimulating discussion about strength training, pulse intervals, nutrition or something else in this area. Michael and I still do not understand why the others always started to shake their heads and looked so strangely at us when we started in on these discussions and distractions.

My own department is filled with nice people. You have all made me feel welcomed although, as a chemical engineer, I was a long way from home (KC). Thanks for the stimulating atmosphere all of you created together. I would especially like to mention Carina Lindström who provided delicious morning coffee or tea and Getachew Darge who assisted me with his technical knowledge. It is easy to take your services for granted and not appear to give them enough show of appreciation during hectic times. Thank you.

A lot of people both at Anox AB and Cenox helped me in various ways. Dr. Anders Ternström and Dr. Alan Werker proof read parts of my manuscript, Åsa Malmqvist always had time for creative discussions, and Stig Stork made those very tedious runs for new batches of whitewater. I was encouraged by everyone's anticipation of when I was going to come back to Anox AB. Hopefully, I interpreted the concern in the right way and was missed; it could be that you just wanted to figure out how many happy days you had left.

I am very grateful to Prof. Erik Dahlquist who took the time to read my thesis and travelled to Lund to discuss the work with me during my licentiate seminar.

Finally, my thoughts turn to my room-mate at IEA, Sabine Marksell, who has become very dear to me and a part of my life. Thanks Sabine for always encouraging me and boosting my self-confidence.

Lund, July 09, 2003

Tomas Alexandersson

Contents

Chapter 1

Introduction

1.1 Problem definition

Pure water is fundamental to life and is today due to pollution close to becoming a limiting resource in many countries. Increased environmental awareness about the effects industries and large population of humans have on nature have led to increased demands on what and how much that is allowed to be released in waste streams. Pulp and paper mills are industries that historically used a lot of water in theirs processes. Development of new processes and other technical improvements have decreased the fresh water consumption over the years. This progress has been stimulated by harsher demands from environmental authorities and a wish by many companies to be regarded as environment-friendly. The ultimate goal for the pulp and paper industry has been an effluent-free factory with no negative impact on the environment. This type of factory does not exist and is probably a utopia but with advanced water management and recycling of different process streams there are operational paper mills demonstrating very low fresh water consumption.

There are, however, problems associated with this reduction in fresh water consumption in the paper mills and they start to appear at a certain degree of closure. The produced paper and the whitewater, which is the process water from the paper machine, could start to smell badly. Corrosion and slime production are other examples of occurring problems. The major part of these problems is caused by the growth of microorganisms in the whitewater system. These organisms nourish on the organic compounds, which accumulate in the whitewater as a result of the increased closure.

One solution to overcome these problems is to treat the whitewater in an in-mill biological treatment plant. This would reduce the compounds in the whitewater, which function as a substrate for the microorganisms. In order to reuse the effluent additional treatment methods like settling, filtration, chemical precipitation and ozonation could be necessary.

Nutrients, like nitrogen and phosphorous, have to be added to the biological treatment plant in order to achieve efficient reduction. Since these elements normally are limiting microbial growth in the whitewater, their concentrations in the effluent should be low. Otherwise the growth in the whitewater system could be promoted and the situation worsened. At the same time as the concentration of nutrients in the effluent should be low, the efficiency of the biological treatment should be as high as possible. There is, consequently, a need for an automatic control system for controlling the addition of nutrients to the in-mill biological treatment plant.

The project

In order to approach the problems related to paper-mill closure a project with the acronym ClosedCycle was put together, which obtained financial support from the European Commission's *Energy, Environment and Sustainable Development* programme in the Fifth Framework Programme. The consortium behind the project consists of five different partners with expertise in different fields. Areas covered are biological and chemical treatment, paper making technology, paper quality testing, separation techniques, determination of organic compounds, paper production, automation and process control. The project is primarily targeting products, such as packaging grades from recycled fibres, printing paper from mechanical pulp/recycled fibre and liner from kraft pulp/recycled fibre.

This thesis represents part of the work for the automation and control work package. The author is fully responsible for it and although the European Commission finances the project, the thesis does not represent the opinion of the Community.

Other projects

The huge importance of the pulp and paper industry has lead to the formation of several multi-national and national projects regarding development of improved pulp and paper processes. One of the larger projects in Sweden was the KAM-project with the title "The Ecocyclic Pulp Mill". In this project different technologies were reviewed and evaluated as resources for a closed cycle kraft pulp mill. The potential of using the pulp and paper production as an energy producer was another of the investigated issues. This project continued for six years during 1996 to 2002 and received funding from participating companies and MISTRA – The Foundation for Strategic Environmental Research.

Several projects aiming at the pulp and paper industries have also been initiated within the European Union. The project "Separation Methods for Closed-Loop Technology in Bleached Kraft Manufacture" was part of the 4th framework programme and was carried out between December 1996 and November 1999. The project "Towards Zero Effluent Papermaking" ended in July 2002 and it was part of the COST-programme. Another COST-project is "Effective solutions to reduce the impact of waste arising from the papermaking", which is running at the moment and should end in September 2005.

Challenges

There are several different challenges related to this project. Since it spans over several different subjects it is first of all important to have knowledge about the different areas, which are included in the project. The most important ones are wastewater treatment, pulp and paper production, control and instrumentation. One important milestone of the project is the development of a control strategy. The challenge is to achieve efficient treatment while maintaining low nutrient concentrations in the effluent. This is difficult since the concentrations should be very low, near the detection limits for on-line instruments. This task also raises a lot of practical questions. Is it possible to do measurements on the whitewater and are the on-line instruments of such quality that they can be used for control? What equipment should be used for data gathering and how should the controller be implemented?

1.2 Overview

Knowledge about the background of a problem is usually a necessity before the problem itself can be solved. This means gathering information about the different processes involved and judge different solutions from every possible angel. If the overall system is not understood efforts to solve a specific problem could create more problems. This happened in Canada where some chemists developed a solution to scaling problems. They dosed phosphoric acid to the whitewater system, thereby removing deposits of carbonate. The idea was correct from a chemical point of view but from a microbiological perspective it was a catastrophe. The addition of the acid to the whitewater boosted the growth of the microorganisms in the system resulting in different severe problems.

In this thesis, Chapter 2 provides some background of the different involved processes. First there is an introduction to the different methods to transform cellulose fibres into paper. This is followed by a short summary of different chemical, physical and biological methods for wastewater treatment. Different brands of instruments are presented in Chapter 3 together with information about how these types of instruments are used at municipal treatment plants in Sweden. Chapter 4 begins with a presentation of the benefits with closure of whitewater systems. Problems associated with the closure are also included in the chapter. One possible solution to the problems is to treat the whitewater with an in-mill internal kidney consisting of a biological process combined with chemical and/or physical methods. This solution is further presented in Chapter 5 together with experimental results. An important issue is the control of the nutrient addition to the biological process and in Chapter 6 control strategies of varying complexity are presented. In Chapter 7, conclusions are summarized together with a number of ideas for future work.

1.3 Main results

In most control applications it is important to acquire information about the actual status of the controlled system. For a biological treatment process, which is part of an internal kidney, this could be achieved with on-line instruments measuring different interesting parameters. A market survey was conducted with the purpose to collect information about available brands of on-line instruments for measurements of ammonium, phosphate and organic matter. Experiences from the operation of such instruments were gathered by a telephone survey of municipal treatments plants. From this survey material three different on-line instruments were chosen as suitable for use in a control system of a biological treatment process.

The possibility to use a combined anaerobic/aerobic biological process for treatment of whitewater from liner production from recycled fibres was demonstrated both in laboratory scale and pilot scale experiments. The purpose of the laboratory experiments was also to determine kinetic parameters to be used in a mathematical model. The nutrient requirement for mesophilic anaerobic treatment was determined to 19 mg N/g $COD_{reduced}$

and 2.5 mg P/g $COD_{reduced}$. It was not possible to determine any requirement for the aerobic reactor since the load of degradable COD was too low. During thermophilic degradation the requirement was determined to 24.5 mg N/g $COD_{reduced}$ and 4.4 mg P/g $COD_{reduced}$ for the anaerobic process and the corresponding values for the aerobic process were 37.1 mg N/g $COD_{reduced}$ and 5.5 mg P/g $COD_{reduced}$. There was not sufficient data to determine the half saturation constant for ammonium but the results indicate it is below 0.3 mg/l. A corresponding value for phosphate could not be determined since a breakdown of a vital part of the used equipment damaged the biological system and prevented further experiments. The pilot test was initiated to control the biological process ability to deal with varying loads. Although the load to the combined process varied the removal of COD was not markedly affected.

The variations in the whitewater were studied at two different paper mills producing liner and fluting from recycled fibres. In the paper mill with an open water system the concentrations varied significantly when the production process was stopped. One explanation for this could be a sudden increased demand of whitewater to the broke system, which were met by fresh water since the whitewater storage capacity was limited. In the other mill, which has a closed whitewater system, the concentrations in the whitewater were stable.

On-line measurement using an instrument for total oxygen demand (TOD) and an instrument for ammonium measurement stressed several difficulties with whitewater measurements. It was not possible to get reliable results from the TOD-instrument despite several recalibrations and adjustments of the instrument. The reason for this is not clear but the complex matrix of the whitewater composition is suspected to cause the problems. During measurement with an ammonium electrode pH is raised to twelve with some base. This probably caused calcium carbonate to precipitate on the surface of the electrode, which gave erroneous results.

Preliminary testing of a TOC instrument and a sensor for orthophosphate determination has been successful whereas there have been problems with foam formation in another instrument for measurement of ammonium.

Successful operation of an implemented in-mill biological treatment plant requires control of the nutrient addition. A number of control structures have been proposed for this task with varying degree of complexity ranging from simple manual control to model-based control.

For practical evaluation of proposed control strategies a measuring and data acquisition system has been assembled. It consists of three different on-line instruments for measurement of TOC, orthophosphate, ammonium, COD, nitrate and turbidity. The acquisition is done with a distributed module system and the controller is implemented on a PC. This system will form the basis for the future work of implementing and verifying control strategies for in-mill biological whitewater treatment.

Chapter 2

Processes Involved

This chapter gives a short overview of the different processes that are involved. Firstly the paper production is presented and it starts with a historical introduction. Then the broad diversity of different paper products is explored, followed by an introduction in Section 2.2 to different pulping processes, both for virgin and recycled fibres. Information about paper making with a special emphasis on the water system follows in Section 2.3 and Section 2.4 about whitewater variation finishes the part of paper production. The second part of this chapter deals with wastewater treatment. After a short introduction in Section 2.5 about internal versus external treatment and wastewater composition, there is an overview of different mechanical/physical/chemical treatment methods in Section 2.6. Then some fundamentals of biological treatment are mentioned. In Section 2.8 aerob biological wastewater treatment is discussed and the chapter ends in section 2.9 with anaerobic treatment.

This chapter merely scratches the surface of all the wisdom man has gathered about these processes during the years. Anyone who wants to know more could easily find excellent textbooks. Fapet Oy (2000) has published a whole series of books about papermaking and in the "Dictionary of paper" from Tappi (1996) most of the technical expressions used in the papermaking world are explained. Also the water treatment area is covered in many interesting books. Technomic (1992) has published a library of 8 books about activated sludge, upgrading, toxicity reduction etc. The handbook from Degrémont (1991) covers almost all aspects of water treatment from biological to chemical treatment. Thoroughgoing information about the guys who do the dirty work at the biological treatment plant, the microorganisms can be found in the book by Brock and Madigan (1991).

2.1 Paper

History of paper

Paper is a general term for a sheet of fibres formed on a fine screen from a water suspension. The fibres are usually vegetative but also mineral, animal or synthetic fibres can be used. The name paper originates from the Greek and Roman word for papyrus, which was a sheet made from thin sections of reed (*Cyperus papyrus*). This papyrus was used in ancient Egypt around 4 000 BC as paper. The knowledge to make paper from fibres was first discovered in China in AD 105. For a long time this art was confined to China but after around 500 years it was passed on to Japan. The knowledge then spread westwards through central-Asia to northern Africa and from there to Europe. The point of time when manufacturing of paper was established in Europe varies from country to country. Since the knowledge came from Africa the manufacturing was first introduced in southern Europe. In Spain, the production started during the 11th century and it was not until the 16th century that the manufacturing started in Sweden. For long time, were cotton and linen rags together with straw used as raw material for paper production. It was not until the late 19th century that wood started to be an important source for the fibres.

Paper products

The term paper has both a general and a more specific meaning. The general term paper refers to all products that are produced in the paper industry. They can be further divided into four categories: paper (the specific term), tissue, paperboard and speciality papers. Reprographic paper and papers for writing, printing and copying belongs to the paper category and they are usually classified as either wood-free or wood-containing. Wood-free printing paper is made of at least 90% chemical pulp whereas wood-containing paper consists of a larger part bleached mechanical pulp. Products that belong to tissue are paper towels, handkerchiefs and napkins. Paperboards are usually used for different packaging products and can be further divided into cartonboards, containerboards and special boards. There is no sharp distinction between the categories paper and paperboard but paper is usually thinner, lighter and more flexible than paperboards. In the last category speciality papers are different paper products gathered that do not fit into the other categories. Examples of such products are filter papers, electrical insulation papers for cables, coffee filters and tea bag papers.

Paper production

The transformation of the fibres in the raw material into different paper products can be divided into two processes, pulping and paper production. There are several different pulping methods but they share the same goal to uncover the cellulose fibres in the raw material. When the fibres originate from old paper they are called recycled fibres and fibres from wood are called virgin fibres. Recycled fibres are always repulped with a mechanical method whereas virgin fibres can be produced with both chemical and mechanical methods. The first step in the production of virgin pulp, is debarking of the wood and cutting it into chips. Since the cellulose fibres in wood are strongly associated with hemi-cellulose and lignin the mechanical methods for pulping virgin fibres need to be harsher than the mechanical repulping of recycled fibres. Despite of the pulping method there will always be more or less lignin present in a pulp with virgin fibres. Lignin in the wood has no colour but is colourised during the pulping process. This colour is removed by bleaching the pulp with different chemicals. Pulping together with bleaching produces a white pulp, which is used in the following process, paper production. Here the pulp is diluted with water and mixed with different chemicals. The mixture is then pumped to the paper machine where the paper sheet is formed. In the paper machine water is removed from the pulp and is thereby converted to paper, which is rolled up on large reels in the other end of the paper machine.

2.2 Pulping

Raw material

Although paper has been made from many different materials like rags of cotton and linen together with straw, wood is the mostly used raw material today. The second most common fibre source is old paper. The use of old fibres have increased recently but they cannot completely replace new fibres since they can only be reused 5 to 7 times. For every time the fibre is recycled it gets shorter, which decreases the strength of the final product. Recycled fibres are therefore usually used for products with lower quality demands such as newspapers, liner and fluting. In developing countries, such as China and India, the main fibre source is nonwood. The most commonly used material is straw (both wheat and rice) followed by sugar cane bagasse, bamboo, reed and cotton linters.

Virgin fibres are produced both from softwood and hardwood. Pine and spruce are the mostly used softwood trees and the most common hardwood trees are aspen, birch and beech. In warm and wet climates are other types of hardwoods such as eucalyptus and acacia used. The amount of cellulose fibre is around 40% in both hardwood and softwood. Cellulose is a large linear polysaccharide of glucose units. Besides cellulose fibres the wood also contains hemi-cellulose, lignin and extractive compounds. The hemi-cellulose is a branched polymer with a lower molecule weight than cellulose. It is primarily composed by five sugars found in wood: glucose, mannose, galactose, xylose and arabinose. Both softwood and hardwood contains between 30 and 35% hemi-cellulose and the type of hemi-cellulose the wood is made up of varies with the type of tree. Lignin is a very branched polymer and the monomeric unit that it is made up of differs between softwood and hardwood. Hardwood contains around 27% lignin, which is a little bit more than the 21% that can be found in softwood. Lignin is very strongly associated to the carbohydrates in the wood. The wood also contains around 4% of different extractive compounds. The chemical composition of the wood depends on the type of tree, where it grows and the environmental conditions. Figure 2.1 presents the chemical composition for a Swedish pine tree.

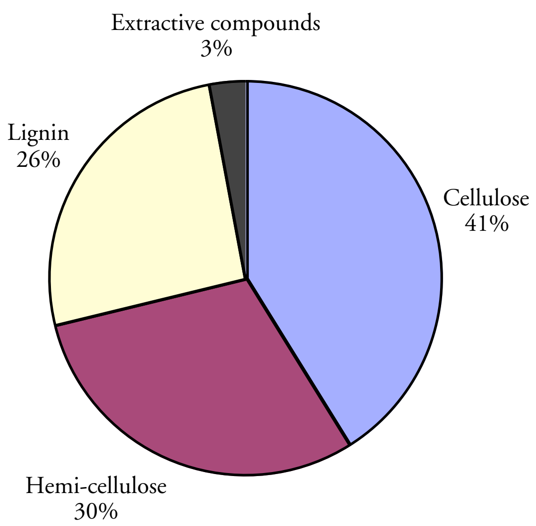

Figure 2.1 Chemical composition of Swedish pine in percentage of wood weight (Gavelin, 1990).

Mechanical pulping

Recycled fibres from different wasted paper products are always repulped mechanically. The raw material is first mixed with water and chemicals. This mixture is then agitated so the individual fibres are released. After cleaning, ink in the pulp is removed in a process called de-inking. To have flexible fibres and a good distribution of different fibre lengths the pulp is refined before it is used. This is done in a machine called refiner, which converts the fibres to a pulp with the wanted characteristics.

There exist three different mechanical pulping methods for virgin fibres. The oldest method produces ground wood pulp (GWP) by grinding wood chips against a wet grindstone. This method have more or less been replaced by the thermo mechanical pulp (TMP) process where the wood chips are grinded against rotating steel plates or drums. The temperature is raised during the process by addition of steam to improve the efficiency. The third method is a development of the TMP-process. Before the chips are grinded they are partly digested by chemical treatment with alkaline 1-5% Na_2SO_3 and the pulp is called chemithermomechanical pulp (CTMP).

One benefit of mechanical pulping is the high yield, 90-97%. The strength of the pulp, however, is lower then chemical pulp since the mechanical grinding shortens the fibres to some extent. Another drawback is the large amount of lignin in the pulp. Mechanical pulp is therefore mainly used for newspaper but is also included in small amounts in other printing products.

Chemical pulping

In chemical pulping, the cellulose fibres are uncovered by degradation and removal of the lignin in the wood. This is done in large digesters where the wood chips are treated in high temperature with different chemicals. Since most of the lignin is removed during the pulping process the exchange is lower compared to mechanical pulping. Normally the outcome is around 45 to 50%. Paper that is produced from chemical pulp has high mechanical strength because the cellulose fibres are not damaged during the pulping process. It is also rather simple to bleach the pulp to a high whiteness.

Chemical pulp is produced by two different methods. The most important is the sulphate-method, which is also known as the Kraft process. The active components during digestion are sodium hydroxide and different sulphide ions. Most of the chemicals are recycled but a small amount of sulphur is lost and replaced by sodium sulphate, which has given the process its name.

The other method is the sulphite-method, which importance has decreased in the last few years. The pH of the digestion solution is low and it contains sulphur dioxide and magnesium or sodium hydrogen sulphite.

Bleaching

The pulp made from wood contains more or less lignin depending on the used pulping method. In the wood the lignin is only slightly coloured but after pulping, especially chemical pulping, the lignin has developed a strong colour. The pulp could, however, be used as it is, if it does not matter if the product is coloured. Other products must be white and for these cases the pulp is bleached. Mechanical pulp is often bleached by some method that modifies the coloured part of lignin. This type of bleaching is often done with hydrogen peroxide, dithionite or sodium bisulphite. The most important bleaching method, however, degrades the lignin and removes it from the pulp. This type of bleaching is only done on chemical pulp. Another benefit of this method besides making the pulp white is that it will increase the strength of the pulp. During the bleaching the pulp is treated with chemicals in several sequential steps with washing of the pulp in between. Chlorine was previously an important bleaching chemical but its use has more or less been stopped due to the production of toxic chloro-organic compounds during the bleaching process. Today bleaching is done with chlorine dioxide, which produces elementary chlorine free pulp (ECF). Development of the bleaching process has made it possible to produce totally chlorine free pulp (TCF). This pulp is bleached with oxygen, ozone and hydrogen peroxide and in Figure 2.2 there is an example of this bleaching sequence.

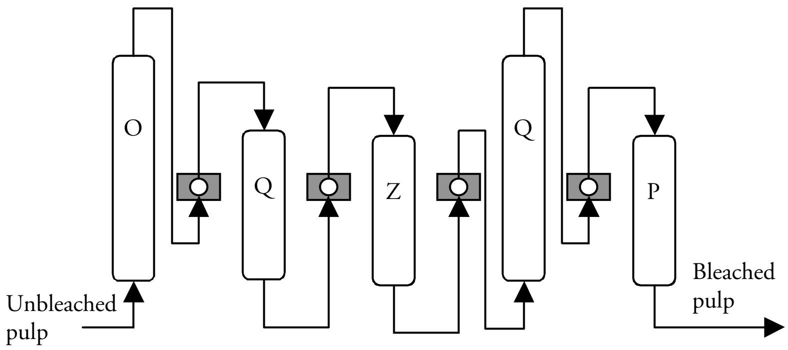

Figure 2.2 Bleaching sequence for TCF pulp.

Unbleached pulp is first treated with oxygen (O) under high temperature (95°C) and alkaline conditions. Dissolved lignin is removed by washing the pulp before it is pretreated with complexing agents (Q) like EDTA (ethylene diamine tetra acetic acid) in order to bind metal ions, which have a negative effect on the next step ozone (Z) treatment. The bleaching sequence is then followed by another complex treatment before the final bleaching with hydrogen peroxide during alkaline conditions.

2.3 Paper making

The paper machine

In the paper mill, the pulp is converted into some type of paper product on the paper machine. A schematic outline of a paper machine can be found in Figure 2.3.

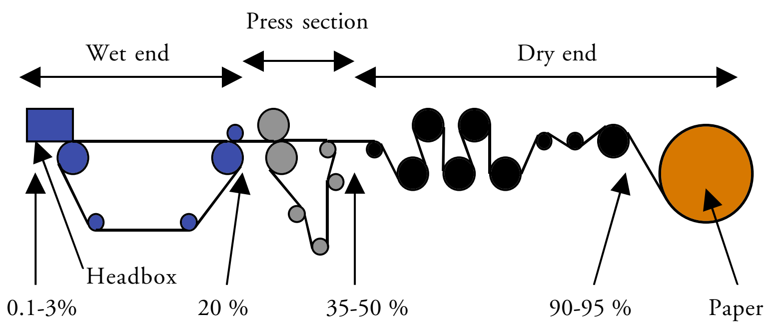

Figure 2.3 Schematic outline of a paper machine. The numbers are approximate values of the dry substance in the transformation of stock into paper.

The main raw material is the pulp, which comes from the pulp mill. Since there is a wish to separate the water system in the pulp mill from the water system in the paper mill the pulp is often transferred between the mills with high consistency. If the paper mill is not part of an integrated mill the pulp normally arrives to the mill in dry form (bales). First, the pulp is diluted with whitewater, which is the name of the process water in the paper mill. The pulp solution is then mixed with different additives like fillers, sizing material, wet- or dry-strength chemicals and dyes. This stock solution is then further diluted to a consistency of 0.1 – 3% before it is pumped to the headbox of the paper machine. There the stock is evenly spread over an endless wire that travels with high speed. During the first part of the paper machine, which is called the wet section, water is removed by gravity and low pressure by suction boxes placed under the wire. Retained on the wire are the fibres and additives, which dry content has increased at the end of the wet section to around 20%.

At the end of the wet section, the paper web is moved from the wet end wire to the press felt in the press section. Here, the paper is pressed between large rolls during its passage. The applied pressure forces water from the paper web into the press felt. Thereby further water is removed from the paper web and the dry content has now increased to around 35-50%.

In the final part of the paper machine, the dry end section, the paper is so strong that it does not need any supporting wire or felt. This section is made up of large steam-heated rolls where additional water is removed from the paper so a dry content of 90-95% is achieved.

The whitewater system

Large volumes of water are handled in the paper mill during the production of paper. All the pipes and vessels that are used for the whitewater are part of the whitewater system. The exact layout of the system differs from mill to mill but there are some similarities. There are two major flows of whitewater in the paper mill, the short and the long circulation. The short circulation is the flow of whitewater from and back to the headbox by the way of the wire, wire pit and fan pump, see Figure 2.4. It is only whitewater from the first part of the wet end section that goes to the wire pit and the short circulation.

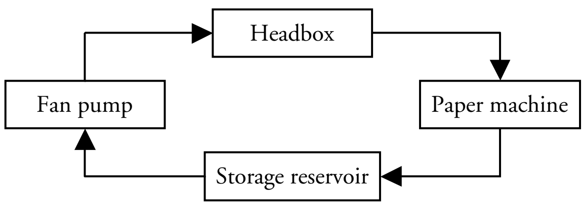

Figure 2.4 Short circulation of whitewater in the paper machine.

Water from the suction boxes and the press section enters the long circulation and is collected in the suction box pit. This whitewater is used for the preparation of the furnish and level control in the wire pit. A part of it is also treated in a saveall unit, which is a physical device for cleaning, usually a disc-filter. This cleaned whitewater could be used for showers in the paper machine. An outline of the long circulation can be found in Figure 2.5.

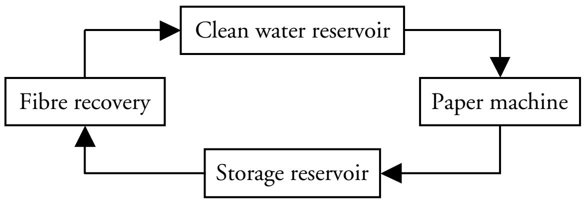

Figure 2.5 Long circulation of whitewater in the paper machine.

Composition of the whitewater

The composition of the whitewater depends on several things, such as, the raw material, the produced product and the type of paper machine. Although it is not possible to give an exact description of the composition, it is possible to mention certain compounds that could be found in the whitewater. Irrespectively of the type and origin, they appear either as particles or are dissolved in the water and constitute both inorganic and organic compounds.

First of all the water contains a lot of fibres, which have not been retained on the wire in the paper web. During the processing of the pulp some of the fibres are broken down into small fragments, which are referred to as fines. These fines could be further degraded so that short chains of polysaccharides are dissolved in the whitewater. Besides the fibres there are a lot of other compounds originating from the pulp. When virgin fibres are used compounds like monosaccharides, disaccharides, resin, waxes and fatty acids can be transferred to the whitewater. The major contribution to the whitewater from recycled pulp is starch, which is an additive to increase the strength of the old product.

In order to reduce the cost and also to produce a product with improved surface smoothness, paper opacity and printability, white pigment powder called fillers are added to the furnish. In some products the addition of filler can constitute around 25% of the paper. The fillers that are usually used are clay, talc and limestone. Although they are considered inert, the filler can dissolve to some extent and influence the pH and the concentration of inorganic ions.

Retention aids are added to the furnish in order to improve the retention of the fibres, fillers and additives. Since the fines and additives are too small to be mechanically retained they must be bound to the fibres in some way. This is done with cationic polymers that bind to several different negatively charged regions causing inter-bonding between fibres, fines, fillers and additives.

One important quality of most paper products is its ability to resist wetting by liquids and especially water. Sizing is the term for that process, which gives the paper the wanted characteristics by addition of different chemicals. The sizing chemicals are applied in two different ways. Either, they are added directly into the furnish, so called internal sizing or they are applied onto the web surface in the dry end, which is referred to as surface sizing. The most used method is internal sizing and it could either be done under acidic conditions with rosin together with aluminium sulfate or at neutral or alkaline pH with alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA). The increased use of calcium carbonate as filler material has lead to an increased popularity for the neutral or alkaline internal sizing. Some other chemicals that are used for sizing are starch, gelatine, modified cellulose and latexes.

Printing paper often needs a smooth surface in order to give neat printout. A coating colour is applied on the paper web to produce this surface. The coating is often made up of three different ingredients: a binder, a mineral and a thickener. The mineral could be chalk, talk or clay and some examples of binders are starch and modified cellulose. The thickener is added to give the coating the right viscosity.

Papermaking is very complex and a lot of different chemicals are used. All these chemicals can be found in the whitewater. Although, many chemicals only are added to the paper in the dry end of the paper machine, small amounts end up in the water system either when the product is recycled or when broke and trim are reprocessed. When there is a break in the paper web the paper machine has to be restarted since the paper is not taking the right passage through the paper machine. This paper is collected for recycling and is referred to as broke. Trim is the edges of the paper web and they are cut of since they have not an even thickness. When the whitewater is characterised it is not possible to determine the exact concentrations of the different compounds in the water. Instead they are lumped together and divided into broader categories like total and dissolved organic carbon (TOC and DOC), total suspended solids and chemical oxygen demand (COD).

The whitewater composition from a recycled paper mill with a fresh water consumption of 1 m^3/ton paper can be found in Table 2.1.

Table 2.1 Whitewater composition in a recycled paper mill (Habets and Knelissen, 1997).

Parameter	Concentration	Unit
COD	35 000	mg/l
Ca	3 700	mg/l
Sulphate	1 500	mg/l
Chloride	550	mg/l
Acetic acid	5 000	mg/l
Propionic acid	700	mg/l
Butyric acid	400	mg/l
Lactate	5 800	mg/l
pH	6.25	
Conductivity	9.0	MS/cm

Mass balances in the whitewater system

The amount of compounds released into the whitewater during mechanical pulping has been reported to be between 20 and 50 kg material/ton of pulp (Lindholm, 1995). During pulping of waste paper somewhere between 20 kg COD/ton paper (Gissler-Weber *et al.*, 1981) and 30 kg COD/ton paper (Barascud M. C. et al., 1992) are released. In laboratory pulping experiments it was found that around 11 kg COD/kg waste paper were released when a mixture of magazines and newspapers were pulped. During the pulping there was a small increase in the COD concentration, which was explained as hydrolysis of the pulp and it was calculated to 1.8 kg COD/(kg recycled paper·h) (Jepsen *et al.,* 1996).

2.4 Variations in the whitewater

The composition of the whitewater is to some extent reflected in the quality of the paper. In order to produce paper with uniform quality from day to day the whitewater composition should be as stable as possible. Due to changes in the paper mill, such as, use of new batches of chemicals, reprocessing of broke and water retained in different pipes and tanks, there are always a variation in the whitewater composition. In a mill producing different types of products there will of course be large variations in the composition during the change from one product to another.

There is also a variation in the whitewater composition from different positions in the system. For example, water from the first part of the paper machine contains more fines than the water collected in the suction boxes.

Results from Rintala and Lepistö (1992), where TMP whitewater was treated anaerobically showed that the composition of the weekly taken whitewater varied a lot. In Table 2.2, some of the measured parameters and their variability are reproduced.

Table 2.2 Concentration range of some parameters measured on weakly samples of TMP whitewater (Rintala and Lepistö, 1992).

Parameter	Concentration range	Unit
COD total	1 800 – 3 700	mg O_2/l
COD soluble	1 700 – 3 500	mg O_2/l
Sulphate	143 – 304	mg/l
SS	31 – 262	mg/l

In the literature, information about the composition of the whitewater can only be found for grab samples and there is often a large variation in the results between different batches from the same mill. In order to design a controller to a process, knowledge about the dynamic behaviour both for the process itself and for the disturbances affecting the process are important. Since no information about the dynamic variation of for example organic compounds in the whitewater has been published, an investigation was initiated at two different mills producing testliner from recycled paper. In this study (Alexandersson, 2002), hourly samples of whitewater from each mill were taken during three different periods. Every sample were characterised for its concentration of dissolved and total chemical oxygen demand (CODd and CODt), dissolved organic carbon (DOC), and total suspended solids (TSS). Some of the important findings in the study are shown below.

Mill no. 1

This paper mill produces testliner (35 000 ton/year) and fluting (20 000 ton/year). The raw material is old corrugated cardboard and newsprint. Testliner and fluting are produced with the same paper machine. The production campaign with liner lasts for 1 – 2 weeks, which is followed by fluting production for 3 – 4 days. The whitewater system of the mill is open and the fresh water consumption is around 14 m^3/ton product. The mill has an internal treatment of the whitewater consisting of a dissolved air flotation unit (DAF). The DAF is made up of two basins, one for the flotation process and one for treated water. Treated water flows from the flotation process basin to the treated water basin through several large tubes. The fresh water inlet point to the mill is in one end of the treated water basin. The samples were taken directly from the tube in the treated water basin that was furthest from the fresh water inlet point.

Mill no. 2

The annual production of this recycled paper mill is 220 000 ton and the production consists of both testliner and fluting. Both products are produced in parallel on different paper machines. The whitewater system is jointly for all paper machines and it is totally closed. This means that there is no effluent from the mill. Water losses due to evaporation and water remaining in the product are compensated with fresh water. The consumption amount to around 1.4 m^3/ton product. The whitewater is internally treated in a DAF unit.

Sampling and storage

The sampling was made with a PSW 2000 from Contronic-Dr Lange and the samples were kept could (+4°C) during sampling with the associated refrigerator. Date for sampling and type of production can be found in Table 2.3. Hourly samples were taken which consisted of 30 aliquots evenly distributed during the hour. The samples were kept cold (+ 4°C) until each sample was divided into one total and one filtered (Munktell MGA) part, which then were frozen until they were analysed.

Table 2.3 Sampling dates and number of samples for the two different mills.

Mill	Dates for sampling periods	Product	Number of samples
No. 1	010829	Liner	24
	010831 – 010902	Fluting	68
	010909 – 010911	Liner	68
No. 2	010917	Liner, fluting	24
	010921	Liner, fluting	24
	010924	Liner, fluting	24

Production disturbances

There was no information from mill no. 2 about disturbances in the production. For mill no. 1 there were two types of disturbances reported, stoppage and interrupt. A stop was reported when something happened and the production and the paper machine had to stop. An interrupt occurred when there was a break in the paper web but the production could be started right away.

Analyses

Chemical oxygen demand (COD) was determined with the Dr Lange test kit LCK 114. Total suspended solids (TSS) were determined according to standard SS-EN 875. DOC was determined on a Shimadzu TOC-5050A analyser. Regular analyses using control solutions for some of the methods have produced significant knowledge about there uncertainty. The coefficient of variation for theses methods is: COD 3.6%, DOC 5.2% and TSS 8.5%.

Results

During the sampling in mill no. 1, the production was disturbed by several stops and interrupts. The concentration of the different parameters mean values for mill no. 1 at times without disturbances can be found in Table 2.4.

Table 2.4 Mean values of the whitewater composition during stable production from mill no. 1.

Sampling period	$COD_{dissolved}$	COD_{total}	DOC	TSS
010829	2 200	2 500	800	160
010831-010903	2 400	2 600	900	80
010909-010912	1 700	1 800	650	100
	mg/l	mg/l	mg/l	mg/l

The disturbances clearly affected the whitewater composition. An example from the second sampling period, 010831-010903, of this can be seen in Figure 2.6 where the dissolved concentration of COD is displayed together with occurred disturbances.

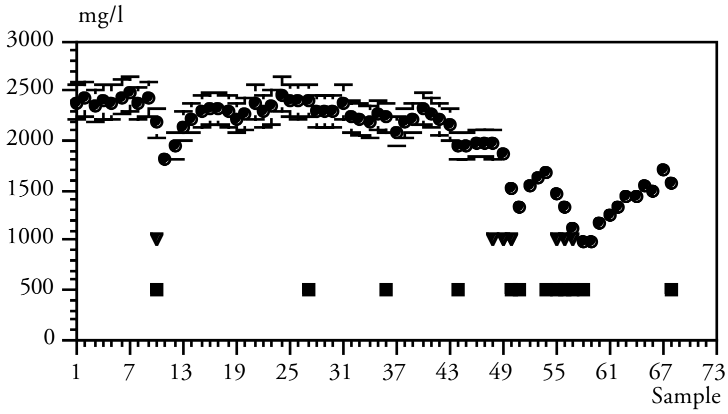

Figure 2.6 Concentration of dissolved COD (•) in whitewater from mill no. 1 during sampling period 010831-010912. In the figure the different disturbances, stop (▼) and interrupt (■) are displayed.

As can be seen in Figure 2.6, dissolved COD was affected whenever the production was stopped. This also happened for total COD and DOC. The effect on TSS was a little more complicated. Sometimes it decreased together with the other parameters and sometimes it increased instead. One explanation to the decreased values at production stops could be a shortage of water in the production process. If there is a break in the paper web, a lot of material is sent to the broke system. When this is to be processed a lot of water is needed and usually whitewater is used. If there is not enough with whitewater due to poor storage capacity, this demand has to be meet with fresh water. This intake of fresh water will then decrease the concentration of various parameters. The increase in the concentration of TSS is a little bit peculiar. In the whitewater there is a lot of different compounds and the whitewater system is a complicated system. It is not impossible that filler or something else inorganic material could settle somewhere in the system and is released into the whitewater during a disturbance.

It was more difficult to perform the sampling in mill no. 2 since the water contained higher concentration of TSS. The mean values of the whitewater composition from mill no. 2 can be found in Table 2.5.

Table 2.5 Mean values of the whitewater composition from mill no. 2.

Period	CODd	CODt	DOC	TSS
010917	32 700	34 800	13 400	2 800
010921	25 300	31 700	11 700	2 800
010924	32 400	34 000	12 600	880
	mg/l	mg/l	mg/l	mg/l

The concentrations of all parameters were much higher for mill no. 2 due to its closed whitewater system. The conditions were more stable in mill no. 2 compared to mill no. 1. This can be seen in Figure 2.7, where the dissolved COD from the third sampling period 010924 is displayed.

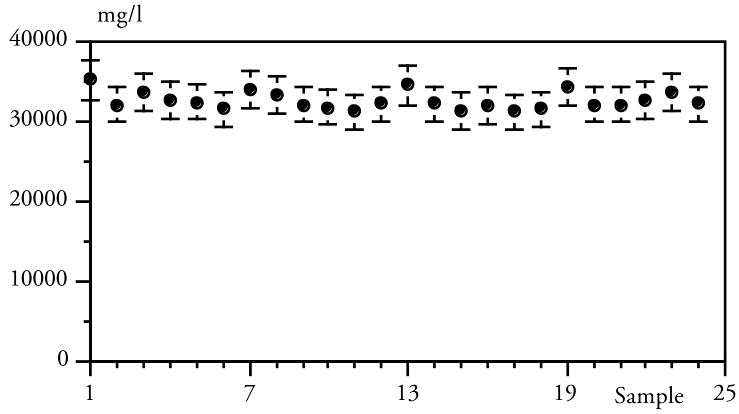

Figure 2.7 Concentration of dissolved COD (•) in whitewater from mill no. 2 during sampling period 010924.

The other parameters showed the same tendency. The important conclusion from this study is that the variation in the whitewater during normal production in a closed mill is rather small. There are however, some variations in the concentrations of the different parameters. It is important to have knowledge about the normal variation of the concentrations, if the signals from the on-line instruments are going to evaluated in some way before the controller use them. A too large change in a signal from an instrument could indicate on an error and this value should not be used. Instead an alarm should be set since something in the control system is malfunctioning. The range for the different parameters found in this study, together with the maximum and minimum rates during these changes can be found in Table 2.6.

Table 2.6 Range of concentration and rate of change for dissolved COD, DOC and TSS during hourly whitewater sampling in one open and one closed recycled paper mill producing fluting and liner.

Parameter	Range in open mill	Range in closed mill	Unit
COD dissolved	1 000 – 2 500	30 000 – 35 000	mg/l
Rate of change for COD dissolved	(-225) – (+150)	(-800) – (+800)	mg /(l·h)
DOC	200 – 900	11 000 – 14 000	mg/l
Rate of change for DOC	(-80) – (+90)	(-250) – (+500)	mg /(l·h)
TSS	30 – 270	2 000 – 3 400	mg/l
Rate of change for TSS	(-20) – (+30)	(-300) – (+240)	mg /(l·h)

2.5 Wastewater treatment (WWT)

Introduction

Already in ancient times skilled cultures developed different systems for supply and removal of water. These systems were more focused on transportation of the fluid than of its treatment. It was not until the industrialisation started at the end of the 19^{th} century and large cities started to form that there were a necessity to introduce some kind of treatment of the wastewater. One major reason for this was the severe epidemics of waterborne diseases that spread in the metropolises. The methods that were developed at the turn of the century were physical methods for removal of particles like settling and the more special methods that used sieves and screens. Later on came biological methods like trickling filter and activated sludge. With time and with increased awareness about the impact untreated wastewater had on the environment, treatment of both municipal and industrial wastewater became more and more common. Increased research and development in this field especially during the last part of the 20^{th} century, has come up with several new treatment methods and increased knowledge about the underlying processes. Today there is a whole spectrum of different mechanical, physical, chemical and biological methods that can be combined in different ways in order to achieve cost efficient wastewater treatment.

Internal versus external WWT

Today most industries have some sort of treatment of its wastewater, either by an on-site treatment plant or by transportation of the wastewater to a nearby municipal treatment plant. Both types can be referred to as external treatment. The wastewater, which in this case is regarded as waste, is treated only with the purpose not to have a negative impact on the recipient.

The other type is called internal treatment and the difference compared to external treatment is that the main purpose is to retrieve some valuable resource in the wastewater or to remove impurities that have a negative influence. The fact that either a compound in the water or the water itself is going to be reused places other and perhaps more demands on the internal treatment process compared to the external. An external treatment process can be regarded as an independent unit placed between the industry and the recipient. The internal treatment plant is more a part of the industries' production process and as such it should not only be able to perform the treatment but it must also function in close cooperation with the other processes. It is important to make a thorough evaluation of the different demands that the surrounding has on the outcome from the internal treatment so the right treatment process can be chosen.

Wastewater composition

The composition and the amounts of different substances in a wastewater vary very much depending on the source of the wastewater. The large number of different possible compounds makes it impossible to give an exact characterisation of the contents in a sample of wastewater. In a characterisation specific analysis on different compounds are performed together with other types of analyses, which lumps different groups of compounds together.

One fundamental division is between dissolved substances and particular matter. This is usually decided by filtration. The compounds that are retained by the filter are said to be solids and the compounds that remain in the water phase are regarded as dissolved. Which type of filter that is to be used differs from country to country and also between different methods. The most common pore sizes are 1.2 μm and 0.45 μm. There are also many methods that give different results due to varying treatment of the sample. Common methods are analyses of total solids (TS), total suspended solids (TSS) and volatile suspended solids (VSS).

Another large division is between inorganic and organic compounds. Inorganic compounds are usually measured by some specific method. The determination of ammonium-nitrogen, orthophosphate and nitrate-nitrogen are examples of some of these specific methods. Organic compounds are usually measured by lumping methods, such as total organic carbon (TOC) and dissolved organic carbon (DOC).

When a pollutant is degraded in the environment, oxygen is consumed in the degradation process. A lot of methods have been developed in order to determine how much pollutants a wastewater is made up of and they measure the amount of oxygen needed to oxidise the sample. The difference between these methods is the strength of the oxidation agent. Examples of these methods are chemical oxygen demand (COD) and biological oxygen demand (BOD).

These different methods represent the most common ones in the wastewater treatment field. The most important method for characterising the wastewater is COD. Other methods like TOC could also be used but then they have to be correlated to COD. The amount of degradable matter in the wastewater can be determined with BOD but this method while only give an estimate. The actual reduction will probably be larger than what the BOD result indicates since the micro-flora in the treatment process will be more adapted to the wastewater compared to the inoculum used in the BOD analysis. VSS is the best measure of the amount of microbial biomass in the wastewater treatment plant. TSS could also be used but inorganic matter could bias the result and cause an overestimation of the amount of microorganisms in the system.

There are of course many more methods besides those mentioned in this section, which is used for characterisation of wastewater and evaluation of treatment plants. Specific analysis is used for determination of one single component, such as ammonium and nitrate and there are methods for determination of wastewater characteristics, e.g. degradability or toxicity.

2.6 Mechanical/physical/chemical methods

Settling

Settling is the most frequent method to separate solid particles from the liquid phase. Particles that have a higher density than the surrounding liquid settle and accumulate at the bottom as sludge. Three different theories, discrete particle settling, flocculent settling and hindered flocculent settling are used to describe the mechanisms behind the settling process. The characteristics of the settling particles and the concentration of particles decide which theory to use. If the particles do not change their size or density (like sand or carbon powder), they settle as discrete particles. The settling velocity for particles in such systems under conditions with laminar flow follows Stoke's law, which states that the velocity is proportional to the difference in density between the liquid and the particle and to the square of the particles diameter. Flocculent settling is used to describe settling of particles like solids that are produced in a biological wastewater treatment plant. When such solids, usually referred to as flocs, settle they tend to attach to each other under the formation of larger flocs. This phenomenon increases the settling velocity since the particle size increases. This mechanism is highly complex and cannot be described by any mathematical formula. Consequently, the settling velocity will have to be measured in practical experiments. When the interference from surrounding particles increases as the floc concentration gets higher the settling mechanism changes to hindered settling. This normally occurs if the starting floc concentration is larger than 500 mg/l. Also for this type of settling the settling velocity will have to be determined by practical experiments.

For discrete particle settling and flocculent settling the sizing of the settling basin depends on the hydraulic surface loading. This is based on the hypothesis that a particle will settle in a settling tank with a horizontal flow, if the time it takes to reach the bottom is shorter than the time it takes for the particle to move from the inlet to the outlet of the tank. This criterion is fulfilled if the settling velocity is larger than the hydraulic surface loading.

Settling is usually done in large either rectangular or circular basins. These basins are at the bottom equipped with some type of scrapes, which transfers the bottom sludge to an outlet point. There is also another type of settler, the lamellae settler, which is equipped with several parallel plates in order to increase the surface for particle-liquid separation. An example on a rectangular settling basin can be found in Figure 2.8, which shows the settling basins after the activated sludge treatment from Källby treatment plant in Lund.

Figure 2.8 Settling basin at Källby treatment plant in Lund (Photo Michael Ljunggren).

Settling is used in many different applications, such as, primary settling of municipal wastewater, removal of chemical flocculent in drinking water treatment and separation of sludge in an activated sludge process.

Flotation

Flotation is another method for separating solids from a liquid. In the flotation process, solids in the water are concentrated in the top layer of the liquid and an outline of the flotation process can be seen in Figure 2.9. Scrapers continuously move across the surface to remove the concentrated solids from the treated water phase. If the density of the solids is smaller than the density of the liquid, the process is called natural flotation. Induced flotation is used when the particles have greater density than the liquid. This is the normal situation in the wastewater treatment field and the induced flotation used is referred to as dissolved air flotation (DAF). Induced flotation is based on small air bubbles ability to attach themselves on the surface of solid particles and producing a solid-air composite. When a sufficient amount of air bubbles is linked to the solids the density of the composite will be lower than the density of the liquid. This density difference will then force the composite to the surface.

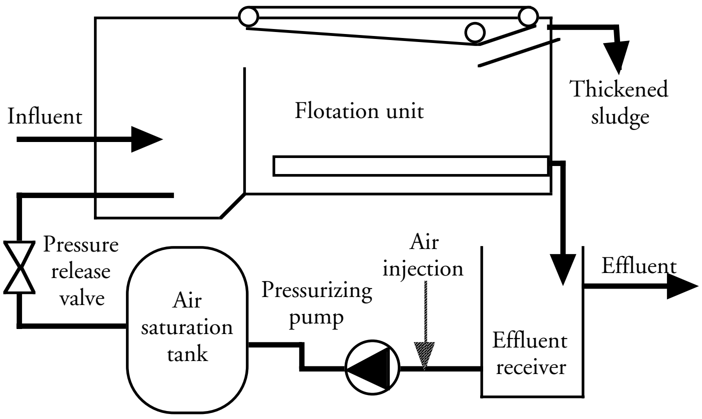

Figure 2.9 Outline of a flotation unit.

It is important to have the right size distribution of air bubbles in order to have an efficient solids removal. The normal diameter of the air bubbles in a DAF process is between 40 and 70 µm. There are several reasons why the air bubbles should be small. First of all, they thereby have a low rising velocity and this promotes the attachment to the solids. The concentration of bubbles in the liquid increases with decreasing size of the bubbles and a high concentration of bubbles gives a high probability that a bubble will come in contact with a particle.

It is not possible to produce such small bubbles as needed in a DAF-process by letting in compressed air even with a fine bubble distribution system. The amount of air that can be dissolved in water increases with applied pressure and this is used in the method. Water is exposed to high pressure (3 – 6 bar) and when the pressure is lowered the water is over saturated with air and small bubbles are produced. Normally recycled treated water is used for high pressure water and the ratio between high pressure water and the water that is going to be treated is normally between 0.1 and 0.5.

In the area of water treatment, DAF processes are used for recovering fibres in paper mill process waters and removing suspended solids after biological treatment.

Sand filtration

Water is pumped into a closed tank or a vessel filled with sand. The size of the sand particles are around 2 mm. Suspended solids in the water are trapped in the sand as the water flows through the sand bed. As more and more particles are retained in the sand the head loss increases. When it gets to large the filter bed has to be cleaned, which is done by backwashing. This is done with water that is pumped in the opposite flow direction. There are also filtration systems where the efficiency of the backwashing is increased by blowing air into the sand bed.

Membrane filtration

Membrane filtration is a separation process and it works, since different compounds have varying selective resistance for transfer through the membrane. It is consequently possible to separate e.g. suspended particles from the rest of the fluid. The separation occurs since water passes through the pores of the membrane to the other side whereas other components are more or less retained. Which type of components that are retained is determined by the size of the pores. Membrane filtration is usually divided into three different operational ranges: microfiltration, ultrafiltration and nanofiltration.

Microfiltration	The membranes have a pore size between 0.02 µm and 2 µm and are capable of separating suspended solids and bacteria.
Ultrafiltration	The pore size is between 0.002 µm and 0.02 µm, which is sufficient to reject large macromolecules.
Nanofiltration	These membranes have a pore size less than 0.002 µm and allow the passage of monovalent ions and bivalent salts to a lesser degree.

Chemical treatment

Chemical treatment can be used for reducing both dissolved and particulate pollutants in wastewater. In the treatment process the added chemicals produce a flocculent, to which the pollutants is either bound or more loosely attached. The mixture of flocculent and pollutants is then usually removed by settling.

The chemicals normally used are different kinds of trivalent positive ions. The most common are iron and aluminium salts together with aluminium polymers. These chemicals react rapidly with water and form a precipitate, the metal hydroxide. Phosphate present in the water will also react with the metal ions to a solid metal phosphate. The formation of the metal hydroxide is important since it helps to trap other particles. During the flocculation phase the flocs tend to aggregate to each other into a large complex , which is positive since large particles have a higher settling velocity.

Due to the special mechanisms chemical treatment is done in three different phases. First there is a fast mixing of the coagulant into the water that is going to be treated. Then the water enters a much gentler zone were the flocculation can occur and finally the produced flocs are removed in a settling phase.

Chemical treatment is used both for treatment of drinking water and for treatment of wastewater. The different methods for treating wastewater are named after the dosing position for the coagulant in the plant. Common methods are pre-precipitation, co-precipitation and post-precipitation.

Ozonation

Ozone is a toxic and reactive gas with the molecular formula O_3 and it is a very strong oxidising agent. It reacts with different cellular components, such as enzymes, proteins and lipids, thereby disrupting their biochemical and physiological properties. It is produced by passing air or oxygen between two electrodes bearing an AC potential, which normally is between 6 000 and 18 000 V. When the oxygen molecule passes the electrical field the kinetic energy of the free electrons is increased. At a certain degree of excitation the oxygen molecule is dissociated into free radicals, which react with other oxygen molecules and produce ozone. If air is used as the feed gas the concentration of ozone from the ozone generator is between 10 and 40 g/m^3normal (1 atm, 0°C). By using oxygen instead of air, higher concentrations can be achieved. Normal values are 10 to 140 g/m^3 normal (1 atm, 0°C) for oxygen. The energy requirement for the production of ozone from air is 13 to 18 kWh/kg and from oxygen 6 kWh/kg. A large part of the energy is transformed into heat, which must be removed by a cooling system.

Ozone is a strong oxidation agent and is used in many different applications like treatment of drinking water, industrial and municipal wastewater. The purpose of using ozone with drinking water is to remove bacteria and virus that contaminate the water. High concentrations of iron and manganese in the drinking water are also a problem since they discolour the water and this can be solved by ozone treatment. These minerals do not have any negative effect on the consumer health but can stain clothes during washing. Ozone is used with municipal wastewater for disinfection of treated water and for deodorization, a purpose that also relates to industrial wastewater. Removing the colour in wastewater from, for example, textile industries is also an example of ozone use. The use of ozone is not limited to treatment of different kinds of wastes. In the pulp industry, ozone is used for bleaching pulp.

Since ozone is very reactive it is a hazardous compound and it ought not to be released into neither the working environment nor the atmosphere. Even a small concentration of ozone in the air is dangerous. Breathing air that contains only 0.0005% ozone for 1 hour will result in injuries to the lungs. When wastewater is treated with ozone it is not possible to use all ozone in the gas. Before this used gas can be released the remaining ozone must be destroyed. The most reliable method for this is thermal treatment. This method is based on that ozone is an unstable compound and disintegrates back to oxygen. At low temperatures this process is very slow but the rate increases at higher temperatures. The destruction is done by heating the used gas to 320°C and then pass it into a reactor with a retention time of around 3 seconds.

2.7 Biological degradation

Different energy and carbon strategies

In biological treatment living organisms are used for purifying waste, which can be a solid, liquid or gas. The substance that is degraded acts as a source of building blocs and/or energy source for the microorganisms so they can fulfil their goal in life, which is to multiply. There is a broad diversity among the microorganisms regarding potential energy and carbon sources. The term autotroph is used to classify any type of organism that uses inorganic carbon, such as carbon dioxid for production of organic cell components. These organisms play an important role on Earth since they are able to produce organic carbon compounds using energy from light or inorganic material. Without autotrophs heterotrophic types of organisms would not exist. These organisms, which include humans, get energy from degradation of organic carbon compounds in coupled redox reactions. During this process the substrate, which functions as an electron donor, is oxidised. Most energy is produced with aerobic respiration where oxygen functions as the necessary electron acceptor. Other compounds like nitrate and sulfate can also function as electron acceptors but the energy yield will then be lower. Such processes are referred to as anaerobic respiration to distinguish them from the case when oxygen is used. If there is no supply of electron acceptors the organisms still can produce energy in a process called fermentation. In this process there is only partial oxidation of the substrate and hence the energy yield is very low. One example of fermentation is production of ethanol from glucose by yeast.

Microorganisms

The term microorganism is used for organisms that are too small to be visible for the naked eye. With a microscope a whole new world appear in a small sample from a wastewater treatment plant as in Figure 2.10. They have the ability to live as free cells or in a cluster unlike the cells in plants and animals, which can only live as part of a multicellular organism. New systematic methods have shown that all cells both from microorganisms and macroorganisms can be classified into three different kingdoms: Bacteria, Archaea and Eucarya.

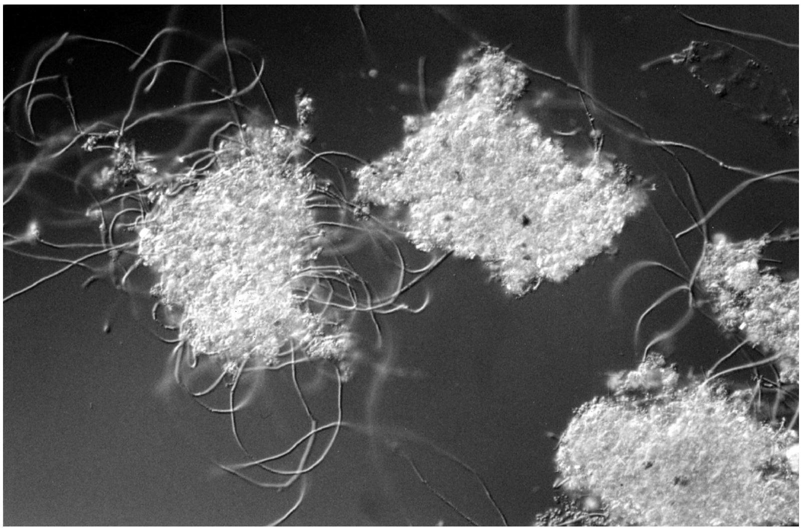

Figure 2.10 Flocs from activated sludge consisting of floc forming bacteria and filaments.

All macroorganisms like plants and animals belong to the Eucarya kingdom but there are also some important microorganisms within this category. The ciliates are unicellular organisms, which are important members of a well-balanced activated sludge. They feed upon bacteria and organic particles. There are ciliate species that are stalked and they stretch out into the void between the floc particles. These organisms filtrate the fluid, which gives a clear supernatant. There are also other ciliate species that are motile and they graze the outer layer of the floc. Within the sludge there exist Eucarya multicellular microorganisms like rotifers and nematodes. Rotifers are more important than nematodes since they help to keep a clear supernatant as they feed upon bacteria.

Very specialised microorganisms like the ones that are producing methane or those which can be found in locations with high salt concentration or high temperature, belong to the kingdom Archaea. In the wastewater area it is only the methanogens that are of any relevance.

In the sludge of a treatment plant there are several hundred different species of microorganisms and most of them belong to the kingdom Bacteria. As a normal microorganism they can live as free cells but the preferred manner of growth for water treatment is as a cluster of several cells, which will facilitate the separation of the microorganisms from the purified water.

Although microorganisms in a treatment plant are small and look similar in the microscope there can be hugh differences between them. The evolutionary distance between two species is measured by comparing the sequence of ribosomal RNA. Such investigations have revealed that there is greater evolutionary distance between almost any two families of bacteria than between e.g. tulips and humans.

Environmental demands

There are a lot of factors that influence the well-being of microorganisms. Aerobes in treatment plants, for example, need oxygen and this is supplied to them by forced aeration. If oxygen is absent some of them can still function if they have the ability to use other types of electron acceptors. This ability is used in the denitrification step in municipal treatment plants where nitrate is reduced to nitrogen gas together with the oxidation of organic compounds. Organisms that cannot use oxygen are called anaerobes and for some of them even small quantities of oxygen are lethal. Therefore is it important to exclude oxygen from anaerobic treatment processes.

As long as it is possible to maintain water in liquid form inside the cell despite the surrounding temperature, microorganisms can survive at extreme temperatures. Microorganisms are found in hot springs where the temperature can be over 100°C and in cold areas like Artic and Antarctic. Although the range for growth extends over more than 100°C the range for a single organism is much smaller – about 35°C. The growth rate is usually increasing with increasing temperature up to an optimum value. If the temperature is further raised the growth rate declines rapidly to zero as the maximum temperature is reached.

pH indicates whether a solution is acidic, neutral or basic and most microorganisms have optimum conditions in the range from 5 to 9. There are of course examples of microorganisms that grow in solutions with a pH-value below 2 and others have their optimum between 10 and 11.

The environmental conditions set the limits for which microorganisms will survive in the treatment plant. In order to have stable process conditions such parameters as pH and temperature should not be allowed to vary too much during a short time period since this will cause a change in the composition of the sludge. Other things like the influent load of wastewater and the amount of microorganisms in the system also influence the result and should therefore be stable.

Nutrient requirements

The ultimate goal of a bacterial cell is to reproduce itself. Therefore the bacteria is increasing its size and multiplying its components so it can be divided into two identical daughter cells. In the cell several different organic and inorganic molecules can be found. Most of the cell by weight is made up of protein followed by genetic material ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). The rest of the cell is a mixture of different lipids, polysaccharides, amino acids and a small quantity of inorganic molecules.

The elements that these different molecules are made up from can be divided into two different groups, macronutrients and micronutrients, depending on their concentrations in the cell. The macronutrients are carbon, oxygen, nitrogen, phosphorous, potassium, sulphur, magnesium and calcium and the micronutrients are iron, zinc, manganese, cobalt, copper and molybdenum. Since there are only small quantities of micronutrients in the cell these elements are normally not limiting the growth of the cell. The composition of the macronutrients in a cell can be found in Table 2.7.

Table 2.7 Macronutrients in a biological cell (Welander, 1991).

Element	% of dry weight
Carbon, C	50
Oxygen, O	30
Nitrogen, N	12
Hydrogen, H	6
Phosphorous, P	1.5
Potassium, K	1.5
Sulphur, S	0.3
Magnesium, Mg	0.2
Calcium, Ca	0.1

If the cell should have optimal growth conditions all macronutrients should be provided in the right ratio. Carbon and hydrogen are of course in most cases originating from the compounds in the wastewater and there is plenty of oxygen in the water. Usually there is also enough potassium, sulphur, magnesium and calcium in the wastewater. Nitrogen and phosphorous, however, are often limiting and if these are not added to the wastewater, the treatment process is not as efficient as it could be.

To get an estimation of the microorganism's nutrient requirements the cell can be approximated with the empirical formula $C_5H_7O_2N$. In an aerobic process the yield is around 0.35 kg VSS/kg COD reduced (Henze *et al.*, 1990). Since the cell contains around 12% nitrogen and 1.5% phosphorous this would mean that the microorganism would require 42 g N/kg COD reduced and 5.2 g P/kg COD reduced. The requirement rewritten so that the P-need is normalised to 1 would then finally be COD:N:P 130:8:1. In an anaerobic process the yield is lower, around 0.1 kg VSS/kg COD reduced (Malina and Pohland, 1992, p. 56) and this would give the following requirement COD:N:P 670:8:1.

These numbers are only to be regarded as rule of thumb since the nutrient requirement is a function of sludge load and wastewater composition.

2.8 Aerobic biological WWT

Biological treatment can be divided into two major fields, aerobic and anaerobic treatment. Each field can then be further divided into several methods depending on how the microorganisms are growing and being handled. Some of the most common methods are shortly described below.

Activated sludge

The activated sludge, which has given this type of process its name, is normally a thick brownish slurry that consists of the microorganisms. Wastewater is mixed with the sludge and the mixture is kept for some time in an aerated basin. The aeration has two purposes, partly it continuously stirs the mixture and partly it provides oxygen to the microorganisms, which need it in order to oxidise the pollutants. When the wastewater has been treated in the aerated basin the activated sludge must be separated from the water. This is usually done in large sedimentation basins where the activated sludge settles to the bottom and is pumped back to the beginning of the process. The cleaned water is withdrawn from the surface of the sedimentation basin. An outline of an activated sludge process is found in Figure 2.11.

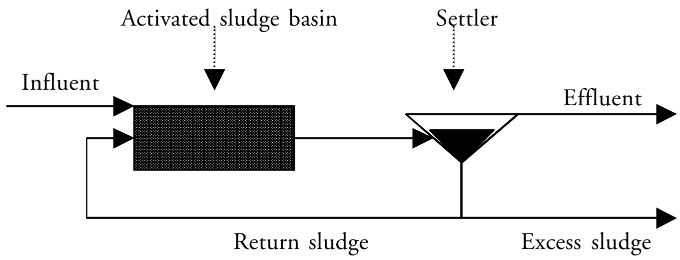

Figure 2.11 Outline of an activated sludge system. The influent is pumped to the aeration basin where it is mixed with return sludge. After treatment water with sludge is transferred to the settler where the sludge settles as sediment and cleaned effluent is withdrawn from the settler surface. Part of the sludge is returned and the surplus of sludge is wasted.

For an activated sludge process is the separation of the activated sludge from the cleaned water, essential. A sludge that is easy to settle is a necessity for a well-functioning process. The sludge should therefore, consist of large compact particles with a high settling velocity. Bacteria have the ability to produce a slime layer around them, which will glue them together into large particles, so called flocs. This happens when the ratio between the amount of food and the amount of microorganisms is low. By having a suitable load of influent wastewater to the process and by recycling sludge from the settler, the growth of floc-forming bacteria is promoted. In a good sludge there is a balanced composition of filaments and floc-forming bacteria. The filaments function as a framework for the floc-forming bacteria and the result is large floc, which settle easily. It is also important to have higher organisms like protozoa and metazoa in the sludge because they feed upon bacteria keeping the supernatant clear and prevents the flocs to become too large.

The advantage of the activated sludge process is its possibility to reach high reduction of pollutants and it is also possible to achieve enhanced biological removal of nutrients. The drawback with the method is that the function of the process is depending on the separability of the sludge. Different kinds of disturbances can also affect the operation for a long time.

Biofilm

In a biofilm process the microorganisms grow attached to a solid surface. Materials that are usually used as growth support are stones, sand or some type of plastic material. An example of some plastic carriers can be found in Figure 2.12. Since the biomass is retained on a solid material in the reactor there is no need for any sludge recirculation system and the treatment process is not so dependent on the settleability of the sludge. The sludge age of the biofilm process tends to be very long, which promotes the development of a long food chain. This is the explanation why the sludge production is usually somewhat lower than for suspended sludge systems.

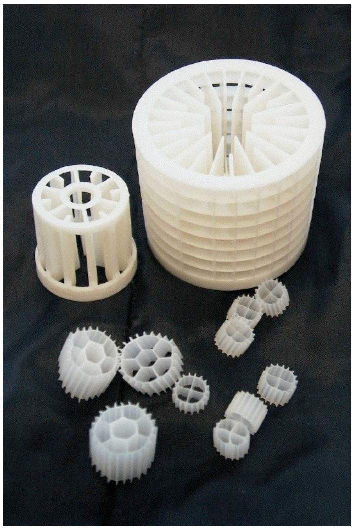

Figure 2.12 Different carriers used in biofilms processes.

In general, it is possible to achieve a higher degree of reduction with an activated sludge system than with a biofilm process but the latter process is not so sensitive to disturbances from variations in the load. The biofilm process also recovers faster after a disorder with toxic or inhibitory substances.

2.9 Anaerobic treatment

Anaerobic treatment is perhaps most known for the digestion of different solid wastes, such as municipal sludge. The method, however, has many advantages making it suitable also for treatment of wastewater. Anaerobic treatment is used in different industrial sectors like brewery, dairy, slaughterhouse and sugar production.

Anaerobic treatment of complex organic waste is a multi step process with several different species involved. The degradation process starts with hydrolysis of large molecules and solid matter by the action of extracellular enzymes into small monomeric substances, such as simple carbohydrates and amino acids, which can enter the bacterial cell. These substances are then fermented in the next step, called acidogenesis, to hydrogen, carbon dioxide and different short chain fatty acids like acetic acid, propionic acid and butyric acid. Some of the fermentation products are further converted into hydrogen and acetic acid by special groups of bacteria in a process named acetogenesis. The treatment is then completed with the methanogenisis, where methanogens produce methane from either acetic acid or hydrogen and carbon dioxide.

One benefit of the anaerobic treatment process is the low sludge production. This is caused by the lower energy yield for anaerobic processes compared to aerobic ones. This is also reflected in the generation times for different types of anaerobic microorganisms, see Table 2.8. It is important to take these different growth characteristics into consideration during the start-up of an anaerobic treatment process. If there is not a balance in the sludge composition between the different types of microorganisms there is a risk for accumulation of fatty acids, which can have an inhibitory effect on the methane production.

Table 2.8 Generation times for different microorganisms involved in anaerobic treatment (Malina and Pohland, 1992, p. 4 and 7).

Anaerobic step	Substrate	Generation time
Acetogenisis	Propionic acid	7 days
Acetogenisis	Butyric acid	3 days
Methanogenisis	Acetic acid	24 h
Methanogenisis	Hydrogen	1 – 4 h

There are several different reactor configurations that have been developed for anaerobic treatment. In general, when sludge and wastewater with a high content of particles are treated a suspended growth reactor, such as the anaerobic contact process is more advantageous. It resembles the activated sludge process since the waste is treated in a stirred reactor together with an anaerobic sludge. The sludge is then removed in some type of separator from the treated water and is returned to the reactor. Wastewater that mainly consists of dissolved components is suitable for treatment in a fixed-film reactor. This reactor could either be a fixed-bed process or an expanded/fluidised bed process. In both processes the microorganisms grow as a biofilm on the surface of some sort of supporting media. Rocks and special plastic material are used for fixed-bed processes whereas sand is often used for the expanded/fluidised bed processes. In both processes, wastewater is distributed in the bottom of the reactor and in the expanded/fluidised bed process the flow is sufficiently high to expand the bed. Whether a process is to be called expanded or fluidised depends on the degree of expansion. When the bed is expanded 15 to 30% it is called expanded and expansion in the range 25 to 300% are called fluidised. The benefits of a fluidised bed are the high biomass concentration and long sludge retention time together with high mass transfer characteristics. One major drawback is the energy costs associated with the pumping in order to keep the bed fluidised.

Chapter 3

On-line Analysers

Whether there is a need to measure a single compound or mixture of different compounds there are always several different techniques that can be used for the determination. The most common techniques for analysis of organic matter, ammonium and phosphate are presented in Section 3.2. In Section 3.3, some of the on-line analysers available on the market are presented. One area where on-line analysers are becoming more common is in municipal wastewater treatment plants. To benefit from the practical experiences about on-line analysers from that area a telephone survey was performed. In the survey, which is presented in Section 3.4, the contacted plant managers were asked questions about what on-line analysers their plant were equipped with and if the signals from the analysers were used for on-line control or only for monitoring purposes. The chapter ends with some conclusions.

3.1 Introduction

When a process is going to be controlled it is important to have fresh information about the systems variables. Analyses of grab samples are good enough if only an indication of the function of the process is required but it is not enough for control. Therefore there is a need for on-line analysis. Process is a general word and could mean almost anything but this chapter will focus on instruments for wastewater treatment.

Before the 1970s there were no suitable on-line sensors available, which made it impossible to incorporate closed-loop control. During the 1970s different nutrient sensors were developed but the stability was still not sufficient and the instruments demanded too much maintenance (Garrett, 1998). The stability of the instruments improved and in the late 1980s on–line sensors were used for the planning phase to upgrade Swedish treatment plants for nitrogen removal and at several plants instruments for monitoring nitrogen were installed. In the early 1990s, the sensors were considered good enough for implementation of on-line control with only little surveillance (Thornberg et al. 1993; Thornberg and Thomsen, 1994). Today there are several plants in Denmark that uses on-line sensors (Olsson et al., 1998) and modelling and on-line measurements are today of sufficient quality to be able to be introduced at municipal treatment plants (Önnerth et al., 1996). But continuing progress of the on-line sensors is still a demand. For example more reliable instruments and sensors not sensitive for lightning and storms are wanted (Huntington, 1998).

The goal of the ClosedCycle project is to develop an in-mill biological treatment of whitewater so that the water can be reused in the papermaking process. One of the projects milestones is to produce an automatic control system for the addition of nutrients to the biological treatment process. To be successful with this task, some information about the treatment process must be available. The type of information that can be retrieved from the treatment process determines how the control should be implemented. However, performing on-line measurements are not always a walk in the park. Since there are no experiences from on-line measurements in whitewater and since it is a new application area it would be strange if an approach could be implemented without any problems. It is important to evaluate all types of information that the control can be based upon. In the treatment process, nutrients are consumed while microorganisms degrade organic compounds. The most interesting parameters to analyse are in this case organic compounds and the nutrients ammonium-nitrogen and orthophosphate. The activity of the microorganisms measured with respirometri or with some other method, as NADH is of course also very interesting. Since they, however, often require an activated sludge process and the chosen instruments should work no matter the type of the treatment process; these methods are not investigated.

An almost complete production of different methods used on wastewater treatment plants can be found in Standard methods (1998).

3.2 Measurement principles

Organic compounds

The only thing that the term organic compounds reveals is that the compounds are made up of carbon. So the compounds in this group can have totally different chemical structures, biodegradability and chemical properties. One way to determine the amount of organic compounds is to utilise the fact that many unsaturated and aromatic substances absorb light of certain wavelengths. Normally the sample is radiated with ultraviolet light (UV) at 254 nm and the amount of organic compounds is proportional to the amount of light that the sample absorbs. Since not all organic compounds absorb ultraviolet light there is a risk that the method gives a too low values and completely miss dynamic changes in the concentration of non-absorbing compounds. On the contrary, if it is found that the method is suitable for the sample it is a very simple and robust method, which normally does not require much maintenance.

A more complicated method is to determine the amount of organic carbon in a sample. In Figure 3.1 there is an example of a TOC-instrument, a Biotector 990+ from Pollution Control system.

Figure 3.1 On-line instrument for analysis of TOC.

The organic carbon is usually measured either as total organic carbon (TOC) or as dissolved organic carbon (DOC). The first step of the method is to remove the total or dissolved inorganic carbon (TIC, DIC). By adding a strong acid to the sample, carbonates in the sample are converted to carbon dioxide. A stream of gas transfers it to an IR-absorption unit where the amount of TIC/DIC is quantified. Then the different organic compounds in the sample are oxidised to carbonates. This can be done in many different ways, for example:

- high temperature in combination with oxygen
- ultraviolet radiation and chemical oxidation with per-sulphates
- ozone under alkaline conditions.

There is, however, a difference between how easy or difficult it is to oxidise different compounds and therefore the results from analyses of the same sample with different TOC-instruments can differ due to the oxidation process. When the sample is oxidised the pH is again lowered, this time in order to quantify the amount of TOC/DOC in the same way as TIC/DIC.

A TOC-instrument is, compared to a UV-absorbing instrument, a more complicated instrument. The sample has to be transferred from the sampling point to the instrument in tubes and the instrument needs different chemicals and gases. Such an instrument demands more maintenance and the risk for clogging is larger. A UV-instrument is placed directly into the water at the measuring point and it is usually equipped with some form of wiper, which automatically cleans the instrument. The signal from a UV-instrument is usually continuous while it takes around 10 minutes to complete a single measurement with a TOC-instrument.

Ammonia

Ammonia is a gas at room temperature and it is soluble in water. Dissolved ammonia acts as a base with ammonium as the conjugating acid. The equilibrium between the acid/base pair is determined by the pH of the water solution, see Figure 3.2. Usually when an analysis of a water solution is expressed in units of ammonia, the term ammonia refers to the sum of ammonia and ammonium. Ammonia can be analysed by several different methods, e.g. gas sensitive electrode, wet chemistry and direct absorbance.

If a measurement is made with an electrode the sample is mixed with a strong base, such as sodium hydroxide. The raise in pH will convert all ammonium to ammonia, which diffuses through the membrane of the electrode into the internal solution. The incoming ammonia will change the pH in the internal solution and this change is detected by measuring the potential between a pH-electrode and a chloride-reference electrode immersed into the internal solution. By calibrating the electrode, the instrument gives a direct reading of the ammonia concentration.

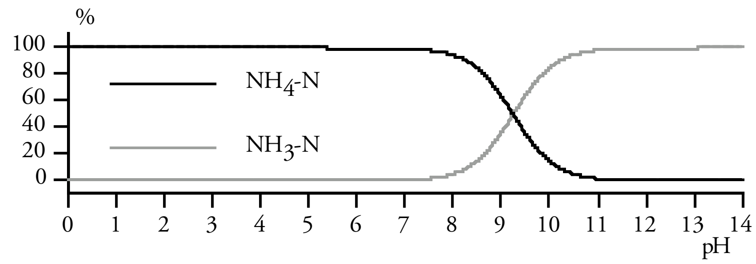

Figure 3.2 Fraction of the conjugated acid/base form of ammonia at different pH.

It is also possible to convert the ammonia into a coloured compound and measure the colour with a spectro-photometer. In the phenate method, ammonia reacts with hypochlorite and phenol with nitroprusside as a catalysator to an intensively blue compound, indophenol. The developed colour is determined by absorption at 640 nm. There is also another method, the modified Berthelot method, where ammonia is converted to 5-aminosalicylate. After oxidation and oxidative coupling a green complex is formed, which is determined by absorption at 660 nm.

It is, however, also possible to measure directly on ammonia with an absorption method without developing a coloured compound. In this method, the sample is mixed with sodium hydroxide and an equilibrium between ammonia in the gas phase and dissolved ammonia in the water phase is established. The amount of ammonia in the sample is determined by a fast Fourier transformation of the UV-light absorption spectrum of the ammonia in the gas phase.

Phosphate

Phosphorous normally occurs as different phosphates either in inorganic form as orthophosphates and condensed phosphates or in organic form as organically bound phosphates. A shortage of phosphorous when a wastewater is treated biologically, is usually met by addition of phosphoric acid, where the phosphorous is in form of orthophosphate. Determination of orthophosphate is usually done with a colorimetric method.

For analyses in the range of 1 to 20 mg P/l, the vanadomolybdophosphoric acid method, which gives a yellow colour, is suitable. In this method, orthophosphate reacts under acid conditions with ammoniummolybdate forming molybdophosphoric acid, which in the presence of vanadium turns into yellow vanadomolybdophosphoric acid. The intensity of the yellow colour, which is proportional to the amount of orthophosphate, is measured by absorption at 400 to 490 nm.

The ascorbic acid method, which gives a blue colour, is more suitable for lower ranges around 0.01 to 6 mg P/l. In this method, ammonium molybdate and potassium antimonyl tartrate react under acid conditions with orthophosphate forming phosphomolybdic acid, which is reduced by ascorbic acid to the intensely coloured molybdenum blue. The intensity of the blue colour, which is proportional to the orthophosphate concentration, is measured by absorption at 880 nm.

In order to determine the amount of total phosphorous the sample first has to be digested with some oxidation agent in order to convert all phosphorous to orthophosphate and then be analysed according one of the previously mentioned methods.

3.3 Market survey

There are a lot of commercial manufactures of on-line instruments today. Some operate only on a national level whereas others are international. It would be good if a survey like this could be complete but finding every manufacture in the world is of course impossible. It is also necessary to limit the number of parameters in the survey since it has been developed on-line instruments for a lot of different parameters. Therefore, this survey has focused on finding commercial instruments for measuring organic compounds, ammonium-nitrogen and orthophosphate. Two different on-line instruments for determination of ammonium-nitrogen and orthophosphate can be found in Figure 3.3.

Figure 3.3 Furthest up to the right is the Evita phosphate sensor from Danfoss A/S with its signal converter beneath and to the left is a multi-parameter instrument (ammonia, COD and nitrate) from Awa Instrument.

Information sources

Information about different brands of on-line instruments has been gathered from several sources. Some brands, for example, have been found in scientific articles. Another important source is wastewater treatment exhibitions. Much information about new brands and specific instruments has also been found on the Internet. A list of available instruments, manufacturers, parameters, methods and other data can be found in Table 3.1. It is important to remember that the manufacturer has provided the information to the table. The determination of for example detection limit and measuring error is probably done at optimal conditions, which could deviate a lot from the actual conditions in a wastewater treatment plant. Therefore, in a real application is it probably difficult to achieve the excellent performance, which some of the instruments claim to have.

Table 3.1 List of available on-line instruments for measuring phosphate, ammonia, organic matter, total organic carbon and biological oxygen demand.

Manufacturer	Model	Parameter	Method	Range	Det. limit	Measuring error	Response time (90%)	Frequency
ABB Instrumentation, GB	8230	ammonia	electrode	0.05-5.0 mg/l	n.a.	±5 % of value or ±0.1 mg/l	< 5 minutes	continuous
Applikon, NL	ADI 2018	ammonia	electrode	0.01 – 17 000 mg/l	n.a.	n.a.	n.a.	n.a.
Contronic, SE	A4620	ammonia	electrode	1 – 1 000 mg/l	n.a.	2%	n.a.	n.a.
Danfoss, DK	Evita	ammonia	phenate method	0 – 20 mg/l	100 ppb	±10% of value or ±0.06 mg/l	10 minutes	continuous
Awa Instruments, F	AM 300	ammonia	stripping + UV-abs	0 – 10 mg/l	100 ppb	±0.05 mg/l	n.a.	5 minutes
Dr. Lange, D	Amtax Inter	ammonia	phenate method	0.01 – 80.0 mg/l	10 ppb	2% DIN 38 402	5 minutes	5 minutes
Hach, US	APA 6000	ammonia	mod. Berthelot	0.02 – 2.0 mg/l	20 ppb	±5% of value or ±20 ppb	n.a.	5 minutes
Skalar, NL	SA 9000	ammonia	mod. Berthelot	25 - 500 ppb	25 ppb	n.a.	n.a.	continuous

Table 3.1 Continued.

Manufacturer	Model	Parameter	Method	Range	Det. limit	Measuring error	Response time (90%)	Frequency
STIP, D	Spectron	ammonia	electrode	0.1 – 50 mg/l	n.a.	n.a.	n.a.	continuous
WTW, D	TresCon OA110	ammonia	electrode	0.10 – 1 000 mg/l	100 ppb	±5% of value	< 3 minutes	continuous
Polymetron, F	8810	ammonia	electrode	0.01 – 100 mg/l	10 ppb	±2% of range	n.a.	5 minutes
ABB Instrumentation, GB	8240	orto-phosphate	vanadate	0 – 20 mg/l	n.a.	±0.05 mg/l or ±5%	11 minutes	continuous
Bran & Luebbe, D	Monitor 90 S	orto-phosphate	n.a.	0 – 0.5 mg/l	n.a.	< 1% of range	n.a.	10 minutes
Danfoss, DK	Evita	orto-phosphate	ascorbic acid	0 – 6 mg/l	50 ppb	±10% of value or ±0.03 ppm	15 minutes	continuous
Dr. Lange	Phosphax Inter	orto-phosphate	vanadate	0.05 – 15 mg/l	50 ppb	2% DIN 38 402	5 minutes	5 minutes
Dr. Lange	Phosphax Sigma	orto-phosphate	ascorbic acid	0.01 – 5.00 mg/l	10 ppb	2% DIN 38 402	10 minutes	10 minutes

Table 3.1 Continued

Manufacturer	Model	Parameter	Method	Range	Det. limit	Measuring error	Response time (90%)	Frequency
Gimat, D	Phosphato-lab	orto-phosphate	vanadate	0.05 – 30 mg/l	50 ppb	±5% of value	n.a.	35 seconds
Hach, US	Series 5000 Low	orto-phosphate	ascorbic acid	0 – 5 000 µg/l	< 4 ppb	±4% of value or ±4 µg/l	15 minutes	continuous
Skalar, NL	SA 9000	orto-phosphate	ascorbic acid	25 – 500 ppb	25 ppb	n.a.	n.a.	n.a.
STIP, D	Spectron	orto-phosphate	vanadate	0.05 – 100 mg/l	n.a.	n.a.	n.a.	n.a.
WTW, D	TresCon OP210	orto-phosphate	vanadate	0.05 – 3 mg/l	50 ppb	±2% of value	< 3 minutes	continuous
Polymetron, F	8810 Phosphate	orto-phosphate	ascorbic acid	0 – 5 mg/l	< 100 ppb	±0.1 mg/l	n.a.	15 minutes
ABB Instrumentation, GB	7320	org. matter	UV-abs.	0 – 100 mg/l	n.a.	n.a.	5 minutes	continuous
Awa Instruments, F	CT 300	org. matter	UV-abs	0 – 20 000 mg/l	n.a.	±10 mg/l	< 10 seconds	continuous

Table 3.1 Continued.

Manufacturer	Model	Parameter	Method	Range	Det. limit	Measuring error	Response time (90%)	Frequency
Dr. Lange, D	UV-Probe	org. matter	UV-abs.	0.01 – 60 abs/m	0.01 abs/m	2% DIN 38 402	1 minute	>= 1 minute
Astro, US	1950 Plus	TOC	$Na_2S_2O_8$ + UV + low temp.	0 – 5, 0 – 20 000 mg/l	50 ppb	±2% of range	<= 8 minutes	continuous
Dr. Lange, D	Toctax	TOC	$Na_2S_2O_8$ + high temp. + pressure	1.0 – 1 000 mg/l	1.0 mg/l	n.a.	n.a.	10 minutes
Pollution Control system, IR	BioTector 990 plus	TOC	high pH + ozon	0 – 25 000 mg/l	n.a.	±3% of value or ± 0.5 mg/l	n.a.	6 minutes
STIP, D	Stip-TOC	TOC	high temp + catalysator	2 – 500 000 mg/l	2 mg/l	n.a	n.a.	3 minutes
Applitek, B	RA-BOD	BOD	oxygen sensor	n.a.	n.a.	n.a.	n.a.	n.a.
Kelma bvba, B	RODTOX	BOD	oxygen sensor	0 – 500 000 mg/l	n.a.	n.a.	n.a.	n.a.

Discussion

For measurements of ammonia there are three different brands of instruments that measure with an electrode but they are all based on the same principle. The sample is transferred in tubes, mixed with a base and perhaps a complexing agent to prevent precipitation. The mixture is then transferred to the electrode for ammonia determination. Usually the instruments are equipped with some form of automatic calibration to compensate for instrument drift. Samples with high concentrations of suspended solids often create problems since they tend to clog the instrument.

There is only one instrument that measures ammonia with absorption in the gas phase and it is the instrument from Awa Instruments. Since the measurement is done in the gas phase the instrument is probably not so vulnerable with regards to high concentrations of suspended solids if the tubes for sample transfer are large enough. Interferences from the sample matrix are also likely to be small.

Instruments that measure ammonia with absorption in the liquid phase can be divided into two different groups. The conventional type uses tubes to transfer the sample and also depends on filtration of samples that contain much particular matter. The new type of instrument, the Evita instrument from Danfoss, uses a completely new approach. The instrument is immersed directly into the measuring point. The ions in the water phase diffuse through a membrane into a carrier solution. This solution is mixed with reagents and the developed colour is then measured in a spectrophotometer. This instrument can be placed directly into an aeration basin without any problems.

Phosphate is always measured with some absorption method. Although there are different chemical methods the main difference between the instruments is related to in the chosen technology. As for the wet chemistry ammonia instruments the phosphate instruments can also be divided into tube and membrane instruments. The drawbacks and benefits from the two different techniques are the same as for instruments that measure ammonia with absorption in the liquid phase.

The least troublesome way to measure organic matter is with an instrument where the measurement is based on UV-absorption. The only maintenance that this type of instrument needs is cleaning of the windows, which separate the sample from the instrument. Most instruments have a wiper, which automatically performs the cleaning. The instruments that measure TOC are more complicated. In order to get a correct answer proper oxidation and sampling are important factors. The Biotector seems to be an instrument that was developed for more difficult wastewater since it allows particles in the water of up to 2 mm in diameter.

Whether the amount of organic matter is determined with UV-absorption or TOC measuring techniques, the value does not reveal how easily degradable the compounds are. It is of course possible to estimate the distribution between easily degradable, degradable and persistent compounds, by performing correlation studies. If, however, the composition of the wastewater varies over time this is not possible. In that case, a respirometric measurement would be much better. However, this type of instrument often requires activated sludge for its function, which excludes plants with biofilm processes to use such instruments.

3.4 Experiences

Introduction

The purification of wastewater is done in several different processes in a wastewater treatment plant. In order to achieve efficient treatment despite variations in the load much effort has been put into finding different control strategies that will optimise the performance of these processes. Usually the strategies depend on the analysis of one or several important parameters like ammonia, nitrate or oxidation-reduction potential. To implement an automatic control system the determination has to be done with on-line instruments. In the literature there are many different examples of such control strategies, especially for nitrogen removal. For example, the completion of the nitrification and the denitrification can be monitored with a sensor that measures the oxidation-reduction potential. This type of sensor has been commonly used to control the treatment process (Charpentier *et al.,* 1987, 1989; Heduit and Thevenot, 1989; Delamenardiere *et al.,* 1991; Sasaki *et al.,* 1993; Wareham *et al.,* 1993; Plisson-Saune *et al.,* 1996; Isaacs *et al.,* 1998). In most cases, however, these strategies have only been tested in pilot scale or during a short period of time in full scale. The number of reported automatic control strategies implemented in full scale are still scarce. Denmark, where the alternating Biodenitro process is common, seems to have many installations of automatic control systems that utilise signals from on-line instruments (Sorensen *et al.,* 1994; Sørensen, 1996).

In a non-exhaustive survey (Jeppsson *et al.*, 2002) of 13 European countries, it was concluded that many WWT plants are equipped with sophisticated sensors but many of these are not used for direct control. A similar result was found in a study (Ingildsen *et al.*, 2001) where a questionnaire was sent to WWT plants in several countries but the majority of answers came from Denmark, Sweden and Australia. On an average, only 23% of the on-line sensors at WWT plants were used for direct control.

The actual situation in Sweden with regard to implemented control strategies, the use of on-line instruments and experiences from the use of instruments could not be found in the literature. Therefore a telephone survey was initiated.

Telephone survey

The managers of wastewater treatment plants in 45 municipalities in Sweden (total number 289) were contacted over the telephone. They were asked the following questions :

- The number and size of treatment plants in their district.
- What experiences they had from on-line instruments.
- If their plant had on-line instruments for the following parameters:
    - chemical oxygen demand (COD)
    - ammonia (NH_4)
    - nitrate (NO_3)
    - phosphate (PO_4)
    - pH
    - dissolved oxygen
    - reduction-oxidation potential
    - conductivity
    - total organic carbon (TOC)
    - turbidity

- suspended solids.

- How they used the signals from the instruments.

Information about sensors like flow meters and level indicators were disregarded since the survey was focused on nutrient analysers.

WWT plants

In the 45 municipalities, the number of WWT plants were 278, ranging from 50 person equivalents (pe) up to 800 000 pe. These were divided into three different groups according to Table 3.2.

Table 3.2 Number of plants categorised according to size.

Category	Size/(pe)	Number of plants
Large plant	> 100 000	13
Medium plant	10 000 – 100 000	28
Small plant	< 10 000	237

On-line instruments

For every parameter it is shown in Figure 3.4, Figure 3.5 and Figure 3.6 the number of plants, which are using this type of on-line instrument. The figures also display how the information from the instruments are used. The legend “Control” specifies the number of plants where the signal is directly used for control purposes. The legend “Monitoring” represents plants where the signal is not used for direct control. In Figure 3.4 and Figure 3.5, the legend “Missing” accounts for the plants that do not have an instrument for that parameter.

Many of the parameters can be measured with several different techniques but this is not taken into account in the results. So in the following figures there is no difference, if for example, the instrument for analysis of nitrate is made with an ion specific electrode or UV-absorption.

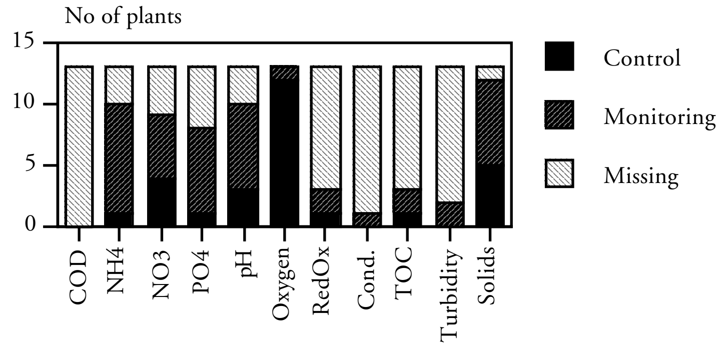

Figure 3.4 Availability and use of on-line sensors at large WWT-plants.

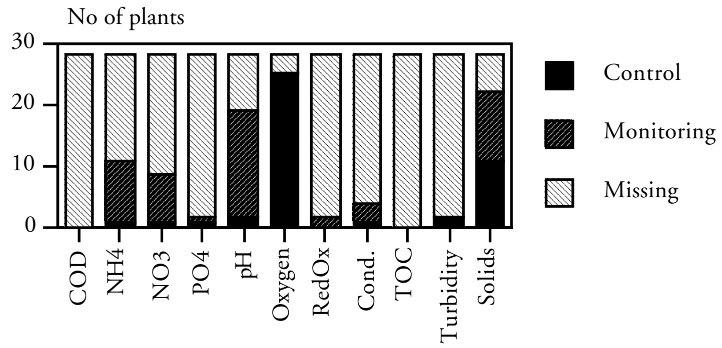

Figure 3.5 Availability and use of on-line sensors at medium WWT-plants.

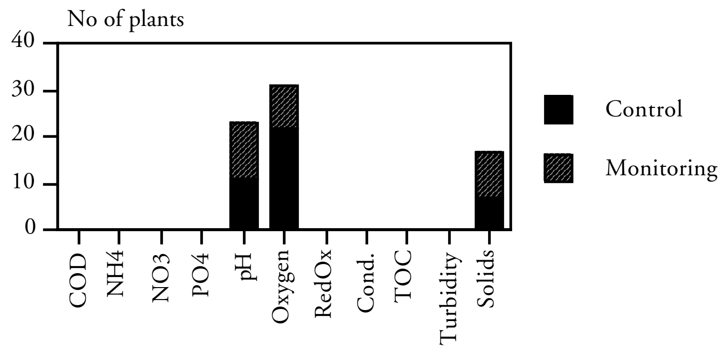

Figure 3.6 Availability and use of on-line sensors at small WWT-plants.

Service and calibration

The need for maintenance and calibration of the instruments varies significantly depending on their position in the plant, importance, type, brand and what type of chemicals that are used. In Table 3.3, the most common calibration and maintenance intervals from the survey are shown for some of the parameters.

Table 3.3 The most common calibration and maintenance intervals for some of the parameters.

Parameter	Calibration interval	Maintenance interval
Oxygen	1 per month	1 per week
pH	1 per month	1 per month
NH_4, NO_3, PO_4	1 per week	1 per week
Suspended solids	1 per month	1 per week

Discussion

Based on the survey, it can be concluded that the number of different types of instruments increases with the size of the plant. Usually there is no instrumentation at the small plants but around 10% have instruments for measurements of oxygen, pH and suspended solids. The main reason for the lack of instrumentation at the small plants is that it would be too expensive to equip them since there are so many of them. The three parameters oxygen, pH and suspended solids are also the most popular to measure at the medium-sized and large plants. The second most popular group of parameters to measure at the medium-sized plants are ammonia and nitrate, which can be found at around 35% of the plants. Phosphate instruments are not installed to the same degree at the medium-sized plants but at large plants there are no difference between these three parameters. They are found at approximately 70% of the plants. Instruments for measurement of TOC could only be found at around 20% of the large plants. There is no plant that has an instrument for measuring COD and there are only a few plants that have instruments for redox-potential, conductivity and turbidity.

One of the largest operational costs for a treatment plant is the cost for aeration. In order to maintain this cost as low as possible without getting shortage of oxygen in the process it is important to monitor the amount of dissolved oxygen. The survey shows that oxygen is the most popular parameter to measure, independently of the size of the WWT plant. Today the oxygen sensor is stable and reliable, which are conditions that must be fulfilled in order to use it for direct control. Almost all plants that have an oxygen instrument use it for direct control of the aeration.

Around 50% of the plants that have an instrument for measuring of suspended solids use it for direct control of the mixed liquor suspended solids (MLSS) in the plant. There is one experience where this type of control did not work due to occurrence of filamentous bacteria and at this plant MLSS were controlled manually.

pH measurements are used in many different ways, but when it is used for direct control, it normally regulates the amount of flocculants added for post precipitation. It is also used for pH control in a sequential batch reactor (SBR) and to trigger various types of emergency procedures, such as automatic sampling during abnormal conditions.

For the remaining parameters there are only a few that are used for direct control. Among the nutrient analysers the most utilised parameter for direct control is nitrate. There are nine large plants that have such instruments and four of them use a nitrate analyser for control of either the addition of external carbon source or the internal recirculation ratio in pre-denitrification processes.

3.5 Conclusions

Whether an on-line instrument or a sensor is going to be used for control depends on how reliable it is. The oxygen sensor is today regarded as very stable and is widely used for control. The situation is a little bit different for other types of instruments. Their complexity and risk for malfunctioning due to clogging has led to that they are mainly used for control. Today, however, new and better instrument have been developed and these are regarded as safe enough to use for control. In the near future will probably the percentage of instruments used for control increase as these instruments become more common in wastewater treatment plants.

Selecting suitable instruments for measurement on whitewater has to be based on the experiences from municipal wastewater treatment and information from manufactures. One important issue to consider is the possibility of a sample with a lot of suspended particles. There are filtration techniques available but finding a solution without filtering would be a better solution. Therefore are the new instruments from Danfoss interesting since they are not using any tubing. Also the Biotector instrument for measuring TOC has potential to be used for analyses of whitewater. This instrument certainly has tubes but since it was designed for samples with particles, the tubes are quite wide and are not likely to clog. Another instrument with a technique different from the rest is the UV-pcx. The instrument for measurement of ammonia is measuring in the headspace and it is not vulnerable against samples with particles. These three instruments are believed to be the most suitable instruments for measuring on-line in whitewater.

All of these on-line instruments are very expensive and the number of projects with unlimited resources for investment in this type of instruments is probably very small. Therefore, in most cases it is important to find the instrument, which can provide most information to a certain cost. In this case, when whitewater is to be treated in a biological treatment and the instruments is going to be used for nutrient control, the most important piece of information would be how much organic matter is loaded to the treatment process. The type of instrument that could be used depends on the composition of the whitewater. If there is a correlation between the UV absorption and the amount of organic matter this type of instrument could be used otherwise it would be necessary to acquire a TOC-instrument.

Chapter 4
Closure of Paper Mills

This chapter is about what happens in paper mills when they are using less fresh water. Firstly, a short description of the different things water is used for in a paper mill, is given. It is followed in Section 4.2 by several reasons why the water system of paper mills is closed. In Section 4.3 some of the problems that might occur when the fresh water consumption is reduced are described. The closure affects the whitewater and what effect this may have on the paper quality is discussed in Section 4.4. After this follows in Section 4.5 some practical examples of how the problems that arise from the closure are solved and a cost comparison between different techniques. The chapter ends with some conclusions.

4.1 Water usage

Although there is nothing in the final product that reminds you of water, a lot of it is used during the paper production process. If the pulp is produced from wood the demand for water starts already with the debarking of the logs, unless dry debarking is used. During the pulp production water is needed both for the pulping liquid and for rinsing and washing of the pulp. In the paper mill water is used for several purposes. The pulp, irrespectively if it is made from wood or recycled fibres, is diluted with water and mixed with additives in the preparation of the stock. This water is then removed from the pulp suspension in the paper machine when the stock is transformed into paper. When the water passes through the wire in the wet end, first by the force of gravity and then with aid from low pressure a lot of fines, fibres and other additives adhere to the wire. To prevent this from stop up the drainage through the wire, it must be cleaned. Therefore the wire is sprayed with water in order to clean it from attached material. Also the press felt in the press section has to be cleaned with water. Besides this water is also used for sealing the vacuum pumps and cooling.

Historically the pulp and paper industry has been a large consumer of water. In the early 1960´s the average water consumption was 240 m^3/t but this consumption gradually decreased over the years (Edde, 1994). How much the consumption has been reduced depends on the type of product and the production process (Webb, 1997).

By replacing fresh water with recycled water the mills have decreased the need for fresh water. It was shown in an analysis (Lindholm, 1998) of an integrated paper mill that around 30% of the fresh water was used for sealing the vacuum system and for cooling purposes. Rinsing and washing of the pulp consumed 30% and the last 40% was used for sprays and lubrication.

4.2 Benefits

There are several different reasons why the mills have put significant effort into reducing their demand for fresh water. One author gave the following reasons (Webb, 1997):

- The availability of fresh water is poor.
- The discharge demands are increased.
- The load on the environment should decrease.
- A wish that the production should be classified as effluent-free for technical and marketing reasons.
- The cost for discharge should be lowered.

A survey (Berard, 2000) listed the following reasons and the degree of citation:

- effluent discharge limits 91%;
- government regulations 52%;
- community perception 48%;
- WWT and fresh water costs 33%.

Besides benefits like no charge for effluent discharge and less dependency on fresh water there is also a reduction in energy requirements since there is less cold fresh water to heat up to the process temperature (Habets and Knelissen, 1997). Also the reuse of warm whitewater can mean further improvements. As an example, an increased reuse of treated whitewater instead of fresh water was possible by the introduction of a filtration unit in a corrugating mill. The treated whitewater was used in different showers on the paper machine. The switch improved the cleaning of the wire and extended its life. There was no thermal chock during the cleaning, as was the case with cold fresh water. The increased recirculation increased the temperature from 57°C to 68°C, which helped to eliminate slime problems (Buchanan, 1980).

4.3 Problems

Closure of the paper mills might generate many different problems. Most of these problems are caused either directly or indirectly by the different compounds in the whitewater. These compounds come from the raw material or the different additives that are used in the production process and they can appear in either dissolved or colloidal form. In a mill with an open water system these compounds are removed from the system with the effluent. Process changes towards a mill with a closed water system lead to accumulation and high concentrations of the compounds creating different kinds of problems. For both wood-free and wood-containing printing paper the critical figure is around 10 m^3/t (Huster *et al.*, 1991). Many of the problems that occur are due to the activity of microorganisms, which feed upon the compounds in the closed water system.

In a survey (Berard, 2000), different paper mills were asked what were the main problems when they closed their whitewater system. The main problems found were:

wet end deposition	58%
mill odour	55%
foam and corrosion	47%
product odour	45%
decreased machine operability	38%
drainage loss	33%

retention loss 32%

Some of these problems are further discussed below.

Microbial growth

Many of the problems appearing in a closed whitewater system are due to microorganims. When the water system is closed organic compounds accumulate in the whitewater and act as substrate for microorganisms. These start to grow in the water and also on the surfaces in the whitewater system as a biofilm. With time the film gets thicker and it may detach from the surface. These biofilm fragments in the whitewater enters the headbox and are spread on the wire together with the stock. In the paper web the fragments take up space, which should have been filled with fibres. The drying process shrink the biofilm fragments and leave a hole in the paper. This is of course deteriorating the product quality.

The whitewater system is very large with a lot of pipes and different vessels. At some positions in the process the water is exposed to the air and oxygen is dissolved into the water. Microorganisms in the whitewater consume this oxygen and an environment without oxygen suitable for anaerobes is produced. When the oxygen is used up and there is no other electron acceptor as nitrate or sulphate the microorganisms starts to ferment instead. In this fermentation process different volatile fatty acids (VFA) are produced. Some of these VFAs have a very unpleasant odour. Accumulation of this type of compounds in the whitewater can lead to a poor working environment. A much worse effect from the paper mill's point of view would of course be if the sale of the product decreased due to its bad smell.

Formation of large amounts of VFAs also affects the chemistry of the whitewater. Retention aids are added in the paper production process for increasing the amount of fibres retained in the web. High concentrations of VFA in the whitewater increase the demand for retention aids.

Corrosion

The closure of the whitewater system leads to an accumulation of both inorganic ions and a conservation of energy, which in turn leads to higher temperatures in the whitewater. High temperature in combination with high concentration of anionic ions create corrosive conditions. It has been established that the corrosive nature of the environment in the whitewater increase with increased levels of different inorganic ions, such as chloride, sulphate and thiosulphate (Danadurai and Rajeswari, 1999). The most aggressive whitewaters are those where the molar amount of chloride exceed that of sulphate (Wensley, 1989).

The metabolic activity of microorganisms can also lead to corrosion. In the whitewater under anaerobic conditions volatile fatty acids (VFA) like acetic acid, propionic acid and butyric acid are produced and they are all corrosive compounds (Blanco *et al.,* 1996).

Explosions

Explosions with deadly outcome have occurred at several paper mills (Rowbottom, 1993). Bacterial hydrogen production was known to be responsible for the accidents at four mills and was suspected at the remaining four. Six of these explosions were initiated by hot work and all explosions happened when the mills were stopped. In tanks and vessels with still process water the environment is changed very fast to an oxygen free environment, which is ideal for the hydrogen-producing bacteria. During normal operating conditions the whitewater is continuously moving in contact with air, which sufficiently aerates the water, making it unfavourable for the hydrogen producers.

Interfering substances

Many different substances are added to the whitewater system and some of them interfere either directly of indirectly with the production process. There are several different types but the most common ones are stickies, pitch and anionic trash.

Stickies are formed in mills using recycled paper. The use of waste paper brings several substances into the system, which can cause different problems. Examples of such substances are adhesive residues, tapes, rubber-like particles and hydrolysed sizing agents. In the water system they produce particulate components that tend to stick to paper machine parts and the final product causing various problems.

Fatty acids or resin acids from virgin fibres can together with hydrolysed sizing agents form something called pitch. This can under certain conditions accumulate on the machine fabric or the press felt and have a negative impact on the paper making process (Meixner *et al.*, 1998; Tardif and Hall, 1997).

During the paper making process different chemicals, so called retention aids, are added to increase the retention of the material in the stock. These are often cationic polymers, which form inter-fibre bonds between the negatively charged fibres. With the use of waste paper as the fibre source, sizing agent and coating chemicals from the old product is also introduced into the whitewater system. Many of these compounds, which are referred to as anionic trash are negatively charged polymers. Since their charge, is the same as that of the fibres they increase the demand of wet-end chemicals added in order to increase the retention of the fibres (Barnett and Grier, 1996).

4.4 Quality relationships

There are a number of substances in the whitewater that affects both the production process and the quality of the paper. These compounds are usually lumped into two categories: dissolved substances and colloidal substances. Dissolved substances could be lignans, polysaccharides and ions whereas colloidal substances are made up of lignin and liphophilic extractives. All of these compounds accumulate when the whitewater system is closed and this influence the production process and the final product.

There are several different methods to determine the quality of the final paper product. Many of these measure the force required to tear the paper. For example the tear strength is the maximum stress developed in a specimen before it is ruptured when opposite force is applied along the paper sheet. The tensile index is the numerical value when the tensile strength is divided with the basis weight of the paper. Other types of quality aspects are also important, for example, light absorption and surface smoothness.

Vendries and Pfromm (1998) studied what effects a closed whitewater system would have on the paper quality. They made hand sheets of linerboard from recycled fibres and simulated the closure by recycling the whitewater. Only the tensile index slightly decreased whereas four other physical parameters were unaffected. In their experiments they did not reach steady state concentrations for the inorganic compounds and they concluded that precipitation for some low solubility ions, such as calcium may eventually occur, which will interfere with the system.

Cations in the whitewater were shown in another study (Sjöström and Rådeström, 1996) to influence the paper strength. This observation was made during the production of kraftliner. At high concentrations of cations the fibres are not as swelled as in pure water and this decrease the number of interfibre bonds, which will decrease the paper strength.

In the whitewater there is also an accumulation of anionic organic compounds, which often are referred to as anionic trash. These compounds have a negative influence on the retention system. Several different types of retention systems exist and it was shown that nonionic retention systems were least affected by the accumulation of organic compounds whereas cationic systems were affected to a higher degree (Hulkko and Deng, 1999).

Dissolved substances in a model TMP-whitewater, such as lignans and polysaccharides reduced the paper strength whereas colloidal matter like lignin and lipophilic extractives reduced the paper porosity and optical properties (Zhang, 2000). These findings are somewhat different from what was found by Rundlöf *et al.* (2000). Experiments with a manufactured whitewater from mechanical pulp showed that the tensile strength decreased with increased colloidal substances and that dissolved substances had no effect. The light absorption did, however, increase for both types of substances.

4.5 Solutions and experiences

There are many different solutions to the problems that arise due to the closure of a water system. Physical, chemical and biological methods have been used in order to overcome the problems. Some of them are discussed in the following text except biological methods, which can be found in chapter five.

Biocides

The most common way to control the amount of microorganisms in the whitewater system is to add biocides. The addition of biocides is often combined with dosing of a dispersion agent, which dissolves the cluster of microorganisms so the biocides can work properly. Also enzymes have been used together with biocides. By controlling slime with enzyme (levanase) together with a biocide, the amount of biocide could be reduced by 25% (Chaudhary *et al.*, 1997).

Most biocides are some sort of organic molecule and there are many different types. Common examples of different classes are organobromides, organosulfurs, isothiatzolinones, thiocyanates and chlorinated phenols. Inorganic molecules have also been used as biocides. One such example is chlorine dioxide, which was reported to be an effective compound for taking care of slime forming bacteria (Latshaw, 1995). Another example is ozone, which was tested with whitewater from a newsprint mill. A dose of 0.02 mg O_3/mg COD (18-26 mg O_3/l) decreased the number of colony forming units (CFU) with 80%. When the dose was doubled the CFU was reduced by more than 99% (Korhonen and Tuhkanen, 2000).

Advanced water recycling

In order to reduce the paper machine water consumption Boyko *et al.* (1999) suggest several different water management operations. It is important to separate different processes from each other. This means that the pulp should be transferred from the pulp mill to the paper mill at the highest possible consistency. Also if there are several paper machines they should be separated from each other. By doing this each process would not be affected by disturbances from other processes and it would be easier to maintain stability. There should also be enough broke storage capacity so that the broke feed can be maintained at a constant rate even during upsets. The cooling water should be collected and reused. The vacuum pumps require a lot of seal water and this should be collected, cooled and reused as seal water.

Some of these ideas have already been implemented in the SAPPI Ltd craft mill in Ngodwana, South Africa (Jonsson, 1984). By installation of a cooling tower the mill could implement a closed-loop cooling system in order to minimise the fresh water use. The same ideas were used for the seal water, which also is working in a closed loop. The flow of seal water to each unit is controlled and the return flow is collected in a sump. From there it can be reused as seal water after being cleaned in an oil separator and a fibre filter.

Evaporation

Millar Western manages two different bleached chemithermomechanical pulp (BCTMP) mills that operate with no effluent discharge. It is the Meadow Lake mill and the Chetwynd mill. The Meadow Lake mill claims to be the first zero-liquid-discharge pulp mill in the world. The effluent from the pulping process is first screened and then treated in a flotation unit. The water is led to a recovery pond, which functions as a storage facility. When there is a demand, water from the pond is screened and treated in an evaporator. The evaporator technology used is mechanical vapour recompression (Webb, 1997). The distillate is after further biological cleaning in an equalisation pond ready to be re-used. The solids from the evaporator is concentrated and sent to a recovery boiler.

StoraEnso is also using evaporation to treat some of the streams in several of its mills (Webb, 1997). Kotka mill, which produces printing paper from TMP, has installed a circulating water evaporator. This has led to a decreased demand of water on the paper machine and decreased the effluent volume in the production line. The evaporation is done using excess heat from the pulp mill. In Varkaus mill, a mechanical vapour system is used to treat wastewater from the debarking process.

Fixing agents

Different chemicals, called fixing agents, are added in order to remove substances from the whitewater, which otherwise would have formed stickies and white pitch. Deposits causing different problems in the paper machine and which are in some way related to coated broke, are referred to as white pitch. The substances are removed from the system since the chemicals interact with them and attach them to the fibres (Meixner *et al.*, 1998). These fixed substances could, however be remobilized when the paper is recycled under alkaline conditions (Kruger *et al.,* 1997).

Enzymes

Enzymes are organic molecules with an ability to catalyse specific chemical reactions. The specificity of enzymes is relatively high, so closely related chemicals are catalysed with different enzymes. The name of the enzyme reveals what the substrate is or what type of chemical reaction they catalyse.

Investigations have been conducted in order to evaluate the possibility to use enzymes for the degradation of different troublesome compounds in whitewater (Zhang, 2000). In this investigation a model whitewater was produced from TMP and the effects from treatment with laccases and lipases were studied. Laccases is an enzyme that oxidise molecules, such as phenols, polyphenols and aromatic amines. It also has an ability to degrade complex organic substances as lignin. Lipases catalyse the hydrolysis of the ester bond in fats. It was found that treatment of the model whitewater with laccases resulted in degradation of most of the extractives and the lipases hydrolysed ester bonded extractives.

Membrane filtration

Ultrafiltration of wastewater from the pulp and paper industry has proven successful in reducing long chain carbohydrates and extractives (Nuortilajokinen *et al.*, 1994). The method is not so successful for reducing small dissolved molecules, which make up most of the COD and lignin residuals. Membrane filtration has, however been installed at one pulp mill and one paper mill (Webb, 1997). The pulp mill application is Store Enso's Nymölla mill in South Sweden where an ultrafiltration system is used for treatment of filtrate from the oxygen delignification stage in order to reduce the COD discharge. The paper mill application is in M-real's Kirkniemi plant in Finland. They are using an ultrafiltration plant for treatment of whitewater from a disc filter and recycle the filtrate to the paper machine. Another ultrafiltration plant is also used to recover coating pigments in the coating machine.

Sand filtration

Hartmann is a waste paper mill producing egg trays. The mill has reduced the fresh water demand to 5 – 10 m^3/ton product by treatment and reuse of process water. The whitewater is treated in a flotation unit before it is used for pulping and regulating the stock consistency. For those processes that need a higher quality of the water, a small stream is treated in a sand filter. Further increase of the water recirculation can only be accomplished if the problems with growth of microorganisms in the system and deposits of inorganic compounds are solved (Jepsen *et al.*, 1996).

A sand filter was also used at the Madison Maine mill when the mill was increasing its production but wanted the water usage to remain constant. Clean warm water from different sources was collected and reused after sand filtering for showers and seals (Laskey and Drechsel, 1983).

Cost for water re-use

The efficiency of a treatment method is of course important but the cost for its investment and operation must also be considered. It is, however, difficult to give the exact cost for different methods since it depends on so many things. The outcome of a comparison between different methods depends on the conditions in that particular case. Some things influencing the cost are: biodegradability of the wastewater, the amount of water to be treated, the water temperature, supply of heat and power, existence of suitable buildings and basins, quality of the treated water and distance between treatment plant and production point.

A cost comparison was made between building a new effluent free greenfield newsprint mill or a conventional mill. The cost for the new mill would only be 1% more than for the conventional mill, which had an external treatment plant for the effluent water (Jantunen et al., 1992). The closed mill, which was developed with a simulation program RAMI, would cost about 390 million USD and should produce 250 000 ton newspaper per year. In the closed mill, process water would be treated both in an evaporation unit and in an ultrafiltration plant. It was also found that it was necessary to increase the storage tank volume to 17 000 m^3, which is around three times that of a conventional mill. In the conventional mill the external treatment plant consisted of biological treatment followed by chemical treatment and sand bed filtration. The cost for investment and normal operation for the closed and the conventional newsprint mill can be found in Table 4.1.

Table 4.1 Investment and operational costs for water treatment in a closed and in a conventional newpaper mill (Jantunen et al., 1992).

Closed mill	Investment cost (M USD)	Operation cost (M USD)/year
Evaporation	3.6	2,9
Ultra filtration	1.1	0,2
Reversed osmosis	n. d.	0,05
Conventional mill		
External treatment	11	2,5

A range of costs for different treatment systems were listed by Metha (1996) in a hypothetical example of an unbleached paper mill producing 1 000 ton/day with recycled fibre as raw material. Increased recycling of water will lead to accumulation of a wide variety of substances, which could be significantly degraded in a biological treatment. Although the biological treatment is efficient in removing dissolved and dispersed substances a tertiary treatment has to be included in order to avoid the build up of solids in the water. Suggested methods for removing solids are: membrane separation, vapor compression evaporation and chemical/mechanical treatment. The range of total installed cost for these options in the hypothetical mill treating 3 800 m^3/day are:

reversed osmosis-system	5-6,7 million USD
mechanical vapor compression	9,5-12,5 million USD
chemical treatment	1,7-2,2 million USD.

The capital and operational costs for different closed cycle techniques were compared with normal treatment and discharge when they were hypothetically applied to treat the effluent from a 550 adt/d TMP-newspaper mill (Gerbasi et al., 1993). The evaluation was done for effluent flow rates ranging from 5 to 20 m^3/t. The different techniques studied were biological membrane treatment, freeze crystallisation and evaporation. They found that the cheapest technique was evaporation but even at the lowest effluent flow of 5 m^3/t conventional external treatment and discharge had lower capital and operational cost. In Table 4.2 all figures for the different cases can be found.

Table 4.2 Estimated treatment costs in million Canadian dollars (1992), for different scenarios (biological treatment combined with membrane filtration (Bio. + Mem.), freeze crystallisation (Freeze), evaporation and activated sludge treatment (AST)) divided into capital (Cap.) and operational costs (Op.) (Gerbasi et al., 1993).

Effluent flow	5 m^3/t (2750 m^3/d)		10 m^3/t (5500 m^3/d)		15 m^3/t (8250 m^3/d)		20 m^3/t (11000 m^3/d)	
Scenario	Cap.	Op.	Cap.	Op.	Cap.	Op.	Cap.	Op.
Bio. + Mem.	19.3	0.71	28.1	2.21	36.8	3.28	44.0	4.19
Freeze	23.3	0.83	33.9	2.27	52.6	3.55	63.2	4.44
Evaporation	18.0	0.55	26.5	2.03	34.8	3.04	42.6	3.91
AST	11.1	0.0	11.5	0.7	11.9	1.0	12.3	1.2

In a study focusing on the implementation of closed cycle operation for different types of paperboard mills a clarifier, a clarified water tank, a screen and a screened water tank was used for treating the water (Lagace et al., 2000). The cost and difficulty to implement closed cycle technology were depending on the process configuration and on what products were produced. The costs were studied for 10 different cases of a chipboard mill and the net cost varied from 1 million up to 6 millions in 1995 Canadian dollars.

4.6 Conclusions

Reducing the water consumption in a paper mill is an extensive process since the paper production in itself is rather complex. It is important to determine the need in terms of flow rate and quality at different positions in the mill. Thereby, can possible ways to recycle water be determined.

Increased recycling and decreased fresh water consumption lead to accumulation of substances and this in turn leads to a range of different problems. The problems can be solved by several different methods. Evaporation is efficient but its use is limited by the drawback of scaling. Development of new and better membranes has strengthened the possibilities for different kinds of membrane filtration to be used. The drawback with this method is its low efficiency for removal of dissolved compounds. A better solution is to combine biological treatment, which is excellent in removing dissolved compounds with membrane filtration in order to remove particulate matter.

Which method or combination of methods that is chosen depends in the end of the costs, which in turn is to a great deal decided by the conditions in the particular case.

Chapter 5
The Internal Kidney

The name internal kidney originates from the resemblance between the function of a kidney and the in-mill treatment process. The purpose is to reject unwanted compounds in the whitewater, which otherwise would affect the production process. In the first part of this chapter, the internal kidney is further presented. In Section 5.2 motives for different types of processes of the internal kidney can be found. It is followed in Section 5.3 by a description of the different parts of the treatment process. Some important design and operating parameters are discussed in Section 5.4 before experiences from experiments are presented in Section 5.5. Practical cases where biological kidneys are used for in-mill treatment are presented in Section 5.6 before the chapter ends with some concluding remarks.

5.1 The internal kidney

In the production of paper, water is used for many purposes, such as transport medium for fibres, solvent for additives and cleaning of machine parts in the paper machine. Part of the whitewater, which is the process water in paper mills, is discharged and replaced with fresh water. The wastewater from the mill is hopefully treated before it is returned to the recipient. This is the scenario in many places were there is a large supply of fresh water of good quality and a recipient that can manage to receive treated wastewater without any environmentally negative effects. The situation is, however, not always like this. There are areas with limited supply of fresh water and sensitive recipients not allowing the discharge of large volumes of even treated wastewater. At these locations, the incentives to reduce the fresh water consumption and to close the whitewater system of the paper mill are much stronger. There are of course also other motives for closure, such as environmental policies and marketing strategies.

The closure implies, regardless of whether the paper product is made from virgin or recycled fibres, an increase of organic compounds in the whitewater, which leads to several problems. The quality of the product can deteriorate due to development of unpleasant odour and holes. Other problems associated with microorganisms in the whitewater are increased corrosion and increased demand of retention aids. One common solution to these problems is to dose biocides in order to suppress the growth of microorganisms in the system. Although this solution is working, it has some drawbacks. Firstly the use of biocides implies exposure of chemicals for the workers at the paper mill, which could constitute a health problem. Secondly, since the biocides are present in the whitewater small amounts of it could be incorporated into the product, which could be a potential health risk. Another and perhaps better solution is to treat the whitewater in some kind of internal kidney to reduce the accumulated substances and thereby prohibit uncontrolled growth in the whitewater system. With this method it would be possible to decrease the use of biocides to a fraction of the normal use or hopefully, eliminate them.

The idea is to incorporate the internal kidney directly to the whitewater system in the paper mill. It should, consequently, be regarded as an internal treatment process working in parallel with the paper production and not as an external treatment connected in series with the production. An implementation of the internal kidney is illustrated in Figure 5.1, where the water circuits between the different processes in the paper mill and the treatment system are demonstrated.

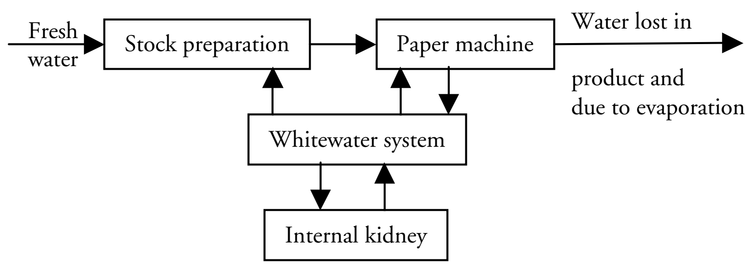

Figure 5.1 Outline of the water circuits in a paper mill with an internal kidney.

The internal kidney could be made up of several components and the exact configuration depends to a great extent on the actual type of production.

The use of different raw materials is reflected in the composition of the whitewater, which results in the exclusion of some methods since they are not suitable. For example would an anaerobic biological treatment process not be suitable when the product is made from kraft pulp. The whitewater would then contain sulphate, which is transformed to unwanted hydrogen sulphide in the anaerobic process. Other methods have to be included since the water from the internal kidney is to be recycled and has to fulfil certain quality limits in terms of particulate matter and colour.

It is necessary, prior to implementation of an internal kidney, to investigate the water need both in terms of flow rate and quality demand of different parts of the paper machine. For some parts it could be sufficient with a less treated whitewater whereas other parts require high quality water. Consequently, the internal kidney could be composed of several different processes but it is not necessary to treat the whole stream of whitewater by all processes. On the contrary, it could be that part of the whitewater stream is returned to the whitewater system after treatment in the first one or two sequential steps whereas only a minor part of the whitewater is treated by all processes constituting the internal kidney.

5.2 Motivation for selection of process

The different processes included in the internal kidney could be some of the methods presented in the previous chapter, such as evaporation, membrane filtration, sand filtration, dissolved air flotation, settling, ozonation and chemical treatment. Another suitable method, which was not described, is biological treatment. As previously stated, the exact configuration of the internal kidney depends on what raw materials are used and what product is manufactured in the paper mill. In the ClosedCycle project, the primary targets for this in-mill treatment of whitewater are: printing paper from recycled fibres and mechanical pulp; packaging grades from recycled fibres and liner from recycled fibres or recycled fibres and unbleached kraft pulp. These different paper products were chosen because they are produced in large quantities and they are also insensitive to slight discolouring, which would not be acceptable for high quality printing paper and journal paper. The first candidate for investigation of different aspects due to implementation of an internal kidney is liner production from recycled fibres.

The first part of the internal kidney should be responsible for reducing accumulated organic matter in the whitewater. The different methods that are more or less suitable for this are evaporation, membrane filtration and biological treatment. Evaporation is efficient for removal of dissolved compounds with boiling temperatures lower than the solvent, which could be water or some organic compound, such as acetone or ethanol. In this application, however, evaporation may not be so suitable. Evaporation needs steam or other types of heating to evaporate the solvent, which in this case is water. In this application, liner production from recycled fibres, there is no surplus of steam or other form of energy from other parts of the production process that could be used. Besides an unfavourable energy consumption the use of evaporation is also limited by other problems. During its operation, different deposits may cover the surfaces in the evaporator, which are responsible for transferring heat to the liquid. This phenomenon is called scaling and it reduces the capacity of the evaporator. Besides evaporation, membrane filtration is also a method that could be used. Everything from particulate matter down to ions can be separated from a liquid by different membrane filtration techniques. This is achieved by using different membranes retaining molecules of different sizes. As more compounds are to be separated there is a demand for a higher applied pressure, which increases the cost for the method. Also membrane filtration is to some degree limited by scaling and clogging of the pores in the membranes. This implies regular washing of the membranes to regain capacity and eventually replacement of the membranes when they are too heavily contaminated. The last method, which could be used for whitewater treatment, is biological treatment. Microorganisms growing on biologically degradable compounds cause a major part of the problems in the whitewater system. One benefit of the last method, biological treatment, is its removal of these biodegradable compounds, which presence otherwise leads to problems. Since it is also a cost efficient method, it was chosen as the most suitable method for removal of the dissolved organic compounds in the whitewater. The high whitewater temperature and the high concentration of degradable matter in the whitewater imply that an anaerobic treatment would be suitable. This type of treatment has several advantages, the sludge production is low and, consequently, the nutrient requirements are also low. There are, however, always some residues of non-degraded matter after an anaerobic process, which must be removed. Therefore, the anaerobic treatment should be combined with an aerobic process, which would also oxidise reduced compounds like hydrogen sulphide that could be produced in the anaerobic process if the wastewater contains sulphate.

The first step, biological treatment, in the internal kidney degrades dissolved compounds in the whitewater and produces particulate matter. Depending on how much is produced and whether it affects the product and production process or not, it may have to be separated from the water. It could also be that only a part of the biologically treated water has to be further treated in order to meet the demand for a recycled water of higher quality. If there is a need for separation of solids this can be accomplished by several different methods. Settling is perhaps not the preferred method since it requires sludge with good settling characteristics and is more space demanding than other methods. A better choice for the removal of particulate matter is dissolved air flotation, since it is more compact and not as sensitive to the quality of the particles, although the operational costs may be higher. An alternative or additional treatment method to dissolved air flotation is membrane filtration and sand filtration.

A slightly darker colour can develop in the effluent from the biological treatment. If recycling of this water leads to deterioration of the product quality further treatment of the water is required. Reduction of colour could be achieved by treatment with ozone, which also may have some positive effects on odour not removed in the aerobic biological treatment.

5.3 The process

Biological process

The efficiency of a biological treatment process is among other things a function of the concentration of microorganisms in the reactor. In order to have an efficient and thereby a small reactor the concentration of microorganisms should be high. There are several different methods available to achieve this. In the activated sludge process, sludge is continuously recycled to the aeration basin to maintain a high concentration of biomass in the reactor. Sludge is also used in sequential batch reactors but in this type of treatment the sludge is maintained in the reactor and the excess sludge is removed together with the effluent. These two types of systems are examples of suspended growth processes. The other existing category is attached growth systems. In these processes the microorganisms grow on the surface of some form of carrier material as a biofilm. Examples of this type of treatment are suspended biofilm processes and fixed film processes. The difference between these two methods is the size of the supporting media. Small carriers, which are able to move around in the liquid is referred to as suspended biofilms process whereas large modules of supporting material placed on top of each other with channels for transportation of water is referred to as fixed film processes.

In an internal kidney with biological treatment as the first method for removal of organic compounds it is suggested to use biofilm processes both for the anaerobic treatment and the aerobic treatment. There are several reasons for this. Some of the most obvious ones are:

- no dependency on a sludge, which is easy to settle;
- no sensitivity to high concentrations of suspended matter in the influent;
- compact design due to the possibility of high loading rates.

There are in general three different types of anaerobic biofilm processes: anaerobic filter, fixed-films reactor and fluidised bed. An anaerobic filter is a reactor filled with a randomly packed filter material and the biofilm is growing on the surface of the material. Much of the biological activity originates from biomass trapped in the void spaces. In the fixed-film process, the reactor is filled with large units of solid packing material and the water is flowing either upwards or downwards through channels in the material. Also the anaerobic filter can be operated in up-flow as well as in down-flow mode. The third type of anaerobic biofilm process is the fluidised bed where biofilm usually grows on the surface of sand particles with a size distribution of 0.2 – 0.5 mm. This gives a high surface-to-volume ratio and together with turbulent conditions, high mass transfer is achieved, which is characteristic of the fluidised bed. The influent is pumped to the reactor and distributed in the bottom. The upward flow expands the bed and when it is high enough the bed starts to fluidise. Usually, the influent flow is too low to keep the bed fluidised so liquid is drawn from the top of reactor in a recycle stream to achieve a sufficiently high flow rate. The risk for clogging is higher with both the anaerobic filter and the fixed-film process. Therefore, a fluidised bed is chosen as the most suitable process type for the anaerobic treatment.

Aerobic biofilm processes can be divided into three different types: rotating biological contactors, trickling filters and submerged filters. In the first type, large disks of carrier material on a rotary axel are partly submerged into the water. The biofilm is growing on the surface of the disks and oxygen is provided to the biofilm when it is exposed to the air. This type of treatment method is more suitable for small systems, such as treatment of wastewater from a few houses or a small industry, since larger applications lead to mechanical and structural difficulties. In trickling filter systems, wastewater is evenly distributed over a carrier material consisting of either stones or plastic modules. Aerobic conditions are maintained since the water passing over the carrier material is in constant contact with the air. Trickling filter is, however, not suitable for treatment of whitewater since it is normally used for less concentrated wastewater and it is also a system that requires a significant amount of space. Submerged filters are made up of some sort of carrier material totally submerged into the water. The carrier material either consists of larger modules with channels for the water flow or small suspended carriers. In both cases, the water flow is a result of the air released into the reactor. The drawback with the fixed submerged filter is the risk for clogging and not achieving an even flow through the whole filter. The suspended carriers are kept in suspension by the air released into the reactor, which thereby limits the risk for clogging. This is one of the benefits of the suspended carrier system and therefore it is selected for the aerobic treatment. Normally, about 50% of the reactor volume is filled up with plastic carriers in this type of system. The carrier is designed with protected surfaces on which the biofilm develops. The outlet of the reactor is equipped with bars to retain the carriers with the developed biofilm in the reactor. Biofilm that has detached from the carriers and other suspended solids (e.g. fibres) can pass through the bars and leave the process with the effluent water.

Separation process

The separation process should remove particulate matter in the treated water from the biological process. Since the water is recycled to the whitewater system and there may be a demand for different qualities of the returned water more than one separation method could be needed. There are many different processes to choose from, such as flotation, sand filtration or membrane filtration.

Additional treatment process

The water can, during the biological treatment, develop an unwanted colour and all fine particles may not been removed in the separation processes. In situations like this when the quality of the water is not sufficient, the treatment process can be extended with some additional polishing step. Treatment with ozone could be used to remove unwanted colour or an unpleasant smell in the water. If it is necessary to remove fine particles or dissolved compounds, chemical precipitation could be used.

The outline of the internal kidney with its different processes can be found in Figure 5.2.

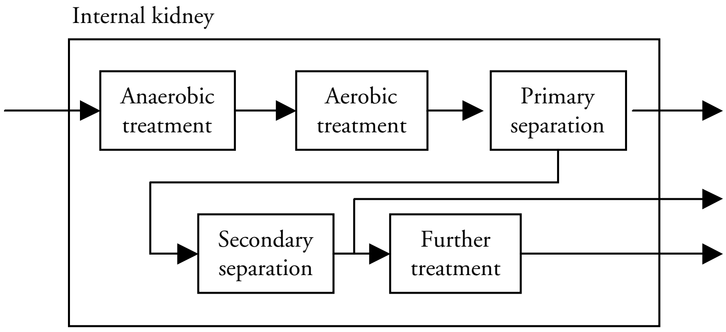

Figure 5.2 Outline of the different processes that constitute the internal kidney and the flow of water between them. Recycling of water from the internal kidney back to the whitewater system can be done from several possible positions.

The whitewater taken from the whitewater system is pumped to the anaerobic reactor for the primary biological treatment. Further degradation of the contents of the water is then achieved in the aerobic reactor following the anaerobic reactor. The effluent from the aerobic reactor is then treated in the primary separation unit to remove most of the particulate matter. If additional treatment is required part of the effluent from the primary separation may be directed to these units.

5.4 Important design and operational parameters

Designing an internal kidney means to decide the exact configuration of the process and to determine the size of the different parts. The purpose of this section is, however, not to produce such data but to address certain important issues.

Several variables determine the size of the reactors, such as the degradability of the whitewater and desired whitewater concentration. The degradability of the whitewater may be improved over time, as the water is recycled. The reason for this is adaption of the microbial composition towards compounds in the whitewater, which are more difficult to degrade. Increasing the size of the reactor volume will lead to a decreased COD concentration in the whitewater system. One critical issue is to determine what the concentration in the whitewater should be. It is important that it is low enough to reduce the problems associated with the closure but if it is too low the reactor size will be unnecessary large, which also results in unnecessary high cost. The goal of the internal treatment process is not to reduce the COD concentration in the whitewater as much as possible, which is the case with external treatment. Instead it is enough to lower the concentration so problems related to uncontrolled growth are maintained at an acceptable level. Nivelon *et al.* (1998) estimated that a concentration of around 8 g/l in the whitewater system would be a suitable concentration to maintain in the system in order to avoid problems. This concentration is similar to what mills with open-loop circuits achieve with a fresh water consumption of 3 to 4 m^3/ton product. The reduction of organic matter would be achieved by implementation of a combined anaerobic and aerobic treatment. The flow to the internal treatment system was calculated to 25 m^3/h and with a production of 200 t/day would give a specific throughput of 3 m^3/ton product. This is in agreement with the conclusions that Huster *et al.* (1991) made from a simple model where treatment of 4 m^3/ton product would result in a COD concentration of 8 g/l. In the model two different cases were compared: combined anaerobic and aerobic treatment with a total reduction of 95% and only aerobic treatment with a reduction of 90%. The results demonstrated no difference in the specific throughput between the two cases.

The removal capacity for an anaerobic system is around 1 kg COD/(kg VSS · day) (Young and McCarty, 1967) so it is the amount of active biofilm in the reactor that sets the loading limits. There are examples where fluidised beds in pilot scale are loaded up to 50 kg COD/(m^3·day) (Hall, 1992). The load on aerobic biofilm systems varies a lot depending on the purpose of the treatment. A load of 2 kg COD/(m^3·day) is considered low and would give almost complete reduction of biodegradable COD. As the load is increased the reduction in percentage is lowered. Biofilm processes are sometimes used as a primary reduction stage removing only 30 to 50% of the COD content. In this type of application, high loading rates of up to 40 kg COD/(m^3·day) used. The actual loading that can be used should, however, be decided in pilot trials.

It is important to achieve an even flow distribution in the bottom of the reactor during the design of the anaerobic reactor. Otherwise there may be stagnant areas in the reactor, which reduces its capacity. The distribution system should also be designed so the bed can be refluidised after a stop and it is important to take into consideration the wear that the moving sand causes. Since the aerobic reactor is also a biofilm process and contains some form of carrier material the flow distribution is important. This is achieved by an evenly distributed aeration. When looking at the surface of the reactor there should be an even flow over the whole surface. In order to minimize the wear of the carriers, the surface of the reactor walls should be smooth with no sharp edges. All tubes in the reactor should be firmly secure since vibrating tubes may damage carriers trapped between the tube and the wall. To prevent the carriers to be clogged at the outlet from the reactor there should be a stream of air forcing them away from the outlet grid.

One important issue distinguishes the internal treatment from the external one; namely the concentration of nutrients in the effluent. Many wastewaters, such as wastewater from pulp and paper, pharmaceutical and chemical industries, have a too low natural concentration of nutrients compared to what is required in order to fully degrade the organic compounds. Therefore nutrients are added during the treatment in order to have an efficient process. The only limitations for an external treatment plant regarding nutrients in the effluent are possible discharge limits and the cost for the nutrients. The purpose of an external treatment is more focused on achieving a far-reaching COD degradation whereas the first objective for an internal treatment process is to ensure low levels of nutrients in the effluent. At the same time, the internal kidney should achieve the largest possible reduction of COD. The exact limit for the nutrient concentration in the recycled water is not known but it is probably below 0.1 mg/l.

The composition of the effluent and especially the concentration of particulate material and its size distribution are important variables, which have to be considered in the design of the separation process. The flow rate is important especially for the flotation process since it requires a certain retention time to allow for a flotation layer to be formed. Sand filtration is besides the flow also dependent on the actual concentration of suspended solids. The load of particulate matter determines how often the sand bed has to be cleaned. If membrane filtration is going to be used knowledge about how often the membranes have to be cleaned is important. This information, however, must be determined by practical experiments, which also is used to try out a suitable type of membrane.

The possibility to use ozon for removing colour and possible odour must also be confirmed by practical experiments. At the same time will information be provided about required amounts of ozon to achieve the purpose of the treatment.

5.5 Experimental experiences

The biological system of a wastewater treatment plant is complex since the composition of the microbial sludge or the biofilm changes as the conditions for the plant changes. New species with slightly different characteristics and environmental needs develop since they are at that particularly moment more suitable. Due to these changes it is important to conduct practical experiments to determine the degradability of a particular type of wastewater and to establish suitable values of model parameters if the system should be described with a mathematical model.

Experiments are also needed for the evaluation of different on-line instruments to determine their suitability for use in a particular application. Although the same instruments have been used for measurements in for example treated municipal wastewater it is not certain that they may be used to measure in whitewater from a paper mill.

Biological process in lab scale

Biological treatment with limiting amounts of nutrients is an area that is not well investigated. Research on industrial wastewater has mostly been done with a surplus of nutrients and where the focus has been on the degradability of the organic compounds. The fate and transformation of nutrients have been investigated in the research of the processes nitrification, denitrification and biological phosphorous removal, which mainly occur in municipal wastewater treatment plants. The effects from limiting amounts of nutrients on the behaviour of activated sludge are well known (Jenkins *et al.*, 1993). As the concentrations of available nutrients decrease the conditions for filaments are improved, which leads to a sludge with poor settling characteristics. With an in-mill application of biological treatment the effects on the degradability during conditions of low concentrations of nutrients are valuable information. The microbial growth is usually described by a Monod equation (5.1) in mathematical models such as ASM1 (Henze *et al.,* 2000).

$$\mu = \mu_{\max} \cdot \frac{S_S}{K_S + S_S} \tag{5.1}$$

In the equation, $\mu_{\max}$ is the maximum growth rate and S_S is the substrate concentration. With this expression the specific growth rate is only limited by the substrate. The last parameter K_S, is the half saturation constant. When the concentration S_S is equal to K_S the growth rate is half of $\mu_{\max}$. When a process with limiting amounts of nutrients is going to be modelled this has to be included in the model. This is done by addition of a term that describes the influence from the nutrients on the growth. If the limitations on the growth, due to low concentrations of nutrients, are described in the same way as the substrate, the expression for the growth rate would then look like equation 5.2.

$$\mu = \mu_{max} \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_N}{K_N + S_N} \cdot \frac{S_P}{K_P + S_P} \tag{5.2}$$

In this equation, the effects from nitrogen and phosphorous are included. In order to have a model describing the behaviour of the biological system in a correct way it is important to know the value of the half-saturation constants. Since the values of these constants probably depend on several things, such as wastewater composition, type of treatment process, operating temperature etc., these have to be determined experimentally. Therefore, experiments were initiated to investigate the combined anaerobic and aerobic treatment of a whitewater from a recycled paper mill during nutrient limiting conditions. The aims were to determine the nutrient requirements under different operating conditions, find out if Equation 2 could described the growth rate and also to determine μ_{max} and the half saturation constants.

For the experiments a diluted solution of whitewater was used. The solution consisted of 30, 40 or 50 volumetric-% whitewater and the rest was filled up with tap water. The whitewater came from a paper mill, which produces fluting and testliner from recycled paper. The whitewater system of the mill is closed and the fresh water consumption of the mill is around 1.4 m^3/ton product. Batches of whitewater were collected at the paper mill approximately once a month and stored at 4°C until they were used. The result from a chemical characterisation of the whitewater can be found in Table 5.1.

Table 5.1 Composition of whitewater.

Parameter, method or standard	Concentration
Total COD, Dr Lange 114	32 000 mg/l
Dissolved COD, Dr Lange 114	31 000 mg/l
Total N-tot, SS028101	46 mg/l
Dissolved N-tot, SS028101	9.7 mg/l
Total P-tot, SS-EN 1189	7.5 mg/l
Dissolved P-tot, SS-EN 1189	6.4 mg/l
NH_4-N, FIA	0.44 mg/l
NO_3-N, SS-EN 13395	<0.05 mg/l
NO_2-N, SS-EN 26777	<0.05 mg/l

The biological treatment plant in laboratory scale consisted of two sets of one anaerobic fluidised bed reactor followed by one aerobic suspended biofilm carrier reactor and the set of anaerobic reactors used for the experiment can be found in Figure 5.3. One set was operating at 37 °C and the other at 55°C. The total volume of the anaerobic reactor was 658 ml and it was made up of reactor 538 ml, tubing 30 ml and pH-control vessel 90 ml. The volume of the aerobic reactor was 135 ml and it was filled with 9.5 g of carrier K1, which corresponds to filling 50% of the bulk reactor volume with the carrier. The anaerobic bed was made up of sand (Ø ~ 1 mm) and the anaerobic biofilm was growing on the surface of the sand particles. The bed was fluidised by recirculation of reactor liquid from the top to the bottom by way of a vessel for pH control. The pH in the anaerobic system was maintained around 7 by automatic addition of 1 M NaOH. The whitewater solution and the nutrient solution were pumped to the pH control vessel. Effluent and produced gas from the anaerobic reactor were led from the top of the reactor to a gas-liquid separator, where particulate matter was separated from the effluent by sedimentation and the liquid was led to the aerobic reactor. Solid material in the separator was manually removed. From the separator the gas was led to a gas volume counter.

Figure 5.3 The two anaerobic fluidised reactors used in the experiment.

The mesophilic reactors (37°C) were operated for 55 days and the load to the different reactors were between 8.6 and 12 kg COD/(m^3·d) for the anaerobic reactor and between 3.7 and 6.7 kg COD/(m^3·d) for the aerobic reactor. The hydraulic retention time in the anaerobic reactor was between 10 and 13 hours and in the aerobic reactor between 2 and 2.7 hours. The reduction in the anaerobic reactor was high during the whole experiment, varying between 85 and 90%. There was some additional reduction in the aerobic reactor, which increased the overall reduction to between 88 and 93%. Both the reduction in the anaerobic reactor and the combined process can be seen in Figure 5.4. The requirement of nutrients could only be determined for the anaerobic step since the consumption was so low in the aerobic reactor due to the low load of degradable compounds. The nitrogen requirement was found to be 19 mg N/g $COD_{reduced}$ and the corresponding value for phosphorous was 2.5 mg P/g $COD_{reduced}$.

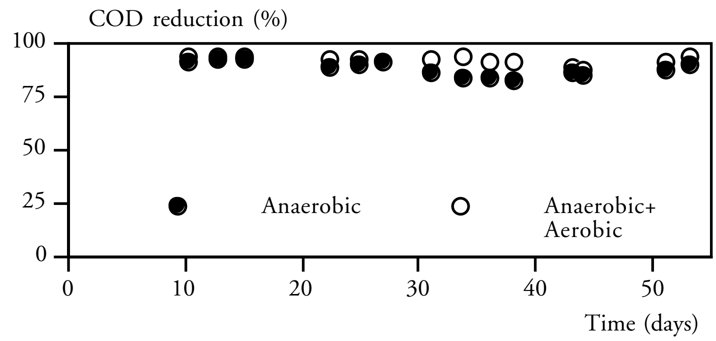

Figure 5.4 Obtained COD reduction in percent for treatment in the mesophilic reactors.

The thermophilic reactors (55°C) were operated for around 90 days and at several occasions there was trouble with the equipment, such as clogged or broken tubes. These disturbances made the evaluation somewhat difficult. However, the load to the anaerobic reactor during thermophilic treatment was around 9.6 kg COD/(m^3·d). The load to the aerobic reactor varied between 10 and 16 kg COD/(m^3·d). The hydraulic retention time in the anaerobic reactor was 16.5 hours and in the aerobic reactor 3.4 hours. It was found that the COD reduction was somewhat lower during the thermophilic treatment compared to the mesophilic degradation. This is probably caused by a lower amount of active biomass in the thermophilic reactor. This parameter was not measured but at regular visual inspection of the reactor contents there seemed to be more microorganisms in the mesophilic reactor. Around 75% COD reduction was achieved after the anaerobic reactor and this was increased to 87% after the aerobic reactor. The nutrient requirements during thermophilic conditions for the anaerobic treatment were found to be a little bit higher than during mesophilic conditions. For the anaerobic treatment the nitrogen demand was found to be 24.5 mg N/g $COD_{reduced}$ and the phosphorous demand to be 4.4 mg P/g $COD_{reduced}$. The corresponding values for the aerobic reactor was 37.1 mg N/g $COD_{reduced}$ and 5.5 mg P/g $COD_{reduced}$.

One purpose of the experiment was to evaluate the effect limited amounts of nutrients had on the COD reduction. Therefore, on day 74 in the thermophilic experiment the content of nitrogen in the nutrient solution was decreased by 25%. The added amount of nitrogen after the decrease corresponded to around 77% of the amount that was consumed during the determination of the nutrient requirements. Despite this decrease there was no immediate influence on the COD reduction as can be seen in Figure 5.5.

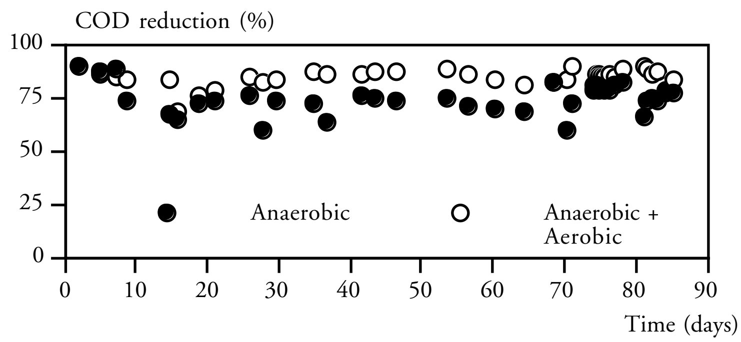

Figure 5.5 Obtained COD reduction in percent for treatment in the thermophilic reactors.

The concentration of NH_4-N in the effluent from the aerobic reactor decreased to values around 0.3 mg/l, which are low but could indicate that there is still enough nutrients. A further decrease was made on day 84 but the effects from this could not be observed since a power failure damaged the pH-control, which in turn raised the pH to 12 in the reactors.

Pilot test and on-line instruments

A pilot test was initiated with the purpose to investigate the stability of a combined anaerobic/aerobic biological kidney with regard to variations in whitewater composition at a packaging board mill. The trial also included testing of two different commercially available on-line instruments to evaluate their possibility to be used as parts of a control system.

The paper mill produces testliner (35 000 ton/year) and fluting (20 000 ton/year) from recycled raw materials, such as old corrugated cardboard and newsprint. The whitewater system of the mill is rather open and the fresh water consumption is around 14 m^3/t. For the trials, whitewater was taken directly from the flotation unit's basin with treated water.

The pilot plant consisted of an anaerobic fluidised bed reactor with a total volume of 36 l and an expanded volume of 20 l. Water was recirculated from the top of the reactor to the bottom, thereby fluidising the sand bed. After the anaerobic stage, the whitewater was treated in an aerobic suspended carrier process with a volume of 13 l filled to 50% with suspended carrier material (Natrix™). The pH in the anaerobic reactor was measured continuously and controlled to a value of 7 by automatic titration of 2M NaOH. Whitewater and nutrients (NH_4Cl and H_3PO_4) were pumped directly to the recirculation loop of the anaerobic stage in a fixed ratio. This ratio was changed during the trials depending on the amount of nutrients remaining in the effluent from the aerobic stage. The effluent was discharged to the wastewater system of the paper mill.

An automatic total oxygen demand (TOD) instrument from Ionics, model 7800, was installed to take samples from the influent whitewater. The instrument was equipped with a 75 µm filtration unit with automatic cleaning of the filter with tap water. In the instrument, a small volume of filtered sample was automatically injected with nitrogen gas containing a small amount of oxygen, directly into a hot oven (900°C) where the sample was catalytically incinerated. The consumption of oxygen was measured and evaluated against a calibration curve resulting in a TOD value for the sample. An instrument from Cerlic for measurement of NH_4-N with an ion electrode was also installed in the effluent from the anaerobic stage. The sample was mixed with potassium hydroxide to transfer the ammonium to ammonia, which was sensed by the electrode.

The hydraulic retention time, HRT, in the anaerobic step varied between 3 and 17 hours and the corresponding organic load between 4 and 44 kg COD/m^3·d. The HRT in the aerobic step varied between 1 and 6 hours and the organic load between 1.5 and 26 kg COD/m^3·d. The removal of soluble organic matter was 78% in the anaerobic step and 86% after the combined treatment at the lowest loading level. The removal efficiency at the highest loading level was about 65% in the anaerobic step and 77% after the aerobic step. The removal efficiency was not markedly affected by the variations in whitewater composition, which was caused by change of production. The variations, however, made the manual control of the nutrient dosage inadequate and resulted in large variations in effluent nutrient concentrations, thereby demonstrating the need for some form of automatic control of the nutrient addition.

The TOD instrument was operated for a year and was during this time at several occasions recalibrated. The instrument, however, failed to show stable and reliable measurements. Identified problems due to clogging of the injection tube were solved by introducing a rinse with deionised water between injections but the measurements remained unstable. The explanation for this was not discovered but the complex matrix of the water was suspected as one major cause. There were also severe problems with the ammonium analyser. The required addition of sodium hydroxide to raise the pH caused inorganic material, probably calcium carbonate, to deposit on the electrode membrane, which led to erroneous readings.

Other experiences

A pilot plant consisting of biological treatment, on-line instruments and data acquisition equipment is at the moment assembled. It is going to be used for practical evaluation of different control strategies, investigation of the operation of biological kidney during low concentrations of nutrients and determination of degradation capacity. The biological treatment consists of an anaerobic fluidised bed reactor with a total volume of 90 l and with a fluidising volume of 50 l. The anaerobic reactor is followed by an aerobic suspended biofilm reactor with a volume of 42 l filled with 21 l carrier material (Natrix™). Three different on-line instruments have been mounted in a stand and are available for gathering information about the treatment process. It is one Biotector 990+ from Pollution Control Systems Ltd (2003) for measurement of TOC. The instrument is equipped with a valve enabling it to sample from two different positions. The second instrument is an Evita sensor from Danfoss Analytical A/S (2003) for measurement of orthophosphate. The last instrument is from Awa Instruments SAS (2003) and it is a multi-parameter instrument called UV-pcx. It consists of three different units and with these it is possible to measure: COD and nitrate, turbidity and ammonium. The signals from these instruments are going to be collected with a data acquisition system from National Instruments (2003). It consists of a distributed module system and the control is going to be implemented using a graphical software, LabView (National Instruments, 2003).

The experiences so far comprise only of preliminary testing of the on-line instruments and are more of qualitative nature. The instruments have been calibrated and measurements have been made on effluent from the pilot plant for almost a month. The TOC instrument has been operating without any problems. Since the analysis is made on a total sample without any filtration there is an obvious risk for clogging of tubes but this has not occurred. For the Evita sensor it was necessary with a special arrangement. This instrument is developed for measurements directly in an activated sludge basin and it was not possible to install the instrument in this way in the pilot plant. Instead the instrument was equipped with a special cup, which can be seen in Figure 5.6. The sample is pumped in a loop and a small flow of sample passes the instruments membrane by a draining hole in the upper part of the cup. The diameter of the draining hole is rather small and a small outlet tube has to be used. With a small tube there is an increased risk for clogging, which also has occurred. Therefore, it is important to either clean the tube at regular intervals or replace it with a new one. This is, however, a problem caused by the actual application, measurement in pilot scale and this problem would not occur in a full-scale implementation.

Figure 5.6 Close-up view of the special cup, which is used together with the on-line instrument Evita from Danfoss.

There have been several problems with the multi-parameter instrument from Awa Instruments. In the ammonia unit, a temperature sensor is mounted directly into the sample. The protecting cover of this sensor broke and the sensor had to be replaced with a new one. There was also a problem with the function of instrument but this was solved as a new software version was installed. The most severe problem with the instrument is with its ammonium unit. In the analysis, the sample is mixed with sodium hydroxide in a reactor tube in order to convert ammonium to ammonia. The sample is then bubbled with air to transfer the ammonia to the gas phase. The gas is pumped into an absorption tube of the instrument where the measurement is performed. The amount of ammonium in the sample is proportional to the absorption at a certain wavelength. The problem arises with samples containing surface-active compounds. When the sample is bubbled foam is formed in the reactor tube and it is carried over into the absorption tube. Water and chemicals cover the lenses in the tube and interfere with the measurement. This has occurred and when it does the instrument has to be thoroughly cleaned. Since the different glass tubes in the instrument is electrically heated with a heating coil wrapped around, as can be seen in Figure 5.7, this is a tricky operation.

Figure 5.7 The glass reactor inside the on-line ammonia sensor from Awa Instrument, which is a part of the UV-pcx instrument.

5.6 Industrial experiences

There are some industrial experiences of implemented biological kidneys and they are shortly described below.

Zülpich Papier

Zülpich Papier is a paper mill producing corrugated medium and testliner from recycled paper (Habets *et al.,* 1997; Habets and Knelissen, 1997). It had been operated under effluent free conditions for almost 20 years when the production was increased from 400 t/d to 1000 t/d in 1996. At the same time it was decided that the product quality had to be increased to the same level as its sister companies, which still had an open whitewater system. The main problem with the products from Zülpich Papier was that they could develop an unpleasant odour during storage.

The problem with increased concentrations of different compounds was solved with an in-line biological treatment consisting of an anaerobic and an aerobic stage. Warm water from the clarified tank is cooled from 55 to 35°C before it is mixed with nutrients in a buffertank. The water is fed into the anaerobic reactors, which are upflow sludge anaerobic blanket (USAB) reactors. The water then goes directly into the aeration tanks and finally to the sedimentation unit.

The load on the treatment plant was 28 ton COD/day and most of this load, around 21 ton COD/day, was reduced in the anaerobic stage under the production of biogas, 9 000 m^3/day. Additional 6 ton COD/day was reduced in the subsequent aerobic stage, resulting in purified water containing 1 ton COD/day, which was returned to the paper making process. During the treatment, 1 ton/day of solids was produced, which was returned to the stock preparation to be used in the product. Before the treatment plant was installed the average concentration of COD in the whitewater was around 35 000 mg/l. This value was decreased to 8 000 mg/l after the plant was started. The concentration of VFA in the product also decreased to a low value, which eliminated the odour problem. Zülpich Papier today belongs to the Kappa Packaging group (2003).

Westfield mill

Westfield mill is a mill within the Inveresk group and it manufactures speciality-coated paper. The mill reuses biotreated wastewater after it has been treated in an existing sedimentation/filtration treatment plant together with a small flow of fresh water (Webb, 1997). Since the wastewater was often cleaner than the fresh water with respect to solids and colour, the cost for coagulation chemicals was reduced.

Gissler & Pass paper mill

At Gissler & Pass paper mill an aerobic trickling filter was installed, which made it possible to completely close the whitewater system. Besides the trickling filter an aerated buffer tank, a sand filter and a sedimentation cone were installed. Produced biological sludge was incorporated in the product. Water losses due to evaporation in the dry end of 5 m^3/h and in other places of 2-5 m^3/h were higher than the amount of fresh water used for pump seal water and suspending starch so more fresh water had to be added (Gissler-Weber *et al.*, 1981).

Hennepin Paper Co.

The mill is located on the Mississippi River and produces coloured uncoated groundwood speciality paper from a mixture of recycled fibres, stone groundwood pulp and kraft pulp. Due to, among other things, fluctuating supply of fresh water this mill initiated a zero discharge program. The main parts of this program were reuse of activated sludge treated wastewater and introduction of a closed-loop cooling system. After the implementation problems with biofouling increased the labor costs and material costs. These were solved by installation of a disinfection system, which dosed chlorine dioxide. There are, however, still some processes within the paper mill that use river water or city water but as a result of the program the monthly discharge volume decreased by 98% to 13 m^3/ton paper (Klinker, 1996).

AssiDoman Lecoursonnois

The mill produces 200 ton/day corrugating media from recycled paper with a permit to discharge 3 ton COD/day. Since the recipient may be used as a source for drinking water this permit was revised to 900 kg COD/day. The mill's management then decided to completely close the water circuits to be able to fulfil the permit. Several actions were taken in order to implement the closure; all cooling water was recycled, dry lining on several pumps, increased buffer tank capacity, clarified water was used to lubricate the water-tightness and biological treatment of the whitewater was initiated. The biological treatment was introduced to remove the compounds that accumulated due to the closure. The efficiency did not have to be very high but should remove enough so that a concentration level of 8 g COD/l was achieved in the whitewater. This would be similar to a mill with a freshwater consumption of 3-4 m^3/ton. The biological treatment consisted of an anaerobic reactor followed by an aerobic reactor and it was installed after the existing flotation unit. Soon after the treatment process was set in operation there was a problem with calcium carbonate scaling in the biological tanks. This was solved with a decarbonisation unit after the aerobic tank. The conclusions drawn from this implementation were that mills using waste fibres are suitable for closed water circuits, the installed treatment system could maintain the COD level at a satisfactory concentration and there may be problems with scaling (Nivelon *et al.*, 1998).

Today, the mill belongs to the Kappa Packaging group (2003).

5.7 Conclusions

Internal treatment of the whitewater in a paper mill is often needed in order to reduce the problems associated with closure. It can be composed of several components and the exact process configuration is decided by the demands of the product and the production process.

Biological treatment is suitable for removing dissolved organic compounds in the whitewater and it must be operated with low concentrations of nutrients in the effluent to enable recycling of the treated whitewater without disturbances.

Further experiments are needed to ascertain the correlation between the activity of microorganisms and low concentrations of nutrients in order to develop mathematical models, which can be used for design of the biological treatment system and evaluation of different control strategies for nutrient addition.

The use of biological treatment has been identified as a possible solution for in-mill treatment. It has also been installed at several full-scale plants. Information regarding how well these systems are working and if biocides still have to be used is in most cases not available. Nor is there any information how the control of nutrient addition is solved.

Chapter 6

Control of the Biological Kidney

This chapter starts with a short description of the concept control and an explanation of some of the fundamental aspects in this area. It is followed by a discussion about what the internal kidney should achieve and a description of the purpose of the control. In Section 6.3 there is a presentation of different variables together with arguments for and against their suitability to be used as control variables. The concentrations of several different compounds in the effluent must be known and the next section 6.4 specifies the necessary measurements. Different control strategies are presented in Section 6.5 together with some important system characteristics, which will influence the controller. It is followed by a discussion of some aspects on simulation and models. Simulation and models are valuable tools and some important aspects are discussed before the chapter ends with a survey of necessary equipment for the implementation of a controller.

6.1 Some elementary control principles

Although most people only associate the word control with regulation of a complicated industrial technical process, much of what humans do every day could also be described as a process with advanced control. One example is an ordinary shower. Since we want it to be a pleasant moment, the water temperature should be in a certain range. We also have some requirements on the water flow. It takes too long time to shower if the flow is too low and it hurts when the water hammers to the body if the water flow is too high. With experiences from previous showers we have a good knowledge about how to turn on the cold and hot water in order to get the right flow and temperature. During the shower, we sense the water temperature and pressure, and if they deviate from what is desired, we make some changes of the water flow. The controller in this example is the human brain. It gets continuous information from the receptors in the skin and determines if and how much it should respond to that information. In this process, other sensors like our sight and hearing are also used.

In an abstract description of the above example, a controller is used to regulate a system, which in this case is the shower. In order to do this the controller receives information about the status of some of the variables that describe the state of the system. These variables are compared to some reference values and if there is a deviation the controller will change its control signal. If the system is controllable and the controller is correctly tuned, the control signal influences the system so that the output values are changed towards the desired values.

The flow of information and signals between the system and the controller is often visualised in a block diagram as in Figure 6.1. This figure shows part of the structure of the control. Since this figure is drawn from the controller's point of view it may deviate from a process engineer's view of the process. In the figure, there are two major blocks, the controller and the system. The controller is able to influence the system with the control variable, $u(t)$, visualised with an arrow from the controller to the system. The system is also influenced by many other things but since they can not be manipulated by the controller they are referred to as disturbances, $v(t)$. The output signal from the system, $y(t)$, presents information about the system. It is referred to as the output variable and the whole purpose with the control is to influence the system so the output variable gets as close as possible to the reference value, $r(t)$.

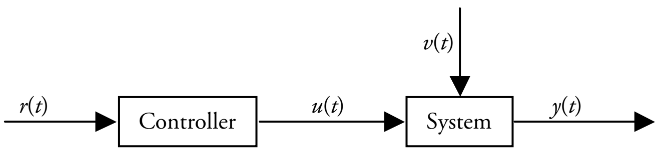

Figure 6.1 Flow of information in a block diagram.

For the design of a controller it is important to have some information about the relationship between the control variable and the output of the system. The dynamic nature of the system can usually be described by differential equations in a mathematical model. For some systems it is impossible or too time consuming to develop a model from the laws of nature. Instead experiments with a transient response analysis are performed, such as step responses and frequency responses.

The next step is to design the controller, which can be done according to two different principles, either open loop or closed loop control. Open loop control is shown in Figure 6.1, and in this type of control the controller receives no information about the actual system output. If this type of controller is going to be successful the model of the system must be accurate. In the other type of control, closed loop control or feedback control, information about the output is sent back to the controller. If the output deviates from the reference signal, the controller changes the control signal in order to minimise the error, $e(t)$. The closed loop principle is depicted in Figure 6.2.

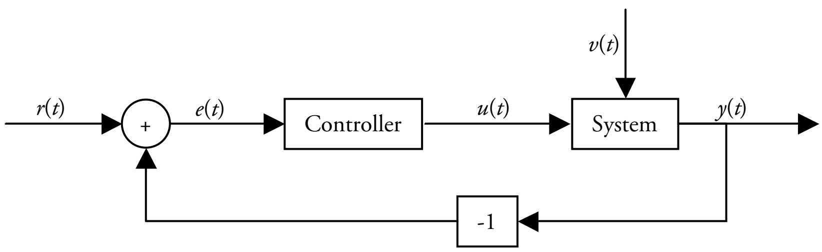

Figure 6.2 Principal outline of a system with closed loop control.

Since the feedback controller receives information about the output variable, it is not so dependent on a correct model of the system as the open loop controller. At the same time, it is not possible to do corrective actions in advance with only a feedback controller because it will not act until the disturbance has caused an error. If it is possible to measure the disturbance the control would be improved if this signal is fed forward to the controller. In this way could the controller act on the disturbance before an error appears.

The On/Off controller is the simplest form of implemented closed loop control. In this type of controller the control signal alternates between two different values depending on the sign of $e(t)$. As a consequence the output is not constant; instead it oscillates around the reference value. If the system responds fast to the control signal the controller will change the control signal with a high frequency. Under these conditions the actuator will probably wear out quickly. To avoid this, On/Off controllers are equipped with a dead band, which is a specified range in the output signal where the controller will not do anything. This will decrease the frequency of the control signal changes but at the same time it will increase the amplitude of the output signal variations.

The PID controller or any version of it, is the most common controller in industrial processes. The name is an abbreviation of its three different control actions: proportional (P), integral (I) and derivative (D). It is not necessary to always include all of the actions in the controller. Instead, it is possible to use different combinations like: P, PI, PD and even DPID. The control signal from the PID controller is a summation of three different parts and is often expressed with the following equation:

$$u(t) = K\left(e(t) + \frac{1}{T_i}\int e(t)dt + T_d\frac{de}{dt}\right) \tag{6.1}$$

The consideration of only the sign and not the value of the error is one of the drawbacks with the On/Off controller. This drawback is avoided in the PID controller where the contribution from the P part is proportional to the error and it will thus give a low gain for small errors. A controller with only a P part can, however, not totally reduce the error. By combining the P part with an I part, the remaining stationary error is eliminated since the integration increases the control signal. With the incorporation of the D part, the controller makes a simple prediction of the future and therefore responds in a better way to changes in the error. In order to avoid problems with derivative kicks, due to changes in the reference value, the derivative is usually calculated from the output variable and not the error. The D part is, however, not so much used since it requires a signal free from noise. If this cannot be provided, incorporation of a derivative will have a destabilising effect. The different parameters K, T_i and T_d in Equation 6.1 are used for controlling how much impact the different components of the controller should have on the control signal. In the common implementation, as in this example, K is affecting all of the three actions. By increasing T_i the impact from the integral is lowered and increasing T_d will increase the derivative action.

In most industrial applications, a PI or a PID controller is sufficient but there are examples where a more complex controller is needed. One such example is if the system contains nonlinearities. In order to solve the control problem in this case, several different controllers would be needed, one in each operating region. Each controller would have its own parameter setting and the range of the output would decide which controller to operate. Using several controllers is of course not a suitable approach and instead a controller with gain scheduling is preferred. In this controller it is possible to store several different sets of parameters. Which set that is currently used by the controller is determined from the actual working condition.

Tuning is the process when the values of the different parameters in the controller are set. For the PID-controller this means that K, T_i and T_d should be given real values. This process is usually a compromise between speed and stability. When the gain is increased in order to make the control faster the risk for instability increases and if the control is made too stable it is usually also too slow. The aim should be to establish a sufficiently fast and stable control. When an accurate mathematical description of the system is available it is used to determine the different parameters. The situation is, however, not always like this. The development of an adequate model is often time consuming and could also be an impossible mission for highly complex systems. Several different methods have been developed for tuning under these circumstances. Some of the most familiar tuning methods are Ziegler-Nichols (Ziegler and Nichols, 1942) and IMC (Rivera *et al.*, 1986). In both these methods the operator disturbs the system with either a step or pulse signal. Suitable control parameters are then determined from the systems dynamic response. The progress both in control theory and microprocessors has led to the development of auto-tuners. These "intelligent" controllers initiate a disturbance and then determine by themselves the most suitable parameters. The only thing the operator must do, is to decide how large the variation in the control signal is allowed to be and perhaps provide some additional information about the system.

More information about practical process control are found in Hägglund, (1991). Fundamentals of control are described in numerous books, for example Glad and Ljung, (1989) and Lennartson, (2000).

6.2 Control purpose for the biological kidney

The overall goal of the biological processes is to reduce the easy degradable components in the whitewater, in order to solve some of the different problems that are caused by the closure of the whitewater system. The internal kidney consists of the biological processes together with additional treatment steps and this unit should produce an effluent suitable for recycling. Since most of the organic reduction occurs in the biological processes the resulting concentrations in the whitewater after an implementation of an internal kidney is a function of the size and efficiency of the anaerobic and aerobic reactor and how much of the whitewater that is treated. In order to reduce the size of the reactors, the biological processes should be operated as efficiently as possible. The treatment process should also be stable and reliable due to the close interaction between the internal kidney and the paper production.

To achieve all of this, automatic control is required for several of the internal kidney components. The environmental conditions in the biological processes should be optimised; otherwise the efficiency will decrease for these steps. In the anaerobic reactor the degradation involves many different types of microorganisms and in the last step methane-producing bacteria converts acetic acid into methane. If this production is reduced due to inhibition caused by the presence of toxic compounds or other disturbances, organic acids could accumulate in the reactor, causing a decrease in the pH. This would further affect the anaerobic reactor and prolong the time it takes for it to recover from the inhibition. During its recovery the anaerobic effluent with low pH could then also affect the next step in the treatment sequence, the aerobic reactor. Therefore, both the anaerobic and the aerobic reactor should be equipped with pH control, in order to adjust the pH in case of disturbances. The fluidisation of the contents in the anaerobic reactor is obtained by recirculation of the fluid in the reactor. This flow must be controlled so it remains in the right operating range.

In the aerobic reactor air is released at the bottom of the reactor and this fulfils two requirements. Partly, the air provides oxygen to the degradation process and partly the air bubbles mix the content as they move towards the surface. One of the major contributors to the operating cost in biological aerobic wastewater treatment processes is the air pump. Therefore, in order to minimise the cost, a constant oxygen concentration should be maintained in the aeration basin by controlling the airflow. It is, however, important that this flow is not decreased below the minimum requirement for adequate mixing.

Controlling pH, oxygen and flow rates are well proven technologies and should not be too difficult to implement. This also applies to the control actions needed in the different additional treatment steps, for example control of pressure and flow in membrane filtration and regulation of ozone production in case of ozone treatment, if the biological process should be complemented with one of those. The challenge in this project is the control of nutrients; nitrogen and phosphorous. Since the whitewater normally is deficient in nutrients, it is important to supply these to both the anaerobic and the aerobic reactor. The term nutrients refers to all essential elements except oxygen and carbon. Normally it is only nitrogen and phosphorous that are limiting the process since they are required in larger amounts. In order to have an efficient treatment process these have to be added. However, since they are so essential to the microorganisms it is also important to prevent the nutrient concentration in the effluent to exceed specified limits, as this will cause microbial growth in the whitewater system. Apparently the nutrient addition must be controlled. This is the major challenge of this work.

6.3 Control variables

As the previous section showed, there are many different aspects of control but the remainder of this chapter will concentrate on how to maintain the required nutrient concentration in the effluent. In this control system the output variables will be the nutrient concentrations and they are influenced by many variables in the biological process. In the biological reactors microorganisms degrade the organic compounds in the whitewater. Most of the degraded material is dissimilated in order to provide energy to the microorganism and the rest is assimilated into different cell components so the cell eventually can be divided. The nutrients are required during the cell growth since many of the molecules in the cell contain other elements than carbon, oxygen and hydrogen. The cell growth is affected by how much organic matter there is to degrade, how much microorganisms there are in the reactor and how much nutrients there are. In the aerobic reactor also the oxygen concentration affect the growth. All of these variables could at least in theory be used as control variables. Other variables, such as pH and temperature, are not suitable since they need to be kept close to desired values so that the treatment is as efficient as possible. Neither oxygen, the biomass concentration nor the load of organic compounds are suitable control variables.

It is obvious that the biomass concentration cannot be used since both reactors are biofilm processes without any return pumping of sludge. Oxygen would only be able to increase the growth if it was initially limited and normally it can therefore only be used to decrease the growth. The load of organic matter could be used to increase the growth with the purpose to assimilate more nutrients. This would only be relevant if the available microorganisms are not working at their maximum capacity. Otherwise, the increased load would not influence the growth. On the contrary, a sudden increase of the load to the biological processes could have a negative effect on the subsequent treatment steps.

The obvious choice of control variables in order to fulfil the described control purpose would be the flow rate of nutrients to the biological reactors. By increasing or decreasing the flow rate it would be possible to maintain the desired effluent concentration despite disturbances in influent organic load. Since the nutrients are only added to the anaerobic reactor the addition should also meet the aerobic demand.

6.4 Measurements and environmental requirements

Biological processes are complex systems since many variables depend on several other variables. In this particular case, the output variables are influenced by the amount of microorganisms in the system, the biological activity and the amount of degradable matter. There are of course several other variables that to a lesser degree affect the system. Gaining information about these variables is helpful when a controller is being designed and the output variables require a special interest in this case. One challenge is to maintain very low concentrations of nitrogen and phosphorous in the effluent from the aerobic reactor. The concentrations should be as low as possible, preferably below 0.1 mg/l. It would be valuable if these concentrations could be monitored but a concentration of 0.1 mg/l is below or close to the detection limit for any on-line instrument. It is thus not possible to measure and determine the output variables in the effluent from the aerobic reactor. It could, however, be valuable to measure in this position anyway but such information could then only be used as part of a warning system in order to detect process disturbances.

The concentrations of nitrogen and phosphorous in the nutrient solution are important information but since they are constant they do not have to be measured on-line. The nutrient solution is added to the anaerobic reactor together with the whitewater. Part of the nutrients is consumed during the anaerobic degradation process and the remaining amounts in the anaerobic effluent should meet the requirements of the aerobic process. The concentrations of nutrients in the effluent from the anaerobic reactor are within the measuring range for on-line instruments and at this position it is consequently possible to achieve reliable information.

Besides nutrients the amounts of organic compounds at different positions also represent important information. By measuring the concentrations in the influent and effluent of the two reactors the actual amount of degraded organic material can be determined. The analysis can be done with a UV-absorbance method or the somewhat more complicated TOC determination. The actual concentrations at the different positions are above the detection limit and there are no limitations as was the case for determination of nutrient concentrations.

The determination of the amount of microorganisms is not straightforward. In fact, commercial methods are aimed at systems with suspended organisms, forming a sludge. Consequently, it is not possible to determine the amount of microorganisms in a biofilm process but the activity could be measured. The gas production is a good measure of the activity in the anaerobic process. Although the gas is only produced in the last step, this reaction is rate limiting and the gas production can therefore give a good indication about the overall performance in the anaerobic reactor. The activity in the aerobic reactor can be measured by respirometry. In this case it would be necessary to do some off-gas analysis in the aerobic reactor since commercial respirometers use activated sludge for the measurement.

Besides information about the different variables that influence the output variables, knowledge about how they are linked to the output variables is also needed.

6.5 Control structures

Now it is time to tie together the purpose of the control and the chosen control variables with available measurements into one working unit. The goal is not to make the most complicated controller. On the contrary, the optimum is to find the simplest controller that will do the job. The exploration for the "ultimate" control starts with the simplest approach, manual control. The nutrient flow rate, which is the control variable, is set to a constant value and this strategy can be seen in Figure 6.3.

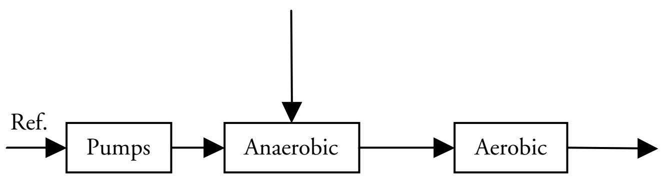

Figure 6.3 Manual open-loop control.

Manual sampling and analysis of the aerobic effluent has to be carried out at regular intervals in order to determine the values of the output variables and to manually correct the flow rate. If the output variables deviate from what is required, the nutrient flow is changed manually. The trouble with this controller is the lack of automatic feedback from the output and the consecutive adjustment to attenuate the disturbances. Of course it is also very labour intensive.

The first choice is to consider a simple feedback controller. By measuring the effluent concentrations of nutrients and feed them back to the controller corrective actions can be made. The apparent difficulty with this solution is its dependency upon measurements in the effluent. Since the nutrient concentrations should be as low as possible, they cannot be determined with any precision during normal operation. The on-line instruments for measuring nutrients can, however, be used in that position as part of a warning system. In order to have an automatic adjustment it is necessary to implement some kind of model based control together with the warning system. The first choice would be to acquire information about the disturbances acting on the system and use this in a feedforward controller. By measuring the flow rate of whitewater and feed forward this information to the controller it could respond to load disturbances. The flow, however, will probably not vary to any larger extent since the treatment plant is implemented in parallel to the whitewater system. It is thus possible to have a relatively constant flow to the treatment plant. The load is more likely to fluctuate due to concentration changes of organic compounds in the whitewater. Since the treatment should be as efficient as possible the feed forward of the flow ought to be complemented with information about the concentration of organic compounds in the whitewater. If the model of the biological system were accurate the feedforward controller would perform well. In reality, however, there are always some errors in models and therefore, the warning system gives an alert if the nutrient concentrations are over a certain value. The proposed feedforward controller with an alarm function can be found in Figure 6.4.

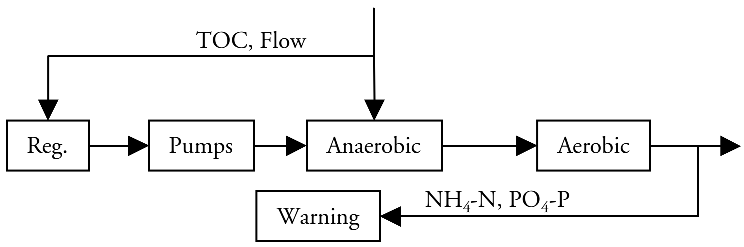

Figure 6.4 Feedforward control of nutrient addition

There are several limitations with the proposed control strategy. First of all, it does not utilise the on-line instruments for nutrient measurement in an efficient way. Most of the time they are measuring on samples where the concentrations are below the detection limit. The controller is not operating the treatment systems as efficient as possible and it is probably necessary to have large safety limits in order to achieve low levels of nutrients in the effluent. Then, the controller does not take into account the division of reduction between the two different reactors. This is important since the nutrient requirements during aerobic degradation are different from that of anaerobic degradation. The controller could still work since the requirement in the aerobic reactor is higher than in the anaerobic reactor. If the efficiency of the anaerobic process for some reason decreases below the expected value, the load on the aerobic reactor would increase. Unless the load on the aerobic reactor rises dramatically the aerobic process should be able to use up all of the nutrients in the anaerobic effluent. The amount of nutrients would not be in balance with the load but the most important goal with low concentrations of nutrients in the aerobic effluent would still be met.

A better use of the on-line instruments is to place them between the anaerobic and aerobic reactor and perform measurement of the anaerobic effluent as in Figure 6.5. In this way it is possible to use the feedback for corrective actions due to errors in the feedforward model.

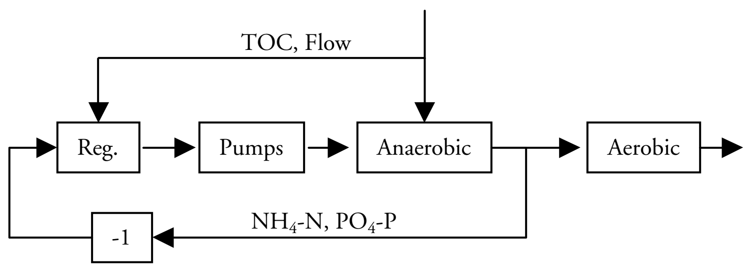

Figure 6.5 Feedforward with feedback.

With this strategy, however, there is no information about the last step, the aerobic treatment. The controller does not know how that process is working and if the load of organic compounds is balanced with regard to the amount of nutrients in the influent. To accomplish this, more information about this part of the treatment process is required and one possible way is to measure organic matter in the water before and after the aerobic reactor. This information together with information about the ammonium-nitrogen and phosphate-phosphorous could then be used to determine the optimal nutrient concentration in the anaerobic effluent. The outline of this strategy with a feedback control of the anaerobic effluent, feedforward of disturbances and an estimation of the reference values can be found in Figure 6.6.

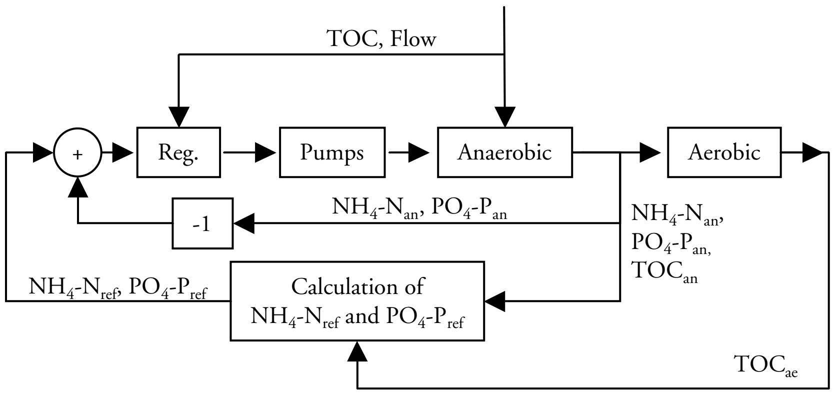

Figure 6.6 Graphical outline of the proposed control structure for the biological treatment plant.

This controller considers the degradation in the aerobic reactor and adjusts the nutrient addition accordingly. The complexity of the strategy could be further increased with better models of the treatment process and automatic update of the models to adjust the controller to changes in the biological system. This model based control strategy can be found in Figure 6.7.

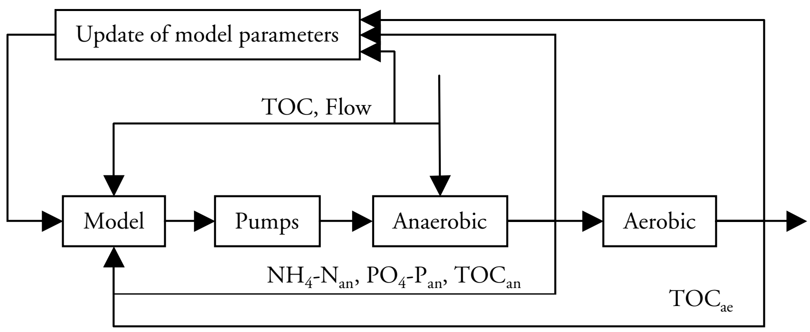

Figure 6.7 Model based controller with automatic update of the model.

One limitation of all control strategies is the dependency of on-line measurements. It is of course necessary to know something about the outcome and preferably disturbances in order to be able to do any automatic control. The drawback with the on-line instruments is their complexity but with proper maintenance this should not lead to any problems.

There are several difficulties in the system that must be handled when the control is implemented. The long detention time of several hours in the reactors leads to a long time delay before a change in the control variable can be detected in the output variables. Also the calculation of the reference values imposes difficulties. It is important to consider the difference between the TOC values. The TOC value in the aerobic effluent is a reduction average of what has been loaded to the aerobic reactor during several hours and the measured TOC in the aerobic influent represents the actual load to the reactor, which will affect the reduction during the next few hours. It is also important to bear in mind nature's great capability to adapt to different conditions. The microbial community in a treatment plant is not constant. In fact, the composition is always changing since some species are favoured at the expense of others due to variations in the wastewater composition and the environment. This may change the behaviour of the systems over time.

Which strategy of all the proposed should then be used? Increased complexity of the controller would hopefully lead to a better control and not just a higher demand of effort for its implementation. It could, however, be that a simpler controller is adequate. The choice has to be based on some kind of evaluation of the different strategies. A preliminary evaluation could be done with computer simulation and the result should then be confirmed with practical experiments in real life.

6.6 Simulations and models

The dynamic behaviour of mechanical, electrical, biological and other types of systems can more or less be described by a set of differential equations. With these equations it is then possible to calculate what effect different variables has on the system. Since the equations are complex it is not possible to formulate an algebraic solution. Instead, the result is found by numerical calculation with a differential solver. Today it is possible to perform computer simulations of complex systems since there has been a tremendous development in the calculation capacity of computers. With computer simulations it is possible to perform different experiments and acquire the results after some minutes or hours. This is a nice feature especially if the practical experiments to do the same thing would have taken weeks and months. With computer simulations it is also easy to make changes in the experimental setup, for example changing the volume of a reactor, which may not be so easy to do in practise.

Obviously there are several advantages with computer simulations. However, the accuracy of the results depends on how well the model describes the reality. It is dangerous to develop a model for certain circumstances and then extrapolate the results to other situations. The formulation of the model may for some systems be quite straightforward while it for other systems requires more effort. For biological treatment several models have been developed and it is today possible to simulate most of the processes that occur in a municipal treatment plant, such as aeration, nitrification, aerobic degradation and denitrification (Henze *et al.,* 2000).

Since there is still much to learn about the bacterial needs and interactions between different species, it is not yet possible to accurately simulate things like the formation of a bulking sludge. In this type of project where a control strategy should be developed for low concentrations of nutrients in the effluent, simulation would be a valuable tool. Instead of performing tedious practical experiments where much time is spent on chemical analysis and maintenance of instruments and equipment, it would be more efficient to investigate the consequences from different control strategies by computer simulations. This cannot, however, be done since there is not enough knowledge about what effects low concentrations of nutrients have on the organic reduction and on the biofilm composition. In order to be able to perform realistic simulations in this area more knowledge has to be accumulated concerning how varying nutrient conditions will affect the organism composition and culture.

6.7 Implementation

There are many different types of hardware that could be used to implement the controller. In this project it is important to have a system with great flexibility since different control strategies should be tested. A computer-based controller fulfils these requirements and the commercial software LabView was chosen (National Instruments, 2003). It is a graphical programming language and can be used for building different software applications. LabView is developed by National Instruments, which also have a broad collection of solutions for data acquisition. For this application, was a module system selected since it offers great flexibility and is easy to expand.

The module system consists of one network module that connects up to nine I/O-modules. During operation the controller should regulate the nutrient dosing pump, which in this case is a membrane pump. The pump is frequency controlled and the pulses to the pump are sent from the controller via a relay module. Three on-line instruments collect information about the process. There is one Evita sensor from Danfoss Analytical A/S (2003) for measuring orthophosphate at one position, one Biotector 990+ from Pollution Control Systems Ltd. (2003) for measuring TOC at two different positions and finally a UV-pcx from Awa Instruments SAS (2003) for measurements of COD, NO_3-N, NH_4-N and turbidity at one position. Since the unit for turbidity measurements is separated from the rest of the instrument, it can be placed at another location. All these instruments are able to transmit a mA-signal, which is proportional to the concentration. The signals are acquired with a 16-bit 8-channel analogue input module. A FieldPoint bus is used for the communication between the I/O-modules and the networking module, which is then connected to the computer by a high-speed Ethernet network.

The intention is to use all this equipment together with a pilot plant of the biological treatment process in the next phase of the ClosedCycle project, for practical evaluation of different control strategies.

Chapter 7

Conclusions

The different findings in previous chapters are concluded in the first section of this chapter. It is followed by suggestions for future work in this area.

7.1 Summary of results

The modern society's need for paper does not seem to be reduced although this was perhaps an anticipated consequence of the increased use of computers with the possibility to distribute electronic documents and correspondence by e-mail. Besides printing paper there is a demand for other paper products e.g. copying paper, journal paper, packaging board, newspaper and tissue. Paper manufacturing is a complex and multidisciplinary science due to the diversity of paper products, used raw materials and different production processes. Besides fibres, either virgin or recycled, different chemicals, water and energy are needed to produce paper. The use of fresh water has decreased significantly during the last decades and there are several reasons for this, such as:

- limited availability of fresh water;
- increased cost for effluent treatment;
- marketing benefits.

This decreased consumption has been made possible by the reuse of process water instead of fresh water. At a certain degree of closure of the whitewater system in the paper mill different problems occur. Many of them are in some way related to the growth of microorganisms in the system. In order to overcome these problems many different solutions have been applied. The probably most common remedy against microbial growth is to dose biocides into the whitewater system and killing the microorganisms. Other methods attack the problem from a slightly different angle. The compounds in the whitewater act as substrate and if they are removed the possibility for the microorganisms to grow is limited. This could be achieved by implementation of an internal kidney consisting of at least a biological treatment step. A combined anaerobic and aerobic biofilm process was concluded to be suitable for internal treatment of whitewater in a paper mill producing liner from recycled paper. Since nutrients, such as nitrogen and phosphorous, normally are limited in the whitewater these have to be added in order to have an efficient treatment process. One major challenge is to operate the biological system with low concentrations of nutrients in the effluent otherwise the conditions in the whitewater system will be negatively affected. Consequently, it is evident that there is a need for automatic control of the nutrient addition. Operation of a biological treatment system with low effluent concentrations of nutrients is not only limited to in-mill applications. This is also of interest for external treatment in plants where additional nutrients are required.

The objective of the implementation of a biological treatment system is to reduce the concentrations of organic compounds in the whitewater. The treatment process should be as efficient as possible without leaking nutrients into the whitewater system. It is possible to control the flow of whitewater to the treatment process but not the actual concentrations of organic compounds in the whitewater, which therefore can be regarded as a process disturbance. An investigation was made at two different paper mills with different degrees of closure to determine the variation of chemical oxygen demand (COD) in the whitewater. The results showed that the whitewater concentration in an open mill could vary a lot whereas the conditions were more stable in a closed mill. This facilitates the control objective of the biological system.

For the control there is a need for information about the process state and output from the system. In this case, for controlling a biological treatment of whitewater, different on-line instruments are needed. First of all, a market survey was conducted in order to get an overview of the supply of suitable instruments. This market survey was limited to instruments for measurements of organic matter, ammonium and orthophosphate. The experiences gathered at several of the Swedish municipal treatments plants were explored in a telephone survey about their use of on-line instruments. One interesting observation was that most on-line instruments were only used for monitoring. The number of instruments used for direct control was low but this number was increasing as new and better instruments are becoming available. As a conclusion of these two surveys, three different brands of instruments were deemed suitable for measurements in whitewater.

Computer simulation is an important tool for evaluation of different controllers. It requires, however, a mathematical model of the system that should be controlled. Laboratory experiments were initiated to determine important parameters for such a model. In these laboratory scale experiments, whitewater from a recycled fibre paper mill was used as influent water to a treatment system consisting of a fluidised anaerobic reactor and an aerobic suspended biofilm process. Both mesophilic and thermophilic treatment resulted high removal of COD of around 90%. The nutrient requirement for the anaerobic mesophilic reactor was determined to 19 mg N/g $COD_{reduced}$ and 2.5 mg P/g $COD_{reduced}$. It was not possible to determine any requirement for the aerobic reactor since the load of degradable COD was too low. For thermophilic degradation the requirement was determined to 24.5 mg N/g $COD_{reduced}$ and 4.4 mg P/g $COD_{reduced}$ for the anaerobic process and the corresponding values for the aerobic process were 37.1 mg N/g $COD_{reduced}$ and 5.5 mg P/g $COD_{reduced}$. One purpose of the experiments was to evaluate how low concentrations of nutrients affected the reduction of COD. A decrease of the added amount of nitrogen to 77% of what was originally consumed did not have any immediate effect on the COD reduction. A further reduction in the added amount of nitrogen was made but the effects from it could not be observed since there was a failure in the equipment.

Pilot tests with the purpose to study both the stability of a biological treatment process and evaluate two different on-line instruments were conducted at a packaging board mill. The results demonstrated that the removal efficiency was not markedly affected from variations of the load to the combined anaerobic/aerobic treatment process. However, it was evident that manual control of the addition of nutrients was inadequate. During this pilot test a TOD instrument from Ionics and an instrument for measurements of ammonium from Cerlic were tested. Both these instruments failed to provide stable and reliable results.

Experiences from other instruments have been gathered during the assembly of a complete system consisting of a pilot plant of a biological treatment process, on-line instruments and data-acquisition equipment. During preliminary testing of the instruments both the TOC instrument Biotector 990+ and the Evita orthophosphate sensor have been operating without any problems. The special arrangement with the sampling cup for the Evita sensor requires, however, regular maintenance in order to achieve a flow of fresh sample across its membrane. The formation of foam, which is transferred into the measuring tube of the ammonium instrument in the multi-parameter instrument from Awa Instruments represents a problem, which has to be solved.

It has been demonstrated that it is possible to use on-line instruments for measurements in whitewater and in this way achieve information about the biological treatment process. This information could be used in several different ways for the control of the addition of nutrients. The objective of the control is to maintain low concentrations of nutrients in the effluent from the biological treatment and at the same time have a reduction of COD, which is as efficient as possible. A controller based on feedback of concentrations of nutrients in the effluent from the treatment process is not possible since the concentrations are near or below the detection limits of the instruments. Therefore, other control structures are suggested ranging from feed forward of the organic load with corrective feedback of concentrations in the anaerobic effluent to more complex model-based control structures with automatic update of model parameters.

7.2 Future work

It is evident both from published results and from the experiments discussed in this thesis that biological treatment is a suitable method for degradation of the organic compounds in the whitewater. It is also necessary to introduce an automatic addition of the nutrients to this process in order to have an efficient process releasing low concentrations of nutrients in the effluent. The first step towards the implementation of one of the proposed control structures would be to develop a mathematical model of the degradation process. It is the operation of the biological treatment process at low concentrations of nutrients that is important to model correctly. Important aspects are the yield of biomass, growth rate and effect of nutrient limitations on the COD reduction. The difficulty with biological treatment is that the composition of the microbiology can change as environmental conditions such as concentrations of nutrients vary. New species, better suited for these new conditions, have probably other characteristics, which in a model would imply new parameters. It is important to find out if one mode of operation gives a set of model parameters that differs from another mode of operation. If so, the effect this has on the overall process performance should be determined. These parameter changes could be so small that the effect could be neglected unless the model should simulate the growth of individual species.

In the model, correct behaviour of the different on-line instruments should also be included. It is not possible to acquire an immediate reading for any instrument. All instruments have some time delay in the response and if this information is not available it should be determined. Besides time delay there is also some uncertainty in the readings, which should be included in the model.

The complete model of the biological system and the different on-line instruments is then used for computer simulations where the efficiency of different control strategies is evaluated. In the evaluation it is important to consider not only the accuracy of the result but also promote strategies that are using few on-line instruments since a complex system with many sensors are more vulnerable and expensive. After identifying the most suitable control strategy its performance should be validated by practical experiments. Before these can be performed the controller has to be implemented in the chosen application, LabView. The practical testing will also be a good evaluation of the on-line instruments to further identify their weaknesses.

The internal kidney is composed of more units than only biological treatment. There is also separation steps and additional treatment. One interesting task is to develop a plant-management system, which would control the combined operation of the different units in an optimal way. This system would be incorporated with the monitoring system of the paper machine in order to receive information about actual production rate and current demands of different qualities of treated water to recycle. Depending on the actual concentrations in the whitewater the manager would control the amount of whitewater treated in the internal kidney. The demand for extensively cleaned water could, for example, control the amount of biological treated effluent, which is directed to a membrane-filtration process. A vital part of such a plant-management system is an early-warning system. Its function is to alert the operator if the state of the treatment system is moving towards an operating point, which could negatively affect the paper production. Examples of such states are: increased levels of nutrients in the recycled water, inefficient decolouring, high concentration of solids or insufficient reduction of organic material.

Finally, it would be interesting to further develop the internal kidney for treatment of whitewater from other types of paper production. The choice for this work was a paper mill with paper production from recycled fibres since this was regarded as one of the less demanding types of production. Other types of paper production will pose different demands on the internal kidney, which has to be considered in the design and operation.

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