FRESH WATER MINIMIZATION BY MEMBRANE FILTRATION IN THE PULP AND PAPER INDUSTRY

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Keywords: closed water circuits, internal purification, water consumption, paper machine, mechanical pulp mill, recycling, circulation water, water reuse, water treatment, water quality, microfiltration, ultrafiltration, nanofiltration, reverse osmosis, fouling

Contents

Summary

The idea of totally or partially closed water circuits in the pulp and paper industry has come to stay. The driving force for fresh water minimization might be the more efficient processes, the lack of water resources, the fresh water and wastewater costs, customer demand etc., but today all parties agree that it has to be done. The question still remains which is the best technique to put it into practice.

A lot has been done during the last decade and many mills are already running with specific water consumption below 10 m^3 per ton. This has been accomplished with water segregation and by applying internal purification methods. The internal purification becomes necessary when the organic and inorganic load in the circulation waters is rapidly increased due to the reduction in the fresh water consumption.

The techniques used today are microflotation, biological treatment, evaporation and membrane filtration. The latter two are approved BAT techniques in the internal purification. However, microflotation and biological treatment have been successfully used for fresh water minimization. Today the performance of the unit processes is rather well known and active research and development work is done in the universities, the research institutes and in the industry to make the unit processes more efficient and cost-effective. It should also be remembered that combining the techniques (hybrid processes) might give the best result. It is also evident, that the best suitable system is not the same for every mill because their water systems are unique. Besides, the circumstances in and around the mill play a notable role.

It is still not known what the toleration limits are for water quality in different mills. Must the reused water really be potable? Or could the reused water contain "something" without harming the product or the viability of the process? Does that "something" differ significantly from mill to mill? On the basis of the knowledge today, it seems that no measured value commensurately describes the papermaking process in such a way that common conclusions could be drawn. Answers to these questions will remain as a challenge in this new millennium.

1. Introduction

The pulp and paper industry is growing with the same rate as Gross Domestic Product in the world. In spite of the growing popularity of the Internet and electronic journals, pulp and paper production is globally steadily increasing. In 1998 the production of pulp and paper in the world was estimated to exceed 300 million tons for the first time. Nowadays the common trend is to establish new pulp and/or paper mills to such areas in the world where the water resources are very limited or non-existent, or where the environmental legislation is very strict; this attracts popularity to the concept of closed water circuits. However, the closed water circuits offer many benefits also to the existing mills:

(a) increased opportunities to maintain or expand production in environmentally sensitive locations;
(b) more favorable market and environmental evaluation of products, including the provision of a more durable solution to future environmental standards;
(c) drastically reduces or even eliminates liquid discharges and the associated water quality problems;
(d) separates and recycles valuable resources;
(e) preserves energy that can be used to reduce cost of production and capital costs;
(f) saves capital and operating costs for effluent treatment as well as saving on chemicals and heat;
(g) reduces the use of fresh water.

During the 20th century specific water use in the paper industry has fallen dramatically from around 300 m^3 per ton at the turn of the century to between 20–30 m^3 per ton today. However, a level of 5–10 m^3 per ton can be achieved rather easily by good water management, for example by the segregation of water fractions according to their degree of "pollution" and by adapting the counter-current principle. The specific water use can further be reduced to the level of about 2 m^3 per ton by internal treatment and reuse of process water. About 0.5–2 m^3 of water per ton of paper is evaporated during the papermaking process and must be replaced by fresh water. However, a question remains: must the water used be potable?

One of the driving forces towards closed water circuits has been, along with seeking better economy and green values, the EU Directive on Integrated Pollution Prevention and Control (IPPC), which came into force in 1999 for greenfield mills and the Cluster Rules in USA. Many of the emission limits stated in the IPPC cannot be reached without limiting the volume of effluents produced. Because the only source of effluent is the incoming fresh water, minimization of fresh water intake has to take place. Moreover, water recycling with or without internal purification has to be arranged.

Membrane filtration is a well-established technology in many lines of industry. By volume most membrane plants are sold to water desalination or to pharmaceutical applications, such as artificial kidneys. Today the market worldwide for membranes is estimated to be worth US$3–3.5 billion.

Traditionally, for example, flotation and evaporation have been widely used as separation and purification techniques in the pulp and paper industry. Since 1980's membrane filtration has also been adapted to these applications. Moreover, along with increasing knowledge and better membranes and modules, membrane filtration has gradually become a more tempting option through its versatility, small room requirement and significantly lower energy consumption compared to evaporation.

Besides the many benefits gained by membrane filtration, one of the major obstacles for wider use of membranes is the membrane fouling. As a function of time, the flux through the membrane decreases because of the solutes accumulating on the membrane surface. This directly affects the economy of a membrane plant by increasing the investment and operating costs. Thus, the focus of recent research on this field has been on the development of low fouling membrane processes for the pulp and paper industry.

In this paper fresh water minimization in mechanical pulp plant (e.g. thermomechanical pulp, pressure groundwood, etc.) and paper mills is discussed. In this context the chemical pulp mills are beyond the scope of this text and are thus not discussed in detail. The chemical pulp mills have similar features as the mechanical pulp mills except that chemical pulp does not release as much dissolved substances in the water circuit as mechanical pulp. Besides, the closing of the water circuits in a chemical pulp mill is usually done with evaporation and incineration.

Some principles of planning closed water circuits are presented. A short review on different internal purification techniques and existing applications is given. Membrane filtration as an internal purification method is discussed in particular and the focus is laid on the development of low fouling membrane processes for the needs of the pulp and paper industry.

2. Surroundings for Closed Water Circuits

2.4. Fresh Water use and Water Segregation in a Paper Mill

Water consumption differs in non-integrated and integrated paper mills. In a non-integrated paper mill purchased pulp is the major fiber source and is delivered at 90% solids. In an integrated paper mill pulp from the pulp mill is stored in a high-density chest at about 12–16% consistency. In both cases the web leaves the press section at about 40–46% solids content. Consequently, there is a net demand for mill water in a non-integrated paper mill and a net surplus of water in an integrated mill. However, in an integrated mill the exchange of water between the pulp and paper mill can change the situation, even though the exchange is nowadays tried to minimize. The production of mechanical pulp is always the primary consumer of water.

In general, mill water is needed for showers in the paper machine wire and press section, dilution of chemicals and process water make-up for level control in the tanks. The fresh water consumption of a paper mill varies widely according to the paper grades produced as well as according to the availability and the price of water. Naturally an important factor is also the technical age of the paper machine: the more modern the paper machine, the lower the fresh water consumption.

Today, in modern paper production fresh water is mainly introduced to the process through paper machine wire and press section showers and is the lead counter currently to various washing and diluting duties in the (mechanical) pulp production plant. In Table 1 different uses of fresh water in paper production are shown.

Unit operation	Printing paper grades	Newspaper grades
Total fresh water consumption, m^3 per ton	***16-26***	***27***
Paper machine showers, m^3 per ton	6–7	5
Dilution/preparation of chemicals, m^3 per ton	2–3	3
Make-up waters in pulp production, m^3 per ton	2–3	
Cooling of process equipment, m^3 per ton	3–10	10
Sealing waters, m^3 per ton	1	6
Power plant, m^3 per ton	2–3	
Miscellaneous, m^3 per ton (washing, sealing etc.)	—	3

Table 1. Fresh water consumption in papermaking. (Sources: Edelmann K., (1999), Water management in papermaking in *Conference on Towards Closed Water Systems in Papermaking*, February 2nd, Arnhem, The Netherlands; Haavanlammi T., (1999), Advanced paper mill watersystem in *AEL-METSKO/Insko Seminar: Closed Water Circuits in Paper Mills*, P907105/99 IV, December 14–15, Vantaa, Finland. 9 pp.)

In many mills which exhibit a high specific water use, the water management is not very well organized, that is, contaminated and clean water fractions are all collected together and then treated as effluent. Until today this has meant that the size of external effluent treatment may become a bottleneck if the producing capacity of the mill is increased or its emission limits are restricted. In many cases also the efficiency of the external treatment plants increases with reduced effluent volumes.

With segregation of clean and contaminated water fractions a significant reduction of effluent volume can be achieved. For example, separate recycling circuits for cooling and sealing waters, which do not become contaminated (except with heat) when used, is worthwhile and rather easily arranged. It is also possible to use new sealing systems, which do not need water. Segregation also provides a possibility to treat process waters or effluents individually close to where they are created.

It has been long believed, that water used for chemical dilution must be very clean and active research has been done. However, a novel retention aid mixer, the TrumpJet™, has now entered the market, in which process water or even head box pulp can be used as a dilution aid.

It has been shown by Curley, et al., that a slight increase in closure, for example from 90% to 95%, would increase equilibrium time by roughly 50%, if the degree of closure is the percentage of the headbox flow returned. Due to this the present development of paper machine short circulation is also heading for lower water volumes and shorter equilibrium times, which is a great improvement for multigrade paper machines. Such new concepts are ShortFlow™, POM or OptiFeed.

2.5. The Process Waters

Paper mill waters carry significant quantities of fiber (losses with effluent 0.5–5% of total fiber amount), filler, fines and other wet-end additives that contribute to the total suspended solids (TSS), the chemical oxygen demand (COD) and the biological oxygen demand (BOD). TSS in paper mill waters varies significantly from mill to mill based on the type of internal clarification equipment used, equipment arrangement and design philosophy. COD depends on the amount of suspended solids such as fiber, fines, and other chemically oxidizable wet-end additives such as starch. BOD is high due to the presence of large amounts of oxidizable materials, such as fiber, fines, starch, wet and dry strength resins, drainage aids, dyes, sizing materials and other dissolved organics.

In the production of mechanical pulp an average of 2–3% of wood material is dissolved during refining and another 2–3% during bleaching. In other words, when producing mechanical pulp from Norway Spruce (Picea abies), which is used for newspaper and magazine paper production, the yield is 95–98% calculated on dry wood. This means that 20–50 kg per ton is lost into the water phase in the form of dissolved and dispersed substances, such as simple carbohydrates, extractive substances and salts. The amount of carbohydrates, which are readily dissolved in water, varies according to the time of year between 1–5 kg per ton. The extractive substances, which are fat soluble components dispersed as oily droplets in water, consist of fats (triglycerides), fatty acids (hydrolyzed fats), rosin acids, sterols, lignans, and stilbenes. The total amount is of the order 10 kg per ton.

The paper mill process waters contain more or less the above mentioned compounds depending on the water arrangements between the mechanical pulp plant and the paper mill. In addition to these wood-originating compounds, various chemicals are added in the papermaking process, such as, for example, retention aids, antifoaming aids, biocides etc. Moreover, in the case of coated paper grades, components of coating color (pigments, binders, latex) enter the white water system with broke. Traces of all of these are found in the process waters, like the white water.

Thus, the resulting white water will contain a wide variety of organic and inorganic substances, which can be classified into three groups depending on the particle size:

- suspended solids: >1000 m^{-9}
- colloidal substances: >50–100 m^{-9}
- dissolved substances: <50–100 m^{-9}

However, the limits of these groups are not strict because during the process, for example, the size of the components may change.

Some of the dissolved and colloidal (DCS) substances are retained in the paper, but some remain in the circulation system levelling at concentrations that depend on the fresh water intake. A portion of the DCS substances is harmful for the papermaking process through their interaction with other compounds in the process waters:

- galacturonic acids are the major components of anionic trash in process waters, which interact with cationic retention aids;
- wood resins can form white pitch with latex and stickies;
- ions like calcium form insoluble soaps with lipophilic extractives;
- chloride and sulfate ions at high concentrations cause corrosion;
- sufficient availability of DCS substances accelarate microbiological growth resulting in formation of slime and deposits.

The counter-current washing principle and the washing of pulp are means to reduce the harmful effects of enriched DCS in the papermaking process. As the water consumption is below 10 m^3 per ton, internal purification is also needed to ensure the paper quality and the viability of the paper machine.

2.6. Potential Problems of Closed Water Circuits

In general closing the mill white water system has the following advantages:

- minimized fresh water consumption;
- lower losses of fiber, fines and fillers;
- reduced cost of water heating;
- environmental compliance;
- reduced consumption of chemicals;
- reduced wastewater treatment costs.

The problems arising from water reuse are broken down into three general classes: those arising from:

(i) the presence of higher levels of suspended solids;
(ii) accumulation of dissolved solids; or
(iii) increased retention of thermal energy.

In the mills these are seen as plugging, corrosion, scale, foaming, slime, sizing and color. With even greater water reuse in paper operations than now occurs, there may be additional difficulties that have not yet been experienced

Difficulties that seemed to arise first were those associated with suspended solids build-up and the subsequent plugging of shower nozzles, small lines and felts. Suspended matter may also lead to deposit formations that may be of biological and/or non-biological nature. An intensification of biological slime difficulties may result as a consequence of more intensive water reuse practices.

The build-up of suspended solids is influenced by first pass retention, performance of filtration equipment such as save all and in-line filters and other factors including the fraction of material rejected by stock cleaning systems, fines and ash content in the furnish. Higher suspended solids are of concern in terms of deposits, lowered filtration capacity of the save all and plugging.

Dissolved and colloidal material present a more serious problem than suspended solids do. After long periods of running under conditions of low fresh water use, the problems of scale (carbonates and silicates) and corrosion (sulfates, chlorides, Fe^{2+} and Al^{3+}) emerge which are caused by dissolved inorganics, anions, and cations. Also brightness reversion (Fe^{2+}) can be caused by dissolved inorganics. Higher dissolved organics content result in higher bacterial growth in the system, possible odor in paper, high BOD and colour in effluents. With very high degrees of recirculation the concentration of dissolved material increases to a point where the wet-end chemistry of the papermaking system may be affected and difficulties with foam and sizing begin to occur.

Higher than desired retention of thermal energy is a concern in terms of sheet formation, internal sizing and vacuum pump capacity. In cases of neutral or alkaline sizing higher pH and higher temperature are favorable conditions for bacterial growth. Closed systems also force more unretained material back into the papermaking process than open systems.

3. Internal Purification

Internal treatment of process water was originally introduced in order to retain otherwise lost fiber and filler, which had a positive effect on the process economy. Further development on the separation of solids from the water lead to high quality “clear filtrate” (i.e. white water clarified with a saveall disc filter), which could be used as shower water in the wire section. However, clarified white water still contains organic and inorganic substances, which can cause various problems as discussed earlier. Some of these problems can be prevented by adding chemicals, such as biocides and dispersants, or elevating temperature above 50 °C or maintaining pH between 8.5–9. The use of chemicals, however, always carries a risk of eventually mixing up the delicate wet-end chemistry of the paper machine and in most cases the two latter mentioned methods are also impossible.

The choice of method for internal water treatment has to be done based on the quality demands of the treated water. In practice, it is necessary to know which components should be separated in order to make the water reusable; is it necessary to remove only suspended solids or suspended solids and colloids or all components from the water? The choice of method follows these requirements. A coarse treatment classification can be made based on the treatment result obtained. These are separation of:

- fiber, leaving pigments and other fines in the water;
- suspended solids giving clear water;
- colloidal substances;
- dissolved substances;
- inorganic salts.

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Biographical Sketch

Jutta Nuortila-Jokinen studied Polymer Chemistry at Helsinki University where she obtained her Master of Science in Polymer Chemistry in 1988. She came to Lappeenranta University of Technology in 1987 and has since worked in the Laboratory of Membrane Technology and Technical Polymer Chemistry as Research Assistant, Researcher and Associate Professor. She continued her studies in Technical Polymer Chemistry and obtained her doctorate in 1997. Her doctoral thesis dealt with the use of membrane filtration as a method for internal purification in the closed circuits of the pulp and paper industry ("Choice of optimal membrane processes for economical treatment of paper machine clear filtrate"). She then joined the Cleantech 2000 project (1997-2000) as Research Professor where she was involved in research in the area of water reduction in the pulp and paper production and membrane technology in particular. In 2000 Dr. Nuortila-Jokinen obtained a five-year office as Senior Fellow from the Academy of Finland and was also appointed as Docent in Membrane Technology in the Pulp and Paper Industry at Lappeenranta University of Technology. Doc. Nuortila-Jokinen has published about 60 scientific papers and has lectured at about 50 international conferences and scientific courses. She is a member of the European Working Party on Membrane Science. She has been a referee for many scientific journals and conferences. She has been leading several projects concerning membrane filtration in the pulp and paper industry, and she is actively co-operating with the related industry.