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Minimum-impact Mills State of the art in Separation Technology for the Pulp and Paper Industry

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1. Instroduction

During the last decade the paper industry has focused a great deal of attention on trying to reduce fresh water consumption in the mills. Recycling of water has become a must, but complete recycling without treatment or only partial purge is not feasible because of the accumulation of harmful dissolved materials inside the plant. This may lead to pitch problems in the paper machine and dark specks on paper. It is obvious that for recycling and reuse of water the potential for including membrane separation process is great. There are at least three potential membrane applications in the pulp and paper industry1.

1) Effluent treatment of mechanical pulp mills using ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) technology
2) Incremental kraft recovery and caustic soda production through electrolysis of weak black liquor
3) Producing of bleaching chemicals using bipolar membrane electrodialysis

The theoretical background and operating principles for the various membrane processes can be found in several textbooks and will not be described in the following sections. Fouling is usually a big problem for these applications. The reduction of fouling is therefore always in focus for improved separation properties. Fouling is discussed briefly in the following sections on Pulp and Paper.

2. Current Applications

Membrane applications in the pulp and paper industries today are mainly aimed towards the challenges of discharge treatment of the mills. Recycling and closing of internal water loops are quit complicated, and there are few standard rules for process solution. Ultrafiltration (UF) and reverse osmosis (RO) membrane for the treatment of mechanical pulp mill effluents and for water reuse are specially in focus.

However, these modules are getting increased competitions from nanofiltration (NF) membrane which naturally will have a higher retention and still an acceptable flux-this is discussed more closely in the following section "Novel Developments". Special membrane modules suitable for the pulp and paper industry have been developed, and integrated solutions with various types of filtration are today in operation. The membrane filtration has proved to be an economical and energy saving solution when good engineering is applied for the process solution and cleaning operation routines. Especially in Canada and the Nordic countries membrane installations of various kinds are today in operation in the pulp and paper industry.

Fouling and process conditions such as temperature and pH are of major importance and must be addressed separately for each process solution.

The major constituents of mechanical pulp mill effluents are various suspended solids, wood resin, lignin fragments and hemicelluloses as well as smaller molecular weight components such as sodium sulfite and sulfate salts. The performance of the membranes are thus evaluated by determining the reduction of certain measureable parameters in the feed solution such as chemical oxygen demand (COD), total organic carbon (TOC), total solids (TS) lignin, etc. In general, the following removals are expected for white water2.

- UF : 100% of TS, colloidal and bacterial matter ; 10-50% of COD ; in principle non- removal of salts (<10%)
- NF : >95% of TOC; >65% COD (UF+NF>80%) ; 20-50% sodium ; removal of Cl and SiO2 depends on bounding to organic matter
- RO : >95% COD and all salts

A main point to notice is that with UF-membranes the salts will go through with the water, which this is not so for the RO-membranes. The RO-membranes have smaller pores for added selectivity where only water goes through, and will therefore demand higher feed pressures (3.5-5.5 MPa or 500-800 psig). In the UF, NF and RO-systems, both the chemical nature of the membrane surface and the composition of the feed stream the permeability and selectivity characteristics of the membrane.

Studies done at Paprican Institute in Canada by Paleologou et al1 document that an ultrafiltration membrane with a membrane flux of 140 L/h m^2 or higher and with low concentration of solids (about 1%), will be more economical than vapor recompression, evaporation and freeze crystallization. It is proposed that the effluents should first be pre-treated through an approach such as settling, screening and flotation to remove suspended solids then followed by recycled back to the mill for reuse. The earlier UF-modules are of the tubular type, while during the last decade, the cross-rotational filter (CR-filter) has become increasingly popular due to a more compact module and high flux. The CR-filters were mainly adapted for the treatment of bleaching effluents and white water as well as concentration of coating color from wash water2. The CR filter (see Figure 1 for illustration) was developed by Raisio Flootek & Engineering around 1990. It can be installed alone or in a series with NF/RO units. A combination of CR filter and NF/RO reduces fresh water consumption and thus the effluent discharge considerably. The CR filter is made up of filter plates (UF-membranes) stacked on top of each other and with rotor blades in between (on feed side). With the help of a throughgoing shaft propelled by an electric motor, the rotors move the waste water at high speed parallel to the membrane surface. Due to high-shear forces and low pressure difference, only a thin layer of contaminants forms and the filter is virtually self-cleaning.The filtrate is removed from the adjunctant compartment2. There should be a prefiltration of the waste water stream before it is fed to the CR-filters, taking the particle size down to appr. 150㎛. A principle flow sheet for a combined UF- and NF-system is shown in Figure 2[2].

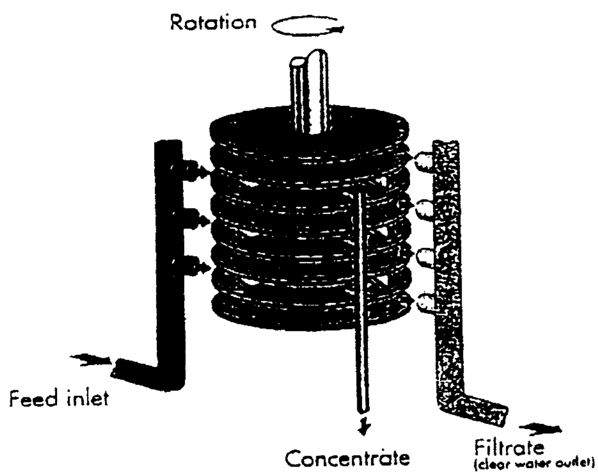

Figure 1. Membrane filter for application at pulp and paper mills. Illustration of the cross-rotational filter (CR) by Raiso Flootek Ltd2.

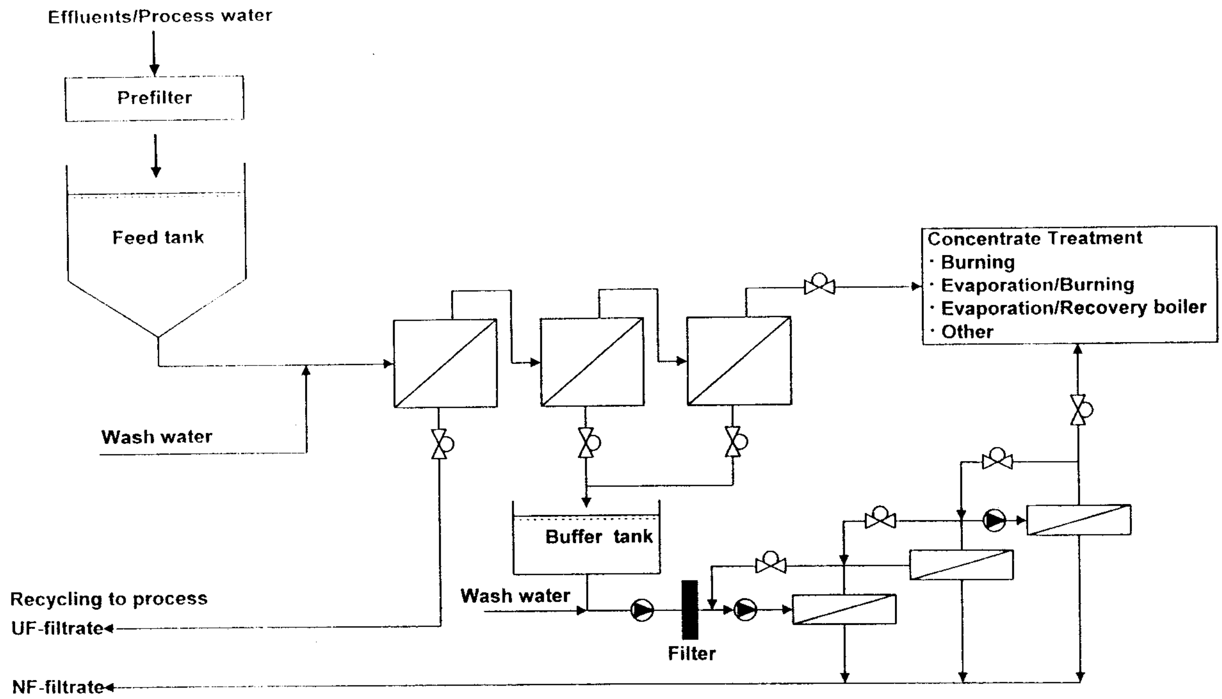

Figure 2. Principal flowsheet of combined ultrafiltration and nanofiltration units for waste water treatment at paper mills (Raisio2)

An alternative to the CR-filter is the vibratory shear enhanced process (VSEP) where the membrane leaf is moved in a vigorous vibratory motion tangential to the face of the membrane. The feed slurry moves at an almost leisure pace between parallel leaf elements. The shear waves induced by vibration of the membrane repels solids and foulants from the surface giving free access for liquid to the membrane pores. The commercial module for the VSEP consists of an array of parallel leaf membrane discs separated by gasket, and spun at high speed in a torsional oscillation. Unlike cross-flow filtration, almost 99% of the energy input is converted into shear at the membrane surface. A variety of materials can be used in range of pore sizes from RO and UF to typically MF-membranes(Scott). The principles of construction of the VSEP-module is illustrated in Figure 3.

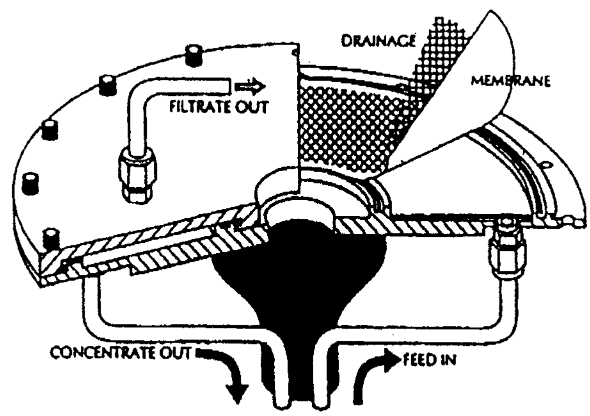

Figure 3. Membrane filter for application at pulp and paper mills. Schematic layout of the vibratory shear enhanced precess (VSEP) filter. (Reprinted from Scott, Handbook of Industrial Membranes. Copyright© (1995), p. 425, with kind permission of Elsevier Science)

3. Novel Developments and Potential

a) Effluent Discharge

The main effort of pulp and paper industry today is treatment of effluent streams in order to use water and recover valuable chemicals. Environmentally the aim is effluents closed systems, and in order to reach this goal, membrane technology has a large potential.

UF-membrane represent the majority of modules in use today, but nanofiltration (NF) membranes are receiving increased attention due to higher retention and still an acceptable flux. These two main type of separations with various types of membrane materials were tested out in the laboratory by Nuortila-Jokinen and Nystrom3 where it was found that in the nanofiltration the membrane structure and the feed pH affected the results the most, but on a whole, very good results were obtained in general by NF--membranes. Fouling was the main problem with UF-membranes. The possibility of pre-treatment with respect to parameters like TOC, COD and TS was obtained with NF when no pre-treatment was done.

In another study reported by Manttari et al.4 different membrane were tested for treatment of the effluent from a thermochemical pulp plant and a paper machine. The reduction in TOC, COD and TS were between 50 and 60% with UF-membranes and even better with NF-membrane (more than 80%) Chloride ions were not retained by either; these were however retained by RO-membranes, but, for this purpose the RO-membranes had too low a permeability for industrial scale application.

The efficient use of UF-or NF-membranes to purify the effluent from paper mills and reuse the water has however been well documented. Thus these membrane units will, in the future, become a standard unit operation module. In each case the composition of the effluents must be carefully considered in order to use the right type. Rosa and dePihno5 have evaluated four different types of UF and NF-membranes for effluent streams with organochlorinated matter and color for two different bleaching sequences. The highest removal of TOC and color achieved by ultrafiltration was 72 and 92% respectively; while more than 90% removal of TOC and total removal of color was achieved with the nanofiltration membranes. Considering the development of membrane biofiltration, it is reasonable to believe that, in the future, these combined membrane processes will also find use in the purification of the effluent stream in pulp and paper industry. This is already implemented at some plants; for example at the Kirkniemi Mill in Finland where they are using both biological waste water treatment, ultrafiltration (CR) modules and nanofiltration in the waste water treatment.

The development of better module design, optimized module configuration and resistant membrane material is continuously ongoing to reduce fouling and wear due to tough process conditions. A novel method under investingation to reduce fouling is the use of ultrasonic fields to control the fouling by eliminating the gel layer.

Experimental tests clearly show that flux will depend on the ultrasonic frequency and the output power6. The method is not yet sufficiently documented, but is found to be very interesting ; and results are reported from applied tests both for pulp and paper effluent stream and oily waste water. Another technique described by Jonsson et al.7 is to reduce fouling by applying "backshocks" to the membrane.

b) Increased Caustic Soda Production

By using membrane electrolysis there is a great potential for increased caustic soda production from recovery of the weak black liquor in kraft mills. The chemical recovery system is often considered to be the bottleneck of the kraft pulping due to its high capital cost. In the conventional recovery systems the sodium and sulfur are recovered as sodium carbonates and sodium sulfide and organics are burnt for steam generation. A recovery process based on electrolysis and a cation selective membrane will recover the sodium as sodium hydroxide.

An example of the integrated membrane process is shown in Figure 41. The proposed solution will take a portion of the weak black liquor (WBL) into an electrolysis cell where pH is brought down to just before the precipitation of lignin, while at the same time high quality caustic soda is produced. As can be seen from the figure, this solution will reduce the size of the process steam going to the multiple effect evaporation. The main challenge is here, as in many industrial process streams, to document durability of the membrane over time.

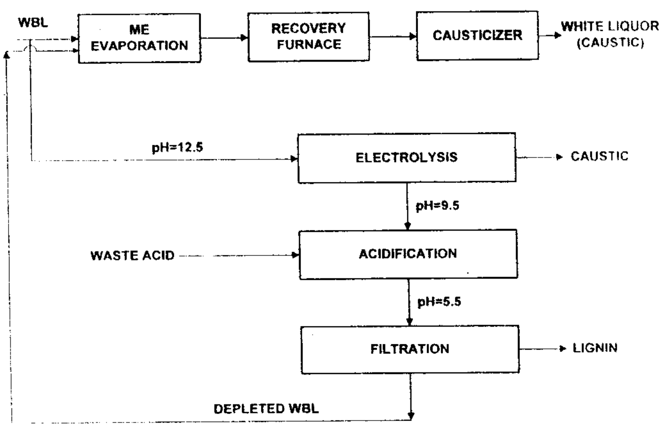

Figure 4. Simplified flowsheet for an integrated membrane process for a proposed incremental Kraft recovery process based on the electrolysis of weak black liquor (WBL= weak black liquor, ME Evap.=multiple effect evap.) (Paleologou1)

c) Recovery of Chemicals

- by the use of Bipolar Membrane Electrodialysis (BME)

The consumption of chloride in the pulp and paper industry is decreasing because of concern about the environmental effects the chlorinated compounds may have. As caustic soda production is currently linked to chlorine production and the demand for sodium hydroxide has remained high, there is a need to find cost-effective approaches for saving or producing caustic soda1. One such method is bipolar membrane electrodialysis (BME). Using this technology, chemical used in bleaching such as caustic and an acid may be produced on-site from a process stream, a waste stream or from water soluble salts. This is schematically illustrated in Figure 51. If a salt solution such as sodium chlorate is fed between the first bipolar membrane and cation-selective membrane, then the positive ions will migrate towards the negative cathode and will "pick up" hydroxide ions produced from dissociation of water within the second bipolar membrane. Thus chemicals like NaOH and HClO3 are recovered. The NaOH may go to bleaching and the HClO3 to a modified chlorine dioxide generator. Several papers are presenting results from research within this field8,9,10 ; purity and current efficiency. The technology has a great potential for the pulp and paper industry, but still there seems to be a way to go before these bipolar membranes are proven technology. Thompson et al.8 has examined the economics of integrating BME into kraft mill operations for on-site productions of caustic and sulfuric acid from sodium sulfate; a by-product from chlorine dioxide generators. The economics were analyzed for a base case in which the acid and base were both credited.

However, the economics of a BME-solution will to a large degree depend on membrane lifetime and cost.

- by the of Membrane Electrodialysis

In the kraft process black liquor is burnt to

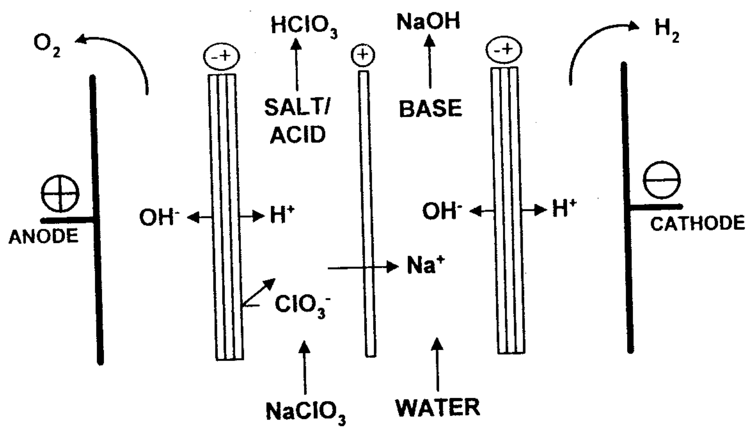

Figure 5. Illustration of a bipolar membrane electrodialysis unit cell for the generation of acid (chloric acid) and base (sodium hydroxide) from salt (sodium chlorate). (Paleologoul)

recover and reuse active pulping chemicals. Heavy loads of dust enriched in chloride and potassium are produced, and collected in electrostatic precipitators (ESP). The dust may then be dissolved in a diluted sulfate solution and feed it to a membrane electrodialysis unit for reuse and recovering of valuable components. The products from the electodialysis process at a diluted (chlorine depleted sulfate/carbonate) solution which may be recycled back to the black liquor, and a concentrated aqueous chloride solution which may be routed to waste water treatment or used in chlorine production for the bleach plant. Good documentation for the economical and efficient removal of chloride from dissolved dust coming from the electrostatic precipitator (ESP) in the kraft process, is given by Pfromm11. In the described process (see Figure 6) it is emphasized that no leaching or pre-treatment of the ESP was needed for successful long-term chloride separation experiments with actual mill materials.

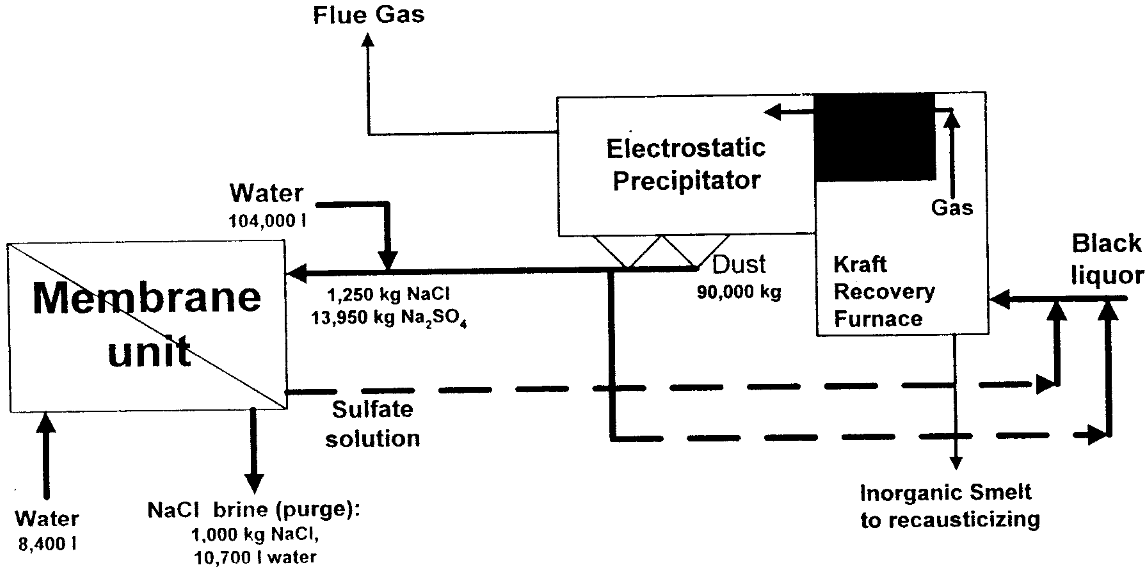

Figure 6. Example for application of electrodialysis to remove chloride from the Kraft process. Electrostatic precipitator dust is dissolved, dechlorinated and recycled to the process (basis : typical daily load of 1000kg NaCl is removed). (Pfromm11, reprinted from Member. Techn., 89, p. 7, Copyright© (1997) with kind permission from Elsevier science)

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