EFFLUENT-FREE PAPERMAKING: INDUSTRIAL EXPERIENCES AND LATEST DEVELOPMENTS IN THE GERMAN PAPER INDUSTRY

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Abstract

Thanks to multiple recirculation of process water, the German paper industry has succeeded in decreasing the specific fresh water demand from an average of 50 m³/t thirty years ago to 13 m³/t today. Although the increasing closure of white water loops creates many problems, it is bound to be part of the German paper industry's ongoing development. Since a few years, in the production of packaging paper, two paper mills are running with a totally closed water system including different process water treatment plants as kidneys.

This paper presents a comprehensive survey of the pros and cons of closed process water systems followed by significant examples of effluent-free production of corrugating medium and test liner. Additionally, operation experiences and economic aspects are discussed.

Keywords

Closed water system, Kidney technology, Papermaking, Process water

Introduction

Water is a most essential, indispensable material in pulp- and papermaking since the early days of this technology. In the beginning of industrial papermaking 200 years ago, paper was produced with high specific fresh water consumption of around 500 m³/t paper. For economical and, in the last decades also for ecological reasons, an increasing proportion of white water from the wet end of the paper machine was recovered and reused as process water. This technological development was only feasible thanks to the increasing closure of white water loops.

This contribution deals with the development of fresh water demand followed by a discussion of the pros and cons of totally closed, effluent-free process water systems as experienced in the paper industry. The current situation in the German paper industry is shown with reference to two paper mills which have established biological treatment plants as so-called kidneys in their effluent-free process water systems.

Water Management in the German Paper Industry

According to **Fig. 1**, the decline of the specific waste water volume was significant in the past 30 years, starting at about 50 m³/t paper produced and approaching almost 10 m³/t paper in the year 2001. This development was mainly driven by economical forces represented by the German Effluent Tax Law which came in force 25 years ago. Paper mills have to pay a certain fee per unit of effluent pollution calculated using parameters such as suspended solids, COD, toxicity against fish and heavy metal content (such as Cd, Cu, Cr, Hg, Ni) of the mechanically and biologically treated waste water. Fortunately, in the case of the paper industry, the tax-like financial burden is only affected by residual suspended solids and residual COD which is in the range of 0.5 to 3 kg O_2 per ton of paper produced.

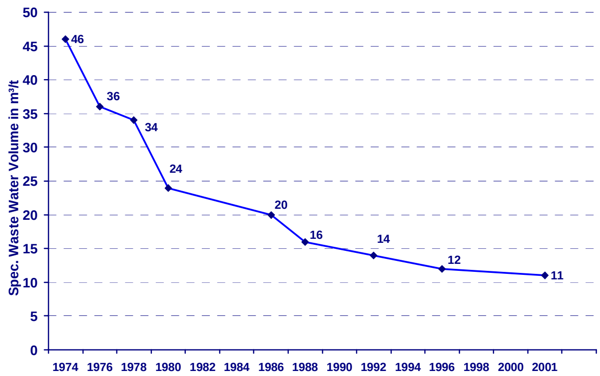

Fig. 1: **Average specific waste water volume of the German paper industry**

Fig. 2 represents the specific waste water volume per ton of paper produced with reference to the most important paper grades in the segments of graphical papers and specialty paper. The specific waste water volume of modern paper mills is in a range of 5 and 22 m³/t of paper with the exception of technical and specialty paper mills which consume up to 100 m³/t on an average of 40 m³/t. In older mills, the specific waste water volume can be higher due to suboptimal process design.

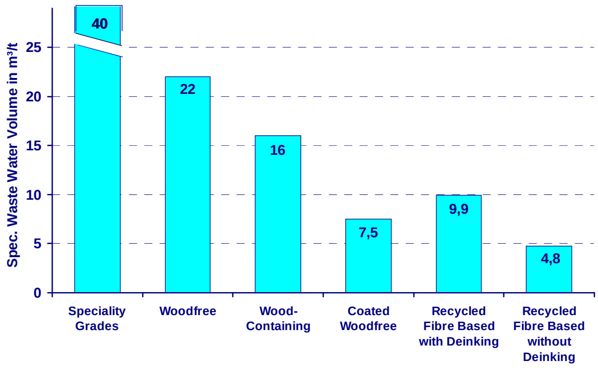

Fig. 2: **Spec. waste water volume of different paper grades in Germany (2001)**

Fig. 3 shows the different types of effluent discharge with reference to the tonnage of paper and board produced today – with a volume of 20 million tons. Before the year 1963, the effluent was only treated mechanically by sedimentation or filtration followed by a direct discharge into the receiving water. Nowadays, there exist five different procedures of discharge:

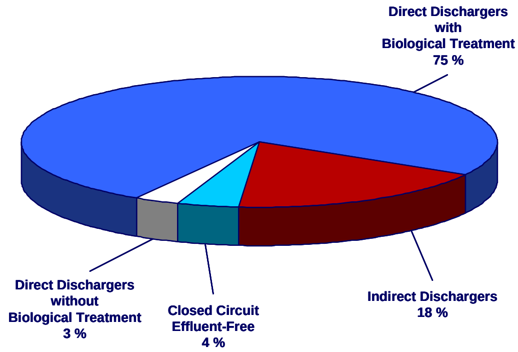

Fig. 3: **Type of effluent discharge in the German paper industry (2001)**

- Direct discharge of mechanically and biologically purified effluent into the receiving water (75 % according to paper production).
- Direct discharge of mechanically but not biologically treated effluent into the receiving water (this refers mostly to very small mills) (3 %).
- Indirect discharge of mechanically pre-treated effluent which is then biologically purified in a municipal multi-user treatment plant before entering the receiving water (18 %).
- A procedure in which there is great current interest is the effluent-free or zero-effluent paper mill with a totally closed process water circuit. In this case, the circulating white water has to be treated internally by means of kidneys to control the performance of the total water system and the runability of the paper mill (4 %).

Totally Closed Process Water Systems - Principle

Environmental and economical pressures are leading to the closure of mill water systems. This process started in brown paper mills in Germany and France producing testliner and corrugating paper from recovered paper and is now slowly spreading to the producers of newsprint, printing/writing and coated. When taking the design of a totally closed water system into account, one has to be aware of the potential risks. The primary risks are corrosion, emission of odorous compounds, increased slime formation, reduced retention, increased consumption of additives, formation of deposits, runability problems, reduced product quality, and increase of complexity of the papermaking process.

Some of the features can be controlled more easily, some others are rather demanding such as the precipitation of calcium carbonate which enters the process in a steady flow via recovered paper. This precipitation can lead to the plugging of shower nozzles and deposits in pipes and on wires, felts and press rolls. Key corrosion sources include chlorine- and sulphur-containing mill chemicals. In order to minimise the risk of corrosion at low fresh water consumption, chloride- and sulphate-containing chemicals should be avoided. Another corrosion risk arises from biological anaerobic activity at the mill which also contributes to the formation of unpleasant smell in the mill's atmosphere and the paper produced as well. Under anaerobic conditions sulphates are reduced to hydrogen sulphide.

On the other side there exist some benefits of an effluent-free process water system. The fresh water consumption, reduced to an absolute minimum of 1.5 m^3/t paper, results in reduced costs for fresh water treatment and in the avoidance of waste water discharge and its costly treatment. Thanks to the closed water loops the receiving water of a paper mill is not affected by chemicals which would leave the mill even in the case of the emission of well-treated waste water. At the same time the river or lake at which a zero-effluent paper mill is located will not experience any thermal load. One of the most significant benefits of a totally closed process water system refers to the fact that no waste water discharge fee has to be paid to the authorities, as would be the case in Germany. Furthermore, a zero-effluent paper mill could be placed at any site and would not require a receiving water with a sufficient flow. Reduced fresh water consumption increases the mill's white water temperature which improves water drainage at the forming section and gives higher solids concentration after the press section. This results in a reduction in the amount of drying energy.

Fresh water resources may also be limited or water consumption may be restricted due to some other reasons such as the volume and the quality of receiving water which is also used as fresh water supply. Special solutions may be needed due to limitations on fresh water supply or effluent loads, high water costs, or space requirement. Mills with such limitations would gain distinct benefits if their process could be effluent-free.

Fig. 4 shows the simplified scheme of a completely closed water system in a paper mill which is equipped with a stock preparation plant and a paper machine as the core equipment. The white water loops are based on the short circulation and on the long circulation of clarified white water from the wire and press section reused for dilution in the stock prep and as shower water in the wire and press section. Fresh water is required for that volume of white water which is evaporated by the dryer section and lost via the solids of the save-all if not completely reused in the stock prep.

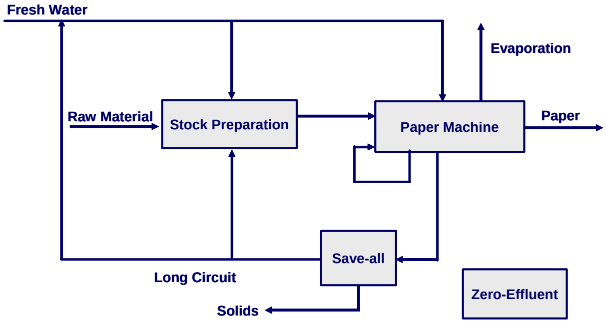

Fig. 4: **Totally closed process water loop without integrated purification systems (kidneys)**

Such an effluent-free water system without any purification would run into severe problems caused by the high concentration of dissolved organic and inorganic substances (e.g. carbohydrates contributing to COD and bad smell and salts contributing to conductivity).The handicaps can be overcome by the installation of kidneys in the closed water systems (**Fig. 5**). These kidneys guarantee an advanced and effective purification of the clarified white water aiming at the removal of dissolved organic matter (which means a significant reduction of COD) in the first place and of dissolved inorganic matter (which means partial reduction of salt content) in the second place. Due to the mode of operation of kidneys most or even all problems of a totally closed process water system can be controlled in the long-term as far as corrosion, odour emissions, runability problems and deterioration of product quality are concerned.

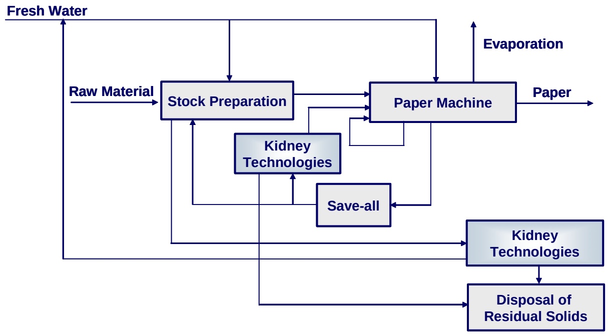

Fig. 5 **Totally closed process water loop with integrated purification systems (kidneys)**

There are several kidney technologies available on the market today. The most common technology comes from state-of-the-art of traditional waste water treatment in terms of biological processes, either anaerobic or aerobic or as a combination of both. Outside of Germany, the membrane technology is a more favourite process which, however, requires a white water clarified to a very low solids content to avoid any plugging of the membranes. In the case of flocculation and precipitation, the water system has to be loaded with additional organic and/or inorganic chemicals. Evaporation might be only feasible when cheap energy is available. A suitable process is based on ozonation and bio-filtration, beneficial for a rather clean white water.

Effluent-free Process Water Systems – Two Realised Cases

The German paper industry was globally the very first which established totally closed process water systems starting already in the year 1973. These mills of the first generation were not equipped with any kidney technology apart from a simple clarification for the separation of solids-free white water and solids to be reused as fibres and fillers. In the short-term, the water system closure runs into problems due to odour emissions and corrosion of the equipment. Therefore, half of the former mills reopened the water circuit to a specific fresh water consumption of about 5 m³/t paper produced. The other mills which continued with the closed cycles had been forced to apply a large amount of biocides in order to control the intensive slime formation caused by the degradation of carbohydrates.

In 1995, the first completely closed mill started in Germany with biological reactors as kidneys in the water system treating a part-stream of the circulating white water volume (one third of the total white water volume is permanently treated mechanically and biologically). This mill is an excellent example for a stepwise progress realised by engaged engineers and a top management which persisted with a consistent strategy in order to master the challenges of a new procedure. Today eight paper mills producing brown packaging papers (testliner, medium) are operating with a closed system. So far, two out of the eight mills are equipped with kidney technology.

Zülpich Mill of Kappa Paper

One of these mills located in Zülpich (close to Cologne) belongs to the Dutch Kappa group and produces 410,000 tons per year testliner made of recovered paper. In the time between 1975 and 1995, the production was realised with a zero-effluent system but without any kidney technology. Because of corrosion and odour problems, in the early 1990s the management decided to invest in an internal white water treatment plant in order to reduce the load of dissolved organic substances in terms of the chemical oxygen demand COD. The implemented kidney arrangement is shown in Fig. 6. Impurity concentrations of the circulating white water are high due to the accumulation in a totally closed system characterised by a COD of more than 30,000 mg O_2/l. Therefore, the conditions are ideal for anaerobic water treatment performed in UASB-reactors in the first biological stage followed by two aerobic units in the second stage. This requires an efficient solids separation before the biological treatment in order to avoid plugging of the anaerobic reactors. Secondary clarification is also required because of an excess of bio sludge produced in the aeration tanks. The final treatment of the biologically purified water is carried out by a sand filter which achieves a minimised solids content below 20 mg/l, a prerequisite for an undisturbed and plugging-free shower operation. The multi-stage purified bio water is now ready to be used for cleaning and dilution purposes. (Diedrich et al., 1997)

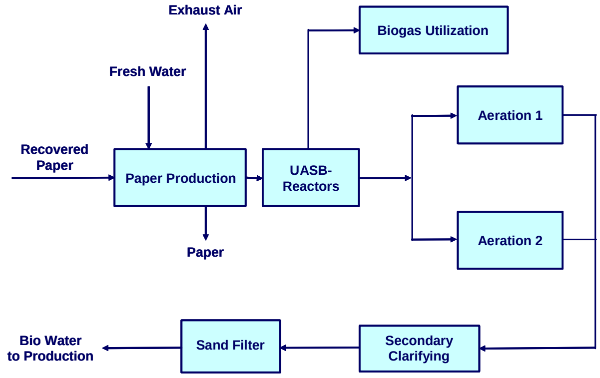

Fig. 6: **Effluent-free process water system of Zülpich Mill of Kappa Paper, Germany**

Fig. 7 demonstrates the success of the investment in the internal treatment plant in the Zülpich Mill of Kappa Paper. The figures shown are related to the operations before and after the kidney arrangement. The most surprising parameter refers to the electrical conductivity which is reduced from 9 to 5 mS/cm despite the fact that no special kidneys for salt removal has been established (no membrane technology was integrated). Some of the hardness salts precipitate in the biological treatment plant resulting in a salt concentration at a reasonable level as is evident with the calcium and sulphate concentrations whereas the chloride concentration, being at a low level, is not affected. Furthermore, the organic substances (in terms of fatty acids) are reduced in a quite effective manner. Finally, the most significant improvement is the reduction of COD by 80 %. In summary, the chosen kidneys have been proven reliable for almost ten years. It took a longer period of time before other paper mills plucked up courage to follow their example which needs much expertise to fulfil the requirements of a sustainable, trouble-free operation.

Parameter	Unit	Before Start-Up of „Kidney“	After Start-Up of “Kidney”
pH		6.3	7.2
Electrical Conductivity	mS/cm	9.0	5.0
COD	mg/l	32,800	6,400
Water Hardness	°dH	375	70
Calcium	mg/l	2,650	505
Sulphate	mg/l	1,350	375
Chloride	mg/l	430	485
Acetic Acid	mg/l	6,300	890
Propionic Acid	mg/l	600	355
n-Butyric Acid	mg/l	350	< 20

Fig. 7: **Effect of water system closure on the quality of process water (Kappa Zülpich)**

Düsseldorf Mill of Julius Schulte Söhne

The most recent establishment of a zero-effluent process of another paper mill with biological kidneys will now be discussed. The medium-sized and privately owned paper mill Julius Schulte Söhne was founded almost 120 years ago outside of Düsseldorf in the open countryside. Nowadays, the mill is located in the centre of a residential area. This situation results in an extremely limited space which is a significant hurdle for any machine investment including a waste water treatment plant. There are operating two Fourdrinier machines which produce 90,000 tons per year of recycled fibre based core board. Before the decision was made to close the water system completely, the specific waste water volume was 3.2 m³/t paper corresponding to a specific fresh water consumption of less than 5 m³/t paper. The paper mill was an indirect discharger of its effluent which was passed into Düsseldorf's municipal sewer system together with other effluents. This includes a biological treatment before discharge to the river Rhine.

The decision to close the mill's water system was stimulated by the effluent fee of 1.50 Euro/m³ for the use of the town's treatment plant. In the future, there might be charged an additional fee for the used volume of ground water taken from the mill's very own wells. Due to the limited mill area (20,000 m²) the space demanding kidney technology of the Zülpich paper mill of Kappa could not be used. On the other hand, other space-saving process technologies for white water treatment, e.g. ultra- and nanofiltration or reverse osmosis, were technologically too elaborate for the mills objectives. (Bülow et al., 2003)

Fig. 8 shows the process configuration developed in cooperation with the Dutch company Paques BV which had developed a space-saving anaerobic reactor, the so-called IC (internal circulation) reactor. The process water is first clarified by micro flotation (not shown in the fig.) and then fed into a pre-acidification tank after its cooling in order to reduce the temperature to 38 °C. The anaerobic degradation takes place in the IC tower reactor. The biogas generated is desulfurised in an alkali washer. Therefore, odour problems due to the formation of hydrogen sulphide (H_2S) in the white water and resulting corrosion risks are under full control.

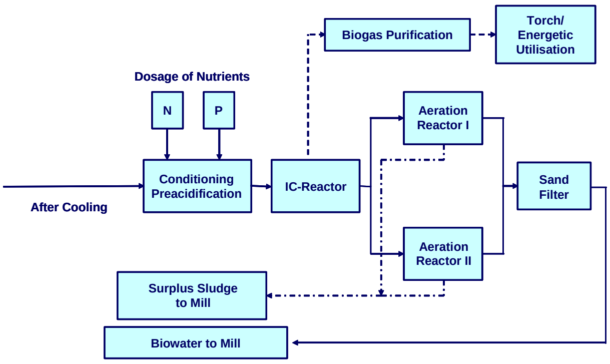

Fig. 8: Process water treatment plant at paper mill Julius Schulte Söhne, Germany

The aerobic part of the kidney plant consists of two aeration reactors into which compressed air is pumped resulting in the precipitation of calcium carbonate ($CaCO_3$) by stripping CO_2 with the effect that the pH-value is increased. The $CaCO_3$ slurry as well as the generated biomass are removed and fed back into the production process. The advantage of the aeration reactors in comparison to an activated sludge system is the fact that they can remove $CaCO_3$ sludge continuously. The last stage of the kidney technology discussed consists of a sand filter, to ensure a solids content in the treated bio water of less than 10 mg/l.

Fig. 9 represents the most relevant data of the whole treatment plant, starting with the hydraulic load, the COD load and the calcium load of the influent into the treatment plant. The variation of the loads is mainly affected by the recovered paper quality and the dosage of the applied chemical additives. The COD reductions of the IC reactor (40-60 %) and of the aeration reactors (10-30 %) are convincing as is also the impressive calcium elimination (50-90 %). The total COD reduction amounts to 70 to 85 %.

Influent Process Water Treatment Plant		
Hydraulic Load	m³/d	600 - 1,200
COD Load	kg/d	2,000 - 6,500
Calcium Load	kg/d	300 - 650
IC-Reactor		
COD Loading Rate	kg/m³d	15 - 40
COD Reduction Rate	%	40 - 60
Biogas Production	m³/d	200 - 1,400
Aeration Reactors		
COD Reduction Rate	%	10 - 30
Calcium Elimination Rate	%	50 - 90

Fig. 9: Data of the process water treatment plant at paper mill Julius Schulte Söhne

An even more specific insight is given in **Fig. 10** which demonstrated the stepwise COD elimination of the total treatment plant starting at a level of 3,585 mg/l. It comes down to 1,190 mg/l after the first biological stage (IC reactor) and to 830 mg/l after the aerobic stage. The residual 830 mg/l remains in the process water as inert COD which does not influence the papermaking process negatively.

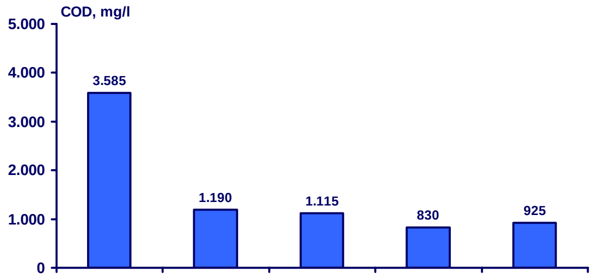

Fig. 10: **COD elimination in the process water treatment plant**

Fig. 11 shows the most important parameters which are affected by the water system before and after its complete closure. When comparing the figures before and after closure, one has to be aware that only one third of the mill's total white water flow is treated by the kidney technology. The figures referring to the situation after the system closure are mean values of both the treated and untreated part streams of the white water. This becomes particularly evident in the case of electrical conductivity which was almost doubled after system closure despite the fact that the conductivity of the treated white water is at the same level of the white water before system closure.

Parameter	Unit	Before Start-Up of „Kidney“	After Start-Up of “Kidney”
pH		6.6	6.6
Electrical Conductivity	mS/cm	2.7	5.1
COD	mg/l	5,070	4,150
Water Hardness	°dH	62	66
Calcium	mg/l	420	450
Sulphate	mg/l	360	475
Chloride	mg/l	215	920
Acetic Acid	mg/l	760	480
Propionic Acid	mg/l	330	305
Butyric Acid	mg/l	< 20	< 20
AOX	mg/l	0.34	0.54

Fig. 11: **Effect of water system closure on the quality of process water at paper mill Julius Schulte Söhne**

The chloride concentration, however, is significantly increased by system closure because there are no special measures taken to eliminate this anion f. i. by membrane technology. Other parameters such as COD, calcium and sulphate concentrations are kept almost constant, whereas acetic acid is partially degraded.

The ultimately positive results of the white water analyses are also reflected in the paper analyses. Strength properties of the paper have not been changed by system closure. There have been no customer complaints since closure that could be related back to the closed process water circuit.

The economical situation of the system closure in combination with the implementation of the multi-stage kidney technology is also a positive feature. The entire treatment plant investment costs were about 1.5 million Euro. Funding from the Federal Foundation for the Environment (which stands for external subsidising) amounted to 0.5 million Euro, of which 0.1 million Euro was to be spent on a comprehensive measuring programme before and after start-up of the plant. The net project costs of 1.1 million Euro can therefore be offset against the annual savings of 0.4 million Euro from the sewage user fee to be paid to the municipal effluent treatment plant.

So far, the kidney-based white water treatment technology has fulfilled the paper mill's expectations. As far as paper quality and exhaust air emissions (odour) are concerned, the closure of the white water circuit has not caused any negative effects. Paper production can proceed without using biocides while maintaining the same runability and production performance as before the complete water system closure. Furthermore, the consumption of chemical additives was also kept on the same level as before system closure.

Conclusions

The installation of closed, effluent-free white water systems with an integrated process water treatment plant in both German paper mills discussed has to be regarded as an innovative development in papermaking's history. Such a complex technology is proved to work successfully fulfilling the papermaker’s expectations to the greatest extent. One has, however, to be aware that further optimisation is required as is always the case with new technologies. The mill operations are more stable due to independent kidneys (biological purification units). The product quality is influenced in a positive manner due to less slime and deposit problems and better process stability. Chemical costs are reduced due to improved removal and degradation of impurities (dissolved organic and inorganic substances) from the paper machine water loop.

Congratulations are well deserved by the small number of papermakers who meet environmental challenges aiming at a considerable saving of fresh water. The kidney and closed circuit technology developed in a highly industrialised country makes even more sense in countries which suffer from ground or surface water shortage. It is, therefore, no surprise that the very last guests visiting most recently the German paper mills concerned and our Institute in Darmstadt came from paper mills which are located in South Africa and Australia poor in water resources.

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