Effects of Increased Closure Water-Loop Systems in Pulp and Paper Industry

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ABSTRACT

Water loop closure in paper mills always results in the accumulation of contaminants which may be classified into: fibre, fines and fillers, colloidal materials, high molecular weight dissolved components, and low molecular weight dissolved components. Water system closure results in the accumulation of non-process elements (e.g. Al, Si, K, Cl, Mg, Mn), suspended solids, dissolved solids, and other pollutants in the closed water system resulting in increased equipment corrosion, detrimental plugging, problematic scaling and deposit formation and can adversely affect the papermaking process.

This paper discusses the impacts of closing the water loop on water consumption and other benefits, and its problems like microbial growth, corrosion, explosions, interfering substances & their effects on production processes and product quality along with some suggestions to solve these problems.

Introduction:

Pulp & Paper industry has been facing the tightening water quality and volume discharge regulations. Development of new processes and other technical improvements have decreased the fresh water consumption over the years. The ultimate goal for the pulp and paper industry has been an effluent-free factory with no negative impact on the environment. By replacing fresh water with recycled water the mills have decreased the need for fresh water. It was shown in an analysis of an integrated paper mill that around 30% of the fresh water was used for sealing the vacuum system and for cooling purposes [1]. Rinsing and washing of the pulp consumed 30% and the last 40% was used for sprays and lubrication. There are different reasons why the mills have put significant effort into reducing their demand for fresh water [2]. For reducing the fresh water consumption, the effluent discharge limit was found to be the main reason [3].

Effluent free process water system has environmental benefits and can also reduce energy and chemical costs. Recycling of process water and closing the water loops have many advantages but some process and product quality issues are also associated with it. The problems associated with increasing recovery of water and closing the water loop system along with few possible solutions have been discussed in this paper.

Problems Of Increasing Water Recycling

Reducing fresh water by recycling increases the accumulation of detrimental substances. These detrimental substances are non-ionic and anionic dissolved and colloidal substances. Anionic trash is a subgroup of detrimental substances. They consume retention aid and thus decrease paper machine wire retention [4]. Detrimental substances can absorb or precipitate onto the surface of fibres, fillers and fines, which adversely affect fibre-to-fibre bonding, brightness, and accessibility of process chemicals. The sources of different detrimental substances are given in Table 1 [5].

Table 1 detrimental substance in recycled water

Detrimental substance	Source
Sodium silicate	Peroxide bleaching, deinking, recycled paper
Polyphosphate	Filler dispersion
Polyacrylamide	Filler dispersion
Organic acids	Pitch dispersing agents
Pitch	Fatty acids or resin acids from virgin fibres together with hydrolyzed sizing agents
Carboxy methyl cellulose	Coated broke
Starch	Recycled paper, broke, strength additives
Humic acid	Fresh water
Lignin derivatives	Kraft pulp, mechanical pulp, lignosulphonates from sulphite pulping
Hemicelluloses	Mechanical pulp
Fatty acids	Mechanical pulp
Stickies (adhesive residues, tapes, rubber like particles and hydrolyzed sizing agents)	Recycled paper

Thus, the key contaminants include ionic constituents, organic contaminants, “stickies and tackies” and suspended solids. Extractives analyses are performed to determine the loading rates of stickies and tackies (glues and adhesives) that enter the process water through recycling, especially in case of secondary fibres like OCC. Cycling up of stickies can lead to deposits and paper breaks resulting in machine downtime and off-spec paper. Sulphate levels had to be monitored due to the potential for $CaSO_4$ scaling (alum is added to the papermaking process). High sulphate levels also interfere with chemical treatment programs on the paper machine.

Organic dissolved and colloidal substances are excellent nutrients for microbial population and according to dissolved oxygen (DO) level in process water either aerobic or anaerobic biological activity cause decreased system cleanliness by slime and smell. Slime deposits by anaerobic activity propagate corrosion because of the release of hydrogen sulphide during the process. The associated problems are described below.

Microbial growth

Many of the problems appearing in a closed whitewater system are due to microorganisms. When the water system is closed, organic compounds accumulate in the whitewater and act as substrate for microbial growth resulting in odour emissions [4]. The growth starts 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 head box 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 shrinks the biofilm fragments and leaves a hole in the paper. This is of course deteriorating the product quality. These can be minimized by kidney technologies comprising biological, mechanical and chemical treatments. Biocides will control slime deposits and reduce odours. Although chemical biocides are the usual agents for treating the waters of pulp and paper mills, enzymes are increasingly seen as potential alternatives. Enzymes are potentially useful for biofilm control in that they are non-toxic in character and biological in origin but a more thorough understanding of their mode of action, limitations and increased synergistic effects obtainable when combined with other slime control chemicals is required [6]. Biofilms in paper machines comprise extra-cellular polymeric substances of microbial origin, fibres, inorganic precipitated matter and microbial cells. Enzymes degrading bacterial polysaccharides can have effects on the formation and integrity of the biofilm matrix, or to damage microbial cells, and they are potential tools in deposit control. Due to the structural diversity of the biofilm components, the combined action of several specific enzymes, possibly together with proteases is in most cases needed. The effect of enzymes on the runnability of a paper machine and the optimal treatment strategy must be evaluated on a case-by-case basis.

The whitewater system is very large with 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 created. When the oxygen is used up and there is no other electron acceptor as nitrate or sulphate, the anaerobic microorganisms start working. In this process, different volatile fatty acids (VFAs) 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 were 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 creates corrosive conditions [4]. It has been established that the corrosive nature of the environment in the whitewater increases with increased levels of different inorganic ions, such as chloride, sulphate and thiosulphate. The most aggressive whitewaters are those where the molar amount of chloride exceed that of sulphate. The metabolic activity of microorganisms can also lead to corrosion. In the whitewater under anaerobic conditions, VFAs like acetic acid, propionic acid and butyric acid are produced and they are all corrosive compounds. Another corrosive compound, hydrogen sulphide may also be produced under anaerobic conditions in the whitewater system.

Explosions

Explosions with deadly outcome have occurred in the past and have been reported in different paper mills [7]. Bacterial hydrogen production was known to be responsible for the accidents at few mills and was suspected at the other mills. Some 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 action of 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 or indirectly with the production process. These are of 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 [8]. Examples of such substances are adhesive residues, tapes, rubber like particles and hydrolyzed 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 hydrolyzed sizing agents form something called pitch. This can under certain conditions accumulate on the machine fabric or the press felt and has a negative impact on the paper making process [9,10].

Effects on Quality of Product and Production Process

Product Quality

There are a number of substances in the whitewater that affect both the production process and the quality of the paper. These compounds are usually lumped into two categories: dissolved substances and colloidal substances [11]. Dissolved substances could be lignans, polysaccharides and ions whereas colloidal substances are made up of lignin and lipophilic extractives. All of these compounds accumulate when the whitewater system is closed and this influence the production process and the final product [12]. Combined fungal-enzyme system has shown promise as one way of decreasing the detrimental substances present within a closed water system, while treatments with different enzyme preparations revealed that fungal laccases play an important role in the removal of white water extractives.

Only the tensile index slightly decreased whereas four other physical parameters were unaffected when the hand sheets of linerboard from recycled fibres and simulated recycling of the whitewater was used [13]. In their experiments they did not reach steady state concentrations for the inorganic compounds and they concluded that precipitation of some low solubility ions, such as calcium might eventually occur, which will interfere with the system.

Cations in the whitewater were shown to influence the paper strength [14]. 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 decreases the number of inter-fibre bonds, which will decrease the paper strength. A combination of wet end chemistry program and purification technique can be implemented to minimize the fresh water consumption and the discharge of contaminants. It is more feasible to stabilize and control the process and reduce the fresh water consumption to a minimum. As long as the paper quality is not affected, the remaining contaminants could be fixed on the web by wet end chemistry control [15].

It has been shown that the amount of *colloidal substances* in the process water, rather than the amount of dissolved substances, is critical for sheet strength [16]. Papermaking system closure increases the number of fines and organic and inorganic substances in process water. This can significantly reduce product quality and process efficiency. Closure of the system brings substantially less strength and increased light scattering. The quality of process water affected the strength properties of different grades of paper. However, in case of *TMP whitewater system*, dissolved substances such as lignans and polysaccharides reduced the paper strength whereas colloidal matter like lignin and lipophilic extractives reduced the paper porosity and optical properties [17]. Light absorption increases for both types of substances. There can be problems with increased concentrations of undesirable substances in effluents, chemical oxygen demand (COD), corrosion and runnability. Closing the paper machine whitewater system can cause *increase in temperature* resulting in higher rate of corrosion. This requires use of suitable material of construction - greater use of plastics as material of construction to avoid the corrosion.

Retention

There is also an accumulation of *anionic organic compounds* in the whitewater, which often are referred to as *anionic trash*. These compounds have a negative influence on the retention system. Several types of retention systems exist and it has been shown that nonionic retention systems were least affected by the accumulation of organic compounds whereas cationic systems were affected to a higher degree [18]. Pectinase enzyme has also been studied to reduce the effect of anionic trash and cationic chemical demand, especially in case of peroxide bleached mechanical grades [19]. The application of pectinase decreased the cationic demand of pulps containing BTMP or BPGW by 46% and 36%, respectively. This resulted in both mills being able to reduce usage of the cationic chemicals, including a strength agent, starch and coagulant. The use of pectinase in the mill using BTMP also eliminated the need for alum to reduce the cationic demand prior to application of a strength agent. Use of pectinase has generated considerable savings in cationic chemicals alone.

The closure of water circuits in recycled paper mills leads to the accumulation of dissolved and colloidal material in the process water. These compounds originate from the recycled paper used as raw material, and can be further specified as anionic trash, secondary stickies, pitch, microorganisms, odour components, salts and calcium hardness [20]. Typical negative effects of the presence of these materials can be: (i) influence on efficiency of papermaking chemicals, (ii) scaling problems, (iii) deposits of sticky material, (iv) slime growth, (v) odours in the product, and (vi) corrosion [21]. The recyclability of paper will deteriorate markedly unless these unwanted materials are removed effectively from the process water. The release of starch, which is present in the furnish, easily hydrolyses into glucose in the process water. In the warm and anoxic environment of the process water, the conditions are optimal for the conversion of glucose into butyric acid, lactic acid, propionic acid and acetic acid (together called volatile fatty acids, VFAs) by acidogenic bacteria. The presence in the process water of high levels of these VFAs is typical for zero discharge recycling mills. They are the main cause of odours in the product and can only be removed efficiently by opening up the circuit or by biological treatment. Anaerobic treatment can be especially efficient because it converts the VFAs into methane gas, which can be used as an energy source. The alternative treatment is by aerobic systems using oxygen. These systems convert the VFAs mainly into bacterial cells. Another important contributor to the waste paper furnish is $CaCO_3$, which is used as filler and coating. The VFAs present in the process water slowly react with $CaCO_3$ and produce CO_2, which leads to foaming and to gas bubbles in the paper fibres. More important might be the increase of dissolved calcium, which can cause scaling in the form of calcium resinate or gypsum. The sulphate required to form gypsum originates firstly from the waste paper furnish because of the use of alum for sizing, and secondly from sulphate pulping. During biological treatment, much alkalinity in the form of bicarbonate is produced, which leads to the precipitation of $CaCO_3$ when CO_2 is stripped out in an activated sludge plant. This inorganic material accumulates in the biomass flocks and thus calcium hardness is strongly reduced during biological treatment. In addition, biological flocks entrap a lot of fillers and fines present in the process water.

In the deinking mills, catalase enzyme is produced in the close water system during the metabolism of aerobic organisms and it catalyses the breakdown of hydrogen peroxide. The catalase enzyme has been implicated in the early problems associated with hydrogen peroxide bleaching in the pulp and paper industry, particularly with deinking processes [22]. Significant improvements have been introduced to control catalase production in deinking plants, notably the increase of peroxide introduction, the thermal treatment of the pulp or process waters and the addition of specific chemicals to deactivate or inhibit catalase.

Bleach plant closure will have major effect on sodium/sulphur balance. Most ECF and TCF bleach sequences will require the addition of sulphuric acid and caustic which, when recycled, will add significant amounts of sulphur and sodium to the liquor loop. In order to control sodium and sulphur levels, it may be necessary to replace caustic with oxidized white liquor and periodically purge sulphur from the liquor system, either at ESP catch or filtrate from acid stage of bleaching where sulphuric acid is added to adjust the pH [23]. The bleach plant effluent will also have problems due to build-up of inerts. In the case of mills that bleach with peroxide, transition metals such as iron, manganese and copper must be purged to avoid peroxide decomposition. These metals are reported to have an adverse effect on chlorine dioxide and also to promote the catalysis of highly oxidative free radicals, which attack cellulose. Under certain conditions, multivalent non-transition metals such as calcium, magnesium and aluminium can form precipitates, which may lead to scale formation in process equipment. Several techniques have been proposed for selectively removing these metals from the acidic bleach plant effluent. The closed cycle mills must establish an ongoing programme for monitoring metal concentrations at key points in the process. Metals intrusion must also be minimized by efficient debarking and other means.

Other effects

With machine closure, temperature and conductivity can increase and pH can fluctuate, upsetting the typical balance between wet end additives [24]. The accumulation of fines can also stabilize foam. Accumulated pitch and scale can block shower nozzles. Water closure will be a higher priority when heat and energy savings and reduced costs of treating incoming and outgoing water are high enough to offset increased operating difficulties. The impact of wet end chemicals on emissions of volatile organic compounds (VOC) must be considered in any strategy for machine closure. With reduced water consumption, equilibrium concentrations of soluble and insoluble materials are reached faster and the level of contaminants in the wet end increases. As most additives have an effect on the electrical charge of the wet end, measurements of conductivity and electrical charge can be useful. Typical loss of paper quality in closed systems includes: lower brightness, difficulties with internal sizing, loss of strength & tensile properties, and loss of bulk & thickness with the use of recycled raw materials.

The other production problem related to closure of the water systems is formation of stickies, pitch, white pitch and slime in the wet-end of the machine. If the slime is ruptured, parts of it can end up in the product as black spots or pinholes. In the worst case, a paper break can be caused. Under the slime layers, anaerobic bacteria can develop corrosion problems. In general, the conditions for bacterial growth are optimal. At the surface of machine parts, where the flow velocity of the process water is moderate, the bacteria attach by producing slime. There are several possible treatments for prevention or control of slime. The most effective method is closing the water system to such an extent that the process temperature increases to higher than 45°C. Above this temperature, the growth of slime-forming bacteria is strongly reduced. The most commonly applied method is dosing with biocides and/or dispersants, sometimes in combination with enzymes [25].

Potential Solutions

New solutions for water recycling include membrane filtration [26], biofilm processes and themophilic biological treatment [27]. Microflotation, biological processes and membrane filtration have all been used to close the water cycles of brown paper mills. Recycled fibre based multiply board mills use membrane filtration to reduce water consumption to 5 m^3/t but without the reuse of press reject water. A novel solution for zero effluent mills utilizes two independent kidney systems. A biological kidney is installed at stock preparation and high quality shower water and chemical dilution water is obtained by membrane filtration from paper machine clear filtrate. Treated water is recycled to stock preparation. Ultrafiltration can be used to remove microstickies and bacteria and to reduce cationic demand. Ultrafiltered water is suitable for high-pressure showers for fabric cleaning. Biological treatment has a much greater effect on BOD, COD and salt content. Despite this, biologically treated water has poor dewaterability. Currently the best mills utilize 7-10 m^3/t water without the use of advanced kidneys. A systematic approach to water resource management uses: a mill audit; conceptual design of potential scenarios for reuse and recycling; development of a steady state simulation model; and a risk and benefit analysis of proposed solutions.

To remove extractives and non-process elements from filtrates in chemical and mechanical pulp mills, a kidney technology system called NetFloc system was jointly developed at the MoDo, Domsjö mill by MoDo and Kemira [28]. The removal of extractives from the process filtrate made it possible to close up the bleach plant. The Domsjö mill was the first totally effluent free chemical pulp mill in the world. This would not have been possible without the NetFloc system. Nordic kraft mills, with interest in TCF and TEF bleaching, were expecting problems with elevated concentrations of detrimental components such as NPE. It is possible to remove metals by employing the NetFloc system as a kidney. The removal will improve the peroxide stability and the oxygen delignification. Removal efficiencies of more than 90% have been documented [29]. The addition of polyethylene oxide (PEO) to the filtrate in the NetFloc System causes extractives to react with the PEO to form pitch sludge, capable of easy removal by filtration. The limited market for the NetFloc system in sulphite pulp manufacturer led to considerable efforts to adapt the NetFloc technology to kraft mills and there are currently several NetFloc kidneys installed in kraft mills for the treatment of filtrates from oxygen delignification stages, from Q-stages and from the paper machine screen room, where kidneys are installed in kraft mills in different positions in the process.

Conclusions

Closing the water loop system gives various advantages to the pulp & paper mills. However, there are some limitations and problems, which need to be properly addressed to implement the closing of water loop to that extent only so that the product quality is not compromised and production process is not adversely affected. The so-called closed cycle mill will never actually be completely closed. In fact, there will always be the need for a continuous purge of dissolved solids as well as more conventional solid wastes such as ash, dregs and slacker grits. Even a zero liquid discharge mill will present serious technical challenges to prevent a build-up of undesirables, which would encourage corrosion or deposition. Process upsets will occur in a closed cycle facility just as surely as they do in a conventional mill. To be truly closed cycle, the mill must have the capability for containment and storage of all process spills, as well as the means for either returning the liquor or filtrate to the process or sending it on to waste treatment. State-of-the-art process controls and information systems will be mandatory for proper monitoring of critical process variables in a closed cycle mill.

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