



THE EFFECT OF pH CHANGE TO THE PGW PROCESS AND PAPER MACHINE'S RUNNABILITY

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ABSTRACT

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The main target of this thesis was to found out the effect of pH change to the pressure ground wood (PGW) process and paper machine's runnability. Thesis contains confidential background material.

Keywords: pressure ground wood, pH, dissolved and colloidal substances, runnability

TIIVISTELMÄ

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pH muutoksen vaikutus PGW-prosessiin ja paperikoneen ajettavuuteen

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Työn tarkoituksena oli tutkia pH muutoksen vaikutusta painehiokeprosessin kemiaan sekä paperikoneen ajettavuuteen. Opinnäytetyö sisältää luottamuksellista taustaineistoa.

Avainsanat: painehioke, pH, liuenneet ja kolloidiset aineet, paperikoneen ajettavuus

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1 INTRODUCTION

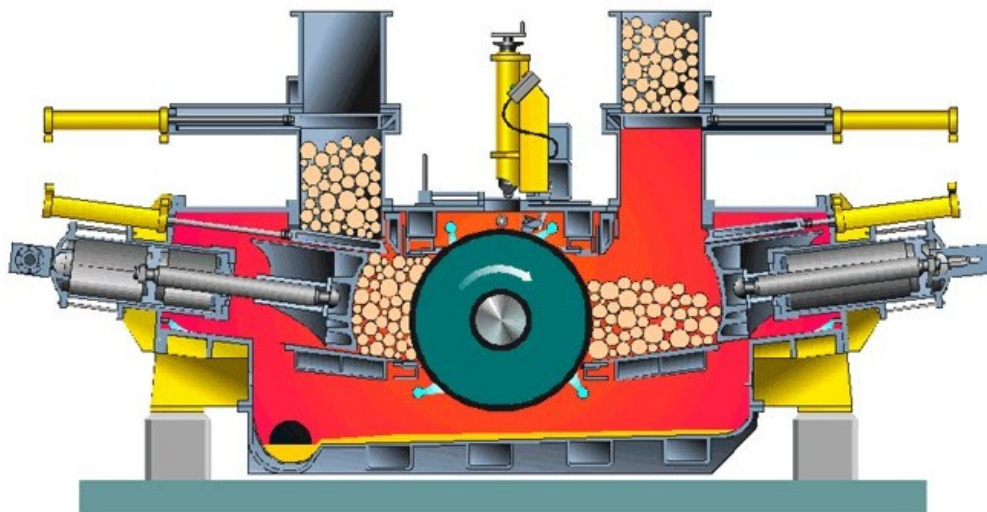
This thesis is the research of the effects of pH changes during the pressure ground wood (PGW) process. The main target is to research how pH changes affects to the dissolved and colloidal substances (DCS) and thus to the runnability of the paper machine.

2 MECHANICAL PULPING

In mechanical pulping process the pulp is made by mechanical treatment to separate wood fibers from each other's and to soften the lignin which wood contains. Mechanical pulp is used to make wood containing paper grades such as newsprint and magazine papers like light-weight coated (LWC) and supercalendered (SC) grades. In mechanical pulping method the yield is very high, 96-98%, and during the pulping from wood is released some wood based materials like for example celluloses, hemicelluloses and lignin to the water. Besides the high yield, mechanical pulping enables to produce low basis weight paper with good opacity and bulk with sufficient strength properties when good runnability and printability is required. (Sundholm, 17-21, 1999)

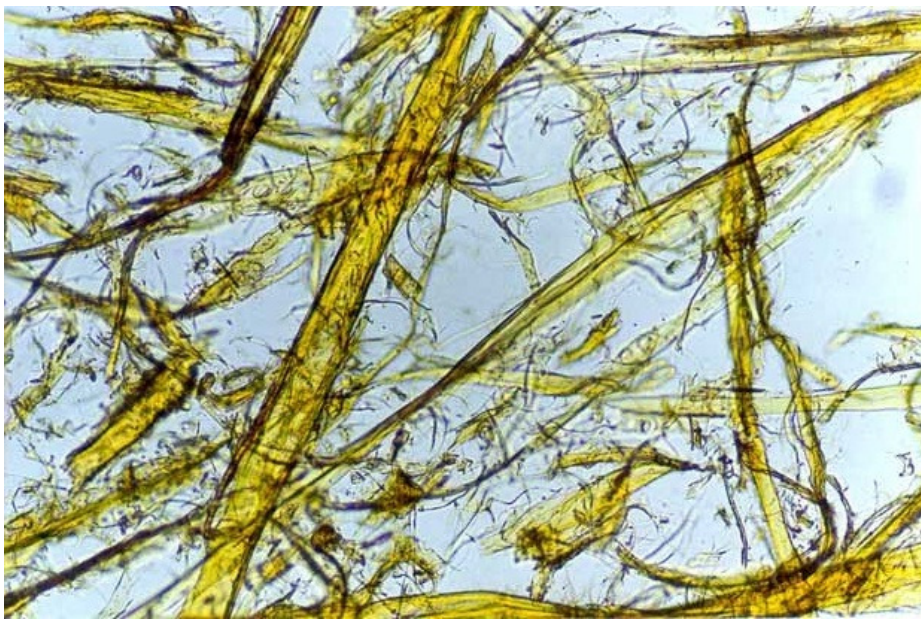
2.1 Grinding

Depending on the mechanical pulping method there are different kinds of names to processes. The most common processes nowadays are Groundwood (GW), Pressure Groundwood (PGW), Thermomechanical pulp (TMP) and Chemithermomechanical pulp (CTMP). In this thesis the pressure groundwood pulp, PGW is especially studied. (Sundholm, 17-21, 1999)



PICTURE 1. Pressure Groundwood machine (Knowpapp, Grinders)

The most used wood specie in PGW is spruce because of its good response in pressurized conditions. The advantages of PGW process are good optical properties. Before pressure grinding wood logs are debarked and logged approximately to 1, 5 m length wood logs. In PGW process mechanical pulp is produced by separating wood fibers from each other's by grinding logs towards to the rotating stone with a high pressure and a lot amount of warm water. During the grinding and pulping process to the process water is dissolved cellulose, hemicellulose, pectins and lignin which are in common called dissolved and colloidal substances (DSC) and can cause later in papermaking process harmful precipitations. (Sundholm, 17-21, 1999)



PICTURE 2. Groundwood fibers. (Knowpap, Grinding)

After grinding pulp is cleaned and screened to separate and retreat various impurities like for example sand, bark, shives and coarse fibers. The main target of screening is to separate wood originating impurities from fibers and then to divide the pulp into different fractions, accept and reject. Accept continues forward to bleaching and reject is processed again so that undefibrated wood is refined and then returned back to the screening and cleaning. (Williamson, 251, 1999)

2.2 Bleaching

In mechanical pulping the pulp is bleached to improve brightness. Most common bleaching methods are dithionite and hydrogen peroxide bleaching. In bleaching of mechanical pulp the main target is to increase pulp brightness by brightening or bleaching colored lignin groups. (Lindholm, 313-326, 1999)

In peroxide bleaching pulp is usually bleached in consistencies of 12-30% but in this case the high-consistency method is used because of the better pulp brightness. In high-consistency bleaching the consistencies are between 30% and 40%. The peroxide bleaching is done in alkaline conditions in retention time between one and two hours. In addition to the hydrogen peroxide, H_2O_2 , bleaching liquor contains also water, sodium hydroxide, sodium silicate and chelating agents, EDTA or DTPA. (Lindholm, 313-326, 1999)

Sodium silicate is used in bleaching because it acts as a buffer, stabilize effect on peroxide and prevent transition metal ions to catalyze peroxide decomposition because of its ability to form metal complexes together with magnesium. Sodium hydroxide is used to adjust bleaching pH. The pH of the bleaching liquor is 11,5, pulp pH right after sodium hydroxide dose is pH 10-10,5 and the end pH in bleaching is 8,5-9. Chelating agent is used to release the metal ions (Mn, Fe, Cu, Cr) from the fibers in order that they cannot decompose peroxide or darken the pulp. (Lindholm, 313-326, 1999)

2.3 Acidification

After bleaching the pulp is acidified by reducing the pulp pH with sulfuric acid (H_2SO_4) or sulfur dioxide water (SO_2). In acidification the pulp pH is normally reduced to pH 5-6 because then the residual alkali cannot darken the pulp when all residual peroxide is consumed. Sulfur dioxide water reduces metal ions to the colorless ions when the brightness of pulp is better but on the other hand it decomposes also residual peroxide which in turn reduces the brightness of the pulp. In acidification process the set pH level affects to the entire paper process like for example to wet end and to water circulation chemistry. (Knowpulp, Acidification)

After whole pulping process, grinding, bleaching and acidification the mechanical pulp is diluted with white water to the storage tank when the pH of the pulp decreases to the pH around 7 because of the white water. From the storage tank the pulp is transferred to the paper machine. To the mechanical pulp can be added necessary amount of chemical pulp to give better strength properties. In addition to the chemical pulp in paper machine phase to mechanical pulp is added also necessary process chemicals like for example retention aids and fillers to allow of paper making and to improve paper properties.

2.4 pH in mechanical pulping

pH is a logarithmic value which define the concentration of the molar hydrogen ion and because of its feature to affected sensitively by external factors, it is one of the most important measurements and factors in papermaking process. All chemical reactions depend on some extent upon pH. (Knowpap, pH control)

Paper machines used pH- areas are divided to acid (pH (4,5-6,5), neutral (pH 6,6-7,4) and alkali (pH 7,5-8,5). Impact of pH in papermaking cannot emphasize too much. It affects strongly to dissolve of wood components and to changes in dissolved substances phases. Increase in pH improves wood components dissolving and thus amount of anionic dissolved and colloidal substances. Also the surface charge of fibers and solubility of extractives increases as well as bacteria activity escalating. When pH decreases precipitations during the process is increased and which are practically insoluble and thus disturb significantly the process. (Hägglom-Ahnger & Komulainen, 148, 2005)

Chemistry of paper making process is very dependent on pH level. pH has to be controlled at the beginning of the process, starting from pulping. The chemistry of paper machines wet end is affected by pH, like for example its charge level and functionality of retention chemicals and especially function of hydrophobic sizes. Measurements of the wet end the pH is the most important right after temperature. pH measurement is the most common online measurement in paper machines. Changes in pH level are always harmful, both in acid and in neutral levels. (Hägglom-Ahnger & Komulainen, 148, 2005)

3 WATER CHEMISTRY

In papermaking water is one of the most important raw materials. Water is used as a transporter in paper making process, as a solvent for used chemicals and raw materials as well as for building hydrogen bonds between fibers. In figure 1 is shown water usage as a raw material at a paper mill. (Holmberg, 205-221, 1999)

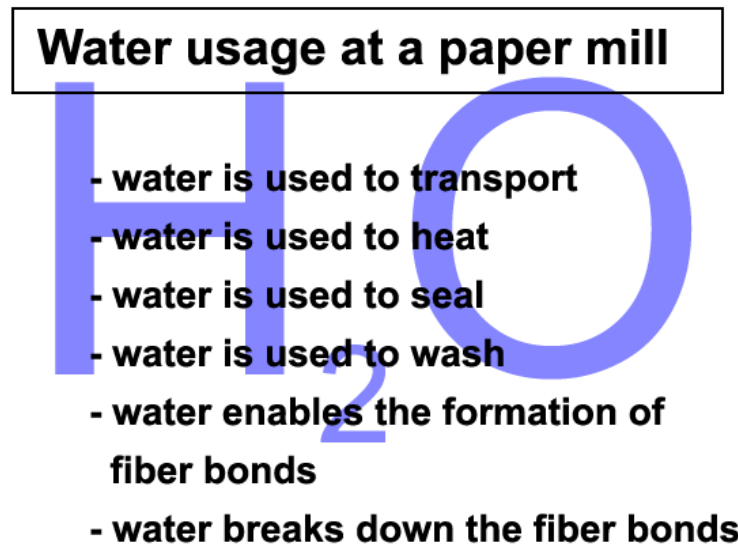


FIGURE 1. Water usage as a raw material at a paper mill. (Knowpap, Water usage in paper production)

During the mechanical pulping process to the water is released some wood based material like for example cellulose, hemicellulose and extractives which cause different kind of precipitations to the paper making process together with other fractions in aqueous phase. One part of fractions into the water phase comes from the paper machines wire section which contains short fibers, fines and fillers. (Holmberg, 205-221, 1999)

Because of the undesirable fractions in water phase, water needs purification with different kind of methods like for example with disc-filtering and chemicals. The wet-end of the paper machine contains the highest amount of water and its chemistry has to be controlled by a variety of chemicals like, retention chemicals, fixatives, de-foaming agents and biocides. (Bergelin, Möller, & Holmbom, 163-175, 2005)

Retention chemicals like bentonite and polymers are used to attach fines and fillers to the web. Wood extracts are attached to the fibers by fixatives which also are used to adjust the anionicity of the paper process. Substances dissolved from the wood can

cause harmful foaming during the process which has to be controlled by defoaming agents. (Bergelin, Möller, & Holmbom, 163-175, 2007)

3.1 Dissolved and colloidal substances

In paper machine used water contains all kind of substances like for example dissolved and dispersed colloidal substances, micro-organisms, solid particles and gaseous particles. Dissolved and colloidal substances are a common description to different kind of harmful substances during the paper making process which can cause together precipitations and thus problems to paper machines runnability and to paper properties. Dissolved and colloidal substances (DCS) in water phase can be called as detrimental substances or anionic trash. (Holmberg, 205-221, 1999)

During the mechanical pulping process some fractions of dissolved and colloidal substances are released from wood fibers to the aqueous phase and which are composed mostly of hemicelluloses, pectins, hydrophobic extractives and lignin. Beside the celluloses and extractives, the aqueous phase contains also many other organic substances and inorganic salts. The composition of this water-based colloidal system in paper machine can vary depending on the produced paper grade, used raw materials as well as on production conditions. (Holmberg, 205-221, 1999)

3.2 Precipitations

Nowadays paper machine's water circulations are more and more closed because of the economic issues and cost of fresh water and that is why many of these dissolved and colloidal substances in water systems give a rise to the formation of deposits and thus increase paper machine's runnability and quality problems.

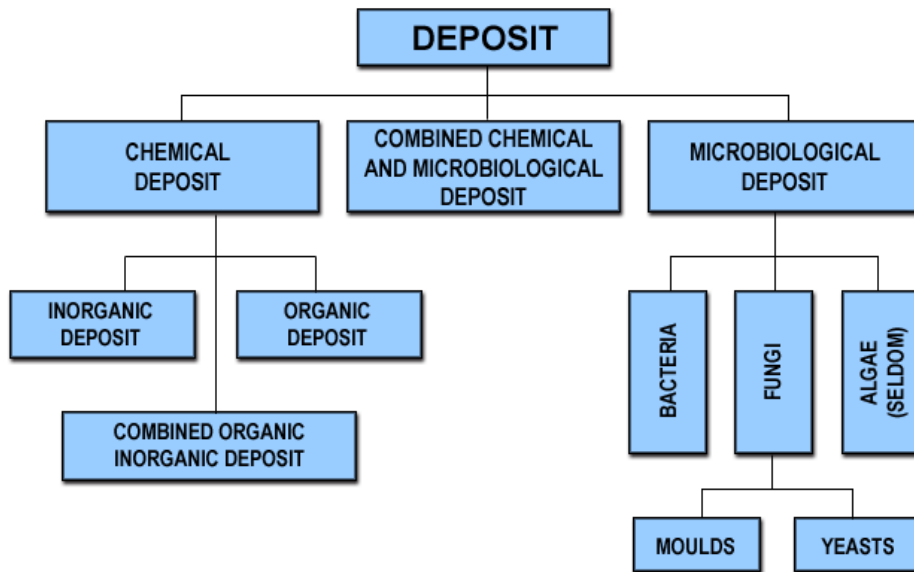


FIGURE 2. Different kind of types of deposits formations. (Knowpap, Chemicals for deposit control)

In figure 2 is shown the main types of deposits formations. Deposits can be in form of chemical deposit, microbiological deposit as well as these two deposits combined. Precipitations are usually formed in places where are pH, temperature and pressure fluctuations as well as into places where two flow are run into each other and where is a high rate of flow.

Because of the problems which detrimental substances cause to the paper process it is important to try to control and predict them by chemicals and cleaning. The most used parameters to measure detrimental substances are pH, turbidity, conductivity, cationic demand and redox potential. The solubility of dissolved and colloidal substances increases when pH increases. (Bergelin, Möller, & Holmbom, 163-175, 2007)

3.2.1 Extractives

Wood extractives are divided to two groups by their chemical properties, to hydrophobic and to hydrophilic groups. Hydrophobic extractives are for example rosin acid, steryl esters and fatty acids. Hydrophilic extractives are lignans, tannins and salts. In papermaking process it is usually talked about pitch when it is meant hydrophobic extractives. The amount of extractives is normally a few percent of the wood but it de-

depends on from the wood species as well as the part of wood like for example it is normally higher in wounded wood. (Björklund, Nilvebrant, 148-159, 2009)

Pitch is one of the most difficult substances to control in papermaking process because of its hydrophobic and tacky properties. Pitch problems caused by pitch deposits can cause runnability problems to the paper machine by tacking and picking in wire and press sections. Sudden changes in temperature or pH can lead to pitch problems. When the pH level varies, the size and amount of pitch change. (Björklund, Nilvebrant, 148-159, 2009)

Extractives are released from wood during the pulping process and they are one part of the dissolved and colloidal substances. The amount and the content of the wood extractives depend on the wood specie and growth conditions. (Björklund, Nilvebrant, 148-159, 2009)

3.2.2 White pitch

White pitch is also a one source to the dissolved and colloidal substances. Consisting of agglomerates from synthetic binders are called white pitch. Synthetic binders in paper making originate from coated broke or coating color.

Most of the coating colors components have an anionic charge and thus have an adverse impact to cationic chemicals which are added to the wet end. Substances present in this harmful white pitch deposits are mostly binders, fibers, hydrophobic chemicals, pigments and wood extractives.

White pitch occurs usually in the press section and in the drying section by tacky deposits in brown or grayish colors. White pitch deposits cause often web brakes and spots and holes in the paper. White pitch appearing is higher when the paper machine is operated in the neutral than in the acid pH range. (Bergelin, Möller, & Holmbom, 163-175, 2007)

3.2.3 Inorganic salts

Into the papermaking process is introduced also some inorganic ions with raw water, chemicals, fillers and pigments. Sodium, aluminum, magnesium, calcium, iron and copper are formed typically cations group and sulphate, sulphite and chloride are among the generous inorganic anions. These ions affects to the hardness of the water and to process conductivity.

The trend of inorganic ions to combine deposits depends on their solubility equilibrium. Deposits by inorganic ions are due to unstably process conditions like changes in temperature, pH and pressure. (Bergelin, Möller, & Holmbom, 163-175, 2007)

3.2.4 Deposit control

Deposit forming can be prevented or removed by different treatments depending on the extent and location of the problem. The deposit controlling method has to be chosen carefully and some issues have to be taken considered like for example the advantages, disadvantages and associated costs. Usually deposit forming is controlled by mechanical cleaning or chemical additive treatment but in some cases some chemicals have to be left out because of its improving impact to deposit forming.

Chemical additives have different mechanism to work and to each case there is best suitable chemical which can be tested beforehand in laboratory tests. Anionic dispersants enhance the stability of colloidal substances by adsorption of anionic groups onto particles surfaces and at the same time the pitch particle proportions are decreased and thus decreases also the possibility to build wider agglomerates. Used dispersants are usually poly-naphthalene sulfonates and lignosulfates.

Aluminum sulfate is one of the oldest chemical in papermaking and its use is one way to solve pitch problems. Alum is a strongly cationic product which enables that dissolved and colloidal substances can coagulate onto fibers.

Fixing agent chemicals are cationic synthetic polymers which build up agglomerates in water phase with colloidal material and bind up them onto fibers so that all ends up in the paper. Most used fixing agents are poly-DADMAC, poly-ethylene-imine (PEI) and

diamine- and dicyanoamide polymers. Poly-DADMAC works as a flocculant and PEI as a coagulant. (Bergelin, Möller, & Holmbom, 163-175, 2007)

4 MICROBIOLOGY

Closed white water systems in paper mills have led to increased microbe problems. Microbes cause for example slime problems to paper process and thus affect to runnability of the paper machine and to the paper properties. Beside the closed water systems also the increased temperatures in paper processes grow microbes faster and more easily. Microbes have to be controlled during the whole paper process by continuously and good housekeeping as well as by chemicals.

4.1 Microbes

Microbes are classified to two different groups, to prokaryotes and eukaryotes. To the prokaryote group belong bacteria and blue-green algae and all rest of the living organisms are eukaryotes like for example fungi, yeast and algae. Prokaryotic organisms are simpler life forms than eukaryote organisms by comparing them structure and membrane-bounds. (Kolari, 2007, 182-196)

All microbes requires to them growth conditions suitable pH and temperature, enough time and available nutrients. In paper process used water contains carbohydrates which are one of the nutrients source to the microbes. The other good nutrient sources to microbes are used chemicals, like starch and impurities caused by kaolin. Microbes can grow in the entire pH range between pH 2 and pH 10. In neutral conditions, pH from 7 to 10, bacteria is the most dominate microbe as well as in high temperatures, from 40°C to 60°C which is the most common temperature area in paper process. Microbes need time to grow so the best places in paper process for microbe growth are for example water storage tanks, broke treatment, long pipelines and stock chests and other wet surfaces. (Kolari, 2007, 182-196)

4.2 Microbe controlling

Microbes can be controlled by biocide chemicals which are used in paper process. Biocides can inhibit or kill the microbes due the mechanism how biocides work. Depending on the process variables like pH and temperature the most correct biocide is used. Biocides can inhibit the growth of microbes either by destroying the membrane cells or by

penetrating through the membrane and thus react with essential cell components. (Kolari, 2007, 182-196)

Beside the biocides, microbes can be controlled also by good housekeeping and mill designing. Efficient housekeeping in paper process means regular washing of tanks and pipelines, water treatments and controlling the purity of used raw materials like chemicals and additives. Mill designing has to be realized so that stock chests and water storage is in effective control as well as places where the flow velocity is slow. (Kolari, 2007, 182-196)



PICTURE 3. Slime problem on the paper machine. (Knowpap, Microbiology)

Microbes can cause to paper process many different kind of problems like slime, runnability, corrosion problems and paper property problems like for example odor and taste problems as well as holes and spots to the paper. Slime bacteria are well protected against biocides and dewatering agents which helps to microbes to adhere onto surfaces. Slime grow the most in pH between 5 and 8 and its growth can be influenced also many process variables like machine speed, temperature and retention. Slime can be controlled by washing critical places and by using biocides. Onto all surfaces in paper making process where water is used can appear microbiological growths which cause also harmful corrosion to these surfaces. (Kolari, 2007, 182-196)

Microbiological growth can be predicted by different measurements like for example redox potential, ATP and applications of plate counting. ATP is the measurement which defines the amount of adenosine triphosphate (ATP), amount of energy, in living microbe cells. Redox potential defines the electronegativity of the substance compared with oxygen. The lower redox potential the higher microbiological growth is in the case. Used plate counting methods are so-called easy-cult method and petri films method. These methods are suitable to detect any contamination occurring in processing aids such as starch slurries and other additives. (Kolari, 2007, 182-196)

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