THE EFFECTS OF A PEO-COFACTOR-BENTONITE SYSTEM ON THE RETENTION OF FINES AND WATER DRAINAGE IN PAPERMAKING

A Thesis

by

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ABSTRACT

Environmental concerns and pressures have made the pulp and paper industry move towards the recirculation of white water. These measures have led to lower volumes of water discharged by those mills recirculating water, and also to increasing problems in the mills. One of these problems is the loss of effectiveness of the PEO-cofactor retention aid systems, due to the increasing concentration of dissolved solids in the water. The results show that the presence of high surface area compounds such as fines, clay and organic compounds, like abietic acid can indeed affect the efficiency of PEO.

The development of a laboratory scale twin wire sheet former has helped study the retention aid system described above under conditions which resemble those found in a mill. This apparatus has helped study the effect the retention aid system had on water drainage and fines retention. The fines retention improved as the concentration of PEO was increased but the water drainage had decreased. Bentonite was added to the system to study its effect on the fines retention and the drainage. Bentonite combined to a PEO-cofactor retention aid system was found to have a positive impact on both the retention and the drainage.

RÉSUMÉ

Les pressions environmentales ont fait que l'indutrie des pâtes et papiers a fait des pas vers la recirculation des eaux. L'adoption de ces mesures a permis la réduction du volume d'eau utilisée par les moulins à papiers, par contre cela a aussi mené a un nombre croissant de problèmes dans les moulins. Des problèmes dûs en grande partie à la concentration plus elevée de solides dissous présent dans l'eau. Un de ces problemes est la perte d'éfficacité du système de rétention PEO-cofacteur. Les résultats montrent que la présence de substances à haute surface spécifique, notamment les fines, l'argile et les produits organiques (tel que l'acide abiétique) ont un impact sur l'éfficacité du PEO.

Le développement d'une machine à papier de double toile pour laboratoire a permis l'étude du système de rétention mentionné précédemment sous des conditions semblables à celles retrouvées dans les moulins à papier. Cet appareil a permis d'étudier les effets que ce système de rétention a sur le drainage d'eau et la rétention des fines. La rétention des fines s'est améliorée lorsque la concentration de PEO a été augmentée, mais le drainage d'eau a diminué. De la bentonite a été ajoutée au système de rétention, PEO-cofacteur, et a eu un impact positif sur la rétention et le drainage.

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" We could run or we could walk, but as long as we're together..."

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a	Particle radius
A	Hamaker's constant
α	Polarizability of non-polar molecule
B	Constant
e	Proton charge
ε	Permittivity of the medium
κ	Debye-Huckel parameter
κ^{-1}	Double layer thickness
KT	Thermal energy
h	Planck's constant
$1/2h\upsilon_o$	Ground state energy of atom or molecule
λ	Constant (in van der Waals forces)
μ	Dipole moment
n_i	Concentration of ion i
ρ	Charge density
r	Distance between molecules
ψ	Potential
υ_o	Frequency of vibration
Φ	Net potential energy
Φ_R	Potential energy from repulsion
Φ_A	Potential energy from attration
z_i	Valency of ion i

GUIDELINES CONCERNING THESIS PREPARATION

Candidates have the option of including, as part of the thesis, the text of a paper(s) submitted or to be submitted for publication, or the clearly duplicated text of a published paper(s). These texts must be bound as an integral part of the thesis.

If this option is chosen, connecting texts that provide logical bridges between the different papers are mandatory. The thesis must be written in such a way that it is more than a mere collection of manuscripts; in other words, results of a series of paper must be integrated.

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Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis. In the case of manuscripts co-authored by the candidate and others, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. Supervisors must attest to the accuracy to such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers.

Under no circumstances can a co-author of any component of such a thesis serve as an examiner for that thesis.

CHAPTER 1

INTRODUCTION

1.1 - BACKGROUND

The pulp and paper industry, like any other industry is in constant search of better products, higher production volumes and environmentally conscious means of production. The higher system closure that is sought by many paper mills, is one way to adapt to the more stringent environmental regulations that are put in place by governments. System closure is a term that can be defined loosely as reusing water run-off (white water) from a paper machine in the papermaking process. System closure leads to lesser water volume being used to make paper, therefore treatment of lesser amounts of effluent. This in turn, saves money to paper mill owners [1,2], and smaller amounts of water used means a smaller impact on the environment.

Now, if the white water is of high consistency, this means that a great deal of the components (such as fillers, fines, wood resins, etc.) in the pulp slurry are not being retained during the papermaking process. The presence of a high concentration of these compounds renders the water treatment more difficult, hence more costly. The method used to ensure that most of these small particles remain in the sheet is by the addition of retention aids [3]. Some of the problems that mill owners can anticipate when closing the loop range, from brightness reversion, decrease in sizing (due to an increase in total hardness and in colloidal substances), and first pass retention will drop if no retention aids are used [4].

Retention aids can be neutral polymers or charged polymers (polyelectrolytes). An example of a polyelectrolyte is polyacrylamide (PAM). This positively charged polymer is an excellent retention aid widely used in the industry. Another cationic retention aid used in the industry is cationic starch. When used in conjunction with alum it has been shown to increase first pass retention significantly [5]. However, in the presence of a large amount of anionic compounds (commonly called "anionic trash") in the pulp slurry, the charge of the polyelectrolyte can become neutral and hence, their effectiveness nullified. One obvious solution to this problem is to increase the use of the retention agents, but this is an unsustainable course of action for mills, simply due to the economic impact this would have. The recycling of white water increases the cationic demand [6] in the pulp slurry tremendously, and hence, the need for a retention system that is little or not affected by the accumulation of these compounds in the mill water is preferred. PEO is an example of a neutral polymer, also called non-ionic polymer. The fact that it does not possess a charge makes it an ideal retention aid for use in conditions where the mill water contains a great deal of anionic trash. The fact that the efficiency of the PEO is increased when it is in the presence of wood resins is an added bonus. The PEO is mainly used in situations where mechanical pulp is involved such as newsprint [7] for example.

Increases in retention have an impact on the quality of the paper produced because since the retention of small particles helps plug the pores in the formed sheet, and the opacity of the sheet increases. This is a very important point to note, since the fibers are so much larger than the fine components. The overlapping and interweaving of such large fibers leaves gaps all over a sheet which must be filled in order to have a good quality product.

The retention on a papermachine works in two ways. For the larger components (notably fibers) of the pulp slurry being injected on the fast moving wire of the machine (speeds of 1000 m/min are quite common) filtration is the predominant effect in their retention. For the smaller compounds (small fines, fillers) their affinity for adsorption (either with themselves or onto fibers) is what will determine their retention.

The constant pursuit for higher machine speeds for higher production, also has a significant impact on the retention of small particles. Because of the higher speed and the need to maintain the drainage at the same level of performance, the hydrodynamic forces encoutered by the particles in the pulp slurry have an increasing importance as the speed of machines increases. The web forms faster and therefore the adsorption of the fines/fillers must occur even more rapidly.

The mechanism by which PEO operates has been the subject of divergent schools of thought for many years. Starting with the knowledge that in most cases where PEO is used it has no adsorption affinity with the pulp or fillers present in the slurry, one of the pioneers in PEO chemistry, Pelton and his group

[8] found that to be most effective, the PEO molecules require the presence of a complimentary molecule. It was found that PEO was most effective in furnishes where there were high concentrations of dissolved chemicals, such as resins. The PEO was less effective in furnishes lacking a notable concentration of these compounds indigenous to mechanical pulps. But, the addition of water soluble phenolic resin accrued the gains in retention [9]. There exists a wide range of these complementary molecules which are termed cofactors or enhancers but they are for the most part very similar to wood lignin and phenolic resins. Lindstrom and Glad-Normark proposed a method by which the dual component retention aid system works [10]. Their research led them to believe that the PEO did not adsorb on either fines or fibers, but rather, it created a polymeric network that fractionated particles according to their size [11]. This network would be capable of capturing the big fillers more easily than the small ones; this was deduced after performing experiments on different sizes of latex.

The network hypothesis was shown to be an unlikely explanation to the way by which PEO and cofactor work. Studies using light scattering [12] and PEO-Cofactor suspension flow through packed beds of fibers [13] concluded in the non-existence of such polymeric networks. Van de Ven and Alince came up with the theory of association-induced polymer bridging [14] as a mechanism by which PEO and cofactor molecules work together. According to their work, a flexible chain (the PEO molecule) will not adsorb on either fines or fillers. But when the chain is stiffened after association with the cofactor molecule, the adsorption of the polymer and hence bridging may take place. The adsorption of the cofactor, linked with the PEO, on the fibrous surface may also occur to allow the formation of a PEO bridge.

The introduction of deinked pulp with the many contaminants (dissolved and colloidal solids) into pulp streams for newsprint has been particularly troublesome for some mills using PEO technology [15]. The presence of stickies, inorganic fillers, non-ionic deinking dispersants were the main culprits in the increased presence of sticky deposits, poor dewatering and wet-end breaks. The introduction of a third particle in the present retention aid system, bentonite added to PEO-cofactor, was a potential answer to the problem. The results of this new retention aid system have proven to be quite good despite the presence of 40 % deinked pulp (DIP). Another entry in the literature relates to improved retention and drainage and lower deposition of sticky material and cleaner papermachine fabrics with the use of a bentonite-PEO-cofactor retention aid system [16]. A great deal of research has been done on the study of bentonite and talc as treatment component for thermo-mechanical white water [17,18,19,20].

1.2 - OBJECTIVES

The goal of this research was two-fold. First, the research centered around finding a compound in deinked pulp that is detrimental to a PEO-cofactor retention aid system. To start, there was an analysis performed on different types of white water and the compounds that were present in the largest amount were singled out for the study. The compounds were then added to a batch reactor containing a 0.2 % solution of TMP. Their effects on the flocculation efficiency of the PEO-CF system used were noted by analysis using a UV-VIS spectrophotometer. The second section of this first part looked at the effect of bentonite on a PEO system in experiments in which the pulp was dispersed in filtered recycled white water.

The second part of this research was to actually use a machine called a lab scale twin wire sheet former and implement a PEO retention aid system on it. Since this was a relatively new machine very little literature was done on this type of set-up. Its purpose was to help in the study of fines retention and drainage of a PEO-CF system by having mill-like conditions in the laboratory. The last section of this research will look at the results obtained by adding bentonite to a PEO-CF system.

1.3 - BASIC THEORETICAL CONCEPTS

In order to understand certain concepts put forth in the subsequent chapters it is important to grasp the basic ideas behind these concepts. This part of the introduction chapter is devoted to give the appropriate background necessary in order to understand the research.

1.3.1 – Interactions in a Colloidal System

Before explaining the interactions present in colloidal systems, one must define the term colloid. In Paul Hiemenz's book "Principles of colloid and surface chemistry"[21], a particle is considered to be a colloid if it has some linear dimension in the range of 1 nanometer and 1 micron. Colloids are found relatively anywhere from soaps and detergents to dairy products to aerosols. Literally every sector of modern industry has colloids present.

In the pulp and paper industry there are a great deal of colloids which makes it an ideal setting for the study of colloidal interactions. Very small fines, a wide range of fillers (clays, calcium carbonates, titanium dioxides, etc.), retention aids (PEO, PAM, PEI, etc.), bond strength agents are all in the colloidal domain [22].

1.3.1.1 - Van der Waals Attraction Forces

There are two main forces of interaction in colloidal systems, not including any brought on by the presence of flocculants. First, there is the van der Waals attraction force and then there are the electrostatic interactions. The most visible hint of the presence of van der Waals force is the occurrence of flocculation in a system. Hiemenz states that the "stability of a dispersion with respect to flocculation depends on the relative magnitude of the potential energy of attraction and that of repulsion of particles involved" [21]. In essence, flocculation is the balance of the attractive forces and repulsive forces.

There are three types of van der Waals dispersion forces [23], that can be categorized by the type of molecules in the system. When there are two molecules both containing a permanent dipole, the interaction is defined by the Keesom formula. Equation 1 calculates the net attraction with Keesom's formula:

$$V_{att} = (- \mu^4 / (4\pi\varepsilon)^2 * kTr^6) \qquad (1)$$

where μ is the dipole moment, ε the permittivity of the medium, kT is thermal energy and r is the distance separating the molecules. If there is one molecule with a permanent dipole and one with an induced dipole, the Debye formula is used, the net attraction is described as such:

$$V_{att} = (- \alpha\mu^2 / (4\pi\varepsilon)^2 * r^6) \qquad (2)$$

where α is the polarizability of the non-polar molecule. And for a system containing two induced dipole particles, the London method is used, the net attraction is given by:

$$V_{att} = (- 3h\nu_0\alpha^2 / 64\pi^2\varepsilon^2r^6) \qquad (3)$$

where $1/2h\nu_0$ is the ground state energy of the atom or molecule, ***h*** is Planck's constant and ν_0 is the frequency of vibration. The combination of these three types of forces can be written in terms of dispersion energy as such:

$$V_{disp} = - \lambda / r^6 \qquad (4)$$

The lambda term, λ, is the result of the charge vibrating around its equilibrium position and depends on the nature of particle.

When adding all the interactions between all pairs of molecules in two colloidal particles, one obtains the van der Waals energy between two colloidal particles. For two spheres of radius a, at short separation distance h, the result is:

$$N_A = -Aa / 12h \qquad (5)$$

where A is the Hamaker constant which is proportional to 8 ($A = B^2 8 n^2$).

1.3.1.2 - Electrical Double Layer

The electrical double layer is a term used to describe the presence of charged ions in dispersed medium in close proximity to a colloidal particle. These charged ions are of the opposite charge of the ions on the surface of the colloid. Because colloidal are neutral when taken in their entirety, the ion density increases as the distance from the interface decreases. This is a phenomenon in which surfaces with charges (high charges or low charges), are "neutralized" by the ions dispersed in solution.

The Poisson equation relates the potential and the charge density as such:

$$\nabla^2 \psi = - \rho / \varepsilon \qquad \textbf{(6)}$$

where ε is the permittivity of the medium, ψ is the potential. The charge density of ions in a solution is quantified in this equation:

$$\rho = \Sigma_i \, n_i z_i e \qquad \textbf{(7)}$$

After combining equations 6 and 7 one obtains the Poisson-Boltzmann equation, as follows:

$$\nabla^2\psi = (- e / \varepsilon)\, \Sigma_i\, n_i^o\, z_i e^{- z_i e\psi / kT} \qquad (8).$$

The solutions of this equation yield the potential, ψ. Literature gives a few solutions to this equation which help a lot in understanding the Poisson-Boltzmann equation. The Debye-Hückel approximation of the equation yielded this formula which help obtain the thickness of the double layer:

$$\kappa^2 = (e^2 / \varepsilon kT)\, \Sigma_i\, n_i^o z_i^2 \qquad (9).$$

The double layer thickness surrounding a colloidal particle in solution is obtained by taking the inverse of the kappa parameter, κ^{-1}. Systems with high electrolyte concentration have particles with smaller electrical double layers when compared to similar particles in a system with little or no electrolytes present. The double layers find themselves compressed when in the presence of high salt concentration, the content of electrolyte in a system will determine which force will be the dominant one, attraction or repulsion. When two colloidal particles, each surrounded by an electrical double layer interact, the interaction energy is given by:

$$\Phi_R = Bae^{-\kappa h} \qquad (10)$$

where B is a constant $\sim \zeta^2$.

Figure 1.1 shows the different types of coverage by polymers that can be encoutered during experiments. As long as the double layer thickness, represented by κ^{-1}, is larger than the thickness of the polymer coverage, the system will remain stable. Another factor that could lead to stability is the coverage of the polymer on the particles. Even if the layer of polymer is thicker than the double layer thickness, if the coverage of particles by the polymer is total the system will be stable, if the layer is sufficiently thick to suppress van der Waals forces.

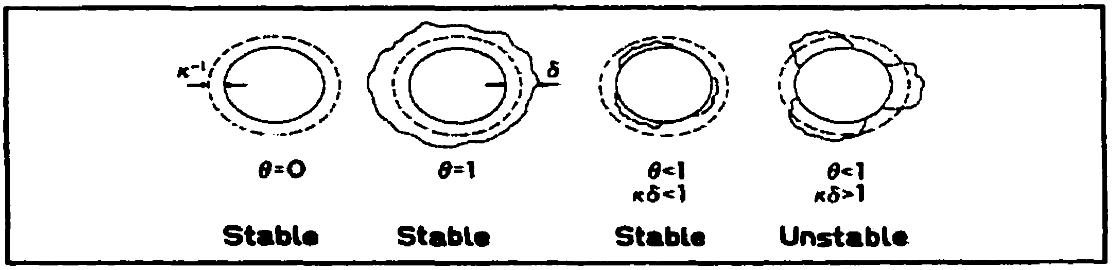

Figure 1.1: Polymer conformation compared with the double layer thickness [24].

1.3.1.3 - DLVO Theory

Derjaguin, Landau, Verwey and Overbeek [25] who worked independently in Russia and the Netherlands postulated a theory for colloidal stability that results from the combination of both the van der Waals attractive forces and the double layer repulsion into one curve [26]. The attractive forces for colloidal particles have a strong dependence on the distance separating each other. The same is also true for the repulsive forces in colloids, due to the electrical double layer; when the electrical double layers of two colloidal particles overlap, repulsion occurs. Equation (11) is the simple way of illustrating the theory:

$$\Phi_{net} = \Phi_R + \Phi_A \qquad (11)$$

Φ represents the potential energy resultant (net) of the two forces present, R (repulsion) and A (attraction). Figure 1.2 shows the resultant curve from the combination of the attractive force with the repulsive force. Although the attractive forces are usually the dominating forces at large distances, at short distances the resultant force depends on the magnitude of both forces. For the first minimum of the resultant force curve in Figure 1.2, also called primary minimum, if the energy barrier is small when compared with the thermal energy there will be a net attractive force and flocculation will take place.

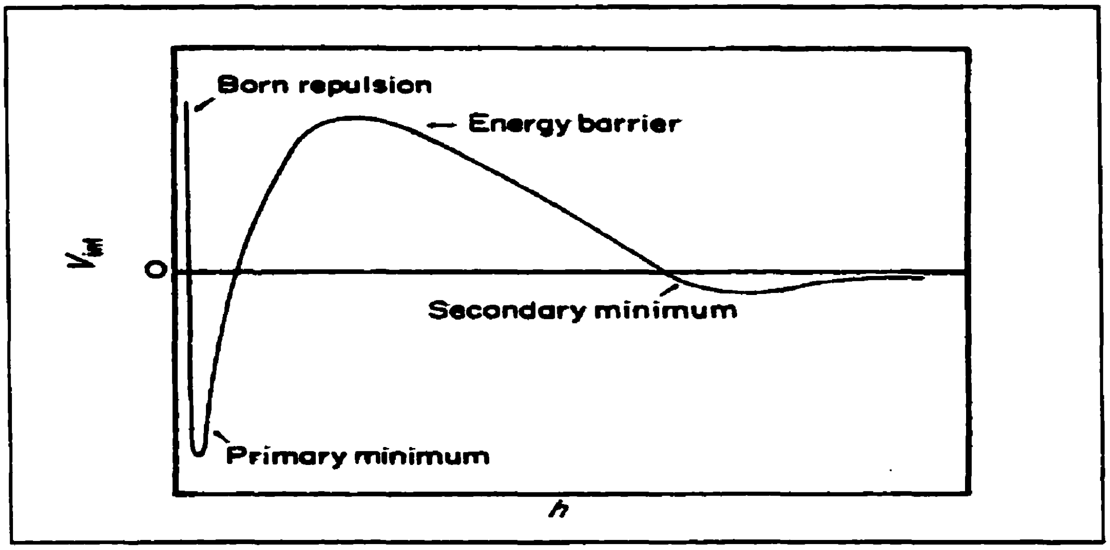

Figure 1.2: **Potential energy curve resulting from the electrostatic repulsion and the van der Waals forces, *h* is the distance separating the two particles. [23]**

However, if the energy barrier is large when compared to the thermal energy then, the system will be stable, in other words the particle will diffuse away from one another and there will not be any flocculation. There are also cases where flocculation may occur in the secondary minimum of the resultant force curve. The difference is, the flocs formed in this minimum will be much weaker, more prone to break up than the flocs formed in the primary minimum. In general, what determines if particles will flocculate or not, is the height of the energy barrier. The Born repulsion is a phenomenon that occurs when the particles are at extremely short distances from one another. This repulsion prevents particles from interpenetration.

1.3.2 - Effect of addition of chemicals

There are three main reasons why, in the pulp and paper industry, chemicals, mostly polymeric in nature, are added to pulp suspensions. They allow to overcome the repulsion forces at the colloidal level in the system, and increase the bond strength of bound particles. The three goals of optimizing the retention of small particles by adding chemicals are well summarized in a paper by van de Ven [27]. First, the optimization of the rate of particle deposition on fibers, second, the minimization of the detachment rate of particles, and third, the capture of fines and aggregates of fillers in the web during the drainage.

The speed of the machines in the industry forces the use of chemicals which possess fast attachment rates. Couture and van de Ven [28] determine that the PEO adsorption on latex particles could be broken down into three steps. (1) A fast diffusion controlled initial adsorption coupled with rearrangement of the polymer, (2) due to a large presence of polymer, the adsorption slows down and there is a dense layer that contains the majority of the molecules adsorbed. (3) The addition of more polymer will cause the adsorption to proceed on top of the initial layer and cause an increase in the layer thickness up to a plateau value.

Their analysis also brought on another interesting point as it pertains to PEO attachment on particles. They found that the adsorption layer thickness of a polymer that is anchored is smaller than without any anchors. This explains and supports the tail contribution to layer thickness. Let's backtrack a little bit. A linear polymer attached on a surface can adopt several positions: the loop, the train and the tail [29] (see Figure 1.3).

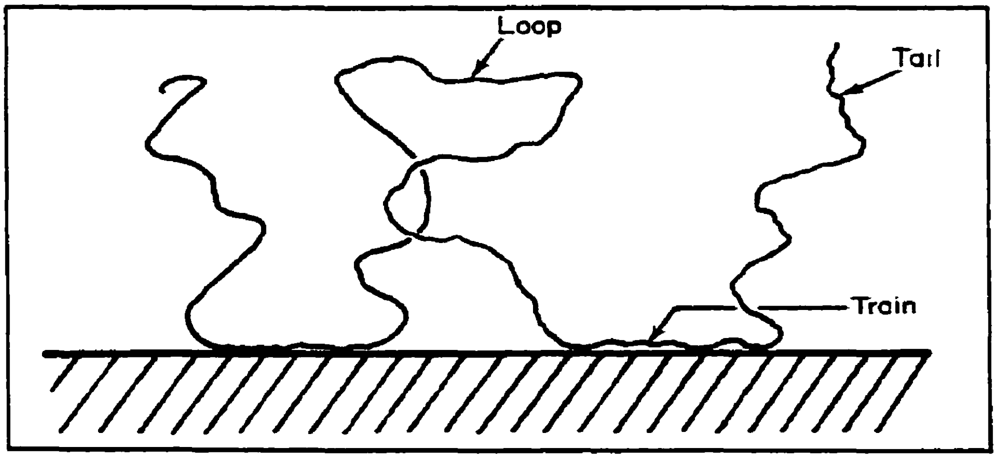

Figure 1.3: Possible conformation adopted by a linear polymer in contact with a surface [23].

This segment distribution is important from the standpoint of increasing the collision efficiency. This is why, if a segment sticks out, like in the tail or loop conformation, it is more likely to overcome the obstacle that is the double layer. Another important contribution of adding chemicals is the collision efficiency between particles. The presence of polymers can greatly enhance deposition or flocculation. While the number of collisions between particles depend on the hydrodynamic forces, the efficiency of those collisions depends on which of the colloidal forces are predominant. If the attractive forces are predominant, the flocculation will be said to have a fast rate. But this fast rate will depend on the ratio of van der Waals forces to hydrodynamic ones [26]. On the other hand if the flocculation rate is deemed slow, the repulsive forces will be the dominant ones at the colloidal level.

The addition of chemicals to a pulp suspension will also have a positive impact on the rates of deposition of the particles and will also decrease the affinity of the particles to be inclined to detachment. Van de Ven, having done experiments using the jet impingement apparatus [30], talks about systems in which the deposition of the particles is controlled by the polymers, and the bond strength between the particles and the surface. He also states that the experiments can yield information about the aging of those bonds. The experiments can also help to study kinetics of polymer adsorption by looking at the kinetics of particle deposition under conditions where both particle adhesion and polymer adsorption compete with each other.

1.4 - LITTERATURE REVIEW OF PEO AND BENTONITE

Polyethylene oxide was first used in papermaking as a single component retention aid. It was found soon after that its performance varied with the type of stock used [31]. The higher the concentration of phenolic type compounds the higher the retention in the system. So, PEO was now used in conjunction with what is called a cofactor to increase the retention in newsprint mills for one. It was also realized that the efficiency of such a system could again be enhanced by the use of a type of clay called bentonite [15]. Bentonite was also found to be efficient in the removal of pitch and other anionic trash found in mill white water [32]. This section of the introduction will give an overview of the published research that has been done on both PEO and bentonite.

1.4.1 - PEO (Polyethylene Oxide)

Polyethylene oxide is most probably the simplest polymer, structure-wise, to be water soluble. One of the reasons for this is the widespread belief that the ether oxygens in PEO are capable of hydrogen bonding therefore allowing to dissolve more easily in water or making it more prone to form association complexes with other compounds [33]. The structure of PEO is quite straightforward, here is the chemical formula for a monomeric section of PEO:

$$-(-CH_2-CH_2-O-)-.$$

The molecular weight of a single monomer is calculated to be 44 a.m.u. (approximated to the nearest integer). There are a number of PEO molecules available on the market, but for papermaking purposes, it was found that PEO of at least 5,000,000 molecular weight are most effective [7]. Of course, the higher the molecular weight of PEO used the harder it will be to dissolve, because it is known that PEO molecule may stay (a small percentage of them) entangled [34]. After the PEO has been dissolved in water and the solution becomes clear, it is in an entangled state, the rate of dissolution to reach that state is given as k_1. In its entangled form, PEO acts like a macromolecule and can stay entangled for a long period of time. When the dissolution of the PEO reaches thermodynamic equilibrium, the PEO is present in both free coils and clusters. The rate to reach this equilibrium state is termed k_2. The terms k_3 and k_4 describe the rates at which the PEO forms clusters and breaks off clusters. Polverari and van de Ven [34] have used dynamic light scattering to determine that above a critical PEO concentration the solution is no longer homogeneous. The following best describes the steps detailed above:

PEO $\xrightarrow{k_1}$ entangled **PEO** molecules $\xrightarrow{k_2}$ thermodynamic equilibrium

dissolution in water (free coils $\underset{k_4}{\overset{k_3}{\leftrightarrows}}$ clusters).

There is the presence of clusters. They determined that between approximately 12 and 18 % of the PEO molecules solutions of at least 250 ppm, which are thermodynamically stable, make up these clusters. They have also shown that in filtered solutions of PEO, there is reappearance of clusters after 1 day.

However, it is to the advantage of papermakers to have such clusters present because they behave as macromolecules and allow for high retention of fines and fillers. Also, Polverari and van de Ven have shown that PEO clusters do not adsorb onto latex particles, while entangled PEO can [35]. In view of this information, the papermakers possess quite a wide range of dissolution state they can play with to obtain the right PEO solution for their purposes.

The dissolution of high molecular weight PEO molecules is increasingly difficult as the molecules used are larger and weigh more. The makedown procedure of solution of PEO has a significant impact on its efficiency in a paper mill [35]. The conclusion was that a reduction in the viscosity of the PEO solutions would negatively impact the retention performance of such a system. Shear effects in the makedown of the PEO solution were thought to break some molecules (shortening of the polymer chains) and therefore lowering viscosity and efficiency.

Adsorption studies [34] on latex revealed that PEO in free coils would adsorb more readily on latex particles than PEO in clusters. This was revealed by experiments using filtered and unfiltered PEO solutions. The data obtained shows that the adsorption of PEO on latex is kinetically controlled. Therefore the equilibrium theories cannot be used to determine the PEO adsorption on latexes. The presence of clusters affects greatly both the hydrodynamic layer thickness (HLT) and the effective diffusion constant. This is of great importance because a smaller HLT is not desirable, a smaller volume is being "swept" by the PEO tails. However, the most important factor determined to control the HLT was the method of addition of the PEO. The one-step and two-step additions have a great impact on the thickness of the PEO layer.

In the pulp and paper sector, PEO, as was previously talked about, works as a retention agent but its effects are maximized when used with an enhancer or cofactor. The first recorded use of PEO in the literature as a retention aid is from work done by Arledter and Mayer [36]. They talked about "synergism in flocculation", that is to say, they discovered that their PEO (Polyox, in their case!) had a much larger effect on the retention of titanium dioxide filler when it was used with a resin (melamine-formaldehyde in their case). Lindstrom and Glad-Normark [37], studied the adsorption of PEO on several types of pulp and concluded that the PEO molecule would mainly bind to pulps where the presence of phenolic lignin residues were detected. PEO would not bind onto an unbleached kraft pulp that had undergone methylation or acetylation. The primary binding sites which are the phenolic protons, would no longer be present to bind to the ether oxygens in PEO. Stack et al. [38] have studied the interaction of phenol-formaldehyde resin (PFR) with PEO and have found a number of important additions to make to the work done by Lindstrom et al. They discovered that the complex formation between PEO and PFR depends on the solubility in water of PFR and the molecular size of the compounds. Their research showed that the appearance of a PEO-PFR complex and the amount of binding of PFR to PEO varied over a small range of pH and ionic strength.

They put forward the hypothesis that the PFR would interact with the PEO molecules by binding to alternate ether oxygens of the latter as is shown by Figure 1.4.

Figure 1.4 shows the interaction postulated by Stack et al. between a PFR molecule and PEO. This type of bonding would decrease the flexibility of a PEO molecule and increase its volume in solution because of the stiffening of the chain.

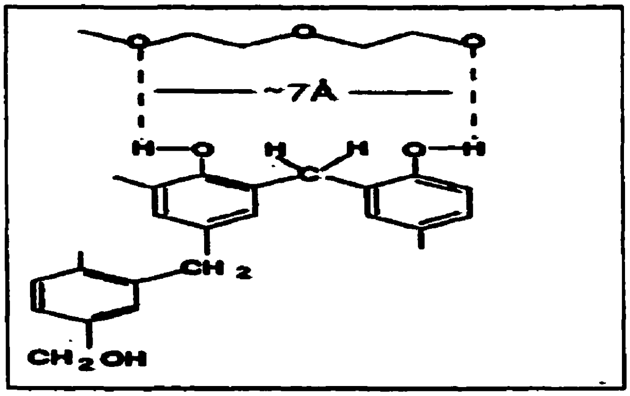

Figure 1.4: The interaction between a PFR molecule and a segment of PEO [38].

In a subsequent publication, Stack, Dunn and Roberts [39], studied several PFR to evaluate their performance in retention when combined with PEO. Although they did not find any correlation between molecular weight and interaction with PEO, they did notice that the highest molecular weight resins displayed the highest amount of interaction with PEO. Whereas the lowest molecular weight resins showed the smallest interaction with PEO. Using the dynamic drainage jar method developed by Britt [40] and furthered later with Unbehend [41], Stack et al. measured the performance in retention of each PFR molecule in the presence of PEO and found that the highest molecular weight resin also gave the highest retention increase. Although no clear trend was observed correlating molecular weight with retention.

Pelton et al.[42] proposed, following experiments in flocculation of latex with PEO-PFR, that a PEO-PFR complex can collapse to an inactive coacervate. Only in the case of very high molecular weight, does the collapse proceed at such a slow rate, that flocculation can still occur. This would back up the implication that only high molecular weight PEO (at least 5,000,000) will work properly as retention aids in the pulp and paper industry. They extend their results into the assumption that microparticle flocculation systems operate by the same mechanism as does the PEO-PFR system.

Takase and van de Ven have also studied the effect of cofactor in the polymer bridging of latex particles to glass with PEO [43]. Their work shows that the use of SKL strengthens the PEO bridge between latex and glass. This was done by changing the PEO conformation which resulted in a thicker expanded layer. The detachment rate depends strongly on the concentration of SKL. SKL acts in increasing the number of tightly bound latex particles, while at concentrations above 1 ppm, it also strengthens the bond of weakly bound particles.

In completely different work, Alince, Porubska and van de Ven [44], showed even hard to retain PCC (precipitated calcium carbonate) using a PEO-SKL system can deposit effectively on fibers. Even though, PEO-SKL is not an efficient system for retention of PCC on fibers, the right dosage of SKL and PEO make it possible for the PCC to be retained almost completely. The right dosage of SKL promotes the adsorption of PEO and therefore the formation of a polymeric bridge between the fibers and the particles.

1.4.2 - Bentonite

The meaning of the word bentonite originates from a particular type of clay discovered near the end of the 1800's near Fort Benton, Wyoming [33]. However, the earliest known use of bentonite was for the fulling of wool and thus the term fuller's earth, which is still in use nowadays [45]. Over the years, this group of clay with its defining characteristics, such as: its capacity to swell in water, to exchange adsorbed cations for other cations and to adsorb organic molecules has been the subject of a tremendous amount of scientific research and industrial applications.

First, let's understand what bentonite really is. It's actually a mixture of different types of clay, namely, montmorillonite, illite and kaolinite. Bentonite can display a wide range of colors, going from pale yellow to a greenish-brown hue. The montmorillonite is the main component in bentonite, it is also the clay that contains the many characteristics mentioned earlier, it usually makes up 90% of the bentonite mixture. Montmorillonites are the sodium form minerals, which are a subgroup of smectites. Another mineral that belongs to the smectite group is hectorite, which is a lithium-magnesium form of smectite [20]. Hectorite is found in anti-static coatings.

The processing of bentonite is quite straightforward. It is mined in open pits or from underground. At this point, bentonite has a moisture content of approximately 30 to 40 %. It is transported to a treatment plant where it is crushed, this step transforms bentonite into very small particles. The bentonite is then transferred into a rotating dryer, once the drying step is finished the moisture content of bentonite hovers around 5 - 15 %, and now it goes through a roller mill. This step, referred to as pulverization, reduces the fineness of the bentonite particle to 90 % through 200 mesh. Bentonite is ready for use in industrial applications.

People have found a wide variety of uses for the bentonite clays, but most of those revolve around the same characteristics: its capacity for water absorption. It is used in the waste industry for the sealing of landfills. They are used in geosynthetic clay liners (GCL) by placing a layer of bentonite between two geotextile layers and needle punching everything together. It is also used on animal farms for retention of waste. It can be added to cements, mortars and concretes where it can measurably decrease bleeding (separation of the water used for mixing). It is also found in foundation works where its presence (especially due to its thixotropic quality) can help reduce the friction of pipes to concrete.

Bentonite's first use in the pulp and paper industry wasn't as part of a retention aid system but as a component in mill water clarification [46]. It is also used as a deinking pulper additive, where it can help control stickies [47]. It finds other uses in pitch control and effluent treatment.

When bentonite is completely dispersed in water, its surface area can go up to 800 m^2/g [48]. This property alone can leave anyone confused. Common clays, for example kaolin clay have surface areas of 10 - 20 m^2/g. How could a clay have surface area that goes up to such a level? The reason lies in the delamination of the bentonite particles into individual platelets of no more than 0.9 nanometer thick, 100 nm in width and 300 nm in length. For a bentonite to cover such a surface it must delaminate and in order to accomplish that it must contain the right cations, the ones which render swelling easy. There are a few clays that can be called montmorillonite, but they are subsequently divided into subcategories depending on which cation they possess in their octahedral sheet. The one of interest is the one containing sodium which swells easily and can exchange cations (if need be!).

As there are a few clays that can be called montmorillonite, it is normal that there is a range of densities for this family of clays. Their densities range from 2.3 g/ml to 2.7 g/ml. The higher values reflect the presence of iron in those clays. The absorption of water can cause large variations in the densities of montmorillonite. For example, a 2.6 g/ml sample of montmorillonite can go all the way down to 1.8 g/ml after having dried in the oven, by having a 46 % water content at an equilibrium with air having a high content of water vapor [45].

The basis behind the idea of using bentonite along with PEO and a cofactor, came up as an extension of the idea of using bentonite with PAM (polyacrylamide, a cationic retention aid). The basic idea of using bentonite is the following, a homogeneous slurry will flocculate after a polymer addition. This causes the formation of weak flocs which are broken up by the hydrodynamic shear forces. The addition of bentonite will allow for a reformation of flocs, but this time, the flocs are much larger and stronger and more capable of enduring the stress of the hydrodynamic shear. The advantages of such a retention system are the following: first, the microporous structure of the web allows for higher drainage and reduced drying costs. Then, the type of floc structure created by a microparticulate system involves everything found in the slurry, therefore the retention of all particles in increased. However, a major drawback to the use of such a system is that the high drainage can cause high sheet porosity, which is most pronounced at lower basis weights.

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CHAPTER 2

EFFECTS OF RECYCLED WHITE WATER ON FINES RETENTION IN A NEWSPRINT MILL

2.1- ABSTRACT

The reuse of white water in paper mills has led to a number of problems caused by the increased presence of dissolved and colloidal solids in the pulp slurry. This study looks at the effect of the white water on a PEO based retention aid system. Various components are looked at in order to determine the detrimental compound present in the white water. From this work, the conclusion is that the biggest culprit present in the white water are components which bring with them a large surface area. This increased surface area will impact the efficiency of PEO by reducing its surface coverage. The second part of the work done here looks at the impact bentonite has on a system using filtered recycled white water for pulp dispersion. The bentonite allows for a greater efficiency from the PEO-cofactor retention aid system in cases where recycled pulp or white water are present.

2.2 - INTRODUCTION

The introduction of recycled paper white water in a paper mill brings about a number of undesirable compounds into the papermaking process. Increases in mill closure due to more stringent water discharge limits, energy conservation efforts lead to higher amount of suspended solids in the mill water [1-4]. Mills usually remove suspended solids from the white water by using filtration and clarification techniques [5]. However, even when with the use of clays and polymer based flocculation agents, dissolved and colloidal solids are difficult to remove from the white water [6]. A neutral polymer such as polyethylene oxide (PEO) is expected to be less affected by anionic trash in the white water than a cationic polymer [7]. Therefore the introduction of white water from recycled fibers should not affect a PEO retention aid system greatly.

PEO has been used in a number of paper mills using mechanical pulp furnish, and its use has been increasing over the past 20 years because of its non-ionic character and because of the increasing degree of system closure found in the industry. Literature extensively describes the increase in PEO efficiency when combined with a cofactor, for example kraft lignin, phenolic formaldehyde resins, modified resins and polysulfonates [8,9]. The explanation of how this dual component retention aid system works can be most clearly describe in the following manner: the cofactor molecules bind to the PEO molecules which are present either as a free coil or in entangled clusters [8]. The cofactor provokes a rearrangement of the PEO coil, which as a result is more prone to bind with fibers or fines. This is what is called association-induced polymer bridging [10]. The PEO-cofactor complex then adsorbs on the surface of either fines or fibers and creates a bridge between fines-fines, fines-fibers or fibers-fibers.

Mill experience shows that the PEO is affected by compounds present in the process water of deinked pulps (DIP). So, an hypothesis was formulated stating that there might be some detrimental compound present in the white water from recycled paper which negatively affects the efficiency of the PEO-cofactor system. An analysis of white water samples allowed us to pursue specific chemicals that were found in rather high amounts in those samples. We analyzed the composition of dissolved and colloidal substances (DCS) in two whitewater samples one from a newsprint mill and the other from a deinking plant. Upon analysis of the data, the chemical compounds that were chosen to see if they were responsible for the loss of PEO efficiency were calcium ions, sodium oleates and calcium oleates, silicates and DTPA.

The research was divided in three parts. In the first part, the effect of white water on the flocculation efficiency of a PEO-cofactor system were studied and compared to the PEO-cofactor's flocculation efficiency in distilled water.

The second part of the research was spent trying to find which compound, if any, would be causing the decrease in flocculation efficiency of the PEO-cofactor system.

And the third part dealt with the effects of available surface area on a bentonite-PEO-cofactor system.

Because some mill using recycled pulp have some difficulties with their PEO system, an experiment was done to show that using bentonite along with a PEO-cofactor system allowed for higher fines retention than with PEO-cofactor alone. The last part dealt with the use of bentonite-PEO-cofactor on a system that used recycled white water to disperse the pulp.

2.3 - EXPERIMENTAL SET-UP

A batch reactor with a spectrophotometer and a flow through cell was used to measure the absorbance of light (at 400 nm) of the suspension that passed through a filter of size 200 mesh. The wavelength selected (400 nm) was chosen after tests that were performed, indicated it gave the optimal response for mixture used. The reactor contained a solution of 1 liter of 0.2 % consistency of TMP pulp (from the Donohue mill in Matane). Throughout the experiments, the filter is cleaned by a brush that turns at 200 rpm. The pulp had a 30 % fines content, the surface area of the pulp was calculated to be approximately 4.6 - 5.3 m^2/g [8, 11].

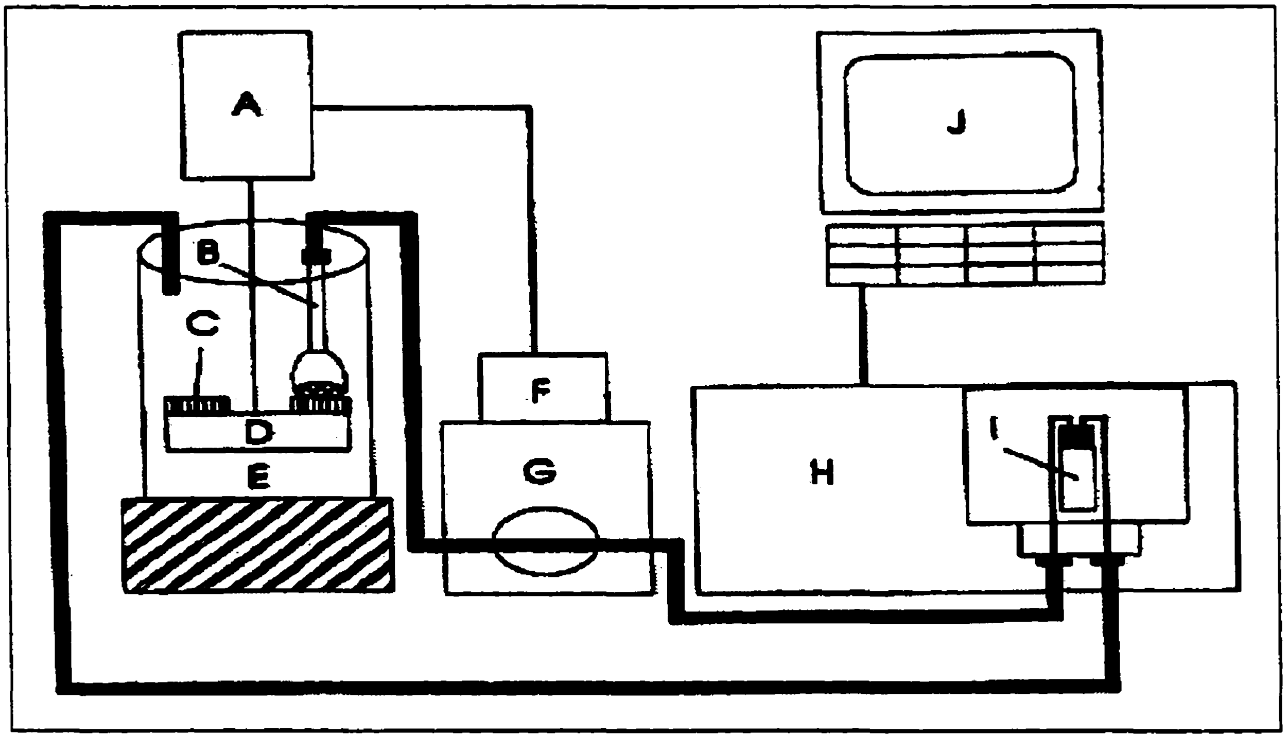

Figure 2.1: Spectrophotometer With Flow-through Cell Set-Up.

A: Stirrer
B: Collecting tube
C: Brush
D: Stirring paddle
E: Beaker
F: Stirring control
G: Pump
H: Spectrophotometer UV-VIS
I: Cell
J: Computer

Figure 2.2 shows a typical print-out from the spectrophotometer. The addition of the cofactor is added at the 3rd minute. The flocculation of the fines occurs a few seconds after the PEO is added at the fifth minute, and the desorption occurs shortly after reaching the minimum absorbance.

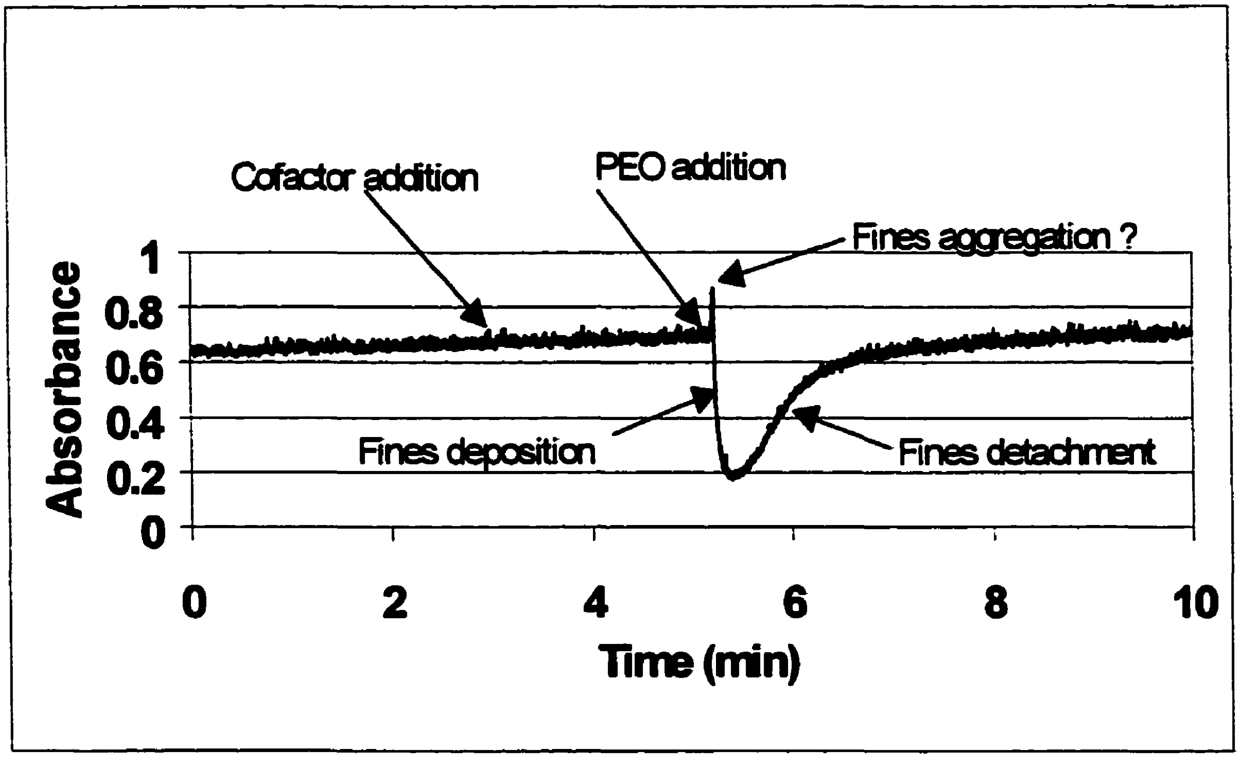

Figure 2.2: **Typical Results obtained from the Batch Reactor Set-up. Graph of Absorbance vs Time for a Blank Trial (cofactor 2 mg/g and PEO 0.5 mg/g) at a wavelength of 400 nm.**

The spike that is observed after the addition of PEO is believed to be the flocculation of fines together in the tubing leading to the spectrophotometer. This phenomenon is very short lasting because such a floc would most probably not be able to pass through the 200 mesh filter, that is present on the tubing. The fact that fines bonding together would create a bigger particle which, would in turn, adsorb more light is the most probable hypothesis. The so-called Reduction in Flocculation is measured by obtaining the magnitude of the absorbance occurring during deposition of the fines on the fibers. The magnitude of the drop in absorbance for each of the subsequent experiment in the same set will be compared to the absorbance drop for the blank trial. For example, a reduction in flocculation of 50 %, means that the drop in absorbance of the sample, at the time of deposition, has only half of the magnitude of the blank sample. This follows from calibration done in the laboratory where the absorbance of fines was measured for selected concentrations of fines in order to determine the relationship between fines concentration and absorbance. The relationship was found to be linear at the fines concentration used, that is to say, it follows Beer's Law.

The PEO (FLOC 999) used had a molecular weight of 6,000,000 and the cofactor (Interac 1323) used was a mixture of sulphonated kraft lignins and modified phenolic resins. The structure of the cofactor is discussed in detail elsewhere [12]. Both the PEO and the cofactor were provided by E.QU.I.P.

The PEO was mixed for 24 hours at very low stirring speed to dissolve it completely after having added it to distilled/deionized water. This stock solution of PEO was prepared at 0.1% concentration (weight/volume). The stock solution of the cofactor was prepared one hour before the start of an experiment by adding a 40 % solution of cofactor to distilled/deionized water and stirring at medium speed. The stock solution of the cofactor had a concentration of 0.1 % (weight/volume). The pulp used was the same sample for all experiments except for the experiments using recycled fibers.

2.4 - COMPARISON OF DISTILLED WATER VS WHITE WATER

This set of experiments was conducted in order to determine the range of the effect that white water has on the flocculation efficiency of a PEO-cofactor system, as can be seen in figure 2.3.

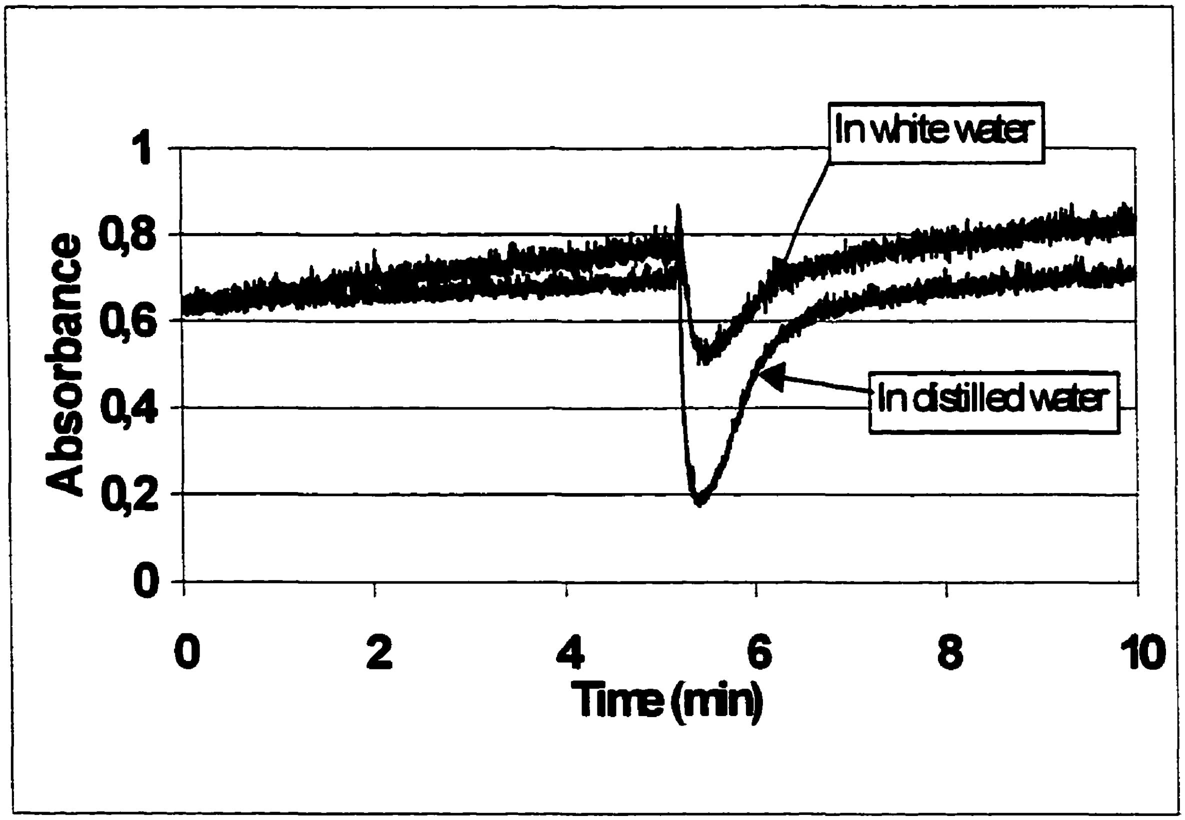

Figure 2.3: Comparison of the effects of white water on the flocculation efficiency of the PEO-cofactor complex.

The effect of filtered white water on the system was noticeable, there was something present in the white water that prevented a full and efficient flocculation like what was observed in the distilled water samples. The observed flocculation in the system using filtered white water had a reduction in flocculation of approximately 60 %.

2.5 - ANALYSIS FOR A DETRIMENTAL COMPOUND

2.5.1 - Calcium ions

Five types of contaminants were studied. Firstly, the effects of calcium ions alone were studied in a concentration range of 50 ppm to 300 ppm. The results show that there were no effects on the flocculation efficiency of the PEO-cofactor system when calcium ions were present in this concentration range. Table 2.1 summarizes the concentrations analyzed and the effects on the flocculation efficiency.

TABLE 2.1: **Reduction in Flocculation as a Function of Calcium Ions Concentration**

Calcium ion Concentration	Reduction in Flocculation
Blank	---
50 ppm	0 %
100 ppm	0 %
150 ppm	0 %
200 ppm	0 %
300 ppm	0 %

Although these results suggest that the presence of high amounts of calcium ions in the white water have no impact on the efficiency of the PEO-Cofactor system, there is evidence of the contrary. Laivins et al. [13] found that calcium ions can have an impact on the flocculation efficiency of the PEO-cofactor system. Their experimental conditions were similar in terms of pulp temperature (60°C) and pH (5.2), but the furnish contained some recycled pulp and the experiments were done in a dynamic drainage jar. The cofactor used in the experiments was the same. The fact that the furnishes used differ from one another, may indeed indicate that the calcium ions may be complexed with a compound that is present in the DIP, therefore accounting for the difference in results.

2.5.2 - Oleates

The second compound that was studied in this part of the research was the sodium oleates. The dosages of sodium oleates ranged from 10^{-6} M to 10^{-5} M. Those are concentrations which are most likely to be found in white water. The results indicated that the oleates did not seem to be the source of the problem. Table 2.2 summarizes the results for this section.

TABLE 2.2: Reduction in Flocculation as a Function of Oleates Concentration

Concentration of Oleates	Reduction in Flocculation
Blank	---
10^{-6} M	0 %
10^{-5} M	0 %

2.5.3 - Calcium Oleates

Further tests were run with oleates, but this time in the presence of calcium ions which would lead to the formation of calcium oleates (or calcium soaps) which can cause a problem since they are not soluble in water (they form precipitates, possibly colloidal particles). Again, these "calcium soaps", ranged in concentration from 10^{-6} M to 10^{-3} M. At concentrations regularly found in mills the calcium soaps had no effect but at higher concentrations the effects were more pronounced. Table 2.3 summarizes the results obtained when calcium oleates were studied.

TABLE 2.3: Reduction in Flocculation as a Function of Oleates Concentration with 100 ppm of Ca^{2+}

[Oleates] + 100 ppm Ca^{2+}	Reduction in Flocculation
Blank	---
10^{-6} M	0 %
10^{-5} M	0 %
10^{-4} M	25 %
10^{-3} M	66 %

2.5.4 - Silicates

The fourth compound studied were silicates. A range of concentrations ranging from 0.038 mg/g of pulp to 38 mg/g of pulp was used in this set of experiments. The only real effect that the silicates had, was observed when it was present in concentrations of 3.8 mg/g and more. The flocculation at these concentrations was so sudden and massive that the filter of the reactor was clogged up. At lower concentrations, 0.038 mg/m and 0.38 mg/g, the silicates were observed to have no noticeable impact on the flocculation.

2.5.5 - DTPA

The final compound to have been analyzed in this part of the research was DTPA. The dosages ranged from 0.201 mg/g of fiber to 201 mg/g of fiber. Only two dosages turned out to have an impact on the flocculation, the 20.1 mg/g of fiber and 201 mg/g of fiber. This is understandable given the large amount of DTPA present. At lower dosages, there was no effect on the flocculation. Table 2.4 summarizes the results from this section using DTPA.

TABLE 2.4: Reduction in Flocculation as a Function of DTPA Concentration

[DTPA]	Reduction in Flocculation
Blank	---
$8 * 10^{-6}$ M	0 %
$8 * 10^{-5}$ M	0 %
$8 * 10^{-4}$ M	40 %
$8 * 10^{-3}$ M	66 %

Other experiments with DTPA were conducted by adding some metal ions into the mixture and observing the change in amplitude of the flocculation. Calcium was chosen as the metal to be added since it is a common ion in the mill white water. There was no significant difference in the flocculation when comparing the two experiments so it was concluded that DTPA was not the detrimental compound. Table 2.5 summarizes the findings of this series of experiments.

TABLE 2.5: Reduction in Flocculation as a Function of DTPA Concentration with 100 ppm of Ca^{2+}

[DTPA] + 100 ppm Ca^{2+}	Reduction in Flocculation
Blank	---
$8 * 10^{-6}$ M	0 %
$8 * 10^{-5}$ M	0 %
$8 * 10^{-4}$ M	25 %
$1.6 * 10^{-3}$ M	50 %

2.6 - STUDY OF THE EFFECTS OF SURFACE AREA ON THE PEO COFACTOR SYSTEM

To study the effects of surface area on the PEO-cofactor system, clay was used because of its high available surface area. Dosages of 5%, 10 % and 15 % of the total pulp present were used for this experiment. Fines and colloidal abietic acid were also used because of their high surface area.

2.6.1 - Abietic acid

An experiment was conducted in order to study the impact of dissolved solids on the flocculation with PEO. To study the effects of organic dissolved solids, abietic acid was used as a model compound since it is commonly found in wood under colloidal form. By having 600 ppm of abietic acid present in the solution the flocculation was reduced by 50 % (see Figure 2.4). Table 2.6 lists the results for all experiments involving abietic acid. Abietic acid, provided by Sigma Co., was dissolved in a small amount of ethanol and then diluted in a distilled/deionized water. The colloids composed of the abietic acid were found to have a diameter of 230 nm, measured by dynamic light scattering. By treating these colloids of abietic acid as spherical particles of 230 nm in diameter, one can calculate their specific surface area.

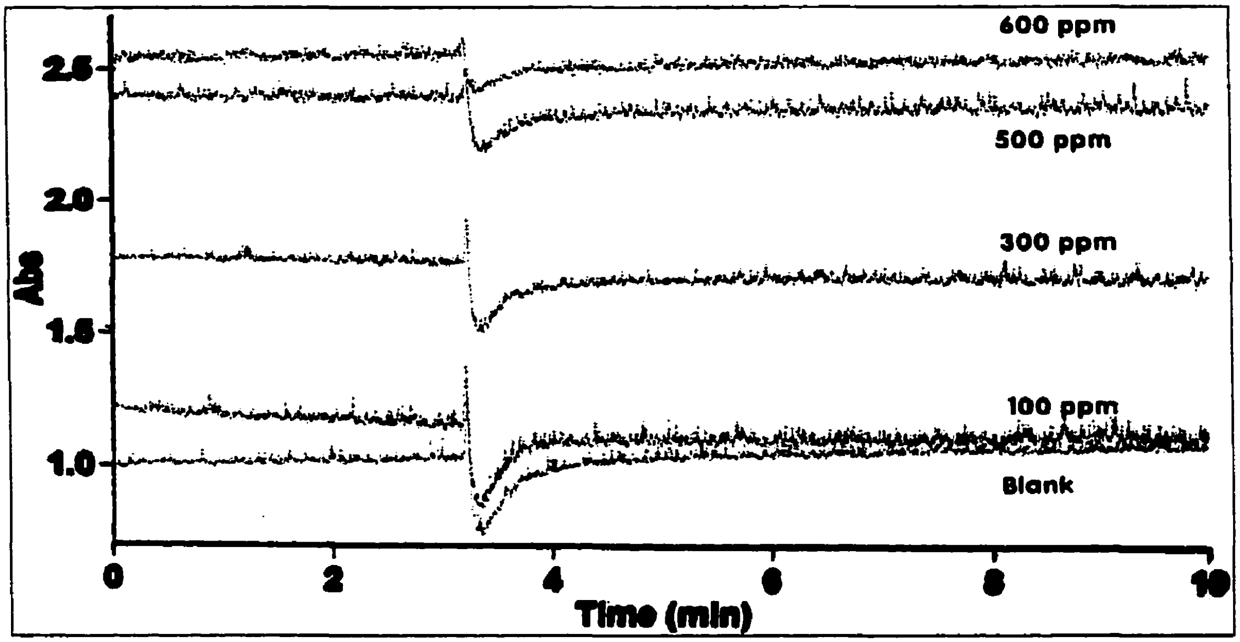

Figure 2.4: Plot of Absorbance vs Time for the Abietic Acid Experiments (λ = 400 nm).

TABLE 2.6: Reduction in Flocculation as a Function of Abietic Acid Concentration and Surface Area of the Added Abietic Acid

Amount of Abietic Acid Used	Reduction in Flocculation	Surface Area of Abietic Acid Added
100 ppm	0 %	2.6 m^2
300 ppm	8 %	7.8 m^2
500 ppm	33 %	13.0 m^2
600 ppm	50 %	15.6 m^2

The analysis of filtered WW obtained from the Masson mill revealed the presence of approximately 620 ppm of dissolved solids. The proportion of organic solids was 73 %, whereas the inorganics made up only 27 % of the total dissolved solids. A literature review mentioned abietic acid and oleic acid as two of the most common material found in recycled white water for a mill using ONP [14]. Since the Masson mill has similar characteristics, abietic acid was used as sole component. A rough approximation of the surface area of the organic compounds in the filtered white water from the Masson mill (assuming the organic portion is entirely made up of abietic acid) was of 8.5 m^2.

2.6.2 - Clay

Clay is known to have high specific surface area and would therefore be the ideal material to use to study the effect of surface area since it is commonly used in the pulp and paper industry. Kaolin clay is known to have a specific surface area of approximately 10 - 20 m^2/g [15]. Experiments were performed with kaolin clay (Georgia Kaolin) present at 5 %, 10% and 15 % of total solids content. These percentage amounts of clay translate into roughly these concentrations in parts per million: 100 ppm, 200 ppm and 300 ppm.

These experiments showed a decrease in flocculation (see Figure 2.5). But most importantly, exhibited a large increase in the light absorbance in the flow-through cell because of the presence of clay in the system. The results are summarized in Table 2.7.

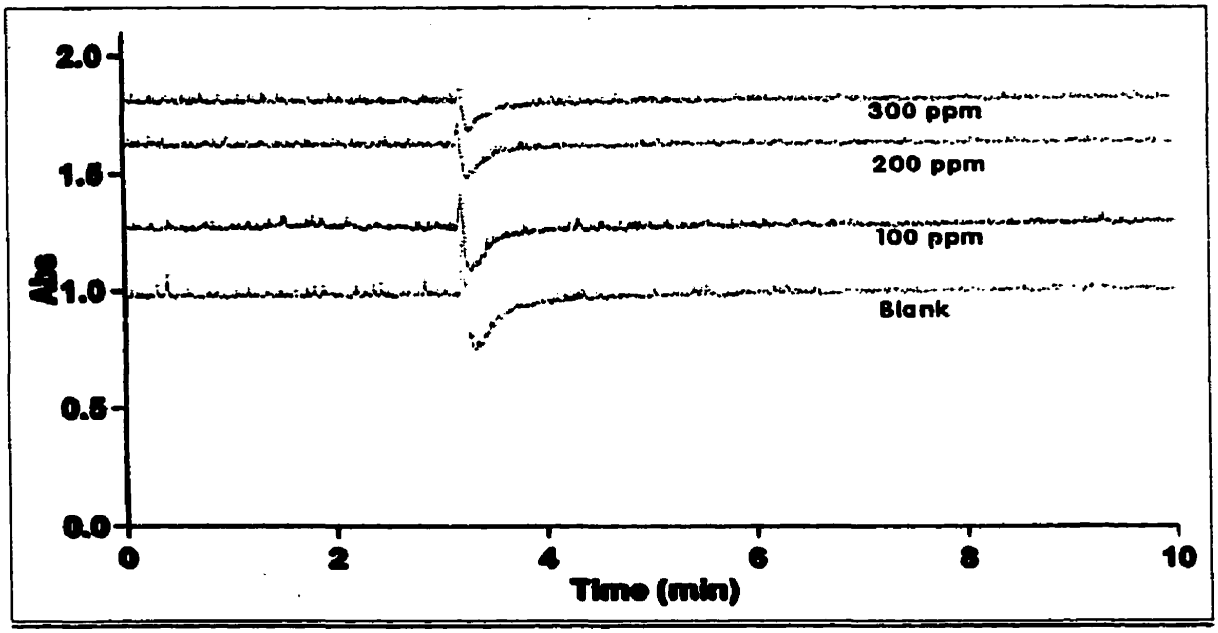

Figure 2.5: Plot of Absorbance vs Time for the Clay Experiments.

TABLE 2.7: Reduction in Flocculation as a Function of Clay Concentration and Surface Area of the Added Clay

Amount of clay added to the suspension	Reduction in Flocculation	Surface area of added clay
Blank (0)	------	------
100 ppm	35 %	1 - 2 m^2
200 ppm	50 %	2 - 4 m^2
300 ppm	60 %	3 - 6 m^2

Other experiments involving the use of clay were performed to study the difference in flocculation between a filtered white water system and a tap water system. At the same time, the impact of clay could be compared using those two different mixtures.

The flocculation was found to be much higher in the tap water systems than in the filtered white water system. In fact, the filtered white water system required twice the amount of polymer to obtain half the amount of flocculation that was observed with tap water.

2.6.3 - Fines

Some experiments were conducted using fines to add large amounts of surface area to the system. The system, already containing 600 ppm of fines, was spiked with similar fines in concentrations ranging from 300 ppm to 1000 ppm (in terms of grams of fines to total volume of solution). There was a substantial effect noticed when comparing the blank and the 1000 ppm of fines added. The reduction of flocculation had decreased a great deal, the light absorbance had also increased. This increase in the light absorbance was due to the increased presence of fine material in the system.

The 300 ppm and 600 ppm trials showed very little decrease in flocculation but were also not adding a great deal of surface area to the system Figure 2.6 shows the impact of the various fines concentrations on the flocculation efficiency of PEO. Table 2.8 gives an overview of the results for the experiment using added fines.

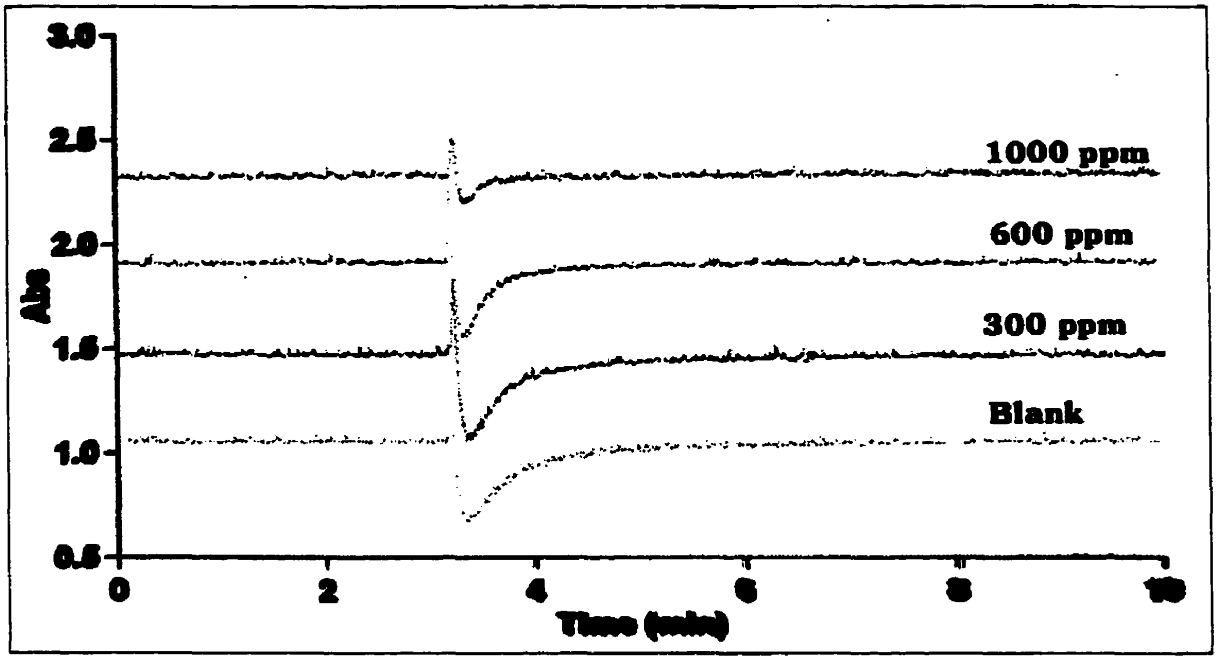

Figure 2.6: Absorbance vs Time for the Added Fines Experiment (λ=400 nm).

TABLE 2.8: Reduction in Flocculation as a Function of Added Fines Concentration and Surface Area of the Added Fines

Amount of fines added to the suspension	Reduction in Flocculation	Surface area of fines added
Blank	-----	-----
300 ppm	0 %	3.9 m^2
600 ppm	25 %	7.8 m^2
1000 ppm	67 %	13 m^2

2.7 - USE OF BENTONITE WITH RECYCLED PULP WHITE WATER

These experiments were done in order to study the efficiency of bentonite on a PEO-cofactor retention aid system in the presence of recycled white water. Some mills have seen a decrease in the retention of fines when recycled pulp was added. It was found that using bentonite could help (increase the retention) in situations where recycled pulp had been introduced. This section looks to corroborate the observations made in the mills.

2.7.1 - Experimentation

The pulp used in this set of experiments was TMP from Donohue in Matane. The preparation of the bentonite (Hydrocol O, from Allied Colloids) was done as follows: the bentonite was weighed and placed in an erlenmeyer flask and the distilled/deionized water was added to create a 3 % stock solution. This was stirred for 24 hours to ensure proper wetting of the bentonite. The bentonite requires at least a 24 hours of soaking in water to be at its optimum efficiency. The sample of bentonite used had been in water for several weeks, so it was assumed to be at optimum delamination.

The PEO and the cofactor were prepared in the same manner as described in the previous section.

The experiments were conducted in the same manner as described previously but instead of using tap water to disperse the pulp, filtered recycled white water was used. The filtration of the white water was performed by using Whatman 42 – ashless filter paper. The recycled white water was obtained at the Masson mill on a recycled feed tube. The experiments consisted of comparing the impact bentonite would have on a mixture made up of recycled white water and virgin pulp.

As seen in figure 2.7, the bentonite was injected in the system after 1 minute. The cofactor was added at the 3rd minute, and the PEO was added at the 5th minute. The dosage of bentonite used for this experiment was 30 mg/g of fibers. The dosage of cofactor and PEO were of 2 mg/g and 0.5 mg/g respectively.

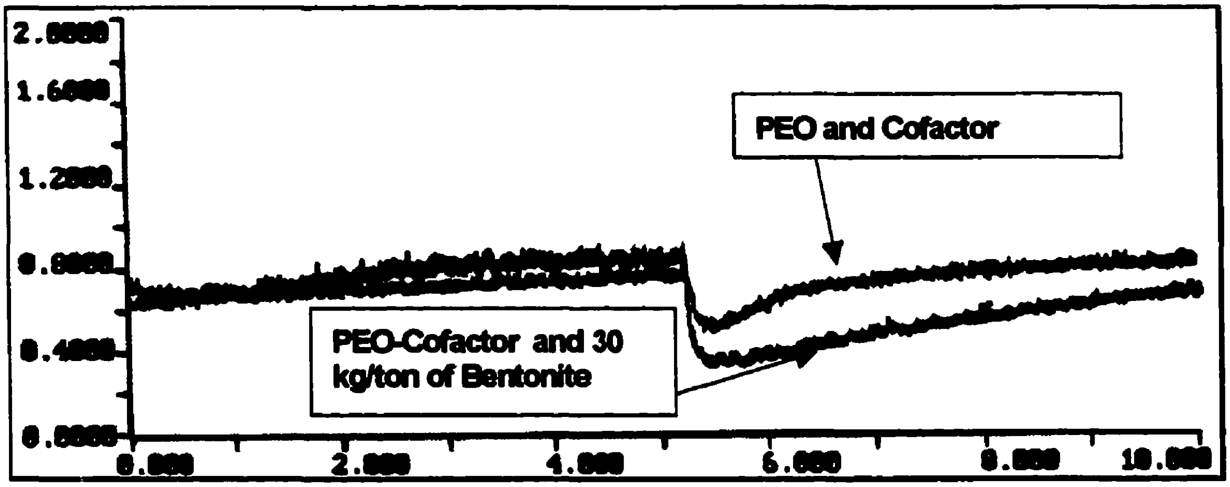

Figure 2.7: Flocculation of fines in recycled pulp white water with and without bentonite (λ = 400 nm).

2.7.2 - Results & Discussion

The difference in flocculation in a system with recycled white water with bentonite and without was clear. The flocculation of the system that did not use bentonite was slightly lower than 60 % of the magnitude of the flocculation of the system were bentonite was used. The idea behind these results is that the bentonite that was injected in the system acted as a scavenger in the system and adsorbed some of the undesirable colloids present. The adsorption of chemicals such as oleic acid and triolein, which are major components of wood resin, was studied by Rogan using talc treated montmorillonites and untreated montmorillonites [15]. In paper mills, the use of bentonite as a third component in a retention aid system has been proposed before [16].

2.8 - CONCLUSIONS

The results from Tables 2.6, 2.7 and 2.8 give a good indication that the problem with these types of systems is the amount of surface area available. The presence of fine material, clay, and dissolved organic and inorganic solids can all contribute to affect negatively the flocculation efficiency of PEO-cofactor systems.

The reduction in PEO flocculation efficiency is mainly due to the adsorption of PEO on colloidal material present in the white water, such as wood resins, clays, etc.

The results of these experiments are a good indication that the problems encountered by mills using recycled fibers with a PEO system are at least partly due to the increase in surface area brought on by the recycled matter. Other effects from calcium ions (seen by Laivins et al.) may also compound the negative effect on the PEO system.

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CHAPTER 3

THE STUDY OF A COFACTOR-PEO-BENTONITE SYSTEM ON A TWIN WIRE SHEET FORMER

3.1 - ABSTRACT

The development of a twin-wire sheet former at McGill University has led to a number of projects using this apparatus. One of these was to study the retention and drainage of a PEO retention aid system in something other than a dynamic drainage jar. There are a number of parameters of this machine which are similar to papermachines commonly found in the industry. The first step that was taken was to determine the reproducibility of the machine between runs. Once the measurements proved satisfactory, the reproducibility of the retention aid system was then studied. After, a wide range of PEO concentrations (50 g/t to 450 g/t) was used and the retention and drainage were determined. The retention increased as the dosage of polymer increased, but at the same time, the drainage of the web decreased. The impact of bentonite as a third component of the retention aid system was looked at. A range of concentrations of bentonite of 1 kg/t to 5 kg/t was used. The retention of the system was even better with bentonite and PEO than with PEO only. The drainage showed a marked improvement with an optimum at a bentonite dosage of 2 kg/t.

3.2 - INTRODUCTION

The retention of fines is a factor that has a great deal of importance nowadays in the papermaking industry. The role fines play is essential for paper quality, which is why their retention is such an important consideration. Fines allow fibers to bridge together in the final sheet formation so as to impart greater strength to the sheet. Because they scatter incident light, they play a major role in giving a sheet greater opacity. But the disadvantage of having an increased amount of fines in the sheet is that during the paper formation, the fines block water channels; this "plugging of the gaps" slows down the drainage of the webs. The study of retention aids is aimed at increasing the amount of fines retained while, at the same time, minimizing the negative impact on drainage this will have.

PEO-cofactor systems are among the more popular retention aid system found in newsprint mills these days. One of the main reasons for this is, that they are more effective than charged polymers in an environment where there are high concentrations of DCS (dissolved and colloidal solids) such as wood resins. PEO-Cofactor systems have been studied in dynamic drainage jars, in batch reactors, on pilot paper machines but never were studied on a laboratory scale twin wire sheet former. This papermachine was used to recreate some of the papermaking conditions found in industry. While a dynamic drainage jar (DDJ) allows for a PEO systems to undergo realistic shear conditions, that is the only variable that can be studied with this method. The dynamic drainage jar does not take into account the drainage profile that is seen on a commercial papermachine.

Drainage on a papermachine consists of two mechanisms: filtration and thicknening. Parker [1] has shown that they are not mutually exclusive but that the filtration process dominates in dewatering. With a dynamic drainage jar set-up, the dominating dewatering mechanism is thickening [2] , since the pulp slurry is in constant turbulent state. Britt et al. [2] go on to explain that the filtration process can be overcome by the thicknening process with a large enough series of pulses, which they have done in the laboratory. The reasoning behind this would mean that drainage on a twin wire sheet former would be dominated by the thickening process, due to the series of pulses the wires undergo during their stay in the drainage section. The advantage of the experimental machine [3] used over the use of DDJ is the fact that the experimental machine will recreate a drainage that resembles more closely what is seen on commercial machines due to the two-sided drainage than a DDJ will with its one-sided drainage.

Some work that has been done using the DDJ involved the use of a cofactor-PEO-bentonite system and its effect on the retention of fines in newsprint furnish [4]. It has found that the presence of bentonite yielded higher retention values than with PEO and cofactor only. The results obtained on the papermachine were similar to what was observed in the laboratory.

The lab-scale twin wire sheet former allows researchers to recreate shear conditions in a paper mill, allows to study this under wire speeds similar to what can be seen in a mill. It also allows researchers to study the whitewater collected from the machine in terms of consistency, volume collected and fines-fibers distribution.

3.3 - MACHINE DESCRIPTION

The schematic of the twin-wire sheet former developed and used at McGill University [3] is shown in Figure 3.1. A picture of the actual machine is shown in Figure 3.2. There are three main sections on this machine: the headbox section, the drainage section and the sheet pick up section.

The headbox section is comprised of the vat where the pulp suspension is mixed before it is injected into the tubing leading to the papermachine. The presence of a three-way valve allows for the pump to recirculate the pulp suspension back to the vat to increase the efficiency of mixing of the suspension. The pump is then set to the desired flow rate, the headbox opening is set to the proper thickness and the wires are set to their desired operating speed, then the valve is switched and the flow is directed towards the wires.

The headbox converts the tubular flow into a flat, broad sheet of pulp suspension, which then reaches the contact point between the two wires. This pulp suspension goes through what is called the drainage section of the machine where it undergoes a series of drainage created by pulse action. Most of drainage occurs at the point of initial contact between the pulp flow and the wires, what is called the primary forming roll. The following section where there is significant drainage occurring is at the secondary forming roll, which is found immediately after the primary forming roll. The forming section (containing the primary and secondary rolls) usually accounts for approximately 70 % or more of all the water drained during each experiment.

Further drainage is performed by a series of six alternating blades, which compose the blade section of the machine. The last drainage apparatus that is set-up on the machine is a group of three vacuum boxes at the top of the machine. These form what is called as the vacuum section of the machine.

The wet web is collected after the vacuum section and it is tested for water content. The measurements obtained will help in determining the effectiveness of the machine in the removal of water.

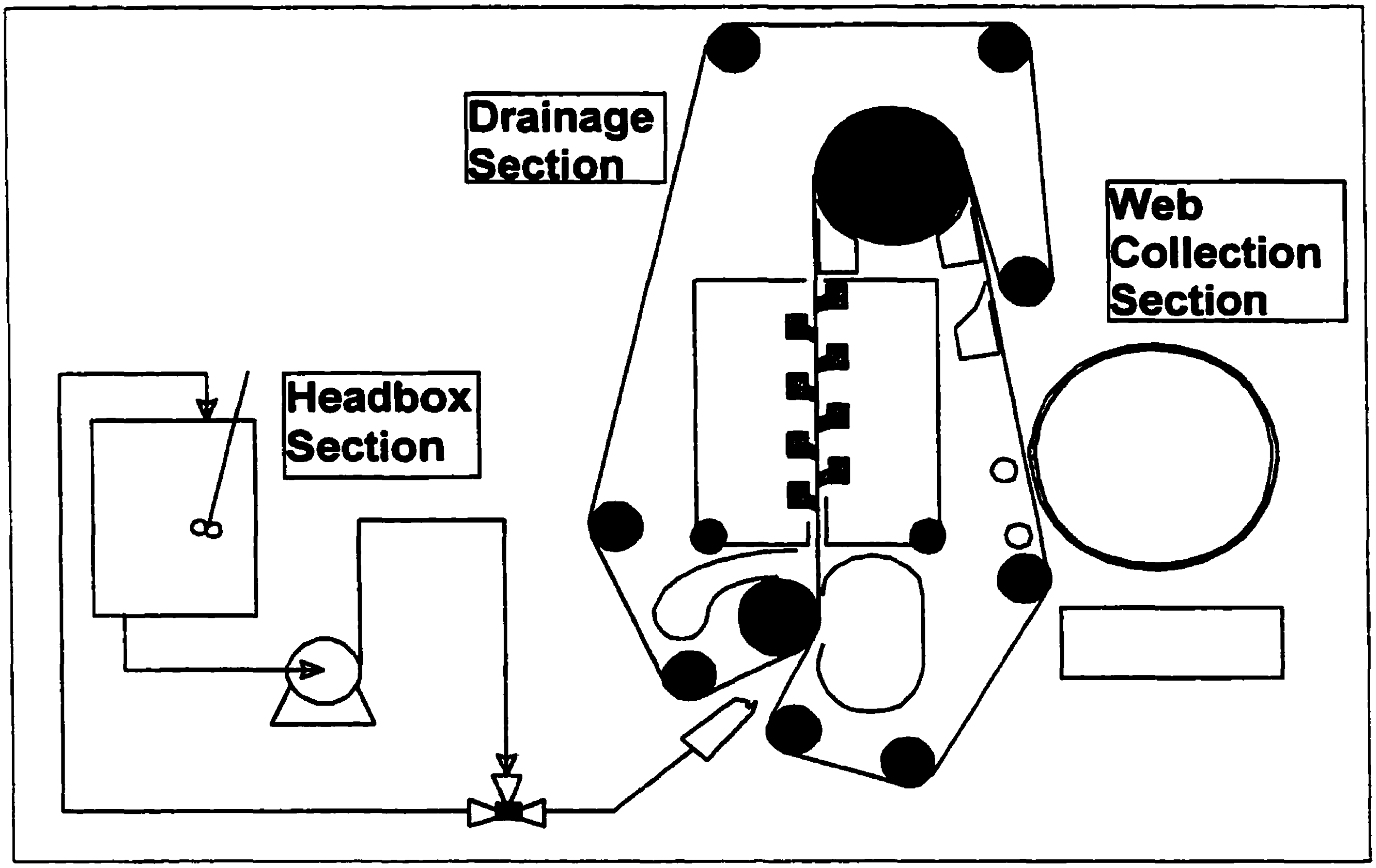


Figure 3.1: Schematic drawing of the laboratory scale twin-wire sheet former.

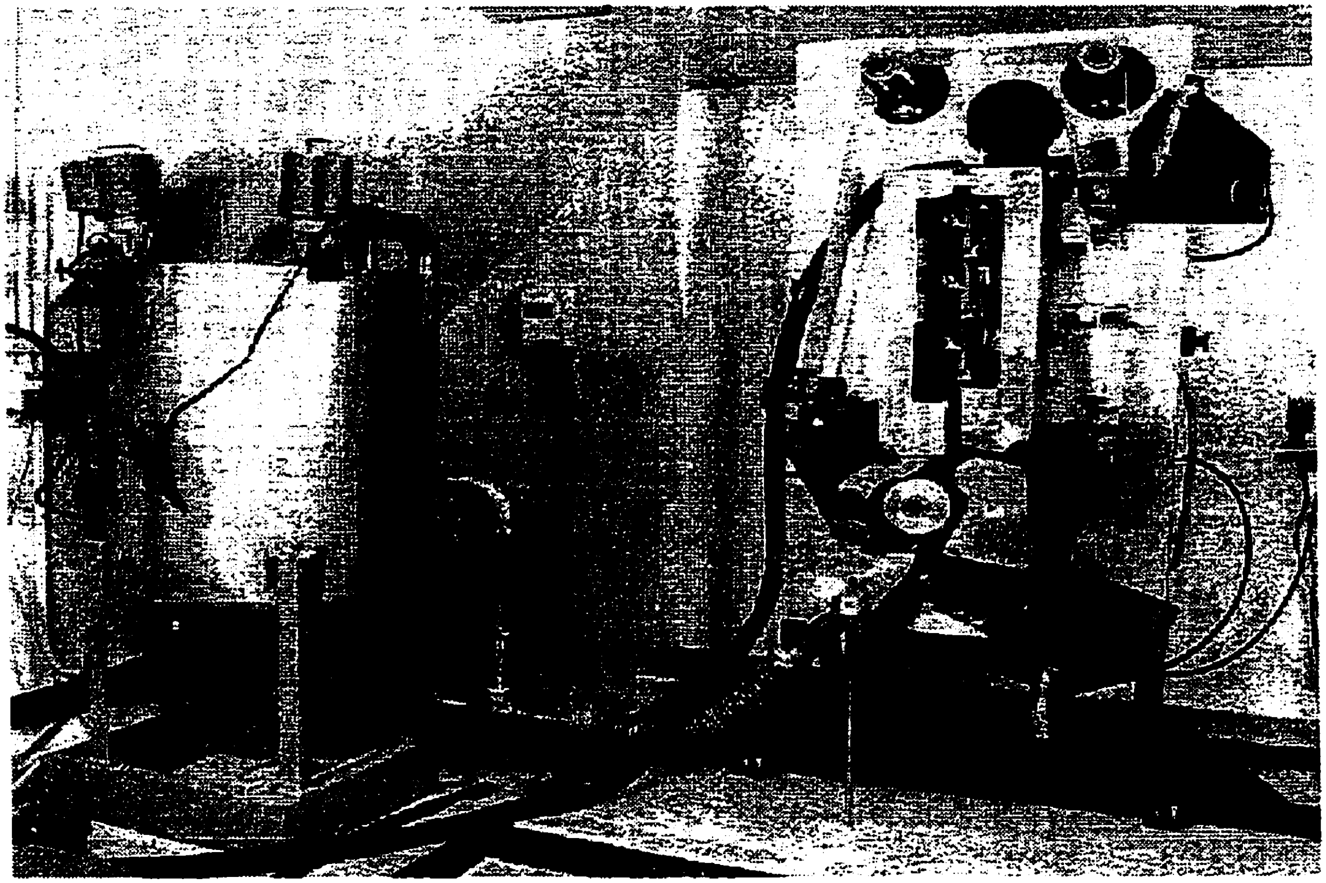


Figure 3.2: **Laboratory scale twin- wire sheet former.**

3.4 - MACHINE SPECIFICATIONS

The papermachine can use pulp slurries of consistencies varying from 0.3 to 1.2 %. The pulp can flow at speeds of up to 1.3 m/s, but it is used at 1.07 m/s (out of the headbox the speed of the jet is approximately 6 m/s). The maximum wire speed at which the machine can operate is 5 m/s. This is also the wire speed that was used for all the experiments performed on this machine. The basis weight of the sheet produced is 22 g/m^2.

The design of the machine allows for a multitude of different injection points, therefore various residence time of the injected solutions before they reach the headbox. The injection points that were used for the purpose of this work were the following. The PEO was injected 5.18 m from the headbox, giving it a residence time (or contact time with the pulp slurry before reaching the headbox) of approximately 4.9 sec. The PEO was injected at a velocity close to 1.8 m/s. The bentonite was injected further down the tubing at around 2.46 m from the headbox, this gave it a residence time of 2.3 s. The bentonite was injected at a velocity of 1.35 m/s.

3.5 - EXPERIMENTAL PREPARATION

Approximately 4.4 kilograms of sheets of BCTMP pulp (Black Spruce with 26 % fines content, freeness of 126 ml, provided by Uniforet, Port Cartier) were placed in large containers with water and were left to soak for 24 hours. The sheets were then disintegrated with the help of two mixers until the mixture was homogeneous. The disintegrated pulp was again left to soak in the water for 24 hours. The correct amount of pulp required to conduct one run was added into the vat of the papermachine, the pulp was then diluted to a consistency of approximately 0.5 - 0.6 %.

The PEO was weighed and added to a beaker containing distilled/deionized water. The PEO solution was left to mix overnight at low stirring speed to properly dissolve it. The solution prepared was of a 0.1 % concentration. The PEO stock solution is then taken and diluted to the required concentration for each experiment.

The cofactor (Interac 1323), which is a mixture of sulphonated kraft lignins and modified phenolic resins, is prepared one hour before the start of the experiments. It is dissolved in distilled/deionized water and stirred at medium speed for 20 minutes. The concentration of the stock cofactor solution is 0.4 %. The required amount of cofactor will then be taken from the stock solution and diluted to the appropriate concentration for each experiment.

3.6 - OUTLINE OF EXPERIMENTS

First, there was an experiment done to determine the reproducibility of the results obtained. This experiment consisted in comparing the fines retention of four blank runs, in other words runs in which no chemical compound have been added to the pulp slurry.

The second set of experiments consisted in performing runs to determine the reproducibility of a system using cofactor and PEO.

The third set of experiments was done in order to determine the efficiency in fines retention and the effect on drainage versus different concentrations of PEO used.

The fourth and last set of experiments was performed using a PEO-cofactor-bentonite system. There had been previous work showing that bentonite coupled with PEO and a cofactor would help the retention of fines and the drainage [4]. This experiment would allow the study of the phenomenon.

3.6.1 - REPRODUCIBILITY EXPERIMENTS FOR THE MACHINE

As was previously explained, this set of experiment was done to verify that the papermachine would work reproducibly from one run to the next. A series of four experiments using the same type of pulp (BCTMP) was run on the twin wire sheet former. The results of the retention and drainage were obtained from the white water that was collected at the various drainage sections: primary and secondary forming, foils section and primary and secondary vacuums.

The values for fines retention at different sections on the machine are obtained by calculating the amount of fines present in the web at a specific point in the machine divided by the initial amount of fines at the headbox. The results obtained gave us a standard deviation for fines retention measurement of 2.5 %. This result is used as the standard deviation for the results of all the subsequent fines retention measurements in the research. This was adequate for the needs of the research. The fines retention for each machine section can be studied by looking at Figure 3.3.

The results obtained for the web consistency (Figure 3.4) gave us a standard deviation of 0.3 %. This value is used as the standard deviation for the web consistencies for all subsequent experiments. This value was adequate for the intended purposes.

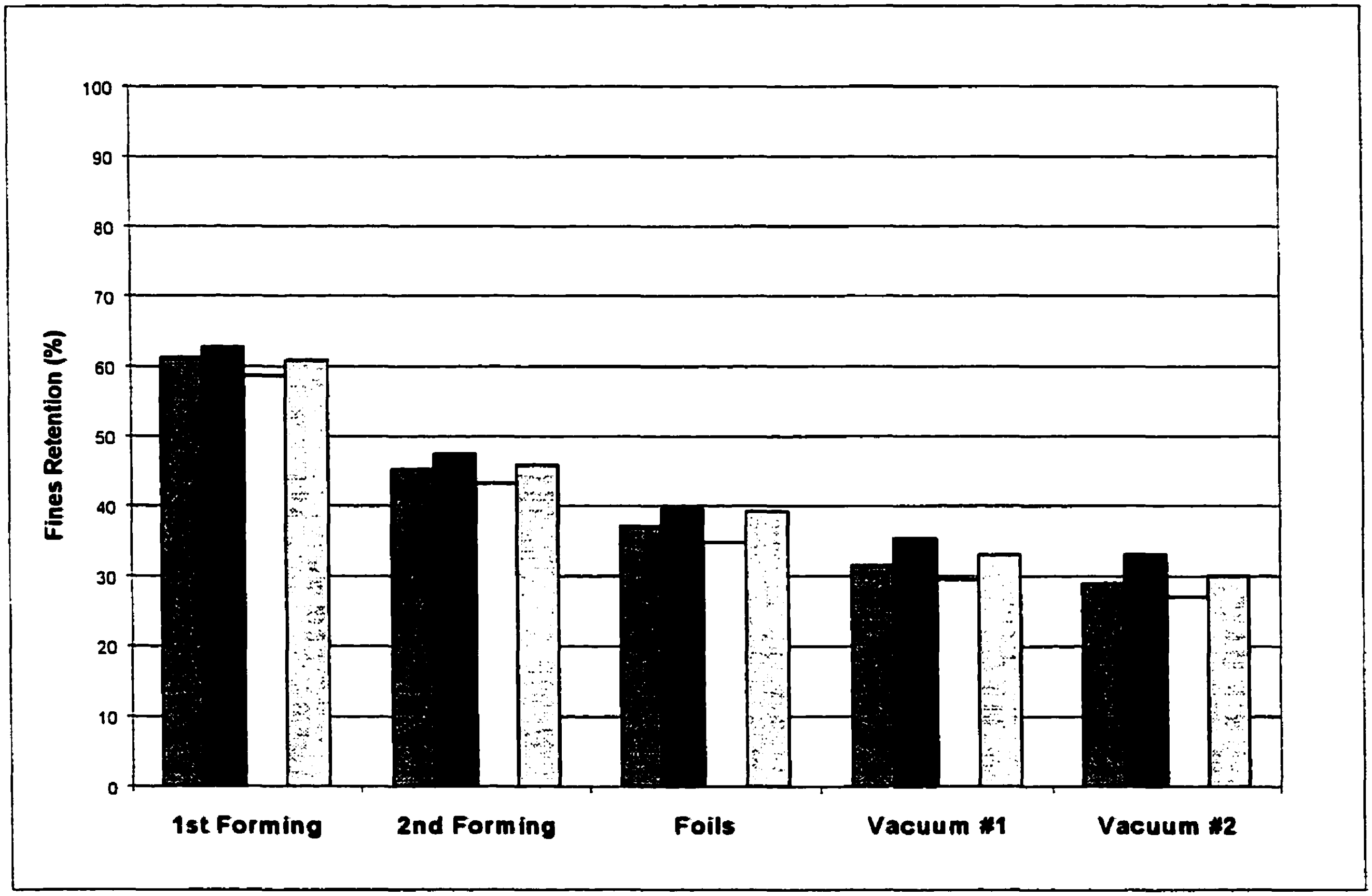


Figure 3.3: Fines Retention vs. Machine Section for Machine Reproducibility Experiment for four different runs

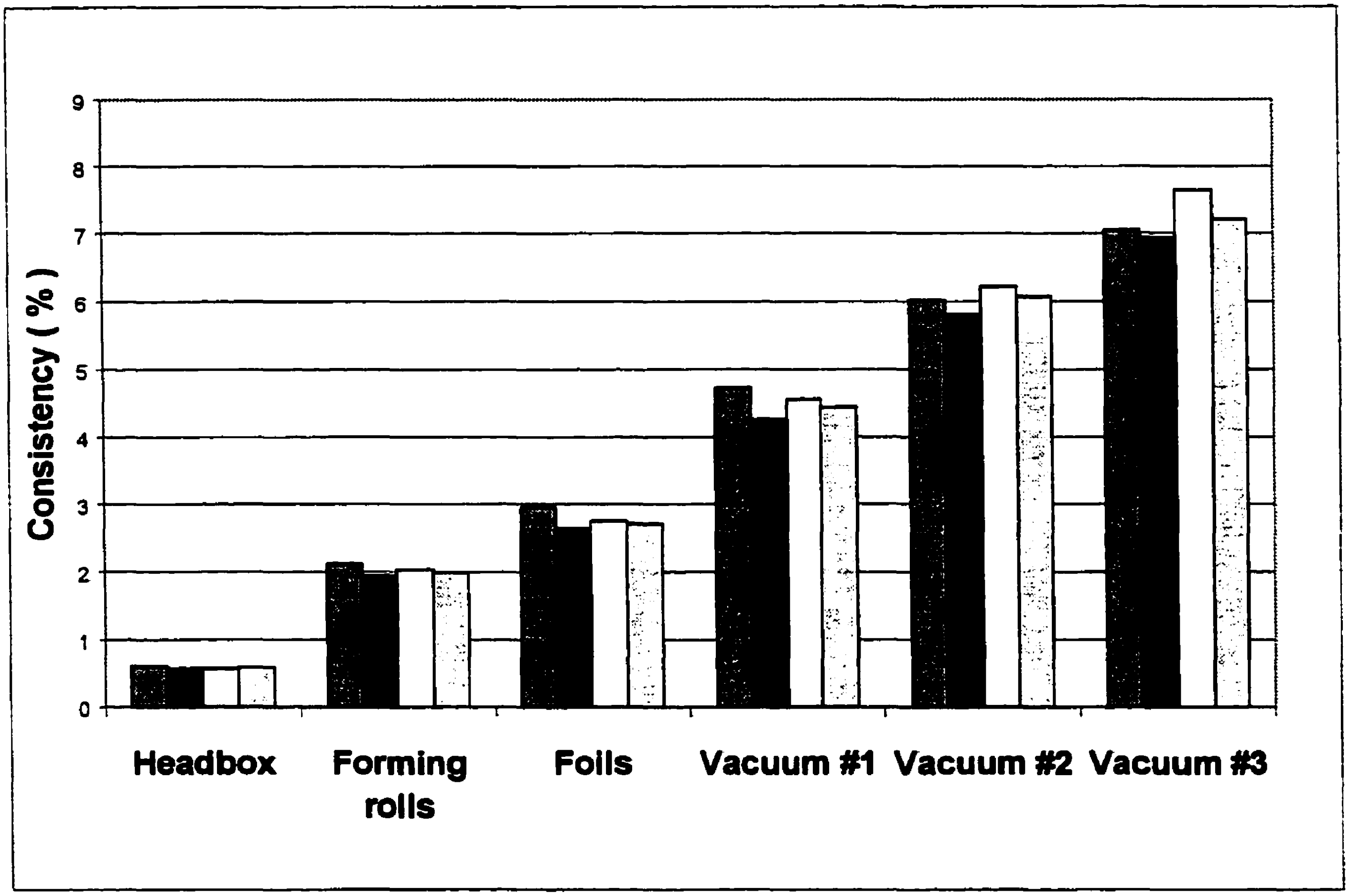


Figure 3.4: Graph of Web Consistency vs. Machine Section for Experiments of Machine Reproducibility for four different runs.

3.6.2 - REPRODUCIBILITY EXPERIMENTS FOR THE PEO SYSTEMS

This experiment was conducted to judge the reproducibility of experiments that used PEO and cofactor. The PEO used for these experiments had a molecular weight of 10,000,000. The cofactor, Interac 1323, was the same as for the experiments in chapter 2, is a mixture of sulphonated kraft lignin and modified phenolic resins.

The weight-to-weight ratio of cofactor-PEO used was 4:1. This means for every gram of PEO used in the experiment there are four (4) grams of cofactor used. This ratio was chosen as the most effective ratio for flocculation, according to some previous work done in our labs.

Figure 3.5 gives the fine retention at various stages of the machine for the experiments of PEO reproducibility. The final retention value, what is obtained at the 2nd vacuum section of the machine, gave a standard deviation of 2.8% for the three runs using PEO. This value was acceptable for the continuation of the work on this machine.

Figure 3.6 shows the web consistency as a function of machine section for the same experiment. The final web consistency, what is obtained at the 2nd vacuum sampling point, was found to have a standard deviation of 0.3%. This was reasonable to allow us to continue the work.

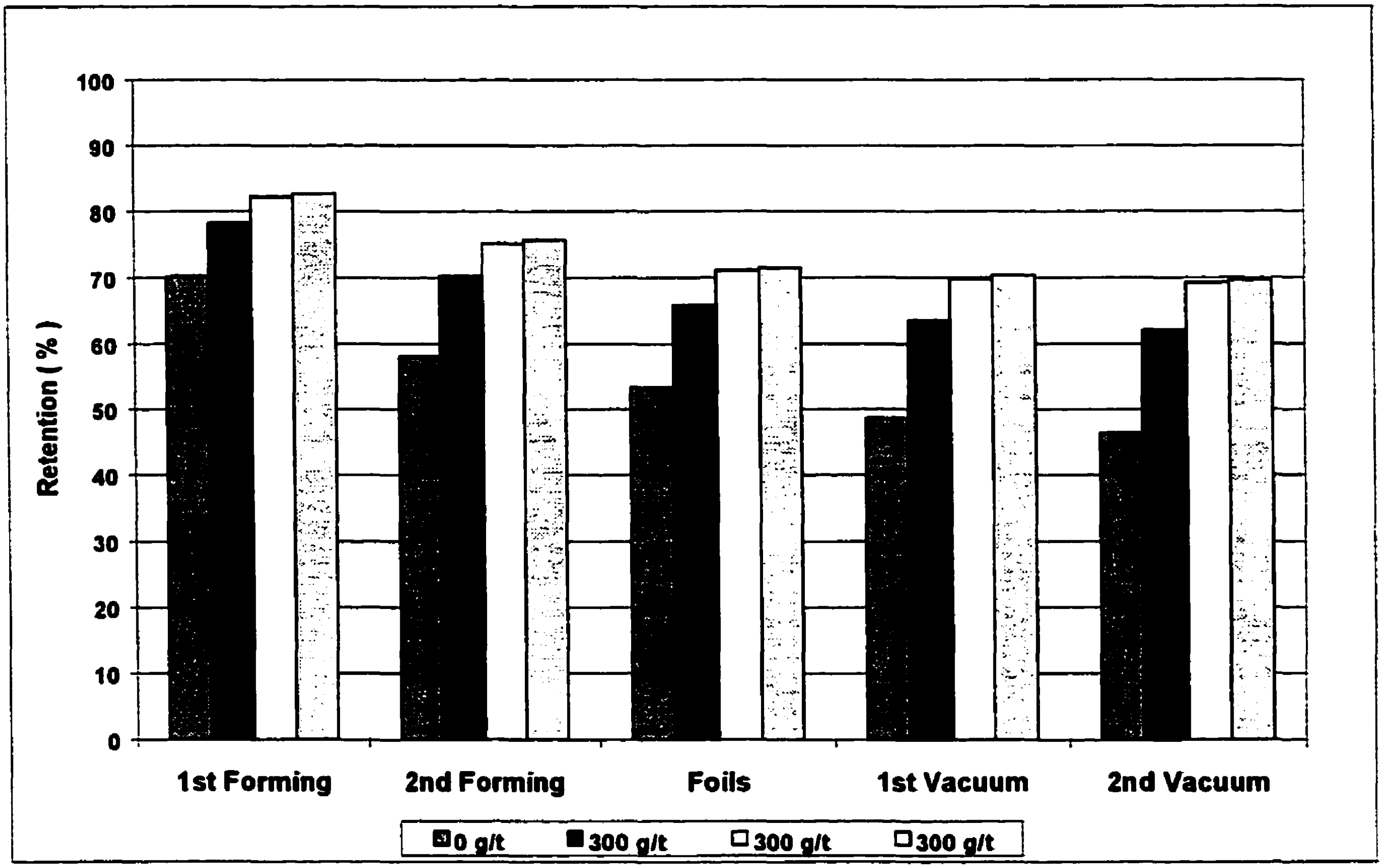
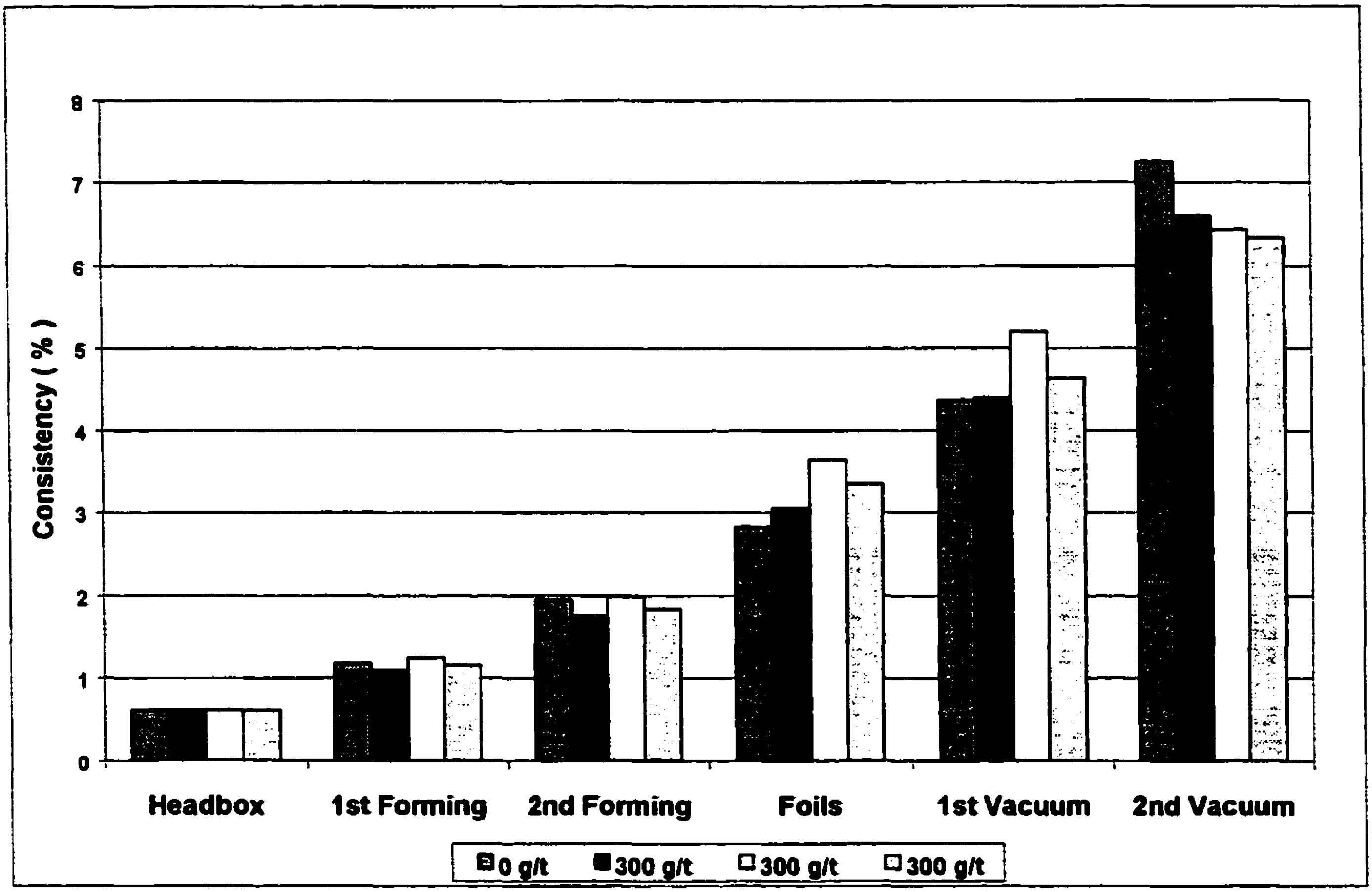


Figure 3.5: Fines Retention as a Function of Machine Section for the PEO Reproducibility Experiment.



<u>Figure 3.6</u>: **Web Consistency as a Function of Machine Section for PEO Reproducibility Experiment.**

3.6.3 - EXPERIMENTS STUDYING FINES RETENTION AND DRAINAGE AS A FUNCTION OF THE PEO CONCENTRATION

Experiments were conducted to study the effect of the PEO concentration on the retention of fines and the overall drainage performance of the machine when using such additives.

The sheet consistency plot (Figure 3.7) shows fairly clearly the drawback of using such a polymeric retention system as it lowers the sheet consistency the more the polymer is added.

As can be determined from the results (Figure 3.8), increasing the PEO concentration increases the efficiency of collision, therefore the retention itself but it is detrimental to the water drainage in the web (Figure 3.7). One explanation for this could be that some of the water channels in the web are blocked by the fines that are being retained.

At dosages of PEO of 300 g/t, the surface area coverage of the polymer on this specific pulp turns out to be approximately 16 %. One can safely deduce from numbers like these, that at dosages three to six times lower the effect on fines retention is increasingly smaller, due to the extremely small percentage of surface covered with the polymer.

Figure 3.9 combines the fines retention graph with the drainage graph and allows for the observation of a trend that by increasing the amount of PEO in the system the drainage of the web will decrease because the retention is higher. Ideally, papermakers would like to have both high retention and good drainage but these two phenomenons seem to counteract one another. It is for this reason that the next section will discuss the use of bentonite in the retention aid system to obtain both good retention and drainage.

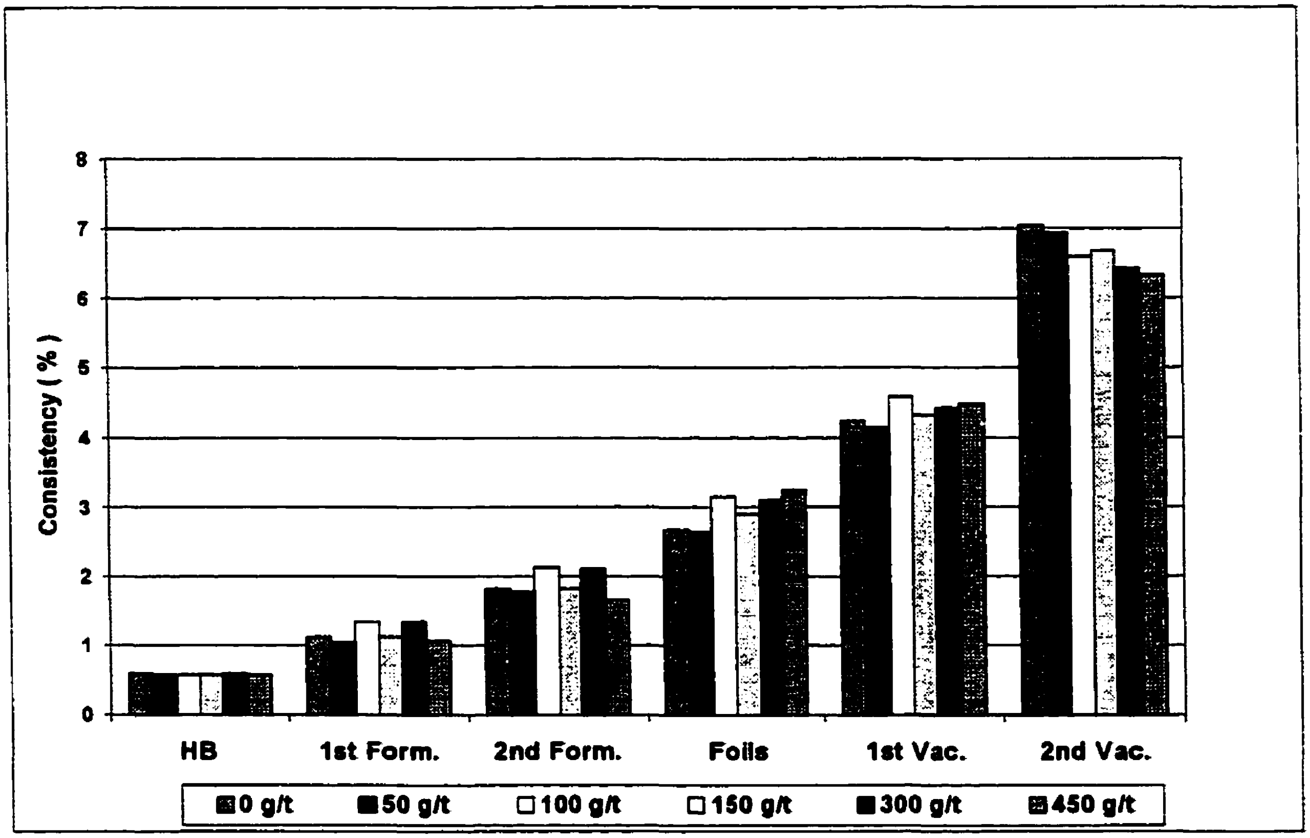


Figure 3.7: Web Consistency vs. Machine Section for Varying PEO Concentrations.

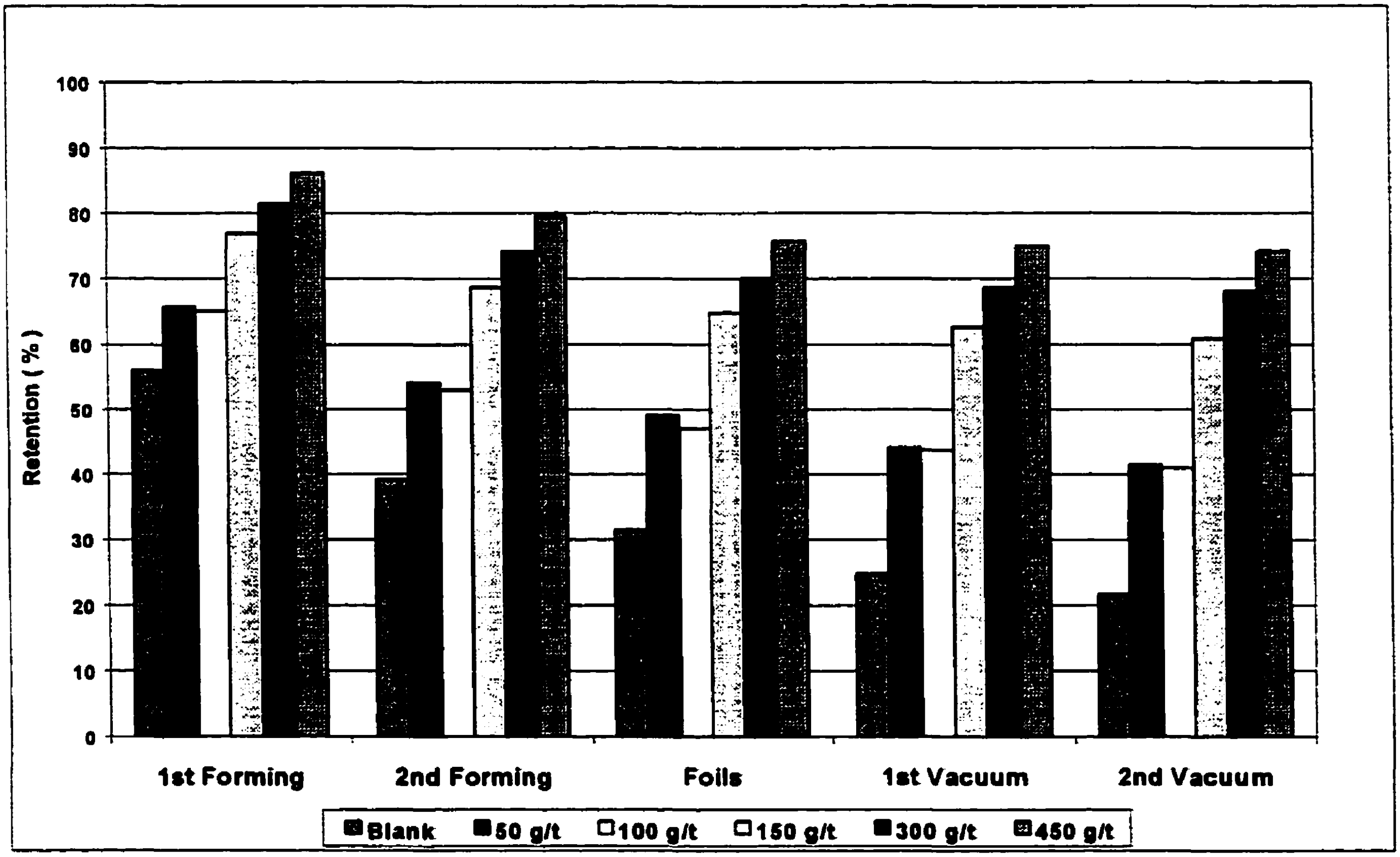


Figure 3.8: Fines Retention as a Function of PEO Concentration.

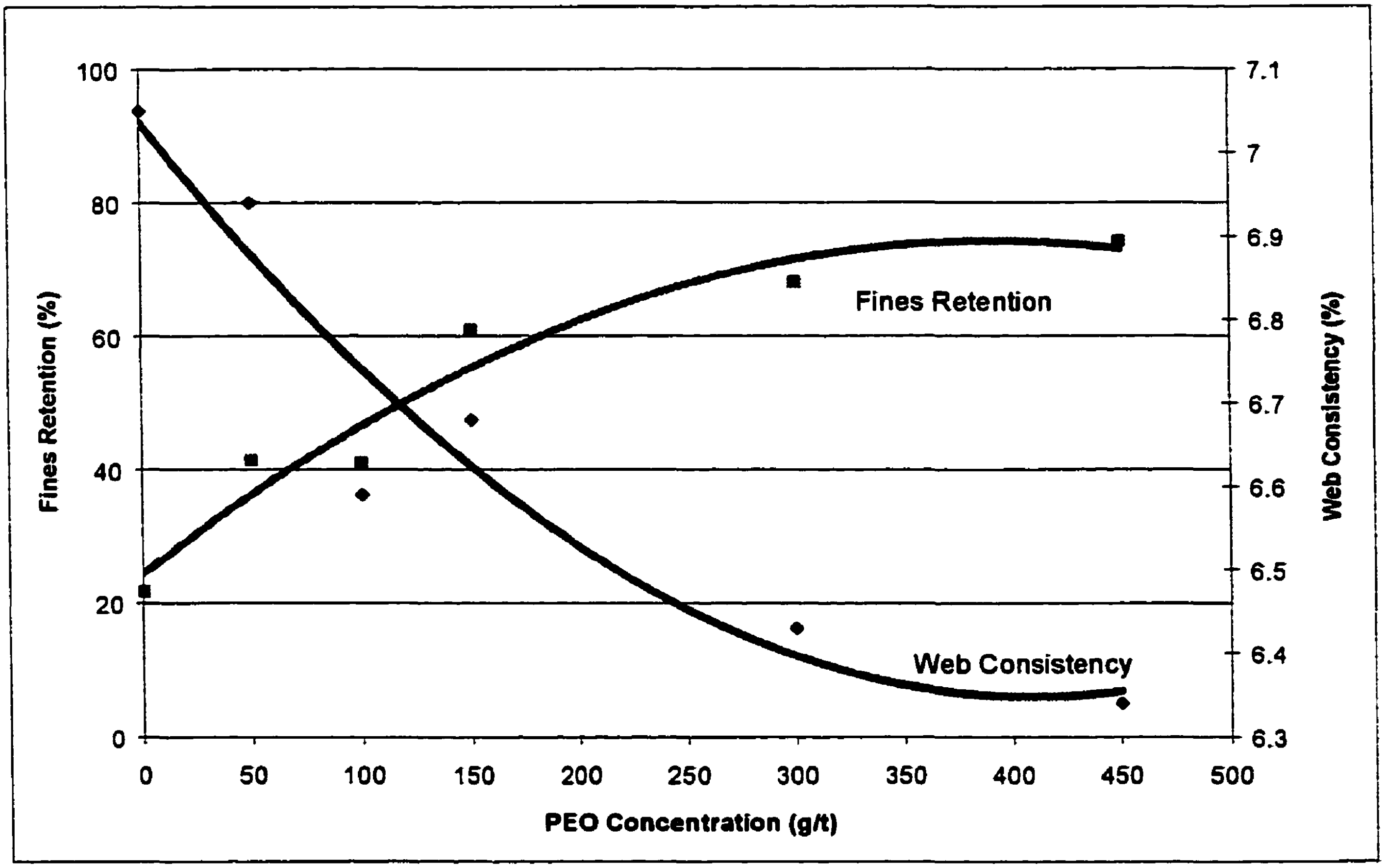


Figure 3.9: Fines Retention and Web Consistency as a Function of PEO Concentration.

3.6.4 - The Impact of Bentonite on the Retention and Drainage

The lab scale twin wire sheet former was used in the same fashion except that an extra injection port was used in order to allow for the injection of bentonite into the flow of pulp slurry. An experiment was conducted in order to look at the impact several different concentrations of bentonite would have on the retention and drainage of the PEO-cofactor system used and described previously. As was previously stated in the Beaudoin et al. [4] paper, there was a successful attempt to introduce bentonite in a PEO-cofactor system. The result was an increase in the retention of fines and the water drainage is maintained. The presence of the bentonite helped maintain the drainage at the same level while the sheet presented a higher fines content.

The experiment yielded comparable results as to what was obtained in the literature, namely the optimum bentonite dosage for the experiments performed at McGill was found to be 2 kg/ton. The bentonite along with PEO and a cofactor was found to increase the retention of fines and the dewatering.

Figure 3.10 shows the results on retention the addition of bentonite has had. There is a clear increase in retention between the system using PEO-cofactor and the systems using PEO-cofactor and bentonite. The optimum retention was obtained during the experiment using 2 kg/ton of bentonite. An excessive amount of bentonite was found to be detrimental to the system.

Figure 3.11 shows the positive impact the bentonite has on the system when compared to the system using only PEO. The best result for the web consistency was obtained by the blank run (without any chemical additive). The next best experiment in relation to the drainage was the experiment using 2 kg/ton of bentonite, the drainage obtained was very similar to the one obtained with no chemicals added. When too much bentonite was injected in the system the drainage suffered. So there is an optimal dosage of bentonite for the drainage aspect.

Figure 3.12 combines the results for the final retention of fines and for the drainage. The presence of bentonite has helped both in increasing the retention of fines when compared to a PEO-cofactor system only and in obtaining better drainage in the situation where the retention has been increased. This is a very desirable situation for papermakers who end up lowering white water consistency, without affecting too much the sheet dryness. The two points on the graph listed as Blank for drainage and Blank for Fines Retention are the values obtained for the experiment that did not use either PEO or Bentonite, they are used to compare the results of the experiments using chemical additives with an experiment using no additives.

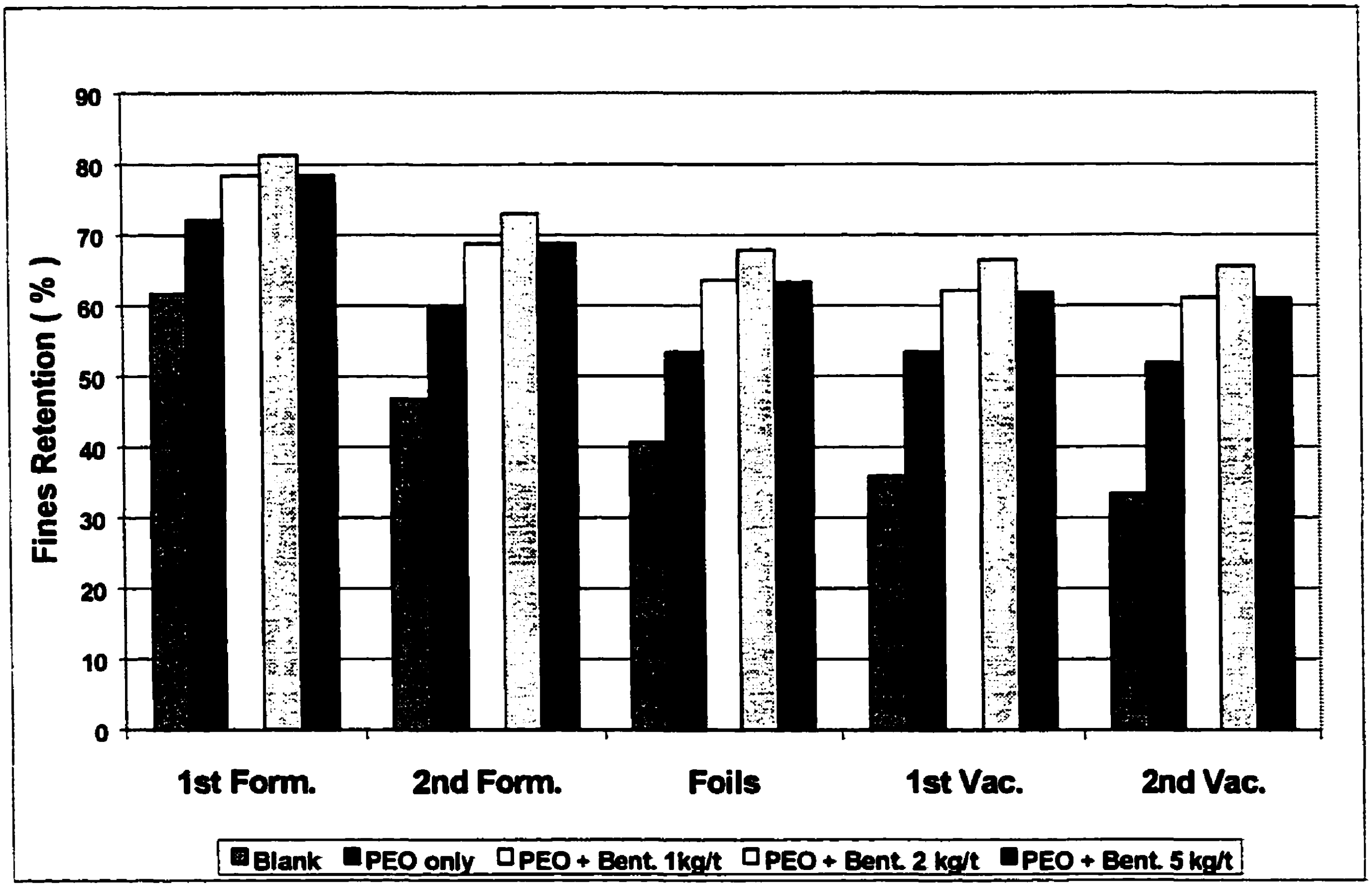


Figure 3.10: Fines Retention vs Bentonite Concentration at Various Machine Sections (PEO dosage of 300 g/t).

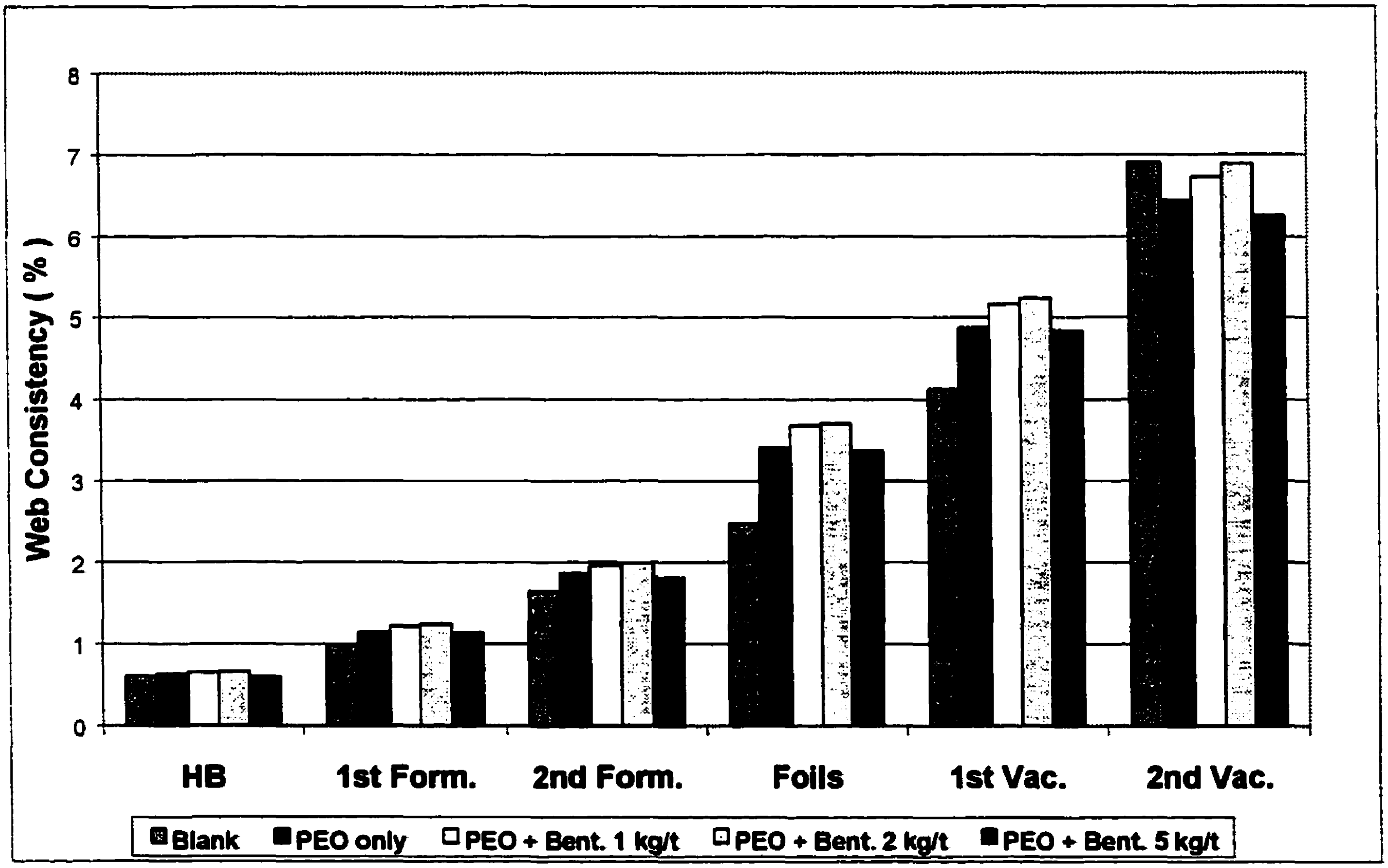


Figure 3.11: Web Consistencies as a Function of Machine Section for Different Bentonite Concentration (PEO dosage of 300 g/t).

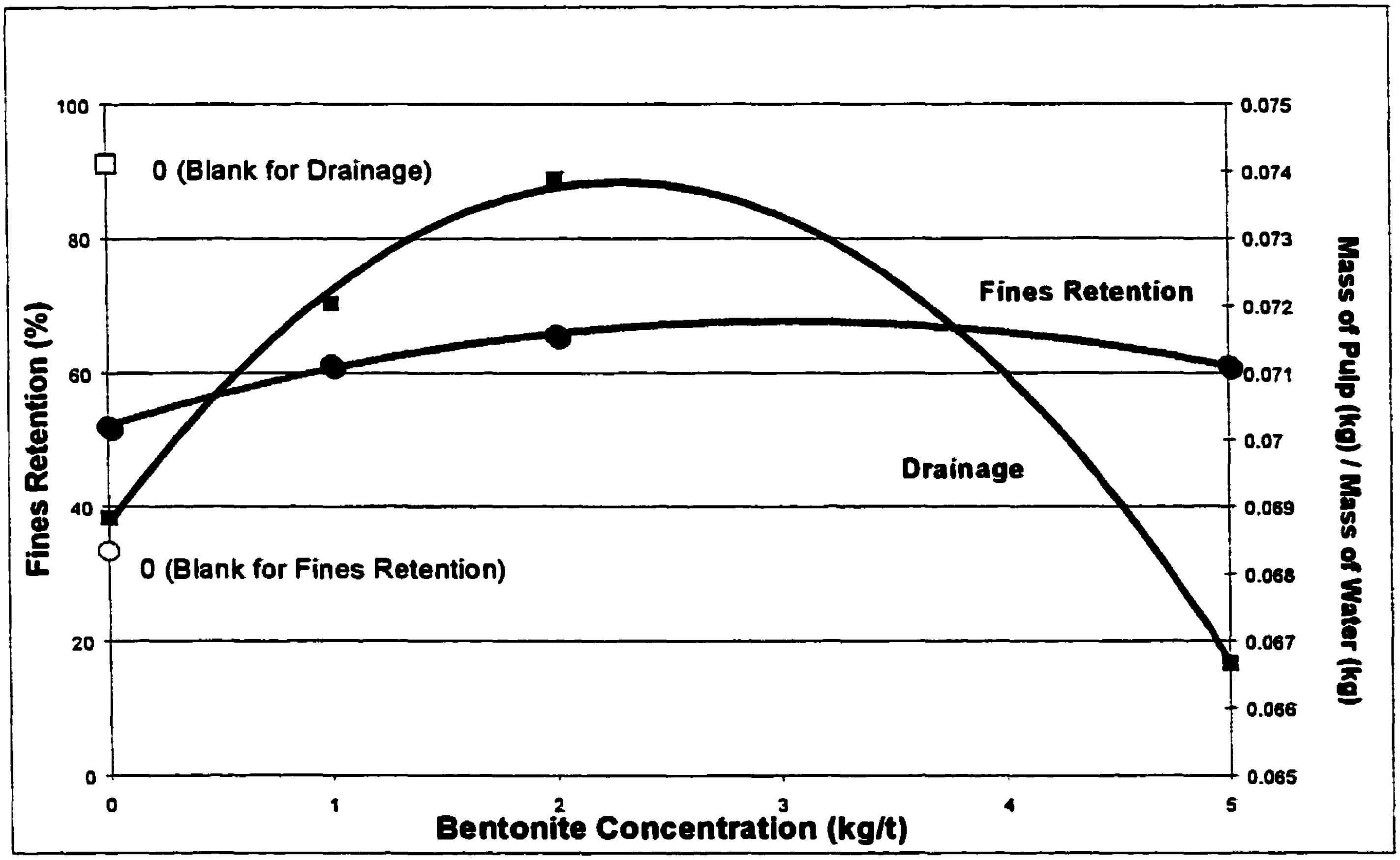


Figure 3.12: Fines Retention and Drainage vs Bentonite Concentration (PEO dosage of 300 g/t).

3.7 - CONCLUSIONS

This chapter covers the establishment of the reproducibility of the twin wire sheet former and then it shows the effects of the PEO-Cofactor system on the retention of fines and the drainage of the sheet.

Figure 3.8 clearly depicts the difficulties encountered when using a polymeric retention aid system. The trend connecting fines retention and drainage when using PEO-cofactor system can be described in this way: when fines retention is increased, the drainage of the sheet is decreased.

A major goal of this research is to increase fines retention without affecting, or with minimal impact, the drainage of the sheet (the web consistency). By adding bentonite in the retention aid system, the retention of fines was increased over a system using only PEO-cofactor (Figure 3.10). The increase had a maximum after which, the addition of bentonite became detrimental to the system. The water drainage of the web exhibited the same tendency, which is to say an increase in drainage up to by using bentonite in the 2 kg/ton dosage (Figure 3.11). After which, the abundance of bentonite in the system led to a decrease of the drainage abilities of the pulp.

Research done by several groups in Europe [5,6,7,8] has shown that the use of bentonite or silica clearly increases the floc strength (resistance to shear). The results of these researches point to the mechanism by which the colloidal silica or montmorillonite (main component of bentonite) act. These microparticles are the bridging element between polymer segments adsorbed on two separate particles. These microparticulate systems have been found to give more strength to the flocs because of the higher degree of flocculation [7]. Swerin et al. [5] determined that the increase in the strength of the flocs is due to an increase in the binding strength of the fiber-fiber contact and to an increase in the actual number of fibers present in the network (floc).

By achieving an increased retention and much better drainage with the use of bentonite as corroborated in the literature [4], the papermachine has proven to be a valid experimental tool for pulp and paper research.

3.8 - REFERENCES:

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CHAPTER 4

GENERAL CONCLUSIONS AND SUMMARY

4.1 - GENERAL CONCLUSIONS AND SUMMARY

The research's main two goals were first, to find out which compound (or compounds) were responsible for the decrease in efficiency of PEO-cofactor retention aid systems used in newsprint mills. The second goal was to use a laboratory scale twin wire sheet former in order to study the PEO-cofactor retention aid system in conditions that resembled those found in mills. The presence of bentonite along with the PEO and the cofactor to form a microparticulate retention aid system, although studied previously in the literature, was studied on this experimental paper machine.

The first part of the research consisted mainly in looking at the effects of compounds found in mill white water on the PEO-cofactor efficiency in retention of fines. Compounds such as calcium ions, oleates, calcium oleates, silicates and DTPA were looked at to see if, at concentrations found in mills, they could affect the flocculation of fines by PEO-cofactor. There was no evidence of any of those compounds having a negative effect on the retention aid system at common mill concentrations.

The second hypothesis stated that it wasn't necessarily a compound that was affecting the PEO-cofactor, but an increase in the surface area of the system which would have an effect on the retention of fines. Indeed, PEO works by adsorbing on a surface and then adsorbs on another surface to create a floc. The desired effect in papermaking is that PEO flocculates fines and fibers together to help in retaining fines. Fines-fines flocculation is also desired as the floc has greater chances of getting trapped in the web during paper formation.

The presence of a large amount of compounds which possess great specific surface area – such as the ones studied: fines, clay, colloidal organic compounds (in this case abietic acid) – can lead to a decrease in flocculation by lowering the % surface coverage of PEO-cofactor. In the presence of many large surface area compounds, PEO can flocculate, for example, clay and fines, clay and clay or colloidal organic compounds. By flocculating these particles the occurrence of fine-fiber or fine-fine floc decreases which in turn leads to a decrease in the retention values. The results proved that indeed at concentration levels found in mills the presence of large specific surface area compounds did lead to a decrease in the flocculation efficiency of the PEO-cofactor system by up to 67 %.

One final experiment was conducted to show that the presence of bentonite in a PEO-cofactor retention aid system was beneficial in that it acted as a scavenger which adsorbed colloidal material. This enabled PEO to work more effectively in flocculating the fines and the fibers. This strengthens the hypothesis that the overabundance of surface area in a given system may be the source of a problem with a PEO-cofactor retention aid system.

The second part of the research used a laboratory scale twin-wire sheet former to study a PEO-cofactor-bentonite retention aid system. These systems are commonly called microparticulate system because of the presence of clay, talc or bentonite as an essential element in the system.

First, the reproducibility of experiments on the machine had to be determined since no retention aids had ever been used on it. The results were deemed adequate for the purpose of this research. Then, the reproducibility of experiments using the retention aid was studied. If the variations between the four experiments were found to be too large when a polymer system was being used, the results of any further work would be questionable. Again, the results obtained showed the machine had good reproducibility when retention aids were used.

The third part of this chapter covered the effects of increasing polymer dosage on the retention of fines and the web consistency. Recall, lower sheet consistency means lower water drainage. The increasing concentration of polymer had the positive impact of increasing the retention of fines in the sheet but it also had the negative impact of lowering the water drainage hence lowering sheet consistency. (This is undesirable for papermakers who would be forced to increase drying time for the paper, this increases tremendously the cost of the paper). The explanation found for such a behaviour is that the increased concentration of fines in the web blocks the water channels that forms when the pulp is pressed between the two wires, by blocking those channels the web retains more water.

The experiments using bentonite-PEO-cofactor were the culmination of the work done in the chapter. The results speak for themselves, the retention is increased when bentonite is used along with the PEO-cofactor. The retention of fines is increased when PEO-cofactor is used when compared to a run with no additives, but this is to the detriment of the web consistency, which decreases in the presence of those additives. The presence of bentonite allows for the formation of larger and stronger flocs, which retain more fines and allow the water to drain out of the sheet almost as well as a system with no additives. The optimal bentonite dosage in this experiment was 2 kg/ton_{pulp}. Published work also pointed at that dosage as optimal for the best fines retention-water drainage combination. The use of bentonite as a scavenger in one instance, and as a retention aid in another, show that such a compound clearly deserves its place in the pulp and paper industry.

4.2 - RECOMMENDATIONS FOR FUTURE WORK

To further study the impact of recycled white water on a PEO system, one could conceivably obtain recycled pulp white water from a mill and perform experiments on the twin wire sheet former. One could look at the gain in retention when using PEO-cofactor compared to a system using no retention aid. Also look at the effect of bentonite on the same type of system, both as a scavenger and a retention aid. The experiments that could be performed on this machine are almost limitless because of its flexibility and ease of use, it allows scientist to perform experiments on a machine that resembles industrial paper machines without the high cost of renting the latter.

The methods used for these experiments can also be used to determine the best PEO-cofactor-bentonite combination for different furnish or different mills.

APPENDIX A

MEASUREMENTS WITH SPECTROPHOTOMETER

A 0.2% consistency pulp solution is prepared the previous day to ensure maximum pulp dispersion. The stirrer is placed in the beaker making sure that the brush on the stirrer is proper positioned in order to sweep the mesh that covers the inlet tube. This is crucial because if the brush does not properly sweep the mesh, the flocs of pulp may block the mesh and the pump will pump air bubbles in the tube. Once the set-up has been verified for proper working conditions, the mixer is set at 200 rpm and the pump is set at 200.

Using the Cary Varian Kinetics software the experiment is recorded as Absorbance vs Time (at $\lambda = 400$nm). The experiments consist in looking at the fines that are capable of going through the mesh into the tubing and the spectrophotometer. When a retention aid is added to the mixture the decrease in the absorbance will indicate the flocculation of fines onto fibers or with other fines creating a particle that cannot go through the mesh. This decreases the absorbance value and hence allows for the measure of flocculation relative to the blank run (where no additives are present).

The reduction in flocculation is essentially the ratio in percentage term of the magnitude of the loss in flocculation (measured by absorbance) of an experiment with the magnitude of flocculation of the blank experiment.

APPENDIX B

MEASUREMENTS WITH THE TWIN WIRE SHEET FORMER

First, approximately 4 kg of pulp are placed in two 150 liters plastic drum with water filled halfway up two days prior to the experiment, this step helps in the disintegration. The next day the drums of pulp are filled almost to the top and stirrers are placed in each drum and disintegration takes place overnight. The PEO is also dissolved the day before the experiment to ensure proper dissolution, it is left stirring overnight at low speed. The day of the experiment the cofactor is carefully dissolved and stirred at low speed. The pulp is then added to the vat connected to the machine and diluted to the appropriate consistency.

The machine's wires are sprayed with water and the experiment is run. The pump is adjusted to the setting 1750 rpm and the motor controlling the wire speed is set at 1750 rpm, at this speed the wires go at 5.3 m/s, both are the maximum settings for this machine. The valve for the pump which was set on "RECIRCULATE" is set to the position "MACHINE" and the pulp flows to the headbox. The water almost immediately starts draining at the collection points: vat, 1st forming roll, 2nd forming roll, blade section, 1st, 2nd and 3rd vacuum boxes. The web is collected in the web collection box. It is collected in the form of a crumpled sheet of pulp. The white water samples collected are in fact only 1 liter of each of the collection points. The sample of web collected is approximately a pound in weight.

The samples collected will be placed in aluminum containers (previously weighed) and weighed and then put in the oven to dry. Once dry the samples will be weighed once more and from this data the consistency can be obtained. The consistency of the white water at each point on the machine allows the operator to calculate the consistency of the sheet at each point in the machine by knowing what has been taken out of the wet web (water and pulp). The headbox samples are done four times to ensure accurate consistency at the starting point. The other sections are measured in duplicates, which is sufficient.

Once the consistency is determined, the measurements for fines content in the white water can take place. Samples of known volumes of each point of collection are analyzed using a 200 mesh fine separator. Knowing the consistency of the solution analyzed, a known volume is taken and diluted to 500 ml and passed through the 200 mesh fine separator. The pulp remaining in the mesh is collected and diluted again to 500 ml and passed again through the mesh. The pulp samples is passed 5 times through the mesh and then it is collected for filtration. The samples are filtered under vacuum with filter papers of measured weight. The samples are placed in the oven to dry. Once dry they are weighed once more. The difference in weight between the filter paper weight and the dried sample weight is the weight of fibers present in the pulp sample collected. By knowing the volume used, the consistency of the solution and the weight of fibers for a known volume, one can determine the percentage composition of fines and fibers in the white water.

Once the composition of the white water is known, the fines content of the wet web can be calculated for each point of the machine. The final retention values are obtained in this manner.