# EFFECT OF COAGULATION AND FLOCCULATION TECHNOLOGY ON BLEACHED KRAFT MILL EFFLUENT QUALITY

by

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## Abstract

Since January 1995 the tertiary colour removal clarifier at Crestbrook Forest Industries' Pulp Division in Skookumchuck, B.C. has removed  $60\pm4\%$  of the biologically treated effluent colour. Over the same period, BOD<sub>5</sub> was reduced by 26% and TSS was increased by 19 mg/L across tertiary treatment. This study revealed that the colour removal system removed 24%, 23%, 80%, and 18% of the COD, AOX, 2,3,7,8-TCDF, and mixed function oxygenase induction, respectively.

A study of the effect that basic effluent parameters had on system performance revealed that the dual polymer system used at Crestbrook Forest Industries operated well over a wide range of temperature, pH, and BOD<sub>5</sub>. Colour removal improved when pH was decreased to pH 3; below this pH the system performance declined. The increased colour removal at lower pH values could not be achieved by an increase in coagulant dose. Decreasing the temperature improved colour removal slightly, and different levels of BOD<sub>5</sub> had no effect on the percentage of colour removed.

Bench scale tests with segregated effluent streams (bleach plant filtrates and pulping area sewers), indicated that there are no possible reductions in polymer usage when these streams are treated separately from the rest of the mill effluent. Polymers used in the full scale system were well suited to treat chlorination stage effluent, achieving acceptable floc formation at relatively low polymer applications. The extraction stage effluent did not produce quality flocs when treated, and required high polymer doses to achieve moderate floc quality.

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## I. Introduction

## **1.1 Canadian Pulp and Paper Industry**

Pulp and Paper is a major industry in Canada, producing over 28 million tonnes of valueadded products, and directly employing 65 thousand people in 1996 (Anon, 1997). In contrast to the financial benefits this industry offers, pulp and paper production has been identified as a major source of pollutants. Pulp production is a water-intensive process that, in spite of recent efforts to re-use water in the process, discharges a vast amount of effluent. Even newly constructed Kraft pulp mills release over 50 cubic metres of effluent for every air dry tonne of pulp produced. Untreated, this effluent has a substantial negative impact on the receiving environment. In response to this, the Canadian government regulates the effluent parameters of biochemical oxygen demand (BOD), total suspended solids (TSS), acute toxicity, and dioxins and furans. A number of provincial governments have applied limits on the discharge of adsorbable organic halides (AOX). Other effluent parameters can be regulated on a site-specific basis, depending on the characteristics of the local receiving waters. In response to these regulations, the industry has implemented treatment technologies and process changes that have dramatically reduced the release of pollutants into the environment.

End-of-pipe effluent treatment systems for pulp mills in Canada are almost exclusively a combination of primary and secondary treatment. Primary treatment is a settling stage that removes larger particulate matter, and secondary treatment is a biological treatment

step, in which microorganisms remove the easily biodegradable material from the effluent.

Over the years, effluent discharge regulations have become increasingly strict. In 1992, the Canadian government introduced legislation that required mills to do an environmental assessment of their discharge on the surrounding ecosystem as part of an environmental effects monitoring (EEM) program (Environment Canada (EC) and Department of Fisheries and Oceans (DFO), 1992a; EC and DFO, 1992b). Recently, the U.S. Environmental Protection Agency (EPA) has introduced stricter regulations on effluent quality as part of their new "cluster rules". Neither country's federal regulatory bodies have implemented limitations on the colour of effluent discharged from pulp mills. Colour has only been regulated on a site-specific basis, primarily because it is believed that the high molecular weight (HMW) molecules that contribute to colour do not exert a substantial environmental impact. Some mills have been required to install a colour removal system as a tertiary effluent treatment stage as a result of the particular characteristics of local receiving environments.

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## **1.2 Kraft Pulping**

Paper is commonly defined as "...a felted sheet of fibres formed on a fine screen from a water suspension...." (Smook, 1992) and pulp is the fibrous raw material used to make paper. In most cases pulp and paper mills utilize wood residuals from sawmills as a fibre source (Smook, 1992). One of the most common techniques to convert wood to pulp is the Kraft process. A Kraft pulp mill cooks wood chips in a solution of NaOH and Na<sub>2</sub>S under high pressures and temperatures to separate lignin from the desired cellulose fibres. A subsequent pressure release blows apart the chips softened by the cooking process into individual fibres (pulp). The pulp is then washed to remove the cooking chemicals and dissolved lignin, and is subjected to screening to remove the uncooked portions of the pulp. The cooking process is not able to achieve full removal of the dark lignin without creating pulp of low quality, so the pulp requires bleaching if white cellulose fibres are needed as the end product.

Bleaching is typically achieved by passing the pulp through a five-stage bleach plant and washing the pulp between each stage. Stages one, three, and five are acidic bleaching (chlorination) stages. Stages two and four are caustic extraction stages. In the acid stages, chlorine and/or chlorine dioxide are added to react with the lignin not removed during the cooking process. Extraction stages use high pH conditions to extract the lignin degradation products (created in the previous bleaching stage) from the pulp. Peroxide and oxygen are commonly added to the extraction stages to achieve higher brightness in the final pulp and to reduce the amount of chlorine-containing bleaching chemicals added in the acidic stages.

Recently, some mills have introduced an oxygen delignification stage prior to the bleach plant. This reduces the lignin content of the pulp entering the bleach plant by approximately 50%, and recycles the removed organics back to the recovery system. After the bleached pulp leaves the bleach plant as a slurry, it is dried in the machine room, and is ready to be shipped to market.

What makes the Kraft process unique is the ability to recover the cooking chemicals (NaOH and Na<sub>2</sub>S). Filtrate from the washing stages after the cooking process, weak black liquor, is concentrated in multi-effect evaporators to make strong black liquor. This concentrated mixture of organics and inorganics is then burned in a recovery boiler, which completely oxidizes the organics into carbon dioxide and water, and recovers the inorganic portion, which is subsequently converted back to NaOH and Na<sub>2</sub>S, ready to be re-used in the cooking process.

## **1.3 Effluent Colour**

For a compound to exhibit colour, it must absorb visible light. This adsorption of light involves the promotion of a bonding electron to a higher energy level (Fessenden and Fessenden, 1982). Radiation in the visible spectrum possesses enough energy to promote loosely held  $\pi$  electrons, to higher energy levels (Bailey and Bailey, 1989). Organic compounds that absorb visible light appear to have colour. Typically these compounds possess a colour-bearing group (a chromophore) conjugated with an extensive network of alternating single and double bonds (Bailey and Bailey, 1989). If long enough, a network of single and double bonds alone can cause colour (Fessenden and Fessenden, 1982). In addition, carboxylic and phenolic acid groups can influence the colour of molecules (Bailey and Bailey, 1989).

Lignin and lignin degradation products are believed to be the main sources of colour in Kraft pulp mill effluent because they possess a large number of aromatic rings and double bonds in conjunction with quiomethides and quinones (Rush and Shannon, 1976). UV-visible spectroscopy of Kraft lignin shows it absorbs radiation strongly at shorter wavelengths, which is responsible for its brown colour in pulp mill effluent (Springer, 1993). Research has been published that challenges the assumption that lignin is the main source of effluent colour from a bleached kraft pulp mill (Ziobro, 1990). Chromophores in Kraft mill effluent consist mostly of high molecular weight compounds (i.e. >1000 Daltons), a quality that most of the colour removal techniques exploit to aid in its removal (Sagfors and Starck, 1988; Rush and Shannon, 1976).

#### **1.3.1 Colour Measurement**

Colour should not be confused with turbidity, which arises from light scattering instead of light adsorbence (Springer, 1993). The standard procedure to measure colour involves measuring the absorbence of light at 465 nm of a sample that has undergone pH adjustment and has passed through a  $0.8 \,\mu\text{m}$  filter (CPPA, 1993a). One colour unit (c.u.) is equivalent to the adsorption of light at the wavelength of 465 nm by 1 mg/L of platinum in the platinum-cobalt standard solution (CPPA, 1993a). The filtering step is to ensure that no suspended solids interfere with the "true" colour measurement (Dorica *et al.*, 1976). Using a filter to remove suspended matter has been subject to criticism; the pore size used still allows some suspended solids to pass through and is small enough to block passage of some chromophoric HMW compounds. Centrifuging the effluent will remove suspended solids, but the radius and speed of the centrifuge are variables that affect the test results (Dorica *et al.*, 1976). Although flawed, filtering allows for better standardization and is considered to be more practical (Dorica *et. al.*, 1976).

#### **1.3.2 Sources of Effluent Colour**

Pulp mill effluent colour comes almost exclusively from three sources: pulp cooking, pulp bleaching, and coloured paper production (Springer, 1993). The colour sources that are of main concern are pulp cooking and bleaching (Springer, 1993). Colour from pulp cooking operations is typically discharged from the filtrate of the last washing stage prior to the bleach plant. The colour from this source is from large lignin molecules that are only slightly soluble in aqueous solutions at neutral or low pH (Adams, 1997). Modern pulp mills recycle this flow back to the recovery process. In these mills, colour from the

chemical pulping area represents only a fraction of the final effluent colour. The filtrates from the washing stages in the bleach plant are difficult to fully recycle within the process, which results in a portion of the filtrates being discharged to the effluent treatment system (Maples *et al.*, 1994). The majority of the colour from the bleach plant effluent comes from the extraction stages, but the acid sewers still represent a significant source of effluent colour. A colour balance recently performed on the effluent sewers at the Weyerhaeuser mill in Grande Prairie, Alberta, quantified the contributions of the main sewers to the overall effluent colour as: alkaline bleaching stages, 50%; acid bleaching stages, 28%; brownstock, 7%; recovery/evaporators, 7%; and others, 8% (Pryke *et al.*, 1994).

### **1.3.3 Impact of Colour on Receiving Environments**

It is a widely-held view that the only negative impact effluent colour has on receiving waters is on those organisms requiring light for growth (Anon, 1994). In a report of laboratory results prepared by the Division of Applied Biology at B.C. Research (Anon, 1974), it was found that both treated and untreated bleached Kraft mill effluent (BKME) had an impact on the growth of green algae (*Selenastrum capricorputum*) in the first meter under the water's surface. Howard *et al.* (1979) performed a study investigating the effect of BKME on algae growth in a lake and concluded that an increase of surface water colour of 100 colour units was required before a significant impact on algae growth was observed. Regulating colour poses a number of difficulties because colour is a property of the effluent and not a specific substance. The impact of compounds

responsible for effluent colour on the environment may differ substantially from one mill to another.

#### **1.3.4 Colour Perception**

If the impact of colour on the receiving environment can only be seen with an increase of 100 colour units, the impetus to regulate the colour of mill discharges which increase the colour of the receiving water less than this amount (100 c.u.), is to preserve the aesthetic qualities of the environment. Concerns about the impact on aesthetic value of surface waters led Maine to pass legislation which limits the increase in colour of the receiving water to less than 25 c.u. for clear streams, or 40 c.u. if background colour is present (Anon, 1994). Regulating colour discharge based on appearance led to a survey on perception of colour in Tennessee's Hiwassee River. Researchers in this study concluded that "...total colour concentrations between 104 and 128 units are not only acceptable, but attractive..."(Prestrude, 1991). In the summary of the study, it was unclear whether the sample group was made aware of the source of the colour increase. According to an NCASI Special Report (Anon, 1994) on human perception of colour from kraft mill effluent, colour increases of 41 c.u. and decreases of 45 c.u. are perceivable by 90% of the population. The ability to detect colour increases was affected by a number of variables such as observation site, bottom visibility, and observer memory (Anon, 1994).

### **1.4 Colour Removal Techniques**

Methods for colour removal have been studied in detail since the 1960s (Springer, 1993). They have received attention recently because of the placement of colour on the list of candidate parameters that was to become regulated in the EPA's "cluster rules" (Anon, 1994). Since colour removal addresses the HMW fraction of organics typically untreated by conventional effluent treatment technologies, studies addressing colour removal are often motivated by the need to assess the effect of each removal technology on AOX reduction.

Due to the high cost of end of pipe treatments for effluent colour reduction, the preferred method to decrease colour discharge is through in-plant modifications (Springer, 1993). By reducing the lignin content of the pulp entering the bleach plant (through such implementations as improved washing or oxygen delignification) and decreasing the use of molecular chlorine as a bleaching agent, the colour of bleach plant effluent can be dramatically reduced. If sufficient colour reduction is not possible by process modifications, a number of colour removal technologies are available, including:

- chemical oxidation,
- biological treatment,
- photocatalysis and photo-oxidation,
- adsorption systems,
- filtration, and
- coagulation/flocculation.

#### **1.4.1 Colour Removal by Chemical Oxidation**

A number of chemicals are capable of oxidizing chromophoric compounds. Using oxidation as a method of colour removal results in the destruction of toxic compounds and no direct sludge formation (Saunamaki and Sorvari, 1992). Oxidants that have been experimented with are oxygen, ozone, chlorine, chlorine dioxide, and peroxygens.

Under ambient conditions, the oxidation of organic compounds with oxygen is not thermodynamically favoured and, therefore, high temperatures and pressures are required to force the reaction to proceed (Portefaix and Figueras, 1978). Sun *et al.* (1989) observed the removal of 60-70% of the colour from an alkali bleaching filtrate in a vigorously stirred reactor under the conditions of 150°C and 150 psi for 40 minutes. Under these same conditions, decolourization was not achieved without the addition of oxygen. From the results of this study, the authors concluded that the reaction of oxygen with the chromophoric material was mass transfer limited.

Oxidation with ozone does not require the severe conditions needed when using oxygen (Amero and Hilleke, 1993). Treating effluent with ozone has been shown to be highly effective in reducing colour, AOX, and chemical oxygen demand (COD) (Saunamaki and Sorvari, 1992). Other benefits of using ozone include high dissolved oxygen levels in the final effluent and the action of ozone as a bactericide (Baumon and Lutz, 1974). Oxygen and ozone treatments can also produce low molecular weight (LMW) reaction products which, if untreated, can exert BOD. Hostachy *et al.* (1996) demonstrated that, although ozone creates five-day biochemical oxygen demand (BOD<sub>5</sub>) at lower ozone concentrations, it reduces the BOD<sub>5</sub> at higher ozone dosages. Complete colour removal is not possible with ozone; Amero and Hilleke (1993) found that 50% of the effluent colour quickly degraded, 40% degraded slowly (requiring large ozone applications), and

10% of the colour was resistant to treatment with ozone. The major obstacle preventing ozone treatment from being applied as a full scale effluent treatment method is the high cost of ozone production. Since it is unstable chemical, it must be produced using an on-site generator, which can lose up to 95% of its energy input as light, sound, and heat (Springer, 1993).

Bleaching agents containing chlorine have been shown to reduce effluent colour (MacNeill, 1984), but concerns over the chlorinated organics generated from this practice make this approach unattractive.

Peroxygens, particularly hydrogen peroxide, are another group of oxidants shown to be effective in reducing effluent colour. Hydrogen peroxide is an attractive chemical to use because most mills already store it on site for pulp bleaching. While peroxide does not remove colour as effectively as ozone, it has been shown that using the two in combination can result in a high level of colour removal, and reduced ozone requirements (Saugier and Vegega, 1991).

#### **1.4.2 Colour Removal by Biological Treatment**

Lignin and its derivatives are hard to degrade because of linkages within the molecule, especially the biphenyl-type carbon to carbon linkages (Prasad and Joyce, 1991). Conventional biological treatment is ineffective in oxidizing lignin and its larger degradation products. The Proctor and Gamble pulp mill in Grand Prairie, Alberta, failed to reduce effluent colour by introducing a genetically engineered bacterium into the

secondary treatment system, which could supposedly metabolize the chromophoric material in the effluent (McNeill, 1984).

White rot fungi, the most effective lignin degraders, are able to completely mineralize both the lignin and carbohydrate components of wood (Reid, 1994). They can also dechlorinate and decolourize pulp mill effluent and be used in the bioremediation of soils (Reid, 1994). Under optimum conditions *Trichoderma sp.* (a Fungi imperfecti) was able to reduce colour by almost 85% and COD by 25% from a hardwood pulp extraction stage effluent sample (Prasad and Joyce, 1991). White rot fungi have been shown to degrade lignin from hardwood better than softwood lignin because of the presence of syringyl lignin in the hardwood (Highley, 1982).

Two patented processes, the MyCoR and MyCoPor processes, use the solid surfaces of a rotating biological contactor (RBC) and polyurethane foam cubes in a trickling filter, respectively, to immobilize *P. chrysosporium* (Eaton *et al.*, 1980; Pallerla and Chambers, 1996). Pallerla and Chambers (1996) achieved colour reductions ranging from 72-80% when treating bleach plant effluent in a fluidized bed reactor with immobilized *Trametes versicolor* on urethane prepolymer cubes.

#### 1.4.3 Colour Removal by Photocatalysis and Photo-oxidation

Radiation and a combination of radiation and oxidants can be used to reduce colour of pulp mill effluents. Archibald *et al.* (1995) found that the HMW compounds which contributed to effluent colour and AOX are "photobleached" in subsurface natural lake conditions from May

to September. McKelvey and Dugal (1975) were able to completely remove the colour from extraction stage effluent in two hours with a 450 W mercury lamp and a 1.0 cm optical path. When compared with a number of possible oxidants (not including ozone), McKelvey and Dugal (1975) showed that sodium hypochlorite was the most effective oxidant to be used with UV-radiation.

When treating effluent, radiation is often used in conjunction with an oxidant or catalyst. It is felt that the UV-radiation activates the oxidant (typically hydrogen peroxide or ozone) by creating the hydroxy radical (Springer, 1993). This radical reacts with the organic material and participates in an autocatalytic reaction. Coburn et al. (1984) used ozone and UV-radiation to treat extraction stage effluent, achieving 86% colour removal after 15 minutes and a colour removal of 99% after 90 minutes, with 20 mg/L of ozone. An increase of BOD<sub>5</sub> of 34% was seen at the completion of the colour removal, suggesting that the removed colour was reduced to LMW organics (authors of this paper did not state the intensity or wavelength of the radiation). Hydrogen peroxide and UVradiation was also able to dramatically reduce extraction stage effluent colour, but it is not as effective as using UV-radiation and ozone (Coburn et al., 1984). Smith and Fraily (1990) were able to remove 78% of colour from extraction stage effluent with a combination of 480 ppm of hydrogen peroxide and 80,000  $\mu$ Wsec/cm<sup>2</sup> of radiation at wavelength of 253.7 nm. Reduction of colour was initially rapid, but the rate of colour reduction decreased as time progressed (Smith and Fraily, 1990).

Metal oxides have been used as oxidizing catalysts in a number of other applications (Immura *et al.*, 1986). For instance,  $MnO_2$  is considered to be one of the strongest oxidizing agents in the absence of oxygen (Immura *et al.*, 1986). Higashi *et al.* (1991) reported that secondary treated bleach kraft mill effluents can be decolourized by using UV-radiation with a titanium dioxide catalyst.

## 1.4.4 Colour Removal by Adsorption Systems

Three systems using resins have been developed to remove colour from high strength streams that are low in suspended solids or other contaminants (Springer, 1993). These systems are the Rohm and Haas process, the Dow process, and the Uddeholm-Kamyr process (Springer, 1993). To remove the chromophoric constituents of the effluent, each of these systems involve passing bleach plant filtrates through a resin bed that can be regenerated using a clean, highly caustic stream.

A full-scale version of the Uddeholm-Kamyr process was installed at a 300 ton/day bleached kraft pulp mill in Sweden in the early 1970s (Anderson *et al.*, 1974). Colour removals of 90% were reported when treating extraction stage effluent, and as an additional benefit, the system was able to reduce the COD and BOD<sub>5</sub> of this stream by 88% and 50%, respectively (Anderson *et al.*, 1974). The resin required regeneration with either 1-2 N caustic or white liquor (Springer, 1993). Acid was used to re-activate the resin bed, and the removed colour was ultimately burned in the recovery furnace.

The Dow process is similar to the Uddeholm-Kamyr process, but because of the resins used (Experimental Resins XD-8704) colour was able to be removed over a wide range of pH (Chamberlin *et al.*, 1975). Excellent colour removal (95%) was reported in lab-scale experiments. Organic carbon removal (43%) was substantially lower than the removal reported from operation of the Uddeholm-Kamyr process (Chamberlin *et al.*, 1975).

The Rohm and Haas process does not use a ion exchange resin, as in the other two resin processes, but a polymeric adsorbent (XAD-8) which has no ionizeable groups (Rock *et al.*, 1974). This process is operated at a pH of 3 or lower, which allows for treatment of the chlorination stage filtrate in addition to the extraction stage filtrate (Rock *et al.*, 1974). In field studies, with a mobile treatment unit treating a combination of extraction and chlorination filtrates, removals of 70-95%, 43%, and 33% were observed for colour, COD and BOD<sub>5</sub>, respectively (Rock *et al.*, 1974).

Using activated carbon has been well established as a method of removing organics responsible for colour, taste and odour from water supplies (Rush and Shannon, 1976). Since activated carbon is more efficient in removing the lower molecular weight chromophores, it is a good polishing step for the colour removal techniques better suited to remove HMW chromophoric molecules (Rush and Shannon, 1976). An application using activated carbon to treat pulp mill wastewaters is the ISEP process (Berry, 1987). The ISEP system is a patented sorption process that includes all the treatment stages in one unit, without having to resort to slurried transport of the sorbent material or batch

sequencing (Springer, 1993). Operation can be broken into three steps: acidification, clarification, and activated carbon adsorption (Berry, 1987). Concentrated  $H_2SO_4$  is added to the coloured stream (extraction stage filtrate) to bring the pH down to between 1.2 - 1.8 to either precipitate the chromophores, or put them in a state more amenable to later treatment. The acidified solution is mixed with a flocculent and clarified to remove any solids. Overflow from the clarification stage is treated with activated carbon in a counter current fashion (Berry, 1987). The ISEP system was a success on a pilot plant scale, but the cost of a full scale process was too high to justify installing it in a mill (Springer, 1993).

### **1.4.5 Colour Removal by Membrane Filtration**

A membrane is a semipermeable barrier that resists passage of some particles and not others. Ultrafiltration and reverse osmosis are two colour removal techniques that utilize membranes. Currently, these technologies are not widely used because of the high cost of membranes and the low solvent flux rates that they offer, but this technology continues to improve and shows promise for future applications in pulp and paper effluent treatment (Springer, 1993). Membranes foul with use and need special detergents for washing (Blackwell *et al.*, 1992). Pejot and Pelayo (1993) found that, even after washing the CARBOSEP<sup>©</sup> inorganic tube membrane 60 times, the general state of the membrane was still good. Two Japanese pulp mills installed ultrafiltration processes to treat extraction stage effluent in the 1980's (Ekengren *et al.*, 1992).

Sierka and Folster (1996) were able to remove 62% and 33% of the colour from extraction and chlorination stage filtrates, respectively, with a membrane with a 10,000 Dalton molecular weight cut-off. Removal of extraction stage filtrate colour was higher than that of the chlorination stage because the chromophoric molecules in the extraction stage filtrate were, on average, of a higher molecular weight (Sierka and Folster, 1996). A colour removal of 20% was achieved when ultrafiltration through a 1000 Da molecular weight cut-off filter was used to treat chlorination stage filtrate from Weyerhaeuser's Grande Prairie pulp mill (Sierka *et al.*, 1996). Increasing the pH to neutrality increased both flux through the membrane and colour removed; increasing the temperature increased the flux through the membrane, but decreased the amount of colour removed by ultrafiltration (Sierka *et al.*, 1996). Pretreatment with either 5  $\mu$ m filtration or ultrafiltration, followed by reverse osmosis, was able to virtually remove all colour from the chlorination stage filtrate (Sierka *et al.*, 1996).

#### **1.4.6 Mechanism of Coagulation/Flocculation**

In common English usage, the terms coagulation and flocculation are almost interchangeable. For this discussion, coagulation will represent the process of destabilization of surface charge on suspended colloids or molecules; flocculation will be defined as the agglomeration of destabilized particles and colloids into settleable or filterable particles (Crawford and Cline, 1990). Both coagulation and flocculation require mixing to induce contact between the polymers and the charged particles, and can either be classified as either orthokinetic (induced by turbulence) or perikinetic (induced by Brownian motion) (Howe-Grant, 1994).

DVLO theory (named after the investigators Derjaguin, B., Landau, L.D., Verwey, E.J.W., and Overbeek, J.T.H.G.) quantifies particle stability in terms of energy changes when particles converge, and can be used to explain why similarly charged particles remain stable in solution (Schwoyer, 1981). Energies of the particles upon approach are the summation of attractive forces (van der Waals - London) forces and repulsive forces (overlapping of electric double layers) (Shaw, 1980). Typically, repulsive forces will be dominant at intermediate interparticle distances, and attractive forces will dominate at near and far interparticle distances (Schwoyer, 1981). Figure 1.4.1 plots two general types of energy curves of approaching particles, where a positive energy of interaction means there exists a repulsive force between the two particles.



Figure 1.4.1 - Total Energy Interaction Curves (Shaw, 1980)

The curves  $V_R(1)$  and  $V_R(2)$  represent two different repulsive energy curves and  $V_A$  is a attractive energy curve. Curve V(1), the summation of  $V_R(1)$  and  $V_A$ , has a region of potential energy greater than zero. Particles represented by these curves will likely

remain stable in suspension (Shaw, 1980). Particles represented by V(2), the summation of  $V_R(2)$  and  $V_A$ , always have negative potential energies and, therefore, there are no electrostatic barriers to agglomeration (Shaw, 1980).

Schwoyer (1981) stated that the removal of waterborne charged particles with polyelectrolytes may "...involve four mechanisms:

- 1. Colloid entrapment or removal via the sweep floc mechanism.
- 2. Reduction in surface charge by double layer compression.
- 3. Charge neutralization by adsorption.
- 4. Bridging by polymers."

Colloid entrapment involves the treatment of wastewater with a comparatively large amount of charged particles, as in the massive lime treatment colour removal process (Tyler and Fitzgerald, 1972). A large, three-dimensional polymer matrix is formed, entrapping solids. The matrix contracts (freeing solvent water) and is dense enough to settle (Schwoyer, 1981). The solids remain entrapped in the matrix as it settles and appear to be swept from the solvent.

Double layer compression, the reduction of the electric double layer, occurs when the ionic strength of the solvent is increased (Schwoyer, 1981). As the ionic strength of the solution is increased, the repulsion due to the electrostatic repulsion of the double layers is reduced, and flocculation is possible (Howe-Grant, 1994). If the charge of the ions forming the double layer is increased by adding ions of higher charge to the solution, the particles can come even closer together and be attracted by van der Waals forces (Howe-Grant, 1994).

Mechanisms three and four are predominant in the colour removal method of a dual polymer coagulation/flocculation system. A highly cationically-charged coagulant electrostatically bonds with the anionic sites of the chromophores and reduces the repulsive forces between the chromophoric molecules (Schwoyer, 1981). If the coagulant bonds to more than one anionic body, a bridge is created between the two particles. Heterocoagulation can occur when the coagulant reverses the surface charge of one anionic particle, creating a positively-charged region, which is attracted to negative regions on other particles (Howe-Grant, 1994). Through bridging and heterocoagulation, particles are brought together during coagulation with charged polymers, but it is likely that flocs of sufficient size are not created (Schwoyer, 1981). High molecular weight flocculents, through electrostatic and hydrogen bonding, adsorb to the destabilized particles from coagulation and bring them together into larger flocs that settle well (Schwoyer, 1981).

### 1.4.7 Colour Removal by Coagulation/Flocculation

Coagulation of chromophoric molecules from pulp mill effluents involves the formation of a sludge phase that can be separated by a density difference. Positively charged metal cations or organic polymers are used to reduce the repulsive anionic surface charge of the chromophores and bring them together into physically removable flocs. A number of coagulants can be used:

- alum,
- iron and magnesium salts,
- calcium (lime),
- flyash, and
- polyamines.

Good colour removal has been achieved with all of these materials (Springer, 1993).

Metal cations need to be either divalent or trivalent to be effective as coagulants in water treatment applications (Schwoyer, 1983). Garcia-Heras and Forster (1989) concluded that salts of low solubility formed when HMW organics with carboxyl groups electrostatically bonded with the products of hydrolysis of trivalent metals ( $Me_x(OH)_y$ +(3x-y)). When the concentration of the metal was high enough to form Me(OH)<sub>3</sub>, and proper pH conditions were maintained, the metal complexes react chemically and physically with the lignin and "sweep" flocculation occurs (Garcia-Heras and Forster, 1989). Colour removals of greater than 80% were achieved with low suspended solids in the supernatant (<15 mg/L) when using aluminium and ferric salts to treat bleach plant filtrates. Stephenson and Duff (1996a) reported that iron and aluminium salts were able to remove 90-98% of the colour from a combination of bleached chemical thermomechanical pulp (BCTMP) and thermomechanical pulp (TMP) effluent. As part of the same study, it was shown that Microtox acute toxicity was dramatically reduced by treating the effluent (prior to biological treatment) with metal salts to induce coagulation (Stephenson and Duff, 1996b).

Acidified fly ash releases metal cations able to act as coagulation agents. Roa *et al.* (1978) used chlorination stage effluent to acidify fly ash and used the resulting slurry to treat extraction stage effluent. The removals of colour and COD were 93% and 73%, respectively. Addition of HCl to the chlorination stage effluent improved the efficiency of the process by releasing more cations from the fly ash (Roa *et al.*, 1978).
Lime is the cheapest and most available coagulant (Springer, 1993), but it does not produce a sludge that settles well when used in pulp mill effluent treatment (Wright *et al.*, 1974). By using a "massive" amount of lime, enough so that the colour bodies only represent a small portion of the final sludge, a sludge that settled well was produced (Smith and Berger, 1968). In the "massive lime" process the mill's full lime supply is slaked with the extraction stage effluent, and the lime is settled, dewatered and used for causticizing green liquor. In a process tried under an EPA grant, 94-95% of the colour was removed from the treated stream (Smith and Berger, 1968). This process provides a method for the destruction of coloured organics in the lime kiln. The lime used for the colour removal process is used in the recaustizing process. Stone-Container, Louisiana used this process until 1984, but due to a severe colour increase across secondary treatment, the practice was abandoned for a tertiary organic polymer colour removal process (Ackel, 1988). Another drawback of the massive lime process is it dilutes the white liquor, which increases the required capacity of the evaporator and recausticizing equipment (Springer, 1983).

The original method of colour removal employed by Crestbrook Forest Industries' (CFI) Skookumchcuk, B.C. pulp mill was rapid infiltration, which relied on ground application of the effluent into calcium-rich soil to remove the chromophoric material (Swaney, 1985). Percolating the effluent through the soil to the groundwater, and ultimately the receiving water body, resulted in a colour removal of approximately 85%, and allowed CFI to meet its discharge permit with respect to colour (Swaney, 1985). Operating the system of seven rapid infiltration basins on a one day on, six days off basis allowed each basin to "recharge" and be able to treat effluent again (Kaukinen and Burns, 1996). Eventually, the soil began to erode, which diminished the performance of the system. In 1994, a new tertiary coagulation/flocculation system was installed, which was similar to the one at Stone Container, Louisiana (Kaukinen and Burns, 1996).

The use of positively charged polyamines as coagulant, in conjunction with polyacrylamide flocculents, can result in greater than 80% of the colour removal from secondary treated bleached kraft pulp mill effluent (Springer, 1993). Cationic polyelectrolytes are typically either polyamines or quaternary amines (Kemmer, 1988). A polyamine requires a low pH to produce a positive charge through hydrolysis of nitrogen atoms, while a quaternary amine retains its positive charge at both high and low pHs (Kemmer, 1988). The sludge produced by organic polymers is less voluminous than the sludge produced by metal coagulants (Kemmer, 1988). Ackel (1988) reported that 95% of secondary treated effluent colour was removed by a dual polymer system using a quaternary charged amine as a coagulant and a HMW, slightly anionic polyacrylamide flocculent. A lower colour removal of 60-80% for secondary treated effluent using a similar process was reported by Stevenson *et al.* (1996).

## 1.5 CFI Pulp Operations in Skookumchuck, B.C.

The Crestbrook Forest Industries Ltd. bleached softwood Kraft pulp mill in Skookumchuck, B.C. began producing fully bleached market Kraft pulp in 1968, and was originally designed for 345 tonnes of production per day. Current daily production has been increased to 660 tonnes per day with modifications in 1977, 1985, and 1993-1994.

Wood residue from sawmills comprises the fibre source for CFI. The chip furnish is: 45% pine, 20% fir, 35% spruce, and 5% other. Chips are cooked in a 59 m. high, 4.9 m. diameter (at the bottom), Kamyr two vessel vapour phase continuous digester. The pulp is washed in a two stage atmospheric diffuser and a Coru-Dek II decker. Screening occurs in HiQ primary knotters, Sunds secondary knotters, and four stage Ingersol Rand pressure screens. Oxygen delignification occurs in an Ingersol Rand oxygen delignification system prior to the five stage bleach plant. The bleaching sequence is  $OD_{100}E_{OP}DE_PD$ , where O, D, E, and P are symbols for oxygen, chlorine dioxide, caustic extraction, and hydrogen peroxide, respectively.

# **1.5.1 Effluent Treatment at CFI**

The effluent treatment system at CFI consists of four main components:

- in-plant spill control,
- primary treatment, neutralization and solids separation,
- secondary (biological) treatment, and
- tertiary treatment (colour removal).

Ten spill pumps, strategically located around the mill, are designed to return spilled fibre and liquor to spill tanks. The recovered liquids are returned to the appropriate process area. A large area running the length of the mill's main corridor captures spills that occur outside of the buildings, and an automatic valve meters the captured material to the treatment facilities.

Effluent neutralization occurs before primary treatment using either lime mud slurry or spent acid from the chlorine dioxide generator. Solids separation is accomplished in a settling pond with a twelve hour retention time. The pond is periodically dredged on an "as required basis" to remove the collected solids, which are subsequently landfilled.

Secondary treatment consists of a serpentine, six pass aeration stabilization basin (ASB). Surface aerators are used to supply oxygen to the microorganisms, with the bulk of the aeration occurring in the first two passes.

CFI's discharge permit (B.C. Provincial Discharge Waste Permit PE 240) stipulates that the colour of the receiving water, the Kootenay River, can not be increased more than 15 colour units. During low flow conditions in the fall months, the release of secondary treated effluent would raise the colour of the river beyond what is allowed by the permit.

### **1.5.2 Colour Removal at CFI**

Colour removal at CFI is achieved in a tertiary colour removal clarifier (TCRC), which treats post-secondary treatment effluent. The effluent flow from secondary treatment can be split at the influent splitter tank so that only a portion of the effluent passes through TCRC. The flow to be treated exits the splitter tank, and a short-chained positivelycharged organic polymer is added to the flow before it enters the coagulant mix tank.

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This mix tank has a retention time of between two and three minutes and ensures that the coagulant is thoroughly mixed with the effluent. From here, the effluent overflows into the flocculent mix tank, and the flocculent (a HMW slightly anionic polyacrylamide) is added through one of two possible addition points. Currently, the flocculent is added at the crossover pipe between the coagulant and flocculent mix tanks. The effluent in the flocculent mix tanks receives gentle mixing for two to three minutes and flows out the bottom in a 183 cm diameter conduit pipe to the centre well of the dissolved air flotation clarifier (DAF). At this point, many of the chromophoric molecules in the effluent have been brought out of solution and agglomerated together into solid flocs.

The centre well provides a zone of gentle mixing for the effluent before it overflows the wall of the centre well into the main body of the clarifier. In the centre well, a portion of the treated effluent which has had air (under high pressure) dissolved into solution is returned to atmospheric pressure. With the release of pressure, dissolved air comes out of solution in the form of numerous tiny bubbles. These bubbles rise to the surface and come into contact with, and attach to, the flocs created from the polymer addition. Buoyant floc/air conglomerates result and a sludge blanket is created on the surface of the clarifier.

The floating flocs are skimmed off the top into collection tanks and mixed with weak black liquor to be pumped back into the liquor cycle. Clarified effluent is removed through one of 16 upflow tubes into an angled skirt which carries the flow to the discharge point from the clarifier.

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# **II Objectives**

The primary objective of this study was determine the impact of the tertiary colour removal system at CFI's bleached Kraft pulp mill on overall effluent quality. Included in the overall objective are three specific goals:

- 1. Ascertain the effect of the basic operating parameters of temperature, pH, and biochemical oxygen demand on colour and soluble COD removal.
- 2. Assess the effect of the full-scale tertiary treatment system on the effluent parameters of colour, COD, BOD<sub>5</sub>, TSS, AOX, dioxins and furans, and mixed function oxygenase inducing capacity.
- 3. Determine the potential chemical savings and system performance associated with segregated treatment of the effluent streams which are the main contributors to overall effluent colour (bleach plant filtrates and the pulping area sewer).

# **III** Materials and Methods

The methods and materials used will be described at the same time, with the materials used being stated in the relevant sections. Two types of data collection were employed: collection from the actual process and data generated in the lab. All effluent and bleach plant filtrate samples were taken at the CFI Kraft pulp mill in Skookumchuck, British Columbia.

This study was comprised of three parts. First, lab-scale (jar tests) studies were conducted to determine the effect of temperature, pH, and BOD<sub>5</sub> on the removal of colour and COD. Second, data was collected from the full-scale treatment system at the mill to determine its performance as characterized by conventional and non-conventional parameters. Third, lab-scale studies were conducted to determine the feasibility of treating segregated acidic and caustic bleaching stage filtrates.

# **3.1 Lab-Scale Jar Tests**

Jar tests are commonly used to determine the effect of operating conditions on the performance of coagulant/flocculent treatment systems. Provided that conditions in the jar test closely mimic those in the full-scale treatment systems, such tests can be a convenient way to generate useful design and operating information (Kemmer, 1988).

### **3.1.1 Polymer Preparation**

The coagulant and flocculent used were the same commercial organic polymers (Callaway 4000 and Callaway 4310HTI) used in the full-scale system at the mill. Callaway 4000 is an epichlorohydrin - dimethyl amine-based quaternary charged cationic coagulant and Callaway 4310HTI is a slightly anionic polyacrylamide flocculent. Figures 3.1.1 and 3.1.2 show the structure of the monomers of each polymer used; more detailed information about the polymers, such as the level of branching, is proprietary information.



Figure 3.1.1 Structure of Callaway 4000



Figure 3.1.2 Structure of Callaway 4310HTI

The coagulant was diluted to a 1% v/v solution by adding  $10\pm0.10$  mL of coagulant to  $1000\pm5$  mL of mill water. Mill water is fresh stream water that has undergone settling and has been mildly chlorinated. It is used as fresh water in all areas of the mill. The flocculent was diluted to 0.1% v/v by mixing  $20\pm0.2$  mL of 0.5% v/v flocculent solution

with 80±0.5 mL mill water. These made-down solutions were vigorously mixed to ensure homogeneity, and a fresh set of diluted polymer solutions was made for each set of experiments.

## **3.1.2 Jar Test Procedure**

In order to accurately determine the effect of operating parameters on colour removal, the test conditions were adjusted to mimic the operating conditions of the full-scale process (Kemmer, 1988). This was achieved by using the jar test procedure.

Jar tests were carried out using a Phipps & Bird Model 7790-400 gang stirrer (General Medical Corp., Richmond VA). A gang stirrer is typically used to standardize mixing conditions between jars. This stirrer consists of a number of paddles (six turbine type paddles in this work) suspended from a single overhead shaft, and an illuminated platform on which the sample beakers rest.

To begin the test, 500±5 mL of effluent were transferred into two different 1000 mL beakers. The beakers were then placed in the gang stirrer and the paddle rotational speed was set at 200 rpm. A measured quantity of 1% v/v coagulant solution was added with a syringe, and the sample was allowed to mix for three minutes. Mixing speed was then lowered to 100 rpm and diluted flocculent was added using a syringe. After three minutes at 100 rpm, the mixing speed was reduced to 50 rpm. Although some floc building occurs in the last stage, this stage serves primarily as an observation period as the slow mixing keeps the flocs in suspension. Without mixing, flocs of sufficient size

will quickly settle. Five mL and 10 mL syringes were used to add the polymers. The error for both of the syringes was determined  $\pm 0.10$  mL (Appendix A.2).

After a total mixing time of twelve minutes, the gang stirrer was turned off and the beakers were removed. Once removed, the flocs were allowed ten minutes to settle, during which time their settling behaviour was observed. The clarified supernatant was then decanted into plastic sampling containers that were refrigerated at 4°C until analyzed. Samples were never kept for longer than 48 hours before testing. Each jar test was done in duplicate, and the supernatant from both of the beakers was mixed prior to storage or testing.

The three standard response variables recorded for the jar tests were qualitative assessment of floc formation and settling, soluble COD, and colour.

Judging the floc quality is difficult to do with quantifiable measurements such as diameter and density. For the jar tests performed for this project, qualitative assessment was chosen as a measure of floc quality. Floc formation was judged by observing the size of flocs, uniformity of floc sizes, settling performance, and clarity of the supernatant. The floc settling rate would only differentiate between good and poor flocs, which is much easier to do by qualitative assessment. Although, judging floc quality is open to interpretation, attempts were made to make sure that the observations were a consistent as possible. Table 3.1.1 briefly outlines some general criteria for floc quality assessment.

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made. It is recommended that future experimenters gain experience with the jar test before making floc quality assessments.

Floc Quality	General Characteristics
Excellent	Flocs > 1 cm in diameter, rapidly settling flocs, clear supernatant.
Good	Flocs > 4 mm & < 1 cm in diameter, rapid settling, clear supernatant.
Fair	Flocs a few mm in diameter, flocs settle well, slightly turbid supernatant.
Poor	Very small flocs, poor settling, turbid supernatant.
Pin	Flocs difficult to see, often only visible after settling, poor settling, turbid supernatant.

 Table 3.1.1
 Basic Guidelines for Floc Quality Assessment

### **3.1.3 Effect of Temperature on System Performance**

In testing the effect of temperature on system performance using the jar-test procedure, the temperature was set and maintained by using a controlled temperature water bath. A fish tank of dimensions that allowed it to be placed into the gang stirrer was filled with water to a level just above the sample beakers' liquid levels. Once the sample containing beakers were placed in the water bath, it was placed into the gang stirrer. The samples were allowed to come to temperature equilibrium with the water bath, prior to performing the jar test. After the jar test was completed, the water bath, containing the test beakers, was removed from the gang stirrer for the settling period.

Elevating the temperature of the water bath was accomplished with a 100-watt fish tank heater, and to cool the water bath, ice was added. Although this temperature control method does not offer the precision of an analytical temperature-controlled water bath, the temperature of the samples was maintained within  $\pm 0.5^{\circ}$ C of the target temperature at all times. When the uncertainty of  $\pm 0.5^{\circ}$ C from the thermometer was included, the total error in temperature was  $\pm 1^{\circ}$ C. The temperature was controlled for both the stirring and settling portions of the jar test.

### **3.1.3.1 Temperature Experimental Procedures**

Our study of the effect of temperature on colour removal with organic polymers was grouped into two experiments. In the first experiment, the coagulant and flocculent dosages were kept constant and temperature was varied. In the second experiment, coagulant dosages were varied and the flocculent dose was kept constant for three sets of jar tests at three different temperatures. In addition to the standard response variables, a modified form of the standard colour test was performed. In the modified test, a 0.45  $\mu$ m filter was used in place of the 0.8  $\mu$ m filter stipulated in the standard colour test (CPPA, 1993a).

For the first experiment the temperature was varied from  $6.7^{\circ}$ C to  $40.0^{\circ}$ C in  $5.6^{\circ}$ C increments. The effluent sample was taken at the inlet to the colour clarifier, and was found to have a colour of 762 c.u. (789 c.u. when using the  $0.45\mu$ m filter paper) and a soluble COD of 506 mg/L. Polymer doses of 100 ppm of coagulant and 9.2 ppm of flocculent were chosen by qualitative observation. At this coagulant dosage higher applications of coagulant gave only a small improvement in floc formation, and a lower dosage gave a significant decrease in floc quality.

The initial properties of the colour clarifier inlet sample used in the second experiment were: colour, 691 c.u.; modified colour, 744 c.u.; and soluble COD, 503 mg/L. The flocculent dosage was fixed at 8.8 ppm for all jar tests. The temperatures chosen to create the isotherms were 6.7°C, 23.3°C, and 40°C. The coagulant doses were 24, 48, 72, 96, and 120 ppm at each temperature. In addition to the standard response variables, the modified colour test (utilized in the first temperature experiment) was performed on the supernatant collected from the jar tests.

### **3.1.4 Effect of pH on System Performance**

To control the pH of the jar test, hydrochloric acid and sodium hydroxide were used. Concentrated HCl and 50% NaOH were used to bring the pH close to the target value, and 1.0 M and 0.1 M solutions of both HCl and NaOH were used for fine adjustments of pH. If the target pH was exceeded during adjustment, the sample was discarded. While adjusting pH, samples were vigorously stirred to reduce localized areas in the solution which exceeded the target pH. The pH of the sample was adjusted prior to the jar test; variations in pH during the execution of the jar test were not controlled.

### **3.1.4.1 pH Experimental Procedures**

The experiments performed to investigate the effect of pH upon colour removal with organic polymers were structured in the same fashion as those used to examine temperature. In the first experiment, coagulant and flocculent doses were held constant while pH was adjusted. In the second experiment, three sets of data were generated by varying the coagulant dosage at three different pH values.

For the first experiment, the pH was increased from 1.5 to 11 in increments of one pH unit (with the exception of the adjustment of 0.5 from 1.5 to 2.0). The coagulant and flocculent dosages for all jar tests were 88 ppm and 8.8 ppm, respectively. The effluent sample, taken at the inlet of the colour clarifier, had an initial colour of 623 c.u. and soluble COD of 435 mg/L.

Removal of soluble COD and colour was examined at pH 4, 7, and 10 in the second experiment. The coagulant dosages for each pH level were 20, 40, 72, 100, and 120 ppm, and the floc dosage was 9.0 ppm. For this experiment, the effluent sample taken at the inlet of the colour clarifier had an initial colour of 638 c.u. and soluble COD of 397 mg/L.

## 3.1.5 Effect of BOD on System Performance

In all tests in which the effect of BOD was examined, the  $BOD_5$  of the effluent was tested before and after the jar test. The lab where the jar tests were conducted was not equipped with a refrigerator; all samples, jar tested or not, were placed in an ice-bath until they were brought back to the lab and placed in a fridge at 4°C.

### **3.1.5.1 BOD Experimental Procedures**

The experiments to test the effect of biochemical oxygen demand levels are structured in a similar manner as the pH and temperature experiments. For the first experiment, the initial BOD<sub>5</sub> level was adjusted by adding a pre-made BOD solution (containing acetic acid, formic acid and methanol) to secondary treated effluent. In the second experiment, BOD was adjusted by taking a high BOD effluent sample from the effluent treatment system, and biologically treating it to varying extents under controlled laboratory conditions.

In the series of tests in which the BOD of the treated effluent was increased, different amounts of a stock solution made from methanol, formic acid, and acetic acid were added to the effluent prior to jar testing. The stock soluble BOD solution was prepared by making up 5 mL of 100% CH<sub>3</sub>COOH, 5 mL of 88% HCOOH, and 3.1 mL of 100% CH<sub>3</sub>OH with distilled water to one litre in a volumetric flask. The COD and BOD<sub>5</sub> of this solution were assayed and found to be 10,500 mg/L and 7,500 mg/L respectively. The proportions of the chemicals in the solution were not set to represent what is found in kraft pulp mill effluent. Kringstad *et al.* (1984) reported that the BOD<sub>5</sub> found in bleaching liquors was primarily methanol and formic acid with small contribution from acetic acid.

To ensure that the same amount of effluent was used in each jar test, the amount of soluble BOD solution was made up to  $10\pm0.2$  mL with mill water and mixed with

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 $490\pm2.5$  mL of effluent for each jar test. For example, to conduct a jar test with 60 mg/L of soluble BOD<sub>5</sub> added,  $16\pm0.2$  mL of BOD solution and  $24\pm0.3$ mL of mill water were added to  $1960\pm10$  mL of effluent. Since the soluble BOD solution decreased the pH of the effluent, the pH of each jar test mixture was brought down to a pH of 5.00±0.02. This ensured that the pH of each jar test was the same, and it avoided increasing the pH after it had been decreased.

The BOD-enriched effluent samples were divided in half; half were used for the duplicate jar tests and the other half was stored for later testing. This was also done with the sample that had no BOD added. Both the samples that were subjected to jar testing and those stored for later testing were tested for the response variables of soluble COD, colour,  $BOD_5$ , and observable floc quality.

The secondary treated effluent sample was taken from the inlet of the colour removal clarifier, and had the following properties: soluble COD, 487 mg/L; colour, 664 c.u.; and BOD<sub>5</sub>, 17.3 mg/L. For each jar test in this experiment, the coagulant and flocculent doses were 80 ppm and 9.2 ppm, respectively. The BOD<sub>5</sub> added to the jar tests ranged from 0 to 150 mg/L in steps of 25 mg/L. In addition to BOD<sub>5</sub>, the standard response variables were tested.

In the first experiment, only soluble, LMW BOD was varied during the jar test. Since pulp and paper effluent BOD is heterogeneous in nature, use of such a BOD solution may not accurately represent the influence of BOD on performance. To obtain a more realistic representation of effluent BOD, a high BOD sample taken from the effluent treatment system was seeded and aerated for varying intervals to reduce BOD to desired endpoints. To carry out these partial treatments, twenty litre translucent Nalgene plastic containers were filled with effluent from the primary treatment outfall. A sample taken from the ASB, near the inlet, was added to supply seed. If more than one Nalgene container was required, the effluent in each container was mixed together thoroughly to ensure that the properties of the effluent in each container were identical. Aeration was supplied using mill air through a submerged plastic tube at a rate high enough to ensure that the biomass remained in suspension and was thoroughly mixed. To reduce possible variations, samples drawn off for testing were filtered through coarse filter paper (Reeve Angel, Grade 202) to remove any fibre or other charged bodies in an attempt to reduce possible variations. For instance, it has been well established that pulp fibres carry an anionic charge (Gallagher, 1992), and will affect the cationic demand of the effluent. Primary treatment normally removes most of the fibre in the untreated effluent, but if there is a significant amount of fibre present in the primary treated effluent it will affect the test results.

Experiments using the primary treated effluent were performed twice. In one set of experiments, pH was readjusted to 7.0 prior to jar testing, while the other set had no pH adjustment. For both sets of experiments, at each BOD level, a series of jar tests were performed at 24, 48, 72, 96, and 120 ppm of coagulant and 8 ppm of flocculent. The initial conditions for each set are given in Table 3.1.2

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BOD Level		Non-pH Adj	usted			pH adjust	ted	
	BOD <sub>5</sub>	Soluble COD	Colour	рН	BOD <sub>5</sub>	Soluble COD	Colour	pH
	(mg/L)	(mg/L)	(c.u.)		(mg/L)	(mg/L)	(c.u.)	
High	85	565	604	7.7	155	605	535	7.0
Medium	74	542	584	7.8	137	584	544	7.0
Low	15	454	660	8.5	36	443	557	7.0

 Table 3.1.2
 Initial Properties of Effluent Prior to Jar Tests

#### 3.1.6. Effect of Ionic Strength on System Performance

Sodium chloride addition was used to test the effect of the concentration of monovalent ions on colour removal with charged polymers. Chloride concentrations in the final effluent in the days prior to sampling for this set of tests were approximately 260 mg/L. To conduct jar tests at multiples of this chloride concentration a solution of 42.9 g/L NaCl was made by adding 42.9 g of sodium chloride to distilled water and making the solution up to 1 L in a volumetric flask. Solutions with sodium chloride concentrations of 0, 10.7, 21.4, 32.2 and 42.9 g/L were made from the initial saline solution, using a 100 mL graduated cylinder. Mixtures consisting of 1920±10 mL of effluent (collected at the colour clarifier inlet) and 80±2 mL of saline solutions were prepared and divided into equal volume samples. The calculated and measured chloride levels in the prepared samples are given in Table 3.1.3.

Saline Solution	Measured Chloride Conc. (mg/L)	Calculated Chloride Conc. (mg/L)
0	180	180
10.7	450	440
21.4	720	700
32.2	970	960
42.9	1240	1220

<b>Table 3.1.3</b>	Chloride Concentration of Effluent for Ionic S	trength Experiments

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One half of the sample was stored at 4°C for later analysis, while the other half was subjected to jar testing. The sodium chloride concentrations used were much higher than those typically found in the effluent. The effluent, taken from the inlet to the colour clarifier, had an initial colour of 644 c.u. The coagulant and flocculent doses were 92 ppm and 9.2 ppm, respectively, for all jar tests.

## **3.2 Performance of Full-Scale Treatment System**

To assess the performance of the full-scale treatment system during the period of the study, samples were taken after primary, secondary, and tertiary treatment. Samples were collected at the outfall of each treatment stage using timed samplers (Sigma 900 Automatic Liquid Sampler for Post-Primary, and Isco 6700 Sequential/Composite Samplers for Post-Secondary and Post-Tertiary). These samplers collected a set amount (10 mL) of effluent every fifteen minutes. Post-tertiary treated effluent was collected in a refrigerated sampler (4°C), and the post-secondary and post-primary samples were collected at room or ambient temperature, depending on the season. In the winter months, the effluent sampling stations were heated to prevent freezing of the samples and sample lines.

### 3.2.1 Full Scale System Testing Schedule for Colour, TSS, and BOD5

The trained mill effluent technicians tested the effluent parameters of colour, TSS, and  $BOD_5$  on a regular basis. Due to their strong experimental technique, which is tested by CAEAL (Canadian Association of Environmental Analytical Laboratories Inc.) on a yearly basis, the author of this thesis felt confident in using these test results to assess the performance of the full-scale system. Timed composite samplers described in the previous section collected the samples. The testing frequency for these effluent characteristics is given in Table 3.2.1.

	Post-Primary	Post-Secondary	Post-Tertiary
Colour	5	7	7
TSS	5	7	7
BOD <sub>5</sub>	2	3	3

### Table 3.2.1 Effluent Testing Frequency (Times/Week)

Both colour and TSS were assayed only five times a week for the primary treated effluent, but this covered the full week. The timed sampler for the post-primary flow collected a composite sample for the entire weekend. Values for this extended composite were taken to represent the value for each day of the sampling period. The sampling frequency dropped to four times a week when there was a holiday weekend, and for these periods the composite sample was taken to represent each day of the extended sampling period. Sampling was carried out for the post-secondary and post-tertiary streams seven days per week for TSS and colour. Colour and TSS were assayed within two hours of sample collection. BOD<sub>5</sub> samples were stored at 4°C, and the assays were performed weekly.

Calculations for the comparison of the monthly averages of colour at different stages in effluent treatment were determined by compensating for the ASB's five-day hydraulic retention period. Post-secondary and post-tertiary colour values were offset by five days backwards prior to the calculation of the averages.

### 3.2.2 COD and Recalcitrant COD

The samples collected for COD testing were obtained from the same composite samples as were used for colour, TSS, and BOD<sub>5</sub> testing. Sample collection for COD assays followed a less strict sampling schedule. On average, between two and three sets of samples were assayed each week, typically on the days on which  $BOD_5$  was assayed.

One of the purposes of this COD testing was to determine the effect that the effluent treatment system at CFI had on the fraction of the effluent that is resistant to conventional treatments. Samples were not assayed to determine their molecular weight distribution or tested to account for the compounds in effluent that are recalcitrant to primary and secondary treatment, so the parameter of Recalcitrant COD was developed for this study. Recalcitrant COD has the contribution of the suspended solids and biologically degradable material subtracted from the COD for the whole sample. This was done by developing a factor for the contribution of TSS to COD, and assuming that the BOD<sub>5</sub> test result represents 65% of the ultimate BOD.

 $BOD_5$  doesn't represent the total oxygen demand of the biodegradable organics in the effluent; it is approximately 60-70% of the ultimate BOD (Tchobanoglous and Burton, 1991). The mean value for this range, 65%, was chosen to calculate the ultimate BOD, which was then equated to the contribution to the total COD from the biodegradable organics.

To determine the impact TSS had on COD, samples were tested prior to, and after filtering. Grab samples were taken at the outfalls of each level of effluent treatment and were tested for COD, soluble COD (see section 3.4.2 for soluble COD procedure), and

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TSS. The difference between the soluble COD and COD was divided by the TSS to give a  $\Delta$ COD/TSS ratio.

Sample Type	∆COD/TSS	# of Samples Used to Determine Ratio
Primary Treated	1.82	6
Secondary Treated (TSS<10)	2.89	3
Secondary Treated (TSS≥10)	1.84	6
Tertiary Treated	1.41	11

### Table 3.3.2 $\Delta$ COD/TSS Ratios

Secondary treated  $\Delta$ COD/TSS values were broken up into the two categories, TSS greater and equal to 10mg/L and TSS less than 10mg/L. This is done because it appeared that there was a definite difference between the ratios of the two ranges.

The formula for the Recalcitrant COD then becomes,

$$Recalcitrant COD = COD - BOD_5 / 0.65 - TSS*(COD/TSS)$$
(1)

The Recalcitrant COD is not a true measure of the dissolved HMW COD, but it does serve as a tool to understand the nature of the COD reduction across the effluent treatment system.

# **3.3 Treatment of High Strength Effluents**

High strength effluent streams are the mill effluent streams that contain the majority of the pollutants. In this work, "high strength effluent" refers to the three mill effluent streams that are the main sources of the colour in the effluent: the bleach plant caustic and acid sewers, and the bleach plant general sewer. The caustic sewer contains the overflow from the filtrate tank of the  $E_{OP}$  bleaching stage, which consists of the filtrate from the  $E_{OP}$  washer and the overflow from the  $E_P$  filtrate tank. The acid sewer is comprised of the overflow from the  $D_{100}$  washer filtrate tank, which also receives the overflows from the  $D_1$  and  $D_2$  washer filtrate tanks. The bleach plant general sewer is so named because it traverses the bleach plant prior to discharge from the mill to the effluent collection system. While this sewer receives flows from the pulping and bleach plant areas, the majority of the colour in this flow is from the pulping area. Colour in this stream typically comes from the knotters and, occasionally overflows from the brownstock washing area. The high strength effluent was collected for two purposes: to establish a crude colour balance for the effluent system, and to determine the treatability of each stream.

To obtain a crude colour balance for the effluent treatment system, the flows of acid sewer, caustic sewer, bleach plant general sewer and effluent to primary treatment were estimated or measured, and samples were collected for later analysis, at approximately the same time during a time of steady operation of the mill. The flows for the acid and caustic sewers were recorded from the mill distributed control system (DCS). The bleach plant general sewer flow was manually measured using a flow velocity measuring device. A ruler was used to determine the cross sectional area of the flow in the sewer. The flow rate of the effluent to primary treatment was estimated by using the measured outflow from the colour removal clarifier; it was assumed that the effluent treatment system was at steady state. One each day of sample collection the flow of effluent to the river was approximately 40 million litres, so it was assumed that the flow was equal to this amount on each of the sampling occasions. The flow measurements do not produce values accurate enough to provide a precise colour balance. The numbers generated are used in calculations, but result generated from these calculations will be discussed with these inherent inaccuracies in mind.

The jar tests on the high strength effluents followed the standard jar test procedure. The effluent samples were filtered through Reeve Angel, Grade 202 paper filters (15cm diameter) and adjusted to a pH of  $5.00\pm0.02$  prior to the jar tests. It is particularly important to filter the high strength effluents prior to testing because they contain significant amounts of fibre.

# 3.3.1 Mixing of High Strength Streams

To determine the interactive effects the mixing of the high strength streams had on colour, a  $2^3$  factorial experiment was performed on two different occasions. Different combinations of the three high strength stream samples were mixed in a 500 mL volumetric flask, and were made up to 500 mL with distilled water.

Run #	Acid Sewer	Caustic Sewer	Bleach Plant Sewer
1	+	+	+
2	+	+	-
3	+	-	-
4	-	+	-
5	-	-	+
6	-	+	+
7	+	-	+
8	-	-	-

# Table 3.3.3 High Strength Sample Mixing Factorial Design

Table 3.3.3 outlines the combinations used in the mixing experiments, the + symbol represents 80 ml of sample, and the - symbol represent 0 ml of sample. The order of addition to the volumetric flask was the same for each run: acid sewer, caustic sewer, and bleach plant sewer. The solution from each mixing combination was tested for colour.

# 3.3.2 High Strength Effluent Jar-Test Procedures

The experiments with high strength effluents were performed on two separate occasions. With all other experimental conditions kept constant, the effect of coagulant dosage on colour and soluble COD removal was examined for the three high strength effluent streams. The effect of coagulant dosage on the combinations of  $D_{100}$  and  $E_{OP}$  filtrate, and on all three stream samples mixed together, was examined with the samples collected on the first occasion. This was done to determine if there were any interactive effects. The amount of each stream used in the mixed effluent samples was determined by the stream flowrates at the time of sampling. For instance, for the  $D_{100}$  and  $E_{OP}$  sample mixture the ratio of  $D_{100}$  to  $E_{OP}$  filtrate in the mixture was 101/85.2. All jar tests performed with the

high strength effluent had the pH of the effluent adjusted to pH  $5.00\pm0.02$  prior to the jar test.

Stream	Flow	Colour	Soluble COD	Flocculent Dosage
	(L/s)	(c.u.)	(mg/L)	(ppm)
D <sub>100</sub> Filtrate	101	871	1661	8
E <sub>OP</sub> Filtrate	85.2	1636	3205	26
Bleach Plant Sewer	85.5	607/104	431	2.6
D <sub>100</sub> and E <sub>OP</sub>	186.2	1218	2303	16
D <sub>100</sub> , E <sub>OP</sub> , Bleach Plant Sewer	271.7	1071	1720	13.2

Table 3.3.4	Experimental Conditions for	r 1 <sup>st</sup>	<sup>st</sup> Set of High Strength Jar Te	sts
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Stream	Colour (c.u.)	Soluble COD (mg/L)	Flocculent Dosage (ppm)
D <sub>100</sub> Filtrate	481	1274	8.8
E <sub>OP</sub> Filtrate	1065	2540	14
Bleach Plant Sewer	1432/381	649	4.4

# Table 3.3.5 Experimental Conditions for 2<sup>nd</sup> Set of High Strength Jar Tests

Tables 3.3.4 and 3.3.5 summarize the data for the sampling of the high strength streams for jar testing. There are two colour values given for each of the bleach plant sewer samples because a colour increase was observed after the pH was reduced to 5. The first colour given represents the sample after the pH adjustment.

# **3.4 Analytical Methods**

The analytical tests done on the effluent from the mill effluent treatment system and the

lab tests included:

- chemical oxygen demand (COD),
- five-day biological oxygen demand (BOD<sub>5</sub>),
- colour,
- adsorbable organic halides (AOX),
- dioxins and furans (TCDD and TCDF),
- total suspended solids (TSS),
- acute Microtox toxicity, and
- mixed function oxygenase (MFO) induction.

Unless stated otherwise, the author performed all tests.

### 3.4.1 Colour

Colour was assayed using CPPA Standard Method H.5 (CPPA, 1993a) using a Pharmacia LKB Ultrospec III Spectrophotometer. Effluent pH adjustment was performed in a 100 mL beaker on a magnetic stirrer with a Teflon coated magnetic stirring bar. All colour measurements for the lab-scale experiments were performed in duplicate. If the measurements did not agree within 5%, the test was repeated. For the lab-scale jar tests, the colour either was tested immediately or the sample was stored at 4°C until it could be assayed. No sample was kept for longer than 48 hours prior to testing.

#### **3.4.2 Chemical Oxygen Demand**

COD tests followed the colourometric procedure outlined by CPPA Standard Method H.3 (CPPA, 1993b), and were performed in duplicate using distilled water as a control.

Commercially prepared reagent vials, 0-1500 mg/L (HACH Ltd, Loveland, CO.), were used.

Absorbence and transmittance of each vial were tested in a Milton Roy Company Spectronic 21. The values of absorbence and transmittance were converted to mg/L of COD from standard curves and averaged to give the mg/L of COD for each sample. The standard curves were developed using 300 mg/L and 1000 mg/L HACH COD Standard Solutions. A standard curve was developed for each package of vials. The standard curves determined for each box of vials were averaged to create one calibration curve for both absorbence and transmittance (Appendix A.1). The slopes for the four absorbence versus COD linear fits had a standard deviation of 3.5% of the average slope; the standard deviation of the exponentials of calibration curves using transmittance was only 0.6% of the average. With these low deviations, it was felt that averaging the curves would reduce variations found in each curve and give calibration curves of improved accuracy.

Typically, only absorbence is used to determine COD, as absorbence and COD have a linear relationship (CPPA, 1993b). In this work, COD values from standard curves for both transmittance and absorbence were averaged to give an overall COD value. This deviates from normal protocol, but was done to reduce the human error associated with reading values from the spectrophotometer.

Results are expressed as either whole or soluble COD. Whole COD, as the name suggests, is the result of the COD test when performed on a sample which has not been pretreated. Soluble COD was determined as follows.

- Filter 100 mL of sample through Whatman 934-AH filter paper (1.5 μm pore size, 15 cm diameter) into Erlenmeyer flask.
- Mix filtrate around the collection flask and dispose.
- Filter an additional 150 mL sample through the same filter paper.
- Test the COD of filtrate from the 150 mL to obtain the soluble COD.

### 3.4.3 Adsorbable Organic Halides

AOX was assayed by a commercial laboratory (Econotech Services, New Westminster, BC) using an AOX analyzer (Mitsubishi TOX-10). The 24-hour composite samples from the full-scale effluent treatment system were collected in sterilized one litre amber glass bottles. These were sent to the commercial laboratory the same day in a non-refrigerated container, and were received by the commercial laboratory on the following day. Prior to shipping, the samples were preserved with HNO<sub>3</sub>.

The coagulant solution contains AOX, but the quality standards of the chemical supplier ensured that no more than 500 mg/L of AOX was present in the undiluted coagulant. A coagulant dosage of 100 ppm to the effluent translates into 0.05 mg/L AOX increase in the final effluent, assuming the maximum value for AOX content of the coagulant.

# **3.4.4 Dioxins and Furans**

Dioxins and furans were assayed according to Environment Canada Reference Method EPS 1/RM/19 using a VG Ultima Autospec mass spectrophotometer equipped with a Hewlett Packard GC by Axys Analytical Services Inc. (Sydney, BC). Samples were collected by a refrigerated timed sampler (Isco 6700FR Refrigerated Sampler) dedicated to only dioxin and furan testing. Toxicity equivalent quotients (TEQ) were calculated using only the 2,3,7,8 isomer and by assigning zero to non-detectable levels (Appendix A.3).

### 3.4.5 Biological Oxygen Demand

 $BOD_5$  was tested in accordance to American Public Health Association (APHA) standard methods (APHA, 1992). Tests to assess the performance of the full-scale effluent treatment system were performed in duplicate, and the tests for the lab-scale work were done in triplicate.

### 3.4.6 Suspended Solids

TSS was assayed in accordance to CPPA Standard Method H.1 using a set sample volume of 250 mL (CPPA, 1993c).

The suspended solids fraction of the tertiary treated effluent contain flocs from the colour removal process not removed in the DAF clarifier. To determine the contribution of these flocs to the total TSS, suspended solids tests were performed on samples with and without these flocs. The procedure was as follows.

- Gently mix sample, enough to make sample homogenous, but not enough to disrupt the flocs.
- Split sample in half.
- Gently filter one half through a fine wire mesh to remove flocs.
- Perform TSS on both halves, the difference is the contribution of the flocs to the total TSS.

# 3.4.7 Microtox<sup>©</sup> Acute Toxicity

The Microtox<sup>®</sup> acute toxicity test was used as a rapid alternative to the 96 hour acute toxicity test. This test measures the toxicity of effluent on the light emitting bacterium, *vibrio fisheri*, which emits light during its normal metabolic processes. When this bacterium is exposed to toxic effluent, the activity of the culture is reduced, and the reduction in light emission is taken as a measure of toxicity. The spectrophotometer used to measure the light was a Microtox model 5000 analyzer. The procedure was carried out on undiluted secondary and tertiary treated effluent in accordance to the procedure outlined in the Microtox manual for the Basic test.

The Microtrox test was performed at the Pulp and Paper Centre in Vancouver, BC. Postprimary and post-secondary treatment 24 hour composite, and post-tertiary grab samples were shipped from CFI in plastic Nalgene sample containers, refrigerated at 4°C upon arrival, and tested within 48 hours of the sampling. CFI periodically uses defoamer to control foaming problems experienced at the point of effluent discharge, so grab samples were taken for the post-tertiary samples to prevent the defoamer from affecting the results.

#### 3.4.8 Mixed Function Oxygenase

Grab samples were collected in plastic carboys at the outfall of each of the effluent treatment stages, and were sent to Queen's University. The post-tertiary sample was

taken prior to defoamer addition. MFO induction was assayed using an H4IIE rat hepatoma cell line, following the methods outlined by van den Heuval (1994).

## **3.4.9 Chloride Concentration**

Chloride was assayed by adding potassium chromate and hydrogen peroxide to the effluent sample and titrating with silver nitrate. The procedure followed was to:

- measure 100 mL of the effluent sample into a 250 mL Erlenmeyer flask;
- place a stirrer bar into the flask, put flask on magnetic stirring place, and set at a moderate mixing rate;
- add 2 mL of 3% hydrogen peroxide and 5 mL of 5% potassium chromate to the sample; and
- titrate with 0.0283 N silver nitrate until the red coloured end point.

The chloride concentration of the sample in mg/L was calculated by multiplying the volume in mL of the silver nitrate used in the titration, by 10.

# **IV** Results and Discussion

## 4.1 Effect of Coagulant Dosage on System Performance

Before the results of the lab-scale jar tests are discussed, it may be helpful to discuss some basic results to lay the foundation for later explanations of observed phenomenon. To do this, some of the results from the work on the effect of pH and coagulant dosage on system performance at pH 7 will be presented and discussed in this section. Only results from this part of the project are used, but conclusions are drawn from experience from other sections of the project.

### 4.1.1. Effect of Coagulant Dosage on Floc Formation

The lowest coagulant dosage at which acceptable floc formation occurs is of economical importance to CFI. This is the application rate at which they want to operate the colour clarifier; any application rate greater than this is considered unbeneficial. When the flocculent dosage is kept constant and the coagulant dosage is increased from zero, the floc formation improves to a peak quality and then begins to decline (Table 4.1.1).

Coagulant (ppm)	Comments
20	No floc formation.
40	Pin flocs, settled poorly.
72	Good to excellent flocs, rapid settling.
100	Good flocs, rapid settling.
120	Fair floc form, settled well.

#### Table 4.1.1 Effect of Coagulant Dose on Floc Formation

The coagulant applications of 20 and 40 ppm result in poor floc quality. After the jar test, the supernatant was more turbid and darker than it was originally. At this point, there

was probably insufficient coagulant added to overcome the negative zeta potential of the chromophores, but there was enough coagulant to effect the chromophores' solubility. The reduction of the anionic nature of these molecules will make them less soluble, and bringing them out of solution will impede the transmittance of light.

Between 40 and 72 ppm of flocculent, floc quality improved with increases in coagulant dose until, at some dosage between these two applications, there was a fair floc quality, where flocs are no more than a couple mm in diameter. Increasing the coagulant dosage past this application resulted in a sharp rise in floc quality, accompanied by a reduction in effluent turbidity, up to the point of acceptable floc quality (flocs approximately 1 cm in diameter) observed at 72 ppm. Beyond this dosage, there was only marginal improvement in floc quality. When too much coagulant is added, the charge on the surface of the chromophores can be reversed and the chromophores will become restablized in the solution (Schwoyer, 1981). This could explain the drop in floc quality as coagulant dose increased from 100 ppm to 120 ppm.

### 4.1.2 Effect of Coagulant Dosage on Colour and Soluble COD Removal

The discussion of the effect of coagulant dosage on soluble COD and colour removal will be focussed primarily on colour removal. Strong similarities between the effect of coagulant dose on soluble COD and colour removal allow conclusions made concerning colour to apply to soluble COD as well. The relation between coagulant addition and colour removal was different than that observed for floc quality. The largest increase in colour removal occurred between zero and 20 ppm (Table 4.1.2). Every increase in coagulant application beyond 20 ppm resulted in a lower marginal improvement in colour removal.

Coagulant (ppm)	Colour Removal	∆Colour/ Coagulant Dose	Soluble COD Removal	<b>∆Soluble COD</b> / <b>Coagulant Dose</b>
20	28%	9 c.u./ppm	12%	2.4 mg/L/ppm
40	45%	5.3 c.u./ppm	21%	1.7 mg/L/ppm
72	56%	2.3 c.u./ppm	27%	0.81 mg/L/ppm
100	61%	1.2 c.u./ppm	27%	-0.11 mg/L/ppm
120	62%	0.1 c.u./ppm	30%	0.8 mg/L/ppm

Table 4.1.2 Effect of Coaguiant Dosage on Colour and Soluble COD Remov	<b>Fable 4.1.2</b>	Effect of	Coagulant	Dosage on (	Colour and	Soluble	COD F	lemova
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The same trend between coagulant dose, floc quality and colour removal has been previously observed (Smith and Malloy, 1990). At a coagulant dose of 20 ppm, 28% of the colour was removed, although there was no observable floc formation. It is possible that polymer addition results in agglomerations of sufficient size, or reduces the solubility of the chromophores enough, to remove them during the filtration step carried out as part of the colour test. This contention is supported by the increased turbidity noted in the floc quality observations. When the coagulant dosage was increased from 40 to 72 ppm (a range over which the floc quality undergoes a large improvement), the improvement in colour removal was only 11%.

Quality floc formation can only occur when the zeta potential is reduced enough to allow the attractive forces to become dominant (Shaw, 1980). In addition, with increased coagulant application there is an increased probability of more than one coagulant
polymer attaching itself to an anionic chromophore, thereby creating more interparticle bridging. More interparticle bridging results in improved floc formation (Howe-Grant, 1994).

The percent colour removal plateaus at higher coagulant doses. This indicates that there is a limit to the amount of colour that can be removed using this type of process. Chromophores with an insufficient number of anionic sites are not good candidates for coagulant-mediated colour removal, and would require a different technique for their removal. However, other colour removal techniques also have the drawback of a limit to the amount of colour that can be removed (Springer, 1993).

The relationship between coagulant dose and removal of soluble COD is similar in nature to the relationship between coagulant dose and colour removal (Table 4.1.2). Increased coagulant dose produces the greatest improvement in soluble COD removal at the lower coagulant applications. Similarities in the dose-response relationships for colour and soluble COD suggest that the soluble COD removed is primarily the chromophores.

It is important to note that the soluble COD test does not differentiate between the organics in the effluent and the polymers. Any discussion about the soluble COD removal should be made with this qualification in mind. That the removal of soluble COD approached a limit with increases in coagulant dose, even to the point of overapplication (120 ppm in this case), indicates that the amount of polymer passing through the filter paper and detected as soluble COD is minimal.

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# 4.2 Effect of Sodium Chloride Concentration on Colour Removal

Sodium chloride concentration has been shown to significantly impact the zeta potential of anionic particles (Shaw, 1980). Addition of sodium chloride can significantly affect a papermachine retention system that relies on electrostatic bonding (Swerin and Odberg, 1996). However, previous work has indicated that the use of charged polymers in wastewater treatment is not affected by monovalent ion concentration (Schwoyer, 1981). In the present study, sodium chloride concentration had no effect on colour removal (Table 4.2.1).

Added NaCl (mg/L)	Initial Colour (c.u.)	Final Colour (c.u.)	Colour Removal
0	597	249	58.3%
429	605	263	56.6%
858	603	257	57.4%
1290	620	256	58.6%
1720	603	259	57.8%

#### Table 4.2.1 Effect of Salt Concentration on Colour Removal

Although the chloride concentrations chosen cover a large range of possible concentrations, the effect of sodium chloride concentrations below what is already present in the effluent was not examined. Perhaps the effect of salt concentration would be significant at values closer to zero. Divalent and trivalent cations, such as calcium and iron, have been demonstrated to have a large effect on colour removal (Garcia-Heras and Forster, 1989). The effect of these compounds was not investigated in this project.

#### **4.3 Effect of Temperature on System Performance**

The temperature of effluent entering tertiary treatment at CFI varies widely, from near freezing in the winter months, to temperatures above 30°C in the summer months. It was known that the treatment system operates well over the full year, but the effect temperature has on the system performance was unknown. Also, if it is desirable to move the process upstream (i.e. after primary treatment or treating segregated high strength streams), how the system would react to higher temperatures would be of importance.

# **4.3.1 Effect of Temperature on Floc Formation**

Floc formation improved with increasing temperature to a peak level, and, as the temperature was increased from 34.4°C to 40°C, the floc quality declined. Since the decrease in floc quality experienced from 34.4°C to 40°C is represented by one set of duplicate runs, it is not possible to discuss it as a trend with any certainty. The clarity of the supernatant was affected by temperature, as temperature was increased, the supernatant became visually more turbid.

Temp.	Comments
67	Good flocs settled well
12.2	Good to excellent flocs, settled very well
12.2	Excellent flocs, settled rapidly
23.3	Excellent flocs, settled rapidly
23.5	Excellent flocs, settled rapidly
34.4	Excellent flocs, settled rapidly
40.0	Good flocs, settled well

 Table 4.3.1
 Effect of Temperature on Floc Formation

Peak floc formation occurred at a temperature between 17.8°C and 34.4°C. Pelton *et al.* (1980) performed work on the effect of charged polymers on the retention of fines in paper machines at different temperatures. While their work failed to yield a definite conclusion on the effect of temperature on retention systems using charged polymers, they found that, for some polymer systems, there was a temperature at which retention, and therefore flocculation, was at a maximum.

The combined effects of temperature on mixing and flocculent performance may explain the peak in floc quality. During mild agitation, changes in the level of Brownian motion are important, and increase the rate of agglomeration of suspended material (Matijevic, 1976). Mixing conditions at 50 rpm in the last stage of the jar test may be mild enough that temperature-induced changes in Brownian motion are strong enough to influence floc formation.

Competing with increased agglomeration of particles with increasing temperature, there is a reduction in the ability of the flocculent to bond with the pin flocs. In addition to the electrostatic bonding from its anionic sites, HMW polyacrylamide flocculents utilize a significant amount of hydrogen bonding (Schwoyer, 1981). Hydrogen bonds decrease in strength as temperature increases (Davis and Day, 1961). Reducing the strength of hydrogen bonds hinders the flocculent's ability to create large, rapid settling flocs. From these observations (Table 4.3.1), it appears that the increase in floc formation due to changes in Brownian motion may predominate at lower temperatures, while the loss of bonding ability of the flocculent becomes more important at higher temperatures.

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# 4.3.2 Effect of Temperature on Colour Removal

There is a definite relationship between final colour and the temperature of the jar test. Final colour rises (with the exception of the result from 28.9°C) as temperature increases.



Figure 4.3.1 Final Colour vs. Temperature

The relationship between final colour and increasing temperature has a strong linear trend, with a  $r^2$  value of 0.91 (calculated with Excel97).

If only the increased colloidal stability and decreased mixing performance at lower temperatures (Matijevic, 1976) were considered, it would be expected that colour removal would decrease as temperature decreased, and yet the colour removed increased. Without more detailed knowledge of the chromophores, it is impossible to quantify the effect of temperature on colloidal stability. A possible explanation for the effect of temperature on colour removal arises from comparing the results of the standard colour test to those of the modified test. The effect on final colour is less pronounced with the modified colour values (Figure 4.3.1). If, at higher temperatures, there is a reduction in the ability of the flocculent to combine the pin flocs from the coagulation step, the pin flocs are not likely to become part of a larger floc structure, and remain in suspension. Any pin floc that passed through the filtering step prior to the colour test would scatter light during the colour test and thereby cause a higher colour result (CPPA, 1993a). Pin flocs would have a greater chance of being removed by smaller pore filter size, and, therefore not scatter light during the test. This would explain the reduced effect of temperature on the final modified colour.

Farley (1997) showed that an anionic body with its surface charge reversed by a charged polymer underwent charge decay. The rate of charge decay increased with increasing temperature of the solution and eventually allowed the surface to become anionic again. Polymer chain length also affected the rate of charge decay; decreasing chain length increased the rate of charge decay. The explanation proposed by Farley (1997) for charge decay is the desorbing and readsorbing of the polymer to the bonding sites. Bond breaking and reconforming would allow the more difficult to reach charged sites on the chromophore to be accessed. This phenomenon is also observed in work done on microparticle retention systems used on paper machines (Swerin *et al.*, 1997). The reconformation of the polymer to the bonding sites of oppositely charged bodies in the pulp slurry was used to explain the increase in polymer demand for this type of retention

system (Swerin *et al.*, 1997). Farley's (1997) work used a HMW poly-DADMAC (diallyldimethylammonium chloride) type polymer, which is different than the LMW charged polymer used as surface charge reducer in this project.

Extending the reasoning of polymer reconformation to colour removal with charged polymers would mean that the anionic bodies would exert an increasing cationic (coagulant) demand as temperature increased. The effect of this would be as if the higher temperature jar tests received lower coagulant applications.

# 4.3.3 Effect of Temperature on Soluble COD Removal

Final soluble COD results from the jar test follow the same pattern as the colour results. There are slight increases in final soluble COD with increases in the experimental temperature (Figure 4.3.2).

The difference in the percent soluble COD removal between the highest and lowest temperatures is 3.8% (most of which is attributable to the 40°C test). The final soluble COD of the 40°C test is high relative to the other results, indicating that there may be a threshold temperature at which the soluble COD removal begins to rapidly decline. While the error in final soluble COD makes the existence of a trend due to temperature uncertain, the consistency of the trend, and the supporting data from the colour values, suggest that the upward trend of final soluble COD with increasing temperature, is reliable.



Figure 4.3.2 Final Soluble COD vs. Temperature

# 4.3.4 Effect of Temperature and Coagulant Dosage on Floc Formation

Observations of the floc formation, when the temperature and coagulant dose are varied, show that, while the colour removal is better at lower temperatures, the coagulant dose required to achieve a given level of floc quality decreased when temperature was increased. For instance, the floc quality at the coagulant dosages of 72 and 96 ppm improved as temperature was increased. From these observations it appears that the improved mixing from increased Brownian motion and decreased colloidal stability at higher temperatures improved floc formation (Table 4.3.2).

Temperature (°C)	Coagulant (ppm)	Comments
6.7	24	No floc formation
	48	Small pin flocs, no observable settling
	72	Pin flocs, very poor settling
	96	Good flocs, settled rapidly
	120	Excellent flocs, settled rapidly
23.3	24	No floc formation
	48	Pin flocs, no observable settling
	72	Poor flocs, majority settled with many flocs left in suspension
	96	Excellent flocs, settled rapidly
	120	Excellent flocs, settled rapidly
40.0	24	Turbid solution, no floc formation
	48	Poor flocs, poor settling
	72	Fair floc, reasonable settling
	96	Excellent floc, rapid settling, clear supernatant
	120	Fair to good flocs, settled well, some flocs remain in suspension

Table 4.3.2	Effect of Coagulant	: Dosage and Ter	mperature on F	loc Formation

#### 4.3.5 Effect of Temperature and Coagulant Dosage on Colour Removal

The final colour versus coagulant dose curves at different temperatures (Figure 4.3.3) show that when temperature was increased, colour removal decreased, over a wide range of coagulant doses. The relatively constant difference in final colour at coagulant dosages that gave fair or better floc quality indicates that the dependence of colour removal on temperature is unaffected by coagulant dose (Figure 4.3.3). The average percent colour removal difference between 6.7°C to 40°C of 5.3% for the coagulant dosages of 72, 96, and 120 ppm is close to the difference of 6.0% over the same range of temperature in the first experiment.



Figure 4.3.3 Final Colour Isotherms (Initial Colour, 691 c.u.)



Figure 4.3.4 Final Modified Colour Isotherms (Initial Modified Colour, 744 c.u.)

Results from the modified colour tests are very similar to the standard colour results (Figure 4.3.4). Colour removal decreases as temperature increases for all coagulant dosages except 24 ppm. As was the case in the first experiment, the magnitude of the change in colour removal at different temperatures was smaller for the modified colour test than the regular colour test. The average difference in percent-modified colour removals between 6.7°C to 40°C at 72, 96, and 120 ppm was 2.8%. This is larger than the 2.0% variation in colour removal over the same range in the first experiment, but gives good agreement for this imprecise comparison.

#### 4.3.6 Effect of Temperature and Coagulant Dosage on Soluble COD Removal

Following a similar trend as that for colour removal, soluble COD removal improved with decreasing temperature (Figure 4.3.5). In the results from the first experiment (Figure 4.3.2) the final soluble COD improved only slightly when the temperature was increased from 6.7°C to 33.3°C and experienced a relatively large increase at 40°C. With the exception of a coagulant dose of 48 ppm, this behavior of the final soluble COD being much higher at 40°C than at lower temperatures occurred over a wide range of coagulant dosages. This supports the conclusion reached in discussion on soluble COD results from the first experiment, that there may be a temperature where the effectiveness of the soluble COD removal rapidly declines.



Figure 4.3.5 Final Soluble COD Isotherms

The possibility of temperature increasing the solubility of compounds, which were previously removed during the filtering stage of the soluble COD test, was not examined. All soluble COD tests were done with effluent returned to room temperature or taken from refrigeration, prior to the filtering stage of the test. Any compounds which had their solubility increased at the higher temperatures would then have to remain soluble upon cooling.

# 4.3.7 Summary

Both colour and soluble COD were more effectively removed at lower temperatures. The colour removal improved by 5% to 6% when the temperature was decreased from  $40^{\circ}$ C to 6.7°C. It would be difficult to justify the cooling of the full effluent flow to achieve this small increase in performance. The increase in the percent soluble COD removal was

lower (4%) as the temperature is decreased over the same range. While colour removal increased in a linear fashion with decreasing temperature over the entire range of temperatures tested, removal of soluble COD did not. Floc formation improved with increasing temperature, up to a point, and then suffered a decrease in floc quality when the temperature was raised to 40°C. A number of possible explanations were proposed to explain the effects temperature had on the colour removal process, but it was not possible to give a definite overall mechanism to explain the effects.

#### 4.4 Effect of pH on System Performance

The pH of effluent has been previously shown to have a strong effect on colour removal with a dual polymer coagulation/flocculation system (Smith and Malloy, 1990). Increasing colour removal by lowering the pH could result in chemical savings even if it didn't reduce the level of polymer application to achieve the desired floc quality. By increasing the colour removal, less effluent would have to pass through the clarifier (i.e. a portion of the effluent could by-pass tertiary treatment) to obtain the required final colour. Bleach plant filtrates are of both high and low pHs, if these streams were to be treated separately the impact of pH on colour removal becomes even more important.

# 4.4.1 Effect of pH on Colour Removal

The initial pH of the effluent had a significant effect on the amount of colour removed; final colour increased with pH (Figure 4.4.1). Final colour decreased with decreasing pH to a minimum at pH 3. Further reduction in pH had a negative impact on colour removal. The final colour values observed at low pH (1.5 - 3) indicated that, at these low values, pH does not have an influence on colour removal. Many of the negative sites on the chromophores would be protonated at these low pHs, and, therefore the amount of coagulant needed to destabilize the anionic material in solution will be significantly reduced. A constant coagulant dosage combined with a lower coagulant demand at low pH may have resulted in overdosing, and a reversal of the surface charge. This, in turn, may have made it more difficult for the flocculent to bring pin flocs together into a larger agglomeration. Low coagulant demand would be desirable from a coagulant dose

reducing perspective, but the bridging induced by the coagulant would be reduced, and the chromophore is then less likely to become part of a floc.





The effect of pH on performance of the dual polymer system is likely due to its effect on the chromophores, the coagulant, and the flocculent.

The anionic nature of the chromophores is due to the presence of a number of ionizable phenolic and carboxylic groups. The pKa ranges for carboxylic and phenolic groups in organic acids are 1-5 and 1-11, respectively (Stumm and Morgan, 1996). The wide range for the pKa values is due to the different configurations of carboxyl and phenol groups have when part of larger molecules (Stumm and Morgan, 1996). The anionic nature of the chromophore will make the extraction of positively charged hydrogen atoms from the functional groups increasingly more difficult with an increasing negative charge of the

molecule; this will also contribute to making the pKa ranges less definite (Stumm and Morgan, 1996). From these pKa ranges, it would be expected that the titration curve, for organic molecules containing significant amounts of both phenolic and carboxylic acids, will gradually decline from pH 11 to pH 5, and then begin a more rapid decrease at pH of 5 and lower. Humic acids, naturally occurring polyelectric acids in soils and waters, also receive their charges from a number of carboxyl and phenol groups (Stumm and Morgan, 1996). The slope of the alkalimetric titration curve of humic acid (Figure 4.4.2) demonstrates this gradual decline and increase in the rate of change at a pH of 5.



# Figure 4.4.2 Alkalimetric Titration Curve for Humic Acid (Stumm and Morgan, 1996)

The effect of pH on colour removal from effluent (Figure 4.4.1) shows a similarity to the titration curve for humic acid. The two solutions contain very different organic substances, but both receive their surface charge from similar functional groups. Dahlman *et al.* (1995) found that the HMW fraction of totally chlorine free (TCF) bleaching filtrate closely resembled aquatic humic substances' polyelectrolytic

characteristics. This indicates that the dependence which colour removal has on pH is strongly related to the reversible reduction in surface charge due to protonation of the functional groups. Although useful, it would be difficult to create a useful titration curve for the secondary treated effluent, since the curve would be dominated by the influence of the CaCO<sub>3</sub> used to neutralize the effluent before treatment (Blackwell *et al.*, 1989).

#### 4.4.2 Effect of pH on Floc Formation

Floc formation is excellent at higher pHs, and as the pH is decreased below a pH of 5, the floc quality begins to decline (Table 4.4.1).

pН	Comments
1.5	Pin floc formation, flocs settled poorly, turbid supernatant
2	Pin floc formation, flocs settled poorly, slightly turbid supernatant
3	Fair floc formation, clear supernatant, flocs settled well
4	Good floc formation, clear supernatant
5	Excellent floc formation, rapid settling
6	Excellent floc formation, rapid settling
7	Good floc formation, rapid settling
8	Excellent floc formation, rapid settling
9	Excellent floc formation, rapid settling
10	Excellent floc formation, rapid settling
11	Excellent floc formation, rapid settling

## Table 4.4.1 Effect of pH on Floc Formation

The anionic nature of the flocculent is pH dependent and as the pH is lowered to 4, the flocculent's carboxylic groups become protonated, and the flocculent becomes charge neutral (Howe-Grant, 1994). Below a pH of 4, the polymer can no longer use electrostatic bonding as a method to bring pin flocs together. There is still reasonable floc formation at a pH of 3, although almost all the charged sites on the flocculent are

eliminated. The flocculent will still have significant hydrogen bonding ability at this pH, and the results suggest this is enough to give a moderate level of floc formation.

Below a pH of 3, floc formation is poor. Since, the flocculent still has hydrogen bonding ability, the obstacle to floc creation at pHs below 3 is likely to be due to the performance of the coagulant. As pH is progressively reduced, the number of the negative sites on the chromophore left available for the coagulant to bond with is progressively reduced. Once pH is sufficiently reduced, poor pin floc formation, or charge reversal, of the chromophores will arise. The flocculent would be unable to induce agglomeration of the poorly formed pin flocs created by coagulant addition, or the fully protonated chromophores.

Even with all the impediments to colour removal at lower pH values, the colour removal was superior to the removal in jar tests performed at pHs 4 and higher. Hydrogen bonding of the flocculent may suffice to form entities large enough to be removed by filtering during the colour test. Another contributor to the colour removals remaining above 69% at pH values less than 3 could be the pH readjustment step of the colour test. Since only a small amount of material settled after the jar tests at a pH lower than 3, even after careful decanting, much of the suspended material was present in the sample collected for testing. During the colour test, when the pH of the sample was brought up to a pH of 7.6, the coagulant and flocculent left in the supernatant became exposed to favorable pH conditions. Under these conditions, the polymer could create flocs of sufficient size to be removed in the filtering stage.

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#### 4.4.3 Effect of pH on Soluble COD Removal

The final soluble COD results (Figure 4.4.3) are similar to those of final colour. Changes in final soluble COD were less pronounced at higher pHs and demonstrated greater deterioration in performance below pH 3 than for final colour.



Figure 4.4.3 Effect of pH on Final Soluble COD

There was a decrease in soluble COD removal above pH 9, which was not observed in the final colour results. Perhaps there was colourless material, or chromophores with a relatively insignificant optical influence, that have their anionic nature increased at pH higher than 9. With sufficient negative charge induced by the high pH values, they may be able to become part of a floc structure.

Soluble COD removal decreased when the pH was reduced below three. This deterioration in performance is much greater than that of final colour over the same pH range. This may be a result of the procedural differences between the two tests. During

the procedure for colour removal there is a pH adjustment step that brings the pH of the sample to 7.6 before filtering, and in the soluble COD test procedure, there is no pH readjustment. With no pH adjustment, the conditions for chromophore removal remain unfavorable, and the unflocculated chromophores may be more likely to pass through the filter paper.

# 4.4.4 Effect of pH and Coagulant Dosage on Colour Removal

The final colour versus coagulant dose curves show a large difference between the colour removed at pH 4 and 7, and a relatively smaller difference between 7 and 10 (Figure 4.4.4). The average difference in the percent colour removal for the coagulant dosages of 72, 100, and 120 ppm are: 10.9%, between pH 4 and 7, and 1.9% between pH 7 and 10. This is in good agreement with the differences of 9.5% and 3.5%, for the same pH ranges in the first pH experiment (Figure 4.4.1).

The final colour curves in Figure 4.4.4 all have roughly the same shape, with decreasing marginal amounts of colour removed with increasing coagulant dose. If the only effect of addition of hydrogen ions was to reduce the quantity of anionic sites on the chromophores, then the shape of the three curves would be different. The greater number of negative sites on the chromophores at higher pHs would require more coagulant to neutralize the anionic surface charge, but once sufficient coagulant was added, the final colour values at higher pHs would be approximately equal to those at lower pHs. The fact that this does not occur suggests that the acidic conditions of the lower pH tests increase the number of chromophores that can be removed.

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Molecules that are more soluble are less likely to become part of the chromophore/polymer matrix (Schwoyer, 1981). Neutralization of the anionic groups of the chromophores with acid addition reduces their solubility, and may increase the likelihood that they will be retained in a floc structure.



Figure 4.4.4 Effect of Coagulant Dosage and pH on Colour Removal

## 4.4.5 Effect of pH and Coagulant Dosage on Soluble COD Removal

The influence of coagulant dose on soluble COD removal at any given pH is similar to that observed for colour; however, the final soluble COD results are different from the results for final colour. The progressively better removal of colour observed as pH was decreased was not seen for soluble COD (Figure 4.4.5).

Similar to final colour results, the lowest final soluble COD values were observed at the lowest pH tested (4). The next lowest final soluble CODs were observed at pH 10 instead of at a pH of 7. Again, the most plausible explanation for the increased soluble COD removal at the higher pH, is that there are compounds in the effluent which become anionic at the higher pHs but do not affect the colour. At first, this explanation appears to contradict the earlier contention that an increase in the anionic nature of a molecule would increase its solubility (and therefore make it less likely to removed in this dual polymer water treatment method). This would only be the case if the effect of the solubility outweighed the effect of increased anionic charge. No work was done to identify factors affecting this balance.



Figure 4.4.5 - Effect of pH and Coagulant Dose on Soluble COD Removal

# 4.4.6 Effect of pH and Coagulant Dosage on Floc Formation

Observations concerning floc formation are in contrast to the improvement seen in colour

removal as the pH is lowered (Table 4.4.2).

pH	Coagulant (ppm)	Comments
4	20	No floc formation
	40	Pin flocs, settled poorly
	72	Fair flocs, settled well
	100	Good flocs, settled very well
	120	Fair flocs
7	20	No floc formation
	40	Pin flocs, settled poorly
	72	Good to excellent flocs, rapid settling
	100	Good flocs, rapid settling
	120	Fair flocs, settled well
10	20	No floc formation
	40	Fair to good floc formation, settled rapidly
	72	Good flocs, settled rapidly
	100	Good flocs, settled rapidly
	120	Fair to good flocs, settled well

# Table 4.4.2 Effect of pH and Coagulant Dosage on Floc Formation

Improved floc formation was expected at lower coagulant dosages for the jar tests performed at lower pHs because of the possibility of added hydrogen ions reducing the cationic demand of the solution. Superior floc formation occurred at lower coagulant dosages at pH 10 instead of at pH 4. There was little difference between the quality of flocs formed at pH of 7 and 10. Perhaps the pH of 4 was too low to experience improved floc formation at a lower coagulant dose. The decreased electrostatic bonding ability of the flocculent at pH 4 may have outweighed the benefits of the lower pH.

#### 4.4.7 Summary

Colour removal is pH dependent. The percent removal of colour improved from minimum removal of 54.3% at a pH of 11 to a maximum removal of 71.1% at a pH of 3. While significant, this improvement in colour removal was less dramatic than previously reported by Smith and Malloy (1990). This difference in the effect of pH could be the result of using a different coagulant (for instance, tertiary amines are more pH sensitive than the quaternary amine used in this work) or to differences in the character of the effluent. Soluble COD removal varied from a high of 43.3% at pH 3 to a low of 34.8% at pH 9. Below a pH of three, removal of soluble COD and colour, and floc quality all declined. The decrease in available anionic sites at this pH level hampers the ability of both the coagulant and flocculent to induce agglomeration. Flocculation performance appeared to increase as pH was increased, and acceptable floc quality occurred at a lower coagulant dose as the pH was increased.

# 4.5 Effect of Biochemical Oxygen Demand on System Performance

Coagulant/flocculent effluent treatment methods have been shown to reduce  $BOD_5$  (Rush and Shannon, 1976), but the effect of the compounds responsible for BOD on colour removal using this technology is unknown. The  $BOD_5$  of the effluent discharged from secondary treatment at CFI fluctuates over the course of a year, from above 30 mg/L in the winter to below 10 mg/L in the summer. This seasonal change in  $BOD_5$  probably does not have a large impact on the colour removal clarifier's performance. If the placement of the colour clarifier was to be moved in the effluent treatment system, or bleach plant filtrates were to be treated prior to conventional treatment, the effect of  $BOD_5$  would become important.

#### 4.5.1 Effect of Low Molecular Weight Organics on System Performance

The LMW organic solution of acetic acid, formic acid, and methanol had no appreciable effect on the colour removal process. The percent colour removed results indicated that there was no relationship between LMW  $BOD_5$  addition and colour removal (Table 4.5.1).

Calculated BOD <sub>5</sub> Addition (mg/L)	Initial Colour (c.u.)	Final Colour (c.u.)	Percent Removal
150	630	272	56.8%
125	645	268	58.4%
100	629	269	57.3%
75	627	269	57.1%
50	634	268	57.8%
25	627	271	56.9%
0	644	276	57.0%

 Table 4.5.1
 Colour Removal at Different LMW BOD<sub>5</sub> Levels

Not only do the LMW compounds have a negligible effect on the percentage of colour removed, but the amount of soluble COD and  $BOD_5$  removed was not affected by the level of soluble BOD addition (Table 4.5.2).

Calculated BOD <sub>5</sub> Addition	Soluble COD (mg/L)			BOD <sub>5</sub> (mg/L)		
(mg/L)	Initial	Final	Reduction	Initial	Final	Reduction
150	687	493	194	120	128	-8
125	640	470	170	124	123	1
100	603	436	168	101	100	1
75	574	399	175	63	60	2.9
50	540	366	174	52	39	12.3
25	496	334	162	28	24	4.3
0	478	299	179	17	12	4.3

**Table 4.5.2** Soluble COD and BOD<sub>5</sub> Removed at Different LMW BOD<sub>5</sub> Levels Having no electrostatic charge, the methanol should not exert any influence on colour removal. Acetic and formic acids are monovalent anions and, therefore, given that the addition of monovalent ions of sodium and chloride had no effect on colour removal (Section 4.2), there is no reason to expect that the monovalent anions of acetic and formic acid would affect colour removal. There were no noticeable differences in the floc quality in any of the jar tests performed.

#### 4.5.2 Effect of Actual BOD and Coagulant Dosage on Colour Removal

In this work, "actual BOD" is taken to represent the material causing BOD found in the mill effluent, not the lab chemicals added to vary  $BOD_5$  in the previous section. Different levels of actual BOD had no substantial effect on colour removal in either of the pH adjusted and unadjusted tests (Figure 4.5.1 and 4.5.2). The colour removed is expressed as percent colour removal because the initial colour of the samples varied with the time of

treatment. Changes in colour were also observed during biological treatment in the full scale system (Section 4.6.1) and has been reported to occur at other mill's effluent treatment systems (Lang and Miller, 1977). Davies and Wilson (1990) observed an increase in colour across secondary treatment and attributed it to evaporation. The amount of evaporation in these experiments was negligible in comparison to the volume of effluent so it would not explain the colour change during biological treatment of effluent performed for this project. In fact, for the non-pH adjusted experiments the colour decreased during a period of the treatment (Table 3.1.2).

# 4.5.3 Effect of Actual BOD and Coagulant Dosage on Floc Formation

The level of biological treatment did not show significant effects on the quality of floc formation (Tables 4.5.3 and 4.5.4). The only set of floc quality observations that is different from the rest is the low  $BOD_5$  data for the non-pH adjusted tests, which shows a lower level of floc quality and the need for a higher coagulant dose to reach peak floc quality. The differences in pH, and the tests being performed at different times, make conclusions about floc quality difficult to make. Given all the factors that change during five days of biological treatment, the observations of floc quality at different  $BOD_5$  within each set of tests show good agreement.



Figure 4.5.1 Coagulant Dosage vs. Colour Removal at Different BOD<sub>5</sub>, Non pH-Adjusted



Figure 4.5.2 Coagulant Dosage vs. Colour Removal at Different BOD<sub>5</sub>, pH Adjusted

BOD5 (mg/L)	Coagulant (ppm)	Comments					
85	24	No floc formation					
	48	Poor flocs, settled poorly					
	72	Good flocs, settled quickly					
	96	Good flocs, settled quickly					
	120	Poor flocs, settled well					
74	24	No floc formation					
	48	Poor flocs, settled poorly					
	72	Good flocs, settled quickly					
	96	Good flocs, settled quickly					
	120	Poor flocs, settled well					
15	24	No floc formation					
	48	No floc formation					
	72	Poor to fair flocs, settled poorly					
	96	Good flocs, settled quickly					
	120	Fair flocs, settled well					

# Table 4.5.3Effect of BOD and Coagulant Dosage on Floc Formation, Non pH-<br/>Adjusted

BOD <sub>5</sub>	Coagulant	Comments						
(mg/L)	(ppm)							
85	24	No floc formation						
	48	Pin flocs, settled poorly						
	72	Fair flocs, settled well						
	96	Excellent flocs, settled quickly						
	120	Good flocs, settled quickly						
74	24	No floc formation						
	48	Pin flocs, settled poorly						
	72	Fair flocs, settled well						
	96	Excellent flocs, settled quickly						
	120	Good flocs, settled quickly						
15	24	No floc formation						
	48	Pin flocs, settled poorly						
	72	Fair flocs, settled well						
	96	Excellent flocs, settled quickly						
	120	Excellent flocs, settled quickly						

# Table 4.5.4Effect of BOD and Coagulant Dosage on Floc Formation, pH-<br/>Adjusted

# 4.5.4 Effect of Actual BOD and Coagulant Dosage on BOD<sub>5</sub> Removal

The amount of actual BOD<sub>5</sub> removed increased with coagulant dose and the percent

BOD<sub>5</sub> removed appeared to increase as the initial BOD<sub>5</sub> was decreased.

<b>Coagulant Dose</b>	Initial BOD <sub>5</sub>					
(ppm)	<b>85 (n</b>	ng/L)	<b>74 (n</b>	ng/L)	<b>15 (n</b>	ng/L)
28	85	0%	75	-2%	16	-4%
48	75	12%	66	11%	13	11%
72	70	17%	63	16%	8	45%
96	61	29%	57	23%	9	43%
120	59	31%	53	29%	12	20%

Table 4.5.5 Final BOD<sub>5</sub> (mg/L) and BOD<sub>5</sub> Removal (%), Non pH-Adjusted

Coagulant Dose	Initial BOD <sub>5</sub>					
(ppm)	<b>155 (</b> 1	mg/L)	<b>137 (</b> 1	mg/L)	<b>36 (n</b>	ng/L)
28	141	9%	120	12%	37	-3%
48	149	4%	111	19%	23	36%
72	128	17%	95	31%	20	44%
96	122	21%	89	35%	15	58%
120	121	22%	96	30%	15	58%

#### Table 4.5.6 Final BOD<sub>5</sub> (mg/L) and BOD<sub>5</sub> Removal (%), pH-Adjusted

The experiment involving the addition of LMW organics showed that this fraction of effluent BOD<sub>5</sub> was not removed by dual polymer coagulation/flocculation. Bacteria in secondary treatment first remove the material which is easiest to consume (i.e. methanol and formic acid), and then the more recalcitrant material (higher molecular weight and colloidal). Therefore, it would seem reasonable to conclude that residual colloidal and non-readily degradable BOD is what was removed in this experiment. Supporting this conclusion, the overall percent BOD<sub>5</sub> removed is higher at low BOD<sub>5</sub> than at the higher

 $BOD_5$  levels (when taking the average of the  $BOD_5$  removals at the coagulant dosages of 72, 96, and 120 ppm for both experiments).

Experiment	BOD <sub>5</sub> Level				
	High	Medium	Low		
Non pH-Adjusted	26%	23%	36%		
pH-Adjusted	20%	32%	54%		

#### Table 4.5.7Average BOD5 Removals at the Coagulant Doses 72, 96, 120 ppm

The percent removal was taken as an average of the removal at the three coagulant dosages that gave reasonable floc formation in effort to reduce the effect of the error associated with the BOD<sub>5</sub> test. Since the initial BOD<sub>5</sub> concentrations at the high and medium levels were not substantially different, it may not be prudent to compare the BOD<sub>5</sub> removed at these levels to each other. Instead, it may be more desirable to compare the low BOD<sub>5</sub> values to the medium and high values. In both experiments, the removal was higher at the low BOD<sub>5</sub> level than the higher levels. If the LMW components, similar to those used in the first BOD experiment, had a higher percent reduction during biological treatment than the rest of the BOD, the harder to degrade material would represent a larger portion of the total BOD<sub>5</sub> in the effluent with low BOD<sub>5</sub>. Since readily biodegradable material was not removed during the experiments with added LMW BOD, it is reasonable that the BOD<sub>5</sub> removal was higher at low BOD<sub>5</sub>.

#### 4.5.5 Effect of Actual BOD and Coagulant Dosage on Soluble COD Removal

The percent removals of soluble COD were similar to the removal of colour, in that the percent removal of soluble COD was independent of the initial value of BOD (Tables 4.5.8 and 4.5.9).

Coagulant Dose	Initial COD					
(ppm)	<b>565 (</b> )	mg/L)	<b>542 (</b> 1	mg/L)	454 (1	mg/L)
28	456	19%	425	22%	383	16%
48	435	23%	413	24%	351	23%
72	418	26%	416	23%	330	27%
96	398	30%	387	29%	325	28%
120	401	29%	376	31%	317	30%

<b>Table 4.5.8</b>	Final Soluble COD (mg/L) and Soluble COD Removal (%), Non pH-
	Adjusted

Coagulant Dose	Initial COD					
(ppm)	605 (1	ng/L)	584 (1	ng/L)	443 (1	mg/L)
28	545	10%	512	12%	389	12%
48	476	21%	464	20%	345	22%
72	463	23%	438	25%	326	26%
96	444	27%	430	26%	311	30%
120	435	28%	410	30%	306	31%

# Table 4.5.9Final Soluble COD (mg/L) and Soluble COD Removal (%), pH-<br/>Adjusted

As with BOD, biological treatment has a differential effect on different COD fractions. The high molecular weight portion of COD should be unaffected by biological treatment, while LMW organics will be readily removed. With the make-up of the soluble COD undergoing large changes during biological treatment, it is surprising that the percent removal of COD from effluent that has been biologically treated to varying degrees was not significantly affected.

The BOD in these effluent samples only represented a portion of the overall soluble COD, and the percent removals of  $BOD_5$  are similar to the percent removals of the soluble COD. Therefore, even if the removal rate of soluble COD is affected by differences in the removal of the LMW fraction, it will not be apparent when the overall

soluble COD percent removals are examined. For instance, in the pH-adjusted experiment at 120 ppm, the removal of  $BOD_5$  was above 50%, much higher than the soluble COD removal of 31%. This higher removal rate of  $BOD_5$  accounted for only an additional COD removal of 6 mg/L (assuming the  $BOD_5$  represented 65% of the COD from biodegradable material), and did not amount to a large change in the overall soluble COD removal.

#### 4.5.6 Summary

Neither type of biochemical oxygen demand tested (lab prepared or from the treatment system), had an effect on the system performance. The colour removal clarifier could be placed before or after the secondary treatment stage without fear of compromising the effectiveness of the colour removal process. The ASB does provide some equalization of colour through back-mixing, which makes control of the clarifier easier, and will act as a settling stage for contaminants (i.e. fibre) that have a negative impact on the recovery cycle. The BOD<sub>5</sub> constituents of methanol, formic acid, and acetic acid were not removed during the colour removal process, but BOD<sub>5</sub> from the effluent system was removed. Results indicate that the colloidal and non-readily biodegradable BOD were the fractions of the BOD<sub>5</sub> that were removed. The percent soluble COD removed was relatively constant at the three BOD<sub>5</sub> levels tested, even though the composition of the COD was altered before each set of jar tests. This may be due to the differences in BOD<sub>5</sub> removal and the contribution of the BOD to the total soluble COD not being large enough to impact the soluble COD removals.

# 4.6 Performance of Full-Scale System

Although dual polymer colour removal is reported to be reasonably specific towards the chromophores in the effluent (Springer, 1993), it may also be effective in removing other contaminants. The effect of the colour removal process in conjunction with biological treatment on effluent was investigated by testing the effluent at different stages of treatment at the full-scale effluent treatment system at CFI. Since the colour removal process targets HMW compounds and the biological treatment is effective in removing LMW compounds, the combination of the two treatment methods may be effective in removing a wide range of compounds.

#### 4.6.1 Colour

Colour removal across tertiary treatment averaged 60.4% from January 1, 1995 to November 25, 1996. A full summary of the colour data is given in Table 4.6.1.

	Primary Treated	Secondary Treated	Tertiary Treated	Colour Removal Across Clarifier
Average	631 c.u.	649 c.u.	257 c.u.	60.4%
Maximum	1368 c.u.	1100 c.u.	421 c.u.	74%
Minimum	123 c.u.	230 c.u.	135 c.u.	41%
Standard Deviation	173 c.u.	130 c.u.	56 c.u.	4.9%
# of Data Points	656	666	665	664

#### Table 4.6.1Full-Scale System Colour Data, Jan. 1, 1995 to Nov. 25, 1996

The colour removal clarifier was operational before January 1, 1995, but the mill was experiencing fluctuations in operation parameters due to the start-up after the mill modernization. The standard deviation of 4.9% for the colour removal across the clarifier is typical of the steady operation of that stage of treatment. CFI makes only one grade of

pulp, so the character of the effluent is relatively constant. For this reason, the variation of percent colour removal would be expected to be small.

The percent colour removal across tertiary treatment is not dependent on the colour of the effluent after secondary treatment (Figure 4.6.1). This suggests that the colour removal process was not colour concentration dependent, but was instead dependent on the composition of the effluent.



Figure 4.6.1 Colour Removal vs. Initial Colour

The change in colour across secondary treatment was highly variable, with both increases and decreases in the colour observed (Figure 4.6.2). The reason for the inconsistent effect of secondary treatment on colour was not clear. Work has been performed by other researchers on this topic (Larrea *et al.*, 1989; Lang and Miller, 1977). Lang and Miller (1977) published a survey from number of mills that experienced an effluent colour increase across biological treatment. They did make some suggestions as to why this occurred, but did not offer a definite conclusion. The colour increased when post-primary effluent was biologically treated in the lab (section 4.5.2), eliminating the possibility of the colour being accumulated in the ASB and then exiting at different times.



Figure 4.6.2 Monthly Colour Averages after Each Stage of Treatment

If colour data was continued to be collected at these points in the effluent treatment system, attributing the times of the changes in colour to events in the mill, or to conditions in the effluent treatment system, may be possible.
#### 4.6.2 Chemical Oxygen Demand

COD tests were performed on effluent taken from the outfall of each of the treatment stages from June 25 to November 26, 1996. The average reduction in COD across the ASB for this period was 46.7%, which corresponds well to previously reported COD reductions across ASBs for fully bleached Kraft pulp mill effluent (Banerjee *et al.*, 1996; Aprahamian and Stevens, 1990). On average, the COD reduction across the colour clarifier was 24.2% (13.3% of the overall COD).

Table 4.6.2 summarizes the averages of the COD and Recalcitrant COD values as well as some basic effluent parameters, averaged from data taken from the same days of the COD sample collection. Colour is expressed in mg/L by equating this unit to c.u., and kg/ADt is calculated assuming a production of 650 ADt/day and an effluent discharge of 38 million litres per day.

	Treatment Level							
	Primary		Secondary		Tertiary			
Parameter	mg/L	kg/ADt	mg/L	kg/ADt	→ mg/L	kg/ADt		
COD	874	51.1	480	28.1	364	21.3		
Recalcitrant COD	482	28.2	437	25.6	292	17.1		
Colour	633	37.0	714	41.7	300	17.5		
BOD <sub>5</sub>	230	14.4	13	0.76	12	0.70		
TSS	38	2.22	15	0.877	42	2.46		

#### Table 4.6.2 - Effluent Data for Days when COD was Tested

The reduction in colour across the colour clarifier was not matched by the COD reduction. The dual polymer colour removal system did exhibit some degree of selectivity towards the chromophores. The average ratio of removals for Recalcitrant COD to colour was 0.572 with a standard deviation of 0.073.

The relatively small reduction in COD due to colour removal makes it difficult to justify the implementation of such a tertiary treatment system for the primary purpose of removing COD. However, it is noteworthy that the reduction in COD from 28.1 kg/ADt to 21.3 kg/ADt would have allowed CFI to meet the COD limit of 25.4 kg/ADt originally proposed by the EPA in 1993 (McCubbin, 1996).

The Recalcitrant COD decreased by only 9.3% across secondary treatment. This supports the conclusion made in earlier studies that the HMW fraction of the effluent passes untreated through conventional primary and secondary systems (Banerjee *et al.*, 1996). The Recalcitrant COD did exhibit a greater decrease across the colour removal clarifier (116 mg/L), indicating this colour removal process targets the fraction of organics untreated by the previous effluent treatment stages. A larger decrease in Recalcitrant COD was seen across the colour clarifier than for COD, this can be attributed to the increase in TSS.

#### 4.6.3 Five Day Biochemical Oxygen Demand

Using a precipitation/flocculation process to treat pulp mill effluent has long been known to remove  $BOD_5$  (Rush and Shannon, 1976). The colour removal process at CFI is no different, with a 26% reduction in  $BOD_5$  observed across tertiary treatment (Table 4.6.4). The average

 $BOD_5$  concentrations before and after the clarifier were used for this calculation rather than the widely variable average percent removal (standard deviation of 33.6%; maximum and minimum removals of 75% and -200%, respectively). This wide range of values was most likely due to the uncertainty in the results from the  $BOD_5$  test rather than because of large fluctuations in actual removal. In the summer, the secondary treated effluent can have a  $BOD_5$  below 10 mg/L, and therefore small errors in the  $BOD_5$  test can be reflected in large percent variations.

	Primary Treated	Secondary Treated	Tertiary Treated	BOD <sub>5</sub> Removal Across Clarifier
Average	198 mg/L	21.2 mg/L	15.7 mg/L	19.3%
Maximum	336 mg/L	86 mg/L	67 mg/L	75.0%
Minimum	42 mg/L	2 mg/L	3 mg/L	-200%
Standard Deviation	49.6	13.9	9.9	33.6%
# of Data Points	181	270	267	267

Table 4.6.3Full-Scale System BOD5 Data, Jan. 1, 1995 to Nov. 25, 1996

#### 4.6.4 Total Suspended Solids

At CFI, effluent discharged from tertiary treatment had a higher TSS than the secondary-

treated effluent (Table 4.6.5).

	Primary Treated	Secondary Treated	Tertiary Treated
Average	41.2 mg/L	21.6 mg/L	40.1 mg/L
Maximum	336 mg/L	86 mg/L	67 mg/L
Minimum	42 mg/L	2 mg/L	3 mg/L
Standard Deviation	±49.6	±13.9	±9.9
# of Data Points	181	270	267

Table 4.6.4Full-Scale System TSS Data, Jan. 1, 1995 to Nov. 25, 1996

The TSS for secondary-treated effluent varied seasonally, with low TSS in the summer months and high TSS in the winter. This seasonal variation caused the standard deviation for the post-secondary TSS to be over half of its average value. The standard deviation for solids measurement in the tertiary treated effluent was much lower, largely a result of the DAF clarifier.

The colour removal process can increase or decrease the TSS across the system. With the post-tertiary TSS being independent of post-secondary TSS, the colour clarifier would decrease TSS if the final suspended solids from the ASB were higher.

To determine the influence of floc carryover on final effluent TSS, solids determinations were carried out on final effluent, and on final effluent from which the flocs had been physically removed. The percentage of total TSS that can be attributed to floc carryover is 27% (Appendix A.4). The rest of the TSS was made up of pin flocs or polymer that were not part of a larger floc structure. Removing the contribution of larger flocs from the average posttertiary treated TSS would give a final TSS of 29 mg/L. Even if the DAF clarifier were operated so that all the flocs of appreciable size were collected, there would be, on average, an increase in TSS across the colour removal system.

#### 4.6.5 Adsorbable Organic Halides

From October 2 to November 25, 1996, samples from the outfall of each stage of effluent treatment were analyzed for AOX. Table 4.6.5 summarizes the data collected.

	L	evel of Treatme	nt
	Primary	Secondary	Tertiary
Number of Samples	7	8	8
Average AOX	8.3 mg/L	4.8 mg/L	3.7 mg/L
	0.484 kg/ADt	0.278 kg/ADt	0.216 kg/ADt
Standard Deviation	2.54 mg/L	0.85 mg/L	0.59 mg/L

#### Table 4.6.5 AOX Data for Effluent Treatment System

The kg/ADt values were calculated by assuming a production of 650 ADt/day and an effluent discharge of 38 million litres per day. Across secondary treatment, 43% of the AOX was removed, a value that is in good agreement with a recently published study that examined AOX removal from a mill with a bleaching sequence and an ASB that were comparable those at CFI (Banerjee *et al.*, 1996). In a review of the effectiveness of different technologies in removing AOX, Wilson and Holloran (1977) reported that removals of AOX from aerated lagoons ranged from 14-65%.

The decrease in AOX across tertiary treatment is substantially smaller at 22% (13% of the original AOX) than colour removal. This, like the removal of COD, is probably too small to justify the implementation of such a system to treat AOX. There is a strong correlation between the average AOX and average COD at each sample point (Figure 4.6.3). The COD values for this graph are the average of the COD results from the samples taken over the same sampling period as for AOX. The error bars represent the standard deviations of the results at each sampling location.



#### Figure 4.6.3 AOX vs. COD

The similar removal efficiencies for AOX and COD indicate that chlorinated organics, unlike the chromophores, are not targeted for removal by the dual polymer system any more than the other organic material. The AOX content of the effluent entering the colour clarifier was relatively constant (standard deviation of 0.85 mg/L). A wider range of AOX values prior to tertiary treatment would aid in making more definite conclusions about the relation between COD and AOX removal. For instance, it would be interesting to observe the reductions in AOX across the different levels of treatment during a prolonged period when the AOX entering the system was, on average, twice as high as it was in our study.

#### 4.6.6 Dioxins and Furans

The implementation of 100% ClO<sub>2</sub> substitution and oxygen delignification all but eliminates the creation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8tetrachlorodibenzofuran (TCDF) during pulp bleaching (Luthe, 1996). Despite the virtual elimination of dioxin and furan production in a mill, benthal deposits in ASBs can contain significant amounts of these compounds if the mill has a history of operation with chlorine bleaching. Previous work at a different mill site showed that 2,3,7,8-TCDF can be transported into the mill effluent from the benthic deposits in an ASB, causing the mill to exceed permitted levels (Pagoria and Kerfoor, 1996). Feedback of dioxins and furans from benthal sediments in CFI's ASB result in secondary treated effluent 2,3,7,8 TCDF concentrations that exceed the permit level (50 ppq). From March 20, 1995 to August 6, 1996, 25 samples of post-secondary and post-tertiary treated effluent were tested for furans and dioxins. The results from these tests showed that the clarifier removed approximately 79.6% of the congener 2,3,7,8 TCDF, and removed other congeners equally as well (Table 4.6.7).

	Total TCDF	2,3,7,8 TCDF	TEQ
Post-Secondary	116 ppq	62 ppq	6.9 ppq
Post-Tertiary	16 ppq	12 ppq	1.2 ppq
Removal	83.4%	79.6%	81.9%

#### Table 4.6.6Average of Furan and TEQ Results

Amendola *et al.* (1989) and Barton *et al.* (1992) demonstrated that a number of different precipitation/flocculation chemicals were effective in removing dioxins and furans from pulp mill effluent and concluded that the furans and dioxins were associated with the suspended solids and colloidal material in the effluent. The types of treatment used were effective in removing this fraction of the effluent contaminants (Schwoyer, 1981) and, therefore, should be effective in removing furans and dioxins.

In the present study, there was no relationship between the post-secondary TSS and total furan concentration (Figure 4.6.4). The lack of dependence between these two parameters suggests that the dioxins and furans in the secondary treated effluent at CFI are associated to a greater degree with the colloidal material than the suspended solids.



Figure 4.6.4 Post-Secondary Suspended Solids vs. Total Furans

After being skimmed from the surface of the DAF the furan rich flocs are mixed with black liquor and sent back to the recovery cycle prior to incineration. The harsh conditions of the recovery boiler should ensure that the furans are destroyed (Luthe *et al.*, 1997).

To meet the stipulations for colour discharge in their permit, CFI needs to operate the colour clarifier only for the part of the year when the river is low (late summer and early fall). They currently operate the clarifier on a year round basis for furan removal. The excellent removal of furans in the colour removal clarifier allows CFI to continue operating without having to

undergo remedial dredging of the ASB or construct an entirely new secondary effluent treatment stage.

### 4.6.7 Microtox<sup>©</sup> Acute Toxicity

The colour removal process did not noticeably increase the acute toxicity of the effluent. Both post-secondary and post-tertiary treated effluents had  $EC_{50}$  values consistently above 100% (Table 4.6.7).

Sample Date	Level of Treatment				
	Primary	Secondary	Tertiary		
March 10	-	>100%	>100%		
March 24	0.32%	>100%	>100%		
March 31	23.8%	>100%	>100%		
April 1	22.5%	>100%	>100%		
April 7	27.5%	>100%	>100%		

### Table 4.6.7Acute Microtox<sup>©</sup> Toxicity Expressed as EC50

There was a high removal of acute toxicity across secondary treatment, which has been found in previous work on biological treatment of pulp mill's effluent (Barr, 1995).

#### 4.6.8 Mixed Function Oxygenase Induction

Due to problems with the tests conducted with fish, rat hepatoma cell cultures were used to determine the level of EROD (7-ethoxyresorufin-O-deethylase) induction. Rats are not typically found in the receiving environment of the mill's effluent discharge, but they should give an indication of possible chronic toxicity due to the mill aqueous emissions.



**Figure 4.6.5 - EROD Induction of 3º Treated SPE-D Fraction (100% methanol eluate)** The solid phase extracted (SPE-D) fraction of tertiary treated effluent did show elevated MFO induction at and above 100% concentration (Figure 4.6.5). It is encouraging that the effect was not seen until the 100% concentration, once the effluent is diluted by the receiving water it is not likely induce MFOs in the organisms in the receiving environment.

The amount of EROD induction was reduced across both secondary and tertiary treatment (Table 4.6.8).

Level of Treatment	EROL	Induction (Treated/C	ontrol)
	Whole Effluent	Non-Particulate	Non-Part/Whole
Primary	5.41	3.50	0.647
Secondary	3.56	3.16	0.888
Tertiary	2.93	2.58	0.881

	<b>Table 4.6.8</b>	EROD Induc	tion at Different l	Levels of Treatment
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MFO potency has been linked to poly-aromatic hydrocarbons (PAHs) and in particular TCDF and TCDD (Martel and O'Conner, 1992). The colour removal process effectively removed furans, and the chromophores removed are likely to have been highly aromatic, so the colour removal process is likely to lower the MFO induction caused by the effluent. The percent reduction in EROD induction across tertiary treatment was very similar for the whole and nonparticulate fraction of the effluent (17.7% and 18.3%, respectively).

Secondary treatment resulted in a much greater percent reduction in whole effluent EROD induction (34.2%) than the non-particulate fraction (9.7%). A large part of the whole effluent EROD induction in primary treated effluent appears to be due to the particulate fraction. Historically, discharge of suspended solids has been associated with negative environmental impacts such as reduced light transmission, covering the floor of the receiving water body and interfering with the oxygen transfer at fish gills (Tchobanoglous and Burton, 1991). Our results suggest that perhaps some of the MFO inducing compounds associate themselves with the particulate fraction of the effluent at this point in the effluent treatment system.

The author of this project are unaware of any previously published work on the ability of different effluent treatment techniques to reduce the level of MFO induction of pulp mill effluent. Without other results to which to compare the results presented here, it is difficult to speculate on the effectiveness of the dual polymer colour removal process in reducing EROD induction.

### 4.6.9 Summary

The reductions in effluent parameters, other than furans, were not as substantial as the removal of colour (Table 4.6.9). The process does appear to be selective towards chromophores, and improvements in overall effluent quality were probably due to their removal.

Parameter	Removal Across					
	2º Treatment	3º Treatment	2° and 3° Treatment			
Colour	-2.85%	60.4%	59.3%			
BOD <sub>5</sub>	89.3%	19.3%	92.1%			
TSS	47.6%	-85.6%	2.67%			
AOX	42.6%	22.4%	55.4%			
COD	45.1%	24.2%	58.4%			
2,3,7,8-TCDF	-	79.6%	-			
MFO Induction	34.2%	17.7%	45.8%			

 Table 4.6.9
 Effect of 2° and 3° Treatment on Effluent Quality Parameters

#### **4.7 Treatment of High Strength Effluent**

Using the dual polymer colour removal process to treat the high strength effluent was investigated to determine if there are benefits to treating the high strength streams separately from other effluent flows and to increase the understanding of the performance of the full-scale system. The high strength effluent sewers were sampled a number of times to establish an average colour for each sewer flow. Samples from each high strength sewer, alone and in combinations, were tested at a number of coagulant doses, in an attempt to determine the system performance using these segregated streams.

#### 4.7.1 Colour of High Strength Flows

Results from the sampling of the high strength flows (Table 4.7.1) showed that the caustic sewer ( $E_{op}$  filtrate tank overflow) consistently had the highest colour of the three streams

Date	Caustic Sewer		Acid Sewer		Bleach Plant Sewer		Combined Effluent	
	Colour (c.u.)	Flow (L/s)	Colour (c.u.)	Flow (L/s)	Colour (c.u.)	Flow (L/s)	Colour (c.u.)	- Flow (m <sup>3</sup> /s)
August 12	2118	44.2	384	101	147	77.9	667	461
August 15	1921	41.0	460	101	262	74.3	623	461
August 26	3530	44.2	720	101	166	60.0	615	461
September 6	2429	56.8	715	88.3	517	77.3	659	461
September 16	2414	56.8	958	114	162	63.2	793	461
October 1	1388	63.1	593	101	98	75.7	618	461
October 4	1225	63.1	536	101	74	56.7		
October 11	962	63.1	451	101	1234	60.2	540	461
October 17	1748	75.7	667	101	6472	115	2157	461
November 1	1641	85.2	860	101	104	85.5	776	461
Average	2038	59.3	634	101	191	74.5	661	461

 Table 4.7.1
 Survey of High Strength Effluent Colour

From October 1 onward, the acid sewer ( $D_{100}$  filtrate tank overflow) flow meter was not operational, and was assumed to be 101 L/s for each of these days. This assumption was arrived at by performing a water balance around the filtrate tank, and observing the flow rates measured on earlier dates. On October 17, there was an overflow from a pulping group sewer that is normally diverted back to the pulp process, into the bleach plant sewer causing the colour of the bleach plant sewer and combined effluent to be much higher than normal. For this reason, these colour values were ignored. The average colour of the effluent entering primary treatment for this survey agrees well with the long term average colour for the post primary treated effluent (631 c.u., Table 4.6.1). During the times of sampling the pulp mill operation was close to steady state, but the colour of the acid and caustic sewers varied widely. Flow variations within the bleach plant, the bleaching conditions (Wohlgemuth *et al.*, 1997), and the lignin content of the pulp entering the bleach plant (Graves *et al.*, 1993) can all have a large effect on the colour of the effluent streams exiting the bleaching process.

The contribution of each high strength flow to the combined colour was calculated in two ways. First, as a percentage of the calculated combined colour, and then as a percentage of the effluent colour entering primary treatment. The calculated combined colour was determined by assuming the three high strength flows were the only streams with colour, and there were no interactive effects when the streams were mixed.

High Strength Flow	Percentage of C	ombined Colour
	Calculated	Actual
	(432 c.u.)	(661 c.u.)
Caustic Sewer	60.7%	39.7%
Acid Sewer	32.1%	21.0%
Bleach Plant Sewer	7.20%	4.68%
Total	100%	65.4%

 Table 4.7.2
 Contribution of High Strength Streams to Effluent Colour

The caustic sewer is the source of most of the effluent colour (Table 4.7.2). Studies at other mills have also shown the filtrate from the extraction stages in the bleach plant to be the main source of effluent colour (Dence and Reeve, 1996).

The calculated sum of the three streams tested only contributed approximately two thirds of the colour entering primary treatment. The calculated value was not expected to closely match the actual value because of the inaccuracy associated with the flow measurements and colour contributions from other effluent streams. However, due to the size of the difference, the source of the difference was investigated. A possible explanation for the large colour difference is that the assumption of no interactive effects from the mixing was false. Carefully conducted colour surveys at other mills have reported that the colour at the influent to the effluent treatment system can be 15-30% higher than predicted by a sewer balance (Springer, 1993). In our study, when the samples from each high strength stream were mixed in different combinations in a factorial experiment, an effect from mixing the bleach plant sewer effluent became evident. The samples used for these factorial experiments were the samples collected for the high strength flow colour survey (Table 4.7.1) on the days of October 1 and 4. Table 4.7.3 summarizes the results from these experiments, the mixing combinations can be found in Materials and Methods (Table 3.3.3).

Run #		October 1			October 4	
	Calculated Colour (c.u.)	Actual Colour (c.u.)	Percent Increase	Calculated Colour (c.u.)	Actual Colour (c.u.)	Percent Increase
1	333	411	23%	293	348	18%
2	317	317	0%	282	298	6%
3	95	103	8%	86	86	0%
4	222	223	0%	196	200	2%
5	16	31	98%	12	32	166%
6	238	239	0%	208	204	-2%
7	111	197	78%	98	355	264%
8	0	0	0%	0	0	0%

## Table 4.7.3Results from Factorial Design Experiment on Mixing of High<br/>Strength Streams

Dorica (1991) reported that the observed colour increase upon mixing the effluent streams was a result of alkaline hydrolysis of the effluent from the chlorination stages. Run #2 (a mixture of the acid and caustic sewer samples) showed that this was not the case with the effluent streams at CFI. The effect of each stream on the change in colour (Table 4.7.4) was determined using the method outlined by Hines and Mongomery (1990) for calculating effects in a  $2^3$  factorial design. The factors that had the largest effects were the dilution of the bleach plant and caustic sewers, and the largest interactive effect was from the mixture of bleach plant and caustic sewers. From these results, it appears that the colour increase is due to the dilution and subsequent increase in pH of the bleach plant sewer sample. Runs number one, five, and seven show the largest

increases in colour, and all were mixtures of effluent where the pH of the bleach plant sewer sample was reduced. The negative effect of the caustic sewer sample dilution indicates that the high pH of this sample can prevent the colour increase caused by the dilution of the bleach plant sewer sample.

Effect	October 1	October 4
Acid Sewer (A)	1.38	15.3
Bleach Plant Sewer (B)	23.9	54.8
Caustic Sewer (C)	-20.1	-50.8
A*B	-0.63	14.3
A*C	4.38	-9.25
B*C	-18.13	-52.8
A*B*C	6.38	-10.3

 Table 4.7.4
 Effects from Factorial Experiment (% Colour Change)

The colour increase from the reduction in bleach plant sewer pH probably was not the only cause of the discrepancy in the actual and calculated combined colours in the full-scale system, but it does give some insight into the cause of the colour increase.

#### 4.7.2 Acid Sewer Jar Tests

Peak floc formation achieved in both sets of jar tests performed on the acid sewer effluent was excellent (Tables 4.7.5, 4.7.6). The full-scale system is typically operated at the lowest coagulant application where good to excellent floc formation is observed. Colour removals at the lowest coagulant dose for which excellent floc formation was observed in each set of jar tests ( $1^{st}$  set = 41%,  $2^{nd}$  set = 26%) were both considerably lower than the colour removed in the full scale system (60.4%). Organics found in the acid sewer are

predominantly LMW and highly soluble (Dence and Reeve, 1996), not the types of compounds that are removed well from the effluent using this type of treatment process.

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
24	18%	4%	No floc formation
48	28%	7%	Pin flocs
72	35%	7%	Fair flocs, settled well
96	41%	10%	Excellent flocs, settled rapidly
120	44%	10%	Excellent flocs, settled rapidly
144	51%	11%	Excellent flocs, settled rapidly
192	53%	12%	Good to excellent flocs, settled rapidly
264	55%	13%	Poor flocs, settled slowly

Table 4.7.5	1 <sup>st</sup> Set of Acid Sewer Effluent (Initial Colour, 860 c.u.; Initial Soluble
	COD, 1661 mg/L) Jar Tests

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
24	13%	3%	No floc formation
48	21%	5%	Good flocs, settled rapidly
72	26%	6%	Excellent flocs, settled rapidly
96	38%	8%	Excellent flocs, settled rapidly
120	38%	10%	Good flocs, settled rapidly
180	50%	10%	Poor flocs, settled slowly

Table 4.7.62nd Set of Acid Sewer Effluent (Initial Colour, 481 c.u.; Initial Soluble<br/>COD, 1274 mg/L) Jar Tests

The soluble COD removals were much lower in relation to colour removal than what was previously observed with secondary treated effluent. To allow for the calculation of these averages of the ratio of removals, it was assumed that the ratio of soluble COD removal to colour removal was independent of coagulant dose.

1 <sup>st</sup> Set		
Coagulant	(Soluble COD Removal)/	
(ppm)	(Colour Removal)	
24	0.228	
48	0.249	
72	0.211	
96	0.246	
120	0.225	
144	0.217	
192	0.234	
264	0.245	
Average	0.232	

	2 <sup>nd</sup> Set
Coagulant	(Soluble COD Removal)/
(ppm)	(Colour Removal)
24	0.199
48	0.252
72	0.243
96	0.213
120	0.265
180	0.198
Average	0.228

Table 4.7.7 Ratio of Soluble COD to Colour Removals for Acid Sewer Samples

The averages of the ratios were 0.232 and 0.228 for the  $1^{st}$  and  $2^{nd}$  set of experiments, respectively (Table 4.7.7). These are low when compared to the ratio of 0.56 for the full-scale treatment system. The ratio for the full-scale system was calculated by calculating the Recalcitrant COD without taking into account the reduction in BOD<sub>5</sub> across tertiary treatment (Table 4.6.2). Comparisons in COD removal between the post-secondary and acid sewer effluents are difficult to make because much of the LMW COD has been removed from the post-secondary effluent, material which is not removed well with this type of colour removal process.

#### 4.7.3 Caustic Sewer Jar Tests

The floc formation in the jar tests with effluent from the caustic sewer, at best, only achieved fair floc formation (Tables 4.7.7, 4.7.8). This result was not anticipated because the effluent from the caustic sewer represented the largest portion of the colour in the final effluent. The polymers used functioned well with the final effluent, so it was expected that they would perform well when treating the largest colour source, the caustic

sewer effluent. This demonstrates how charged polymers can be application specific (Howe-Grant, 1994).

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
124	0.4%	6%	No floc formation
248	19%	21%	No floc formation
372	47%	31%	Pin flocs, settled poorly
496	54%	35%	Poor to fair floc, settled poorly
620	60%	38%	Fair floc, settled well
744	69%	41%	Poor to fair floc, settled poorly

<b>Table 4.7.8</b>	1 <sup>st</sup> Set of Caustic Effluent (Initial Colour, 1636 c.u., Initial Soluble
	COD, 3205 mg/L) Jar Tests

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
100	-13%	9%	No floc formation
200	36%	28%	No floc formation
248	41%	28%	Pin to poor flocs, settled poorly
300	46%	32%	Fair flocs, settled well
400	56%	35%	Fair flocs, settled well
500	41%	37%	Poor to fair flocs, settled reasonably well

## Table 4.7.92nd Set of Caustic Effluent (Initial Colour, 1065; Initial Soluble COD,<br/>2540 mg/L) Jar Tests

The maximum percent colour removals for the caustic sewer effluent at the coagulant dosages tested were only slightly higher than maximum removals for the acid sewer, but the maximum percent soluble COD removals were much greater. Organic molecules present in the filtrate from the extraction stages are, on average, larger than those found in the filtrate from the chlorination stages (Sagfors and Starck, 1988). Coagulation and flocculation processes typically are better at removing larger molecules (Schwoyer,

1981), and, therefore would be expected to give better colour removal for a caustic sewer sample than one from the acid sewer sample.

	1 <sup>st</sup> Set
Coagulant	(Soluble COD Removal)/
(ppm)	(Colour Removal)
124	15.9
248	1.121
372	0.662
496	0.642
620	0.632
744	0.598
Average	0.731

	2 <sup>nd</sup> Set
Coagulant	(Soluble COD Removal)/
<b>(ppm)</b>	(Colour Removal)
100	-0.645
200	0.790
248	0.693
300	0.692
400	0.612
500	0.901
Average	0.738

Table 4.7.10 - Ratio of Soluble COD to Colour Removals for Caustic Sewer Samples The ratio of soluble COD removal to colour removal (Table 4.7.10) was approximately three times higher than the same ratio for the results from the acid sewer jar tests, suggesting that the chromophores represent a higher percentage of the COD in the caustic sewer effluent than in the acid sewer effluent. The ratios at the lowest coagulant dosage for each set of tests were considered outlying data points. If the ratios are considered independent of coagulant dosage, each result can be considered a repeated test. The result from the lowest coagulant dose for each set was at least three standard deviations away from the average of the ratios (averages and standard deviations were calculated with the ratios for the lowest coagulant doses included).

#### **4.7.4 Bleach Plant Sewer Jar Tests**

For each set of jar tests on the bleach plant sewer effluent the colour removal was high (Tables 4.7.11 and 4.7.12), reaching a maximum of 97% removal in the first set of tests. A higher quality of flocs was achieved in the second set of experiments.

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
5	90%	16%	Poor flocs, settled poorly
10	81%	24%	Poor flocs, settled poorly
15	97%	25%	Poor flocs, settled poorly
20	97%	25%	Poor flocs, settled poorly

<b>Table 4.7.11</b>	1 <sup>st</sup> Set of Bleach Plant Effluent (Initial Colour, 607 c.u., Initial Soluble
	COD, 431 mg/L) Jar Tests

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
10	32%	4%	No floc formation
20	73%	14%	No floc formation
32	90%	27%	Poor flocs, settled poorly
44	77%	28%	Excellent flocs, settled rapidly
56	66%	30%	Good flocs, settled rapidly

## Table 4.7.121st Set of Bleach Plant Effluent (Initial Colour, 1432 c.u., Initial<br/>Soluble COD, 649 mg/L) Jar Tests

Results from the jar tests on the samples from the bleach plant sewer require more interpretation than the results from the other high strength sewers. The colour removals are based on the colour of each bleach plant sewer sample after its pH was reduced to 5. The chromophores in the bleach plant sewer were unbleached dissolved lignin from the pulping process, which are only able to be dissolved in water at pH values above 11.5 (Adams, 1997). Bleach plant sewer effluent pH was initially quite high, 11.8 for the first set and 11.9 for the second set, so initially the chromophores should have been stable in solution. When the pH was reduced to below 11.5 the acidic groups on the lignin macromolecules were likely close to being fully protonated, and, therefore no longer stable in solution. Initially, at pH 5, the bleach plant sewer effluent maintained its brown colour that it had at its original pH. After a few hours of storage at 4°C, the effluent lost its initial brown clear appearance, and became a turbid solution of lightly coloured,

visually detectable colloids. These small colloids did not appear to dissolve back into solution after the pH adjustment of the colour test, and some of these colloids were observed in the filtrate from the filtering step of the colour test. Material not dissolved in solution interferes with the colour test.

Although some of the colloidal material in the pH-reduced bleach plant sewer effluent passed through the 0.8  $\mu$ m filter paper used in the colour test, they were not visually observed when this effluent was filtered through 0.2  $\mu$ m filter paper. Final colour values from the colour test using the 0.2  $\mu$ m filter paper were much lower, and showed a more consistent trend than the standard colour test results (Table 4.7.13). The lower colour values of the modified test indicate that fewer colloids passed through the smaller pore size filter paper.

Coagulant (ppm)	Final Col 0.8 μm	our (c.u.) 0.2 μm
0	607	99
5	64	24
10	116	19
15	17	14
20	16	13

# Table 4.7.13Final Colour Values for 1st Set of Bleach Plant Sewer Effluent JarTests

A colour increase was also seen in the experiment involving the mixing of the high strength streams (Section 4.7.1) when the bleach plant sewer effluent pH was reduced. The 0 ppm results represent the bleach plant sewer sample with pH lowered to 5 and no flocculent added. Colour tests with bleach plant sewer effluent conducted without a pH

reduction pretreatment showed no interference from molecules coming out of solution. Perhaps the chromophores' loss of solubility occurred slowly enough to allow for an accurate initial colour measurement.

	1 <sup>st</sup> Set
Coagulant (ppm)	(Soluble COD Removal)/ (Colour Removal)
5	0.180
10	0.291
15	0.260
20	0.260
Average	0.249

	2 <sup>nd</sup> Set
Coagulant	(Soluble COD Removal)/
(ppm)	(Colour Removal)
10	0.137
20	0.188
32	0.320
44	0.359
56	0.454
Average	0.288

## Table 4.7.14 Ratio of Soluble COD to Colour Removals for Bleach Plant Sewer Samples

The ratios of soluble COD removal to colour removal for the bleach plant sewer samples are low (Table 4.7.14), suggesting that much of the soluble COD was not chromophoric. Ratios for the second set of tests appear to increase with increasing coagulant applications. This is most likely due to the decrease in colour removed at the higher coagulant doses and not an increase in the quantity of soluble COD removed in comparison to chromophores removed.

#### 4.7.5 Combined High Strength Effluent Jar Tests

Jar tests with the mixture of acid and caustic sewer effluent samples produced excellent flocs at a coagulant dose of 360 ppm (Table 4.7.15).

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
72	27%	14%	No floc formation
144	38%	18%	No floc formation
216	49%	21%	Poor flocs, settled poorly
288	58%	26%	Fair to good flocs, settled well
360	63%	29%	Excellent flocs, settled rapidly
432	65%	29%	Good flocs, settled rapidly
504	66%	31%	Fair to good flocs, settled reasonably well

### Table 4.7.15Combined Acid and Caustic Sewer Effluent (Initial Colour, 1218 c.u.,<br/>Initial Soluble COD 2303 mg/L) Jar Tests

The ratio of each sample in the mixture was roughly 50/50 (46% acid effluent, 54% caustic effluent) and yet the poor floc formation observed in the jar tests with the caustic sewer effluent was not observed.

The colour removal at the coagulant dose where excellent floc formation was observed (63%) agrees well with the average colour removal for the full-scale system (60.4%). As these two streams are the major contributors to effluent colour, this result was not unexpected.

Coagulant	(Soluble COD Removal)/
(ppm)	(Colour Removal)
72	0.508
144	0.471
216	0.439
288	0.448
360	0.456
432	0.448
504	0.467
Average	0.462

Table 4.7.16Ratio of Soluble COD to Colour Removals for Combined Acid and<br/>Caustic Sewer Samples

The average ratio of percent soluble COD removal to colour removal (0.462) is in good agreement with the weighted average from the acid and caustic effluent ratios (0.463, Table 4.7.17).

Sewer	(Soluble COD Removal)/ (Colour Removal)	Volume Percent of Combined Sample	Contribution to Total Ratio
Acid	0.232	54%	0.125
Caustic	0.731	46%	0.338
		Total	0.463

## Table 4.7.17Calculated Soluble COD to Colour Ratio of Removal for Combined<br/>Acid and Caustic Sewer Samples

Even with the superior floc formation of the combined acid and caustic sewer sample, in comparison to the caustic sewer effluent, there was no observed interactive effect that gave an improvement in soluble COD removal in comparison to colour removal.

The combination of acid, caustic, and bleach plant sewer samples also achieved excellent floc formation with sufficient coagulant application (Table 4.7.18).

Coagulant (ppm)	Colour Removal	Soluble COD Removal	Observations
52	5%	1%	No floc formation
104	34%	19%	Pin flocs, settled very poorly
156	53%	23%	Poor flocs, settled reasonably well
208	57%	25%	Good flocs, settled rapidly
260	63%	29%	Excellent flocs, settled rapidly
312	66%	29%	Good flocs, settled rapidly

Table 4.7.18Combined Acid, Caustic and Bleach Plant Sewer Effluent (Initial<br/>Colour, 1071 c.u., Initial Soluble COD 1720 mg/L) Jar Tests

Coagulant (ppm)	(Soluble COD Removal)/ (Colour Removal)
52	0.127
104	0.555
156	0.438
208	0.443
260	0.457
312	0.439
Average	0.410

## Table 4.7.19Ratio of Soluble COD to Colour Removals for Combined Acid,<br/>Caustic and Bleach Plant Sewer Samples

The average ratios of soluble COD to colour removals for the combined acid, caustic and bleach plant sewer samples (0.410, Table 4.7.19) agree well with the calculated weighted average of the ratio for the three samples (0.394, Table 4.7.20).

Sewer	(Soluble COD Removal)/ (Colour Removal)	Percent of Combined Sample	Contribution to Total
Acid	0.232	31%	0.0862
Caustic	0.731	37%	0.229
Bleach Plant	0.249	31%	0.0784
		Total	0.394

## Table 4.7.20Calculated Ratio of Soluble COD to Colour Removal for Combined Acid,<br/>Caustic, and Bleach Plant Sewer Samples

As with the combined acid and caustic sewer effluent sample, there does not appear to be a synergistic effect that improves the soluble COD removal in comparison to the colour removal.

#### 4.7.6 Coagulant Demand of High Strength Streams

One of the goals of the bench scale work with the high strength effluents was to determine if treating these streams separately from the rest of the effluent offered any chemical savings. To do this, the coagulant demand of each high strength stream was based on its original colour, and then the average chemical demand was determined using the stream flow and colour surveys from section 4.7.1. This calculated coagulant demand was compared with the chemical application in the full scale system for the same time period. This analysis was done only for the coagulant application.

The full scale system is operated at the lowest coagulant dose where good to excellent floc formation is achieved. Coagulant demand for each high strength stream was calculated as the range of applications above and below where desired floc formation occurred. Acceptable floc formation was not always achieved during the jar tests of the segregated streams. In these cases, the coagulant doses at one application level lower than peak floc formation were chosen.

Stream	1 <sup>st</sup> Set	2 <sup>nd</sup> Set	Average
Caustic	0.303 - 0.379	0.232 - 0.282	0.268 - 0.330
Acidic	0.0827 - 0.110	0.0998 - 0.1497	0.0912 - 0.130
Bleach Plant	0.00824 - 0.0165	0.0224 - 0.0307	0.0153 - 0.0236

## Table 4.7.21 Range of Ratios of Coagulant Dosage Required to Achieve Acceptable Floc Formation to Initial Colour

The caustic sewer had the largest demand for coagulant per colour unit of all the high strength streams (Table 4.7.21). Although flow for the colour sewer was lower than the other sewers, this sewer was the largest consumer of coagulant.

Before using the ratios in Table 4.7.21 to calculate the coagulant demand of high strength sewers, the ability to predict the coagulant demand to reach acceptable floc formation of the

combined samples should be checked. Table 4.7.22 summarizes the actual and calculated results for the combined samples.

Sample	Coag Deman	ulant d (ppm)	Colour I	Removal	Solubl Rem	e COD 10val
	Actual Range	Calc. Range	Actual Range	Calc. Range	Actual Range	Calc. Range
Acid and Caustic	288-360	266-335	59-63%	44-50%	26-29%	20-23%
Acid, Caustic & Bl. Plant	208-260	185-231	57-63%	58-60%	25-29%	19-23%

#### Table 4.7.22 - Actual and Calculated Jar Test Results for 1st Set of Samples

In Table 4.7.22, the actual range represents the range in which the acceptable floc formation first occurs. Calculated ranges were determined by assigning ranges in which acceptable floc formation occurs for coagulant dose, soluble COD removal, and colour removal weighted averages based on their volume percentage in the mixed sample (Table 4.2.22).

This method of calculation showed good agreement for coagulant dose, but was not as good in predicting colour and soluble COD removal. It appears that this technique can be confidently used for calculating coagulant dose of the combined sample, and should be used with caution to predict the colour or soluble COD removed.

Using the results from the bench scale work done with the high strength effluent and the colour surveys of the full scale system, the coagulant dosage required to treat the high strength streams separately from the rest of the effluent would have been 164 - 207 ppm (sum of column D divided by sum of column A, Table 4.7.23) of coagulant for the period from August 12 to November 1, 1996.

Sewer	(A) Average Flow (L/s)	(B) Average Colour (c.u.)	(C) (Coagulant Dose) /Colour (ppm/c.u.)	(D)=(A*B*C) Coagulant Demand (ppm*L/s)
Acid	101	634	0.0912 - 0.130	5842 - 8321
Caustic	59.3	2038	0.268 - 0.330	32391 - 39922
Bleach Plant	74.5	191	0.0153 - 0.0236	218 - 336
Sum	234.8 L/s			38451 - 59579

 Table 4.7.23
 Calculation of the Coagulant Demand of the High Strength Streams

When this range is scaled to allow comparison with the full flow of effluent it becomes 83 to 105 ppm. The average coagulant dose used in the full scale system for the same time period was 86 ppm. From this technique of calculating the chemical application required for treating the high strength flows it does not appear that any chemical savings could be achieved from their segregated treatment.

#### 4.7.7 Summary

Colour surveys performed on the high strength effluent sewers revealed that over half of the effluent colour originates from the caustic sewer. The calculated colour contributions of these high strength streams indicate that these streams make up only two thirds of the overall colour. An experiment investigating the source of this difference indicated that the change in colour of the bleach plant sewer when pH was reduced contributed to this difference.

The polymers used were well suited to treat the acid sewer effluent, while they did not function well with the caustic sewer effluent. This does not necessarily mean that it is impractical to treat the filtrates from the extraction stages with a coagulation/flocculation colour removal process. Other polymers may be able to provide excellent system performance when used to treat this stream. When the high strength streams were mixed, the addition of polymers resulted in excellent floc formation.

When high strength streams were jar-tested alone or in combination, only tests conducted with the bleach plant sewer effluent resulted in a considerably higher colour removal than was typically seen in the full scale treatment system. Mixing the high strength streams was beneficial in terms of floc formation but did not improve soluble COD removal in relation to colour removal.

By creating a ratio of coagulant demand to initial colour for each stream it became evident that the caustic sewer effluent had the largest coagulant demand per colour unit. Reductions in this flow to the effluent treatment system would not only reduce effluent colour, but would significantly reduce the amount of coagulant require to treat the final effluent. By extrapolating from the results of the jar tests for the high strength effluents there did not appear to be any large chemical savings that could be realized by treating these streams separately from the rest of the effluent.

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### V Conclusions

From the study of the tertiary colour removal process at Crestbrook Forest Industries a number of conclusions can be made.

- 1. Colour removal with organic polyelectrolytes is unaffected by increasing the ionic strength of the effluent with monovalent ions.
- 2. The dual polymer colour removal process operates well over a wide range of temperatures, pH, and biochemical oxygen demand levels.
- 3. Colour and soluble COD removal improved as temperature was decreased.
- 4. Effluent pH is an important factor in colour and soluble COD removal. Soluble COD and colour removal improve as pH is decreased to pH 3 and then further reductions in pH hamper system performance.
- 5. The full-scale colour removal system reduced colour, BOD<sub>5</sub>, COD, AOX, 2,3,7,8-TCDF, and mixed function oxygenase induction by 60.4%, 26%, 24%, 23%, 80%, and 18%, respectively.
- 6. The relatively low COD to colour removal implies that tertiary treatment at CFI is relatively specific in removing chromophores.
- Segregated treatment of high strength streams does not appear to offer the potential for polymer savings over the treatment of the combined secondary treated effluent.

#### **VII** Recommendations

- Implement a settling stage after tertiary treatment to reduce the suspended solids being released into the environment. A portion of the TSS discharged from the DAF clarifier will settle quickly and, therefore, a polishing stage after the tertiary colour removal system will reduce the amount of pollutants being released into the environment.
- 2. For a possible long term solution to the furans from the ASB, determine if the colour removal system is able to remove dioxins and furans re-suspended in the effluent from remedial dredging of the ASB.
- Perform more work with high strength effluent to increase the accuracy of coagulant demand estimation. Another series of jar tests with high strength effluent, alone and in combination, may reduce the predicted range of coagulant doses needed to treat the segregated streams.
- 4. Perform a charge demand balance on the mill's effluent sewer system to identify possible contributors to polymer demand that do not necessarily have an effect of effluent colour.
- 5. Continue work with effect of tertiary treatment on mixed function oxygenase induction and other measures of chronic toxicity. As environmental legislation becomes stricter and possibly looks towards regulating sub-lethal toxicity, knowing the effects of additional effluent treatment may become more important.

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# VIII Appendix A

## A.1 Calibration of Spectrophotometer and COD Vials

Table A.1.1 summarizes the data for the calibration of the spectrophotometer and COD vials. The relationship between adsorbence and COD was subjected to a linear fit ( $r^2 = 0.997$ ) with Excel 97 and the equation for the curve is,

$$COD(mg/L) = 2147 * absorbence + 4.60$$
 (2)

Transmittance versus COD had good fit with an exponential curve (calculated with Excel 97,

 $r^2 = 0.996$ ) and can be expressed as,

$$COD(mg/L) = -928 * ln[0.00998 * transmittance]$$
 (3)

Date	COD Standard (mg/L)	Absorbence	Transmittance
June 26, 1996	150	0.068	85.5
June 26, 1996	300	0.144	71.9
June 26, 1996	500	0.225	59.5
June 26, 1996	500	0.230	59.0
June 26, 1996	650	0.310	49.1
June 26, 1996	1000	0.456	35.0
July 22, 1996	150	0.068	85.9
July 22, 1996	300	0.141	72.2
July 22, 1996	500	0.242	57.3
July 22, 1996	1000	0.476	33.5
August 15, 1996	150	0.069	85.7
August 15, 1996	300	0.142	72.1
August 15, 1996	500	0.235	58.3
August 15, 1996	1000	0.467	34.1
September 16, 1996	150	0.059	87.7
September 16, 1996	300	0.131	74.0
September 16, 1996	500	0.219	60.5
September 16, 1996	1000	0.451	35.5

 Table A.1.1
 Data for COD Calibration Curves

## A.2 Summary of Errors Involved with Calculations

The discussion of results in this report does discuss error analysis in detail, but this does not mean the errors do not exist. This appendix section briefly covers the errors involved in this project.

## A.2.1 Syringes

A quantitative estimation of uncertainty was not supplied with the syringes, so it was determined experimentally. Volumes of distilled water at  $20^{\circ}$ C from 5 and 10 mL syringes were measured on a Mettler PM400 Analytical Balance. Using the density of water at  $20^{\circ}$ C (998.2 kg/m<sup>3</sup>) the precise volume of water could be determined. The data from these experiments is presented in Tables A.2.1 and A.2.2.

Volume (ml)	Weight of H <sub>2</sub> 0 (g)	Volume of H <sub>2</sub> 0 (ml)	Error (ml)
1.0	1.08	1.08	0.08
2.0	1.92	1.92	0.08
3.4	3.44	3.45	0.05
4.0	3.98	3.99	0.01
5.0	4.95	4.96	0.04
5.0	4.98	4.99	0.01
6.0	5.95	5.96	0.04
6.0	5.94	5.95	0.05
6.0	5.98	5.99	0.01
7.0	6.92	6.93	0.07
7.4	7.33	7.34	0.06
8.0	7.93	7.94	0.06
8.0	7.93	7.94	0.06
9.0	8.88	8.9	0.10
9.0	8.9	8.92	0.08
10.0	9.88	9.9	0.10

Labic A.2.1 Eliter Data for to hill Syringe	Table A.2.1	Error	Data for	10 ı	mL Syringe
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Volume	Weight of H <sub>2</sub> 0	Volume of H <sub>2</sub> 0	Error
(ml)	(g)	( <b>ml</b> ) · · · · ·	(ml)
1.0	1.06	1.06	0.06
1.0	0.98	0.98	0.02
1.4	1.49	1.49	0.09
2.0	1.97	1.97	0.03
2.0	2.06	2.06	0.06
2.0	2.08	2.08	0.08
3.0	3.01	3.02	0.02
3.0	3.09	3.10	0.10
3.6	3.67	3.68	0.08
4.0	4.04	4.05	0.05
4.0	4.08	4.09	0.09
4.6	4.64	4.65	0.05
5.0	4.91	4.92	0.08
5.0	5.07	5.08	0.08

#### Table A.2.2Error Data for 5 mL Syringe

The uncertainty of the syringes was selected to be largest difference between the volume from the syringe and the actual volume (0.10 mL for both syringe sizes). The standard deviations of 0.029 mL and 0.027 mL for the 5 and 10 mL syringes, respectively, were smaller, but the it was decided to use the more conservative value of  $\pm 0.10$  mL.

### A.2.2 Polymer Dilution

Assuming the only errors were from measuring of the components for dilution, the final uncertainty in coagulant (1 v/v%) and flocculent (0.1 v/v%) concentrations were 0.015% and 0.0017%, respectively. Except for the experiments involving actual BOD, each set of experiments was performed with the same diluted polymer solutions. For this reason, the error from polymer dilution did not exert much influence on results, and were ignored.

#### A.2.3 Polymer Dosage

Uncertainty in polymer dosage arises from two sources, volume of dilute polymer ( $\pm 0.10$  ml) added and volume of effluent used ( $500\pm 5$  mL) in the jar test. Coagulant application uncertainty can be expressed by,

$$0.01^*(X/500)^*(\pm [0.1/X + 5/500])^*10^6$$
(4)

The variable X represents the volume of 1% (v/v) coagulant in mL. Flocculent application uncertainty can be expressed by,

$$0.001^*(Y/500)^*(\pm [0.1/Y + 5/500])^*10^6$$
(5)

The variable Y represents the volume of 0.1% (v/v) flocculent in mL. Uncertainty from polymer dilution was not included in these equations.

#### A.2.4 Colour

The CPPA standard method for colour measurement states that the precision of the colour measurement technique is 5% (CPPA, 1993a)

Another source of uncertainty for colour arises in the experiments for temperature, pH, and BOD when the coagulant dosage was kept constant and the experiment conditions were varied. Differences in coagulant application will result in an increase in uncertainty of the final colour. Unfortunately, for these experiments the relationships of coagulant dosage to colour and soluble COD were not established. These relationships were estimated, using data from the experiments where coagulant dosage was varied, to be 1 c.u. per 1 ppm of coagulant and 0.4 mg/L per 1 ppm of coagulant for colour and soluble COD, respectively. An

experiment conducted using 100 ppm of coagulant will have an uncertainty of  $\pm 3$  ppm, which increases the uncertainty of the final colour and soluble COD by  $\pm 3$  c.u. and  $\pm 1.2$  mg/L.

## A.2.5 COD

When measuring COD it was assumed that the only factors that contributed to uncertainty were the pipetting of effluent into the COD vials and reading absorbence and transmittance from the spectrophotometer. The uncertainty of each element was: 2 mL pipette,  $\pm 0.006$  mL; transmittance reading,  $\pm 0.2$ ; and absorbence reading,  $\pm 0.002$ . The error from calculating COD from absorbance is equal to 0.002 multiplied by the slope of the absorbance vs. COD relationship (2147, Appendix A.1). Uncertainty in determining COD from transmittance has to be determined by calculating the COD from readings 0.2 above and below the desired transmittance. For instance, a transmittance reading of 50.0 corresponds to a COD of 644.7 mg/L, and the transmittances of 49.8 and 50.2 correspond to CODs of 648.4 mg/L and 641.0 mg/L, respectively. The COD from a transmittance of 50.0 therefore can be expressed at 644.7 $\pm$ 3.7 mg/L. The formula for uncertainty in COD measurements is,

$$\frac{(A+T)*[0.006+0.002*2147/_{A}+\pm T/_{T}]}{2}$$
(6)  
Where  $A = COD$  calculated from absorbance  
 $T = COD$  calculated from transmittance

 $\pm T$  = uncertainty of COD calculated from transmittance

#### A.2.6 BOD<sub>5</sub>

BOD<sub>5</sub> tests have many factors that can result in extreme variability in results. The APHA standard method for determining BOD<sub>5</sub> suggests a control limit of 198 $\pm$ 30.5 mg/L of BOD<sub>5</sub> for the standard glucose to glutamic acid standard solution (APHA, 1992). A minimum of twenty five standard checks should be performed to find if the size of three standard deviations fall within the control limit (APHA, 1992). This type of standard deviation determination would be prohibitive if applied to the BOD<sub>5</sub> testing of the pulp mill effluent. Instead, the discussion of results from the BOD<sub>5</sub> tests in this project recognize the variability of the results, but no quantitative value is associated with this uncertainty.

## A.3 Calculation of TEQ

The calculation method for toxicity equivalency quotients (TEQs) was supplied by Axys Analytical Services Ltd. (Sydney, BC). TEQ expresses an overall toxicity an effluent in terms of the 2,3,7,8 congeners of dioxins and furans by weighting the contribution each congener to the TEQ by its level of toxicity. For instance, the most toxic dioxin congener, 2,3,7,8-T<sub>4</sub>CDD, is assigned the NATO international toxic equivalency factor (I-TEF) of 1. When calculating the overall toxicity the concentration of this chemical in the effluent in ppq is multiplied by its I-TEF (1). The summation of all the concentrations in ppq multiplied by their respective I-TEF gives the effluent's TEQ. Concentrations that were non-detectable can be given the value of zero or one-half of the detectable limit, in this report non-detect was taken to be equal to zero. Table A.2.1 catalogues the I-TEFs for each 2,3,7,8 substituted congener.

CONTAMINANT	CONGENER	I-TEF
Dioxin	2378 -T <sub>4</sub> CDD	1
	12378-P <sub>5</sub> CDD	0.5
	123789-H <sub>6</sub> CDD	0.1
	123478-H <sub>6</sub> CDD	0.1
	123678-H <sub>6</sub> CDD	0.1
	1234679-H <sub>7</sub> CDD	0.01
	O <sub>8</sub> CDD	0.001
Furan	2378-T <sub>4</sub> CDF	0.1
	23478-P5CDF	0.5
	12378-P5CDF	0.05
	123478-H <sub>6</sub> CDF	0.1
	123789-H <sub>6</sub> CDF	0.1
	234678-H <sub>6</sub> CDF	0.1
	123678-H <sub>6</sub> CDF	0.1
	1234678-H <sub>7</sub> CDF	0.01
	1234789-H <sub>7</sub> CDF	0.01
	O <sub>8</sub> CDF	0.001

Table A.3.1 International	<b>Toxic Equiva</b>	lency Factors
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Date	Unfiltered TSS (mg/L)	Filtered TSS (mg/L)	Contribution of Flocs
July 29	30.4	22.8	25.0%
July 30	44.0	35.6	19.1%
August 8	40.1	31.7	21.1%
August 12	54.8	40.0	27.0%
August 20	33.4	24.0	28.1%
August 22	34.0	22.7	33.2%
September 5	41.5	27.7	33.3%
September 8	83.1	49.0	41.0%
September 12	40.8	28.1	31.1%
October 1	54.8	32.1	41.4%
October 23	43.3	24.9	19.4%
November 7	31.1	30.1	3.2%
November 19	29.8	20.9	29.9%
Average	43.2	30.7	27.1%
Standard Deviation	14.5	7.9	10.1%

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# A.4 Contribution of Floc Carry-over to Post-Tertiary TSS

Table A.4 - Floc Carryover from Tertiary Treatment

# IX Appendix B

# **B.1 Data from Results and Discussion Presented in Figures**

Temperature (°C)	Final Colour (c.u.)	Final Modified Colour (c.u.)
6.7	306	295
12.2	311	303
17.8	320	306
23.3	334	307
28.9	326	307
34.4	339	314
40.0	352	311

Table B.1.1	Effect of Temperature on Colour Removal (Initial Colour 762 c.u., Initial
	Modified Colour, 789 c.u.)

Temperature (°C)	Final Colour (c.u.)
6.7	347
12.2	349
17.8	351
23.3	354
28.9	354
34.4	354
40.0	367

Table B.1.2Effect of Temperature on Soluble COD Removal (Initial Soluble COD,<br/>506 mg/L)

Coagulant	1	emperatui	:е
(ppm)	6.7°C	23.3°C	40.0°C
24	458	467	473
48	380	393	399
72	326	345	367
96	289	309	322
120	253	269	289

Table B.1.3	Final Colour (c.u.) Results from Effect of Temperature and Coagulant
	Dosage Experiments (Initial Colour, 691 c.u.)

Coagulant	Temperature		
(ppm)	6.7°C	23.3°C	40.0°C
24	462	450	462
48	365	373	379
72	314	328	338
96	275	289	297
120	243	252	261

Table B.1.4	Final Modified Colour (c.u.) Results from Effect of Temperature and
	Coagulant Dosage Experiments (Initial Modified Colour, 744 c.u.)

Coagulant	Temperature		
<u>(ppm)</u>	6.7°C	23.3°C	40.0°C
24	395	387	433
48	340	343	347
72	324	328	343
96	304	308	334
120	297	304	315

Table B.1.5Final Soluble COD (mg/L) Results from Effect of Temperature and<br/>Coagulant Dosage Experiments (Initial Soluble COD, 503 c.u.)

рН	Final Soluble COD (mg/l)	Final Colour (c.u.)
1.5	282	189
2	265	189
3	247	180
4	252	201
_ 5	271	233
6	272	249
7	276	260
8	280	265
9	284	281
10	276	281
11	278	285

Table B.1.6	Final Colour and Soluble COD Results from Effect of pH on System
	Performance (Initial Colour, 623 c.u.; Initial Soluble COD, 436 mg/L)

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Coagulant	pH		
(ppm)	4	7	10
20	399	458	502
40	281	353	359
72	206	281	296
100	181	247	266
120	178	245	247

Table B.1.7Final Colour (c.u.) Results from Effect of pH and Coagulant DosageExperiments (Initial Colour, 638 c.u.)

Coagulant	pH		
(ppm)	4	7	10
20	333	349	349
40	290	315	304
72	261	289	274
100	265	292	274
120	256	276	276

Table B.1.8Final Soluble COD (mg/L) Results from Effect of pH and Coagulant<br/>Dosage Experiments (Initial Soluble COD, 397 mg/L)

Coagulant	Temperature		
e (ppm)	6.7°C	23.3°C	40.0°C
24	395	387	433
48	340	343	347
72	324	328	343
96	304	308	334
120	297	304	315

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Table B.1.9	Final Soluble COD (mg/L) Results from Effect of Temperature and
	Coagulant Dosage Experiments (Initial Soluble COD, 503 mg/L)

Coagulant			
(ppm)	85 mg/L	74 mg/L	15 mg/L
0	604	584	660
24	435	430	496
48	376	364	397
72	353	331	344
96	298	292	325
120	275	264	336

<b>Table B.1.10</b>	Final Colour (c.u.) Results from Effect of BOD and Coagulant D	)osage
	Experiments, Non pH-Adjusted	

Coagulant	BODs		
(ppm)	155 mg/L	137 mg/L	.36 mg/L
0	535	544	557
24	399	414	429
48	339	342	363
72	311	310	321
96	271	275	284
120	245	246	255

Table B.1.11Final Colour (c.u.) Results from Effect of BOD and Coagulant DosageExperiments, pH-Adjusted

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