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PREDICTIVE COD MODEL FOR ASBs

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ABSTRACT
In 1995, Georgia-Pacific and IPST began a project to develop a COD treatment model. There were two drivers behind this effort. First, when EPA proposed the Cluster Rule in 1992, they contained limits for COD. In April 1998, the Cluster Rule was promulgated for the bleached subcategory and EPA reserved the right to set limits at a later date. Second, mills must currently meet BOD limits for BOD. The BOD test takes five days to perform. To tightly control performance, a quicker surrogate test is needed. The COD test can be performed in less than three hours. This is adequate for the control of lagoons because they have long retention times.

Historically, it has been difficult to predict effluent COD. There are two reasons for this:

- The COD in mill effluents has not been characterized very well.
- The transformation of COD within a treatment system has not been well understood.

We developed a method of easily fractionating COD into four parts:

- particulate;
- soluble inorganic;
- soluble biodegradable;
- soluble non-biodegradable.

A performance model developed was tested at three mills. It can predict soluble COD within 10% and total COD within 15%. To date, Georgia-Pacific has used the model to increase aeration efficiency and save approximately $500,000.

INTRODUCTION
Mills must currently meet BOD limits, and the BOD test takes five days to perform. To tightly control performance, a quicker surrogate test is needed. The COD test can be performed in less than three hours. This is adequate for the control of lagoons because they have long retention times. Three quarters of our mills treat their wastewater with aerated stabilization basins (ASBs). Also, the performance of these systems is difficult to predict. Therefore, we based our model on ASBs.

Potential Limits
In July 1997, EPA suggested the following limits for market pulp mills.

Monthly Max. (kg/kkg)	**Daily Max. (kg/kkg)**
45.6	64.0

EPA recognizes that the papermaking processes contribute additional COD. However, no new limits have been proposed. The originally proposed limits for unbleached mills are:

Monthly Max. (kg/kkg)	**Daily Max. (kg/kkg)**
24.6	40.2

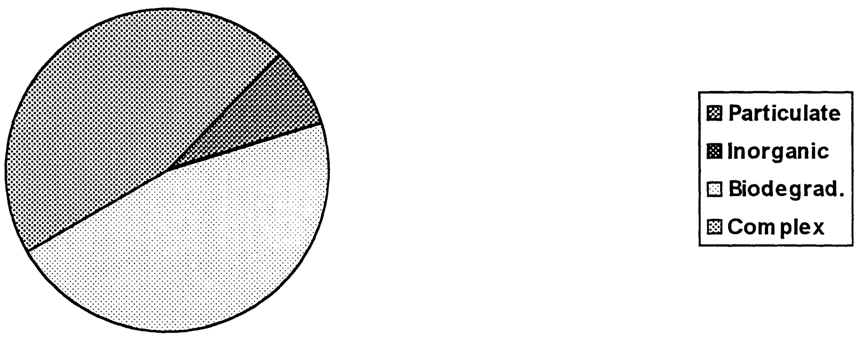
These limits do not recognize the COD contribution from OCC. EPA recognizes the need to collect more data. They are planning to conduct a survey for unbleached mills. We expect that these data will be used to develop new limits.

What is COD?
Before you can model COD, you need to understand what it is. "The chemical oxygen demand (COD) is a measure of the oxygen equivalent of organic matter to oxidation by a strong chemical oxidant."[1] Although all the organics are not completely oxidized in the test, 95-100% are. For example, volatile straight chain aliphatic compounds are not oxidized to any *appreciable extent*[1]. Inorganic compounds including nitrite, ferrous ion and sulfide are oxidized. Ammonia is not oxidized.

The COD in pulp and paper mill effluents can be divided into four groups:

- Particulates
- Inorganic compounds
- Soluble compounds that are easy to biodegrade
- Soluble compounds that are hard to biodegrade

For example, the inlet to Mill A's aerated stabilization basin has the following make-up:



The particulate COD is fiber and biomass. The inorganic COD is mostly bisulfide. At Mill A, we used the immediate oxygen demand (IOD) to estimate its value. IOD can be high during a black liquor spill. Normally, it is low. The biodegradable COD is composed of compounds with a molecular weight equal to or less than 1000. To measure this fraction, we filter the sample through a suspended solids filter. Then we filter the filtrate through an ultrafiltration membrane. We refer to this as "double filtered" COD, or DFCOD. This fraction includes methanol, carbohydrates, and phenolic compounds. The complex COD (CCOD) is the higher molecular weight compounds. These are lignin and lignin degradation products.

COD originates from several sewers in a typical bleached Kraft mill. In a study conducted at Mill B a few years ago, the bulk of the COD was found in the acid and alkaline bleach mill filtrates, with the pulp mill, recovery and evaporator sewers containing smaller quantities. COD correlates with other parameters across the mill. For example, at Mill B, pulp mill and evaporator sewer COD correlates well with BOD, because these materials are biodegradable[2]. There is a strong relationship between COD and color as illustrated in Figures 1 and 2, and there is a good relationship between COD and AOX in the final effluent (but not in the influent) as discussed in reference 2. The relatively high variability across the episodes in Figures 1 and 2 reflects hardwood/softwood swings. Hence, the ability to model COD at the final effluent would also provide insight into the behavior of these other parameters.

Removal in Treatment Systems
Effluent COD from a properly operating secondary treatment system is mostly non-biodegradable carbon. The total COD removal at our mills ranges from 35 - 74 %. IPST studies have shown that 95% of the biodegradable COD can be treated. Almost 100% of the Immediate Oxygen Demand is treated. Five to ten percent of the CCOD is removed.

Model Development
Accurate aerated stabilization basin models have been available for more than a decade[3]. These models predicted biodegradable COD, inorganic COD, dissolved oxygen and suspended solids. They did not predict CCOD. In a study of COD degradation across treatment systems, Larrea et al. aerated Kraft black liquors in batch reactors[4]. They found that the degradable fraction had a first-order half-life of about seven days. This translates to a rate constant of 0.044 hr^{-1}. The COD removal was attributed to two mechanisms:

- polycondensation-adsorption of some lignin structures.
- biodegradation of cellulosic derivatives and the biochemical oxidation of some functional groups of the lignin.

Hence, in principle, if black liquor was the only form of COD released to secondary treatment, then its degradation should follow the above schedule.

However, since COD originates from different locations in the mill, its composition must vary. For example, bleach plant COD will be very different from, say, that in the evaporator sewer. The mechanism of degradation of the CCOD, *i.e.* the non-biodegradable fraction, is unknown, although a combination of oxidation and condensation/settling has been proposed[2].

Despite these complexities, we studied the feasibility of representing the degradation of CCOD by a single first-order rate constant. Over the past few years we have extended and refined the model. The equations for inorganic and biodgradable COD are similar to historical models[3].

We modeled CCOD through equations of the form shown below, where $CCOD_o$, $CCOD_1$, and $CCOD_2$ are CCOD concentrations in fully mixed contiguous compartments, k_A is the first-order rate constant for the degradation of CCOD, q is flow, BMIX is the backmix ratio, and v_1 is the volume of compartment 1. Analogous equations apply to the other compartments.

$$\frac{-dCCOD_1}{dt} = k_A \bullet CCOD_1 - q \bullet \{CCOD_0 - CCOD_1 \bullet (1 + BMIX) + CCOD_2 \bullet BMIX\} / v_1$$

In this paper we demonstrate that a single k_A value is able to adequately model data for three very different mills.

RESULTS AND DISCUSSION

The model was used to evaluate three treatment systems. The three Georgia-Pacific mills listed in Table 1 were modeled with a k_A value of 0.008 hr^{-1}. The treatment systems have different geometries. Mill A has a single basin that receives tapered aeration. Mill C has four lagoons, of which only lagoons 2 and 3 are aerated. The results in Table 1 are for lagoon 2 only. Mill D has two aeration stabilization basins, followed by a polishing lagoon. The results reported are only from the first lagoon.

Despite differences in influent COD and horsepower, among other factors, the COD estimated with a single k_A value compares well with measured data, suggesting that the assumptions made by using a common k_A are reasonable. It is interesting that our field-derived k_A of 0.008 hr^{-1} is of the same order of magnitude as Larrea et al.'s laboratory value of 0.044 hr^{-1}. We conclude that if the value is stable across these various scenarios, then it should certainly be constant for a given mill, which would allow us to include COD in the suite of parameters that are presently modeled.

Table 1: Comparison of actual and estimated effluent COD (ppm)

	volume (m^3)	**flow (m^3/hr)**	**hp**	**influent[1]**		**effluent[1]**		**estimated**
				COD	**BOD**	**COD**	**BOD**	**COD**
Mill A	960,000	6,000	4,790	1,300	160	630	7	580
Mill C	700,000	5,540	240	390 48		300	31	320
Mill D	519,000	7,100	5,100	910		390		420

[1]measured from filtered samples; [2]lagoon 2 only; [3]lagoon 1 only

Model Benefits

The model can be used for many purposes. For example, Mills A and D used the results to conserve energy. The ASBs are designed to handle peak loads. Typically, mills ran all the available aerators all of the time. This practice wastes energy and does not improve effluent quality. The model was used to determine the aeration needed at different daily loads. On the average, we found that 15-20% of the aerators could be turned off without sacrificing performance [5)]. This represents an annual savings of $500,000. Mill C is in the process of converting its non-aerated basin into an ASB. The model was used in the conceptual design.

CONCLUSIONS

Georgia-Pacific and IPST have developed a model to predict COD removal in an aerated stabilization basin. The model has been shown to be accurate at several mills. It can be used to help mills develop cost-effective solutions to meet future limits.

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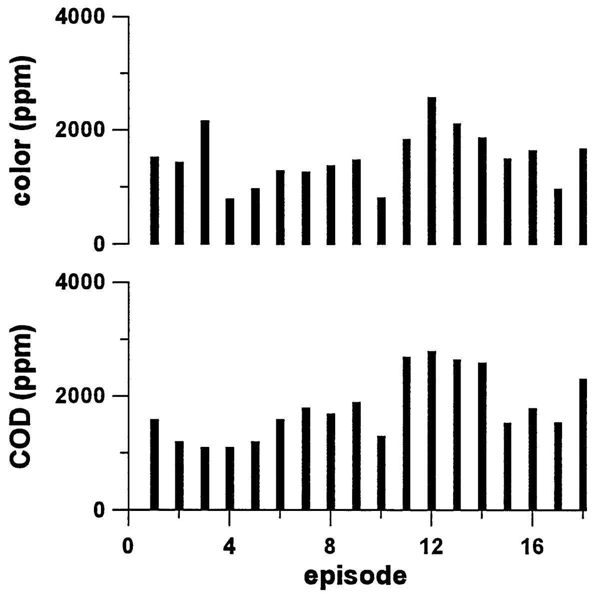

Figure 1: COD-color relationship at the influent from Mill B

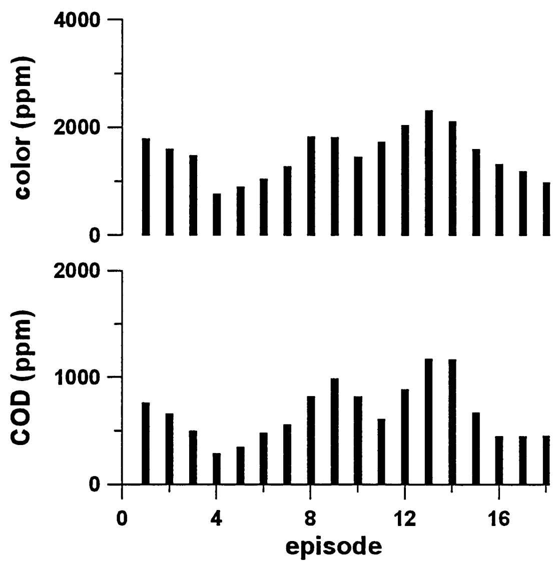

Figure 2: COD-color relationship at the effluent from Mill B