THE EFFECTS OF SULFIDE ON PULP AND PAPER WASTEWATER COLOR REVERSION

Except where reference is made to the work of others, the work described in this thesis is my own or was done in collaboration with my advisory committee. This thesis does not include proprietary or classified information.

Jessica Marie Esty

Certificate of Approval:

Dongye Zhao Assistant Professor Civil Engineering	Clifford R. Lange, Chair Associate Professor Civil Engineering
Willie F. Harper, Jr. Assistant Professor Civil Engineering	Stephen L. McFarland Acting Dean Graduate School

THE EFFECTS OF SULFIDE ON PULP AND PAPER WASTEWATER COLOR REVERSION

Jessica Marie Esty

A Thesis

Submitted to

the Graduate Faculty of

Auburn University

in Partial Fulfillment of the

Degree of

Master of Science

Auburn, Alabama
December 16, 2005

THE EFFECTS OF SULFIDE ON PULP AND PAPER WASTEWATER COLOR REVERSION

Jessica Marie Esty

Signature of Author

Date of Graduation

VITA

Jessica Marie Esty, daughter of Mark and Susan Esty, was born on August 27, 1979, in Waterville, ME. She graduated from Waterville Senior High School as Salutatorian in 1997. In 2001, she graduated from the University of Maine at Orono with a Bachelor of Science degree in Chemical Engineering. During her undergraduate studies, she gained cooperative experience at a local paper mill. From 2001-2002, she worked as an environmental engineer at a printed circuit board manufacturing company. Thereafter, from 2002 until 2004, she was employed at an environmental engineering consulting company. In 2004, she began graduate studies in Environmental Engineering in the Civil Engineering Department at Auburn University.

THESIS ABSTRACT

THE EFFECTS OF SULFIDE ON PULP AND PAPER WASTEWATER COLOR REVERSION

Jessica Marie Esty

Master of Science, December 16, 2005
(B.S. Ch.E., University of Maine, 2001)

139 Typed Pages

Directed By Clifford R. Lange

More and more concern is being given to the aesthetics of wastewater, specifically the color of the resulting effluent. The underlying causes of colored wastewater suggest incomplete pollutant removal and unsuccessful overall treatment. Therefore, monitoring color will soon become a more commonly regulated parameter. Yet, in order to accomplish decolorization as effectively and efficiently as possible, understanding the mechanisms of color reversion, and thereby pin-pointing the color culprit, needs to be achieved first. But, minimal research has been conducted on the generation of color in pulp and paper wastewaters thus far. Therefore, a study of color reversion was conducted in order to observe the effects of sulfide dissolved in pulp and paper wastewater. Color reversion is the yellowing of pulp on exposure to air, heat, certain metallic ions, and fungi due to modification of residual lignin-forming chromophores. The rate and degree of color reversion has been hypothesized to be related to four main mechanisms: 1) anaerobic color reduction, 2) anaerobic color generation via sulfide reaction, 3) aerobic color reversion, and 4) aerobic decolorization. The major goal of this thesis is to elucidate the role sulfide has on color reversion of treated and untreated paper mill wastewater.

Experimentation involving sulfide exposure, aeration, and individual lignin compounds all encompass the efforts of this research. Sulfide exposure yielded as great as 100% color increase in some cases; whereas, in other tests, the results suggested sulfide had relatively no effect on color reversion. The differences appeared to be associated with the initial color of the wastewater—lighter colored samples yielded higher color increases upon sulfide exposure, while the darker samples displayed generally no relationship to sulfide concentration, except at unrealistically high doses.

Aeration appeared to have a reverse effect on sulfide color reversion. However, following this color reduction, other mechanisms became dominant which caused color reversion to recur. These results support the color phenomenon seen across ponds where at times color remains consistent while during other times, it has actually been reported to increase, suggesting another color generation mechanism is involved.

As aforementioned, the underlying differences seen in color reversion appear to be related to the wastewater composition, given the extreme variability of pulp and paper wastewater. The concentrations of lignin derivatives (specifically humic substances) were hypothesized to have direct influences on sulfide color reversion. When different humic functional groups were tested, the catechol and anthraquinone solutions portrayed the greatest effects on sulfide color reversion. The results of this research increase the overall understanding of the color reversion phenomenon, but do not solve this problem in its entirety.

ACKNOWLEDGMENTS

The author wishes to express appreciation to Weyerhaeuser, Rayonier, and Georgia Pacific Pulp and Paper Mills for providing wastewater samples for the purposes of research and analysis.

Additionally, thanks are due to my advisor, Dr. Clifford R. Lange, for his support and invaluable assistance during the course of my research. Moreover, I am much obliged to him for working under a rather tight timeline; for in doing so, he greatly enabled my expedited pursuit of completing graduate school.

Finally, I would like to express my deepest appreciation to my family and friends for their support throughout the course of completing this challenging educational endeavor.

Style manual or journal used: Guide to Preparation and Submission of Theses and Dissertations 2005___________________________

Computer software used: Microsoft Office (Word and Excel)_____________

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

The brown colored effluents discharged by the pulp and paper industry result in poor water aesthetics as well as cause harm and disturbance to the surrounding aquatic environment. These colored compounds are released into the environment from an estimated two trillion gallon wastewater discharge per year and are attributable to various pulping and bleaching operational by-products, resulting from lignin degradation. The receiving waters can potentially experience an increase in temperature and a decrease in photosynthesis as a direct result of the addition of these brown colored effluents (Kringstad and Lindstrom, 1984). Moreover, while being unaesthetic, discharged color bodies can also create considerable problems in terms of contaminant transport as they can mimic chelating agents and form bonds with metallic ions (Dilek and Bese, 2001).

Color reversion is the yellowing of pulp on exposure to air, heat, certain metallic ions, and fungi due to modification of residual lignin-forming chromophores (see Figure 1.1).

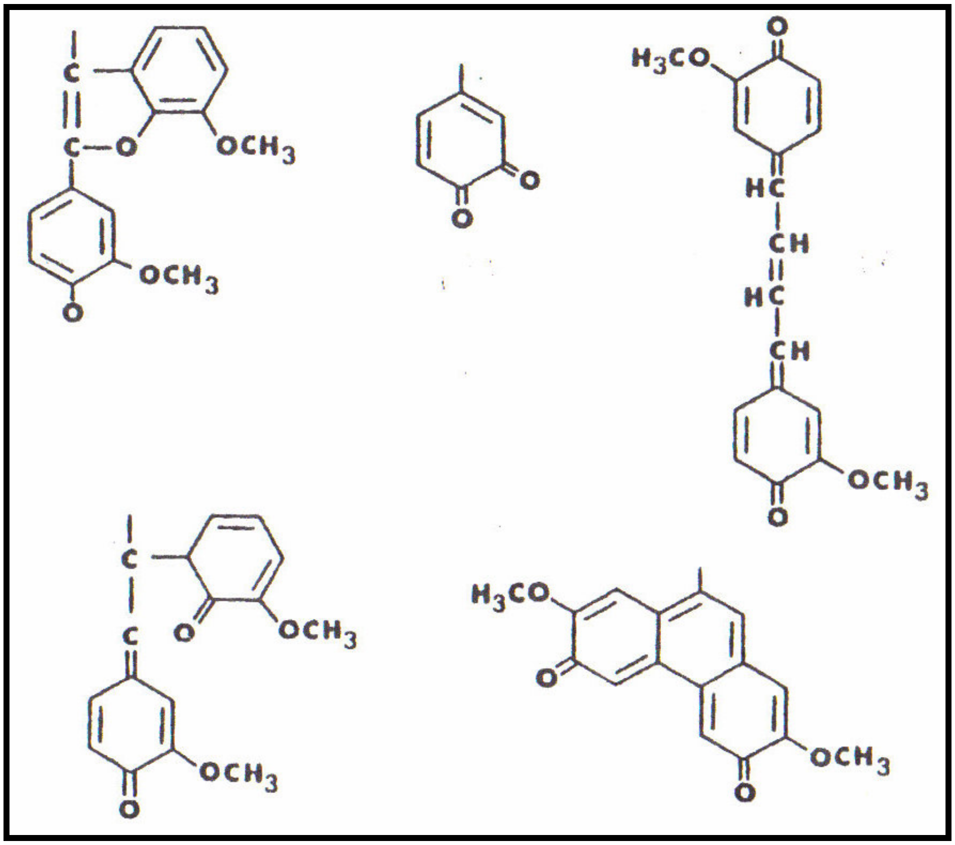

Figure 1.1: Some Proposed Chromophoric Structures (Sjöström, 1981)

As paper product quality parameters have become more stringent, specifically brightness, the unwanted color bodies have increased in wastewater loadings. Moreover, while bleaching has decolorized pulp to meet final paper product standards, associated wastewater color has become intensified. Therefore, recognizing the source of these color-forming compounds is crucial to understanding color reversion.

As pulp and paper wastewater is treated through various steps involving biological technologies which are geared towards biological oxygen demand (BOD) removal, color is at best partially reduced (Perez *et al*., 1997). High amounts of bio-resistant chlorinated lignin derivatives give kraft mill bleachery plants their highly colored effluents. But despite chlorinated organics removal, these effluents keep their characteristic color by remaining stable and unaltered (Tarlan *et al*., 2002).

Yet, while conventional wastewater contaminants such as biochemical oxygen demand (BOD) and suspended solids removal have been the main parameters targeted by environmental legislation, color has been and still is excluded because it is considered a non-conventional pollutant. However, disregarding the fact that official federal regulations have yet to be created, some countries have established permissible color limits for particular pulp mills. For instance, the Grand Prairie, Alberta kraft mill wastewater operating licenses have incorporated color standards such that mill operators are required to be proactively in search for color reduction strategies (Davies and Wilson, 1990). As color is often associated with contaminants arising during the production of paper (i.e., COD), these limits were created in order to protect fisheries and aesthetics. In addition, several Eastern European and Scandinavian countries as well as Japan have followed suit and are instituting chemical oxygen demand (COD) wastewater discharge limitations as this is tantamount to a color parameter. Additionally, a particular mill in Louisiana that discharges into a low flow stream has received much pressure from the state to reduce wastewater color loadings (Joyce and Petke, 1983). Therefore, it appears to be only a matter of time before color compliance is officially incorporated into the monitoring requirements under the U.S. National Pollutant Discharge Elimination System (NPDES).

The rate and degree of color reversion has been hypothesized to be related to four main mechanisms: 1) anaerobic color reduction, 2) anaerobic color generation via sulfide reaction, 3) aerobic color reversion, and 4) aerobic decolorization. The major objective of this thesis is to elucidate the role of sulfide generation during color reversion of treated and untreated paper mill wastewater. The results of this research increase the overall understanding of the color reversion phenomenon, but do not solve this problem in its entirety.

To accomplish the goal of this thesis, several representative pulp and paper mill wastewaters were obtained. The pulp and paper plants that served as the source of the test samples included: three Weyerhaeuser mills, one Georgia Pacific mill, and one Rayonier mill. Samples were taken at various points in the wastewater treatment process including: before primary clarification, after primary clarification, and throughout aerobic biological treatment. It was hypothesized that the addition of sulfide, from biogenic generation in anaerobic portions of a pulp mill wastewater treatment process, could increase color intensity. This hypothesis was based on anecdotal information given by various wastewater treatment plant operators. Therefore, to validate this speculation, the wastewater samples were exposed to various concentrations of sulfide through the addition of sodium sulfide crystals, simulating biogenic sulfide production. Resulting changes in color were measured using Method 701 proscribed by the National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI).

A three phase approach was utilized to determine the effects of sulfide on pulp mill color. In the first phase, sulfide was added to the samples and changes in color were measured at various time intervals. This simulated the effect of biogenic sulfide production occurring in the anoxic zones of sewers, primary clarifiers, and when high organic loadings deplete aeration basin oxygen. Biogenic sulfide production can also occur during lengthy holding periods and during shipping of samples if the temperature is above 4°C.

The second phase of studies involved aeration of the wastewater following sulfide color development. The purpose of the second phase study was to determine if aeration, occurring subsequent to sulfide generation, could lessen or reverse the impacts of sulfide on the wastewater color. This phase would simulate processes occurring in the aerobic portion of the aeration basin, when sulfide is oxidized and stripped off.

The third phase of studies involved exposing lignin, fulvic acid, and lignin monomer compounds to sulfide and measuring the resulting color changes. The goal of this study was to determine which compounds contributed to changes in color due to sulfide. Organic compounds appear to be associated with color in relationship to double bond resonance (Joyce and Petke, 1983). Therefore, several aromatic compounds were used in this experimentation in order to determine the sulfide influence associated with color reversion on various functional groups (see the molecular structures illustrated in Figures 1.2-1.6). The concentrations and amounts of organic matter (OM), specifically the residual carbon of lignin, appear to have a direct correlation to resulting wastewater color. The dark color that is characteristic of lignin is directly linked to the intricacy of its molecular structure which permits extensive double bond resonance.

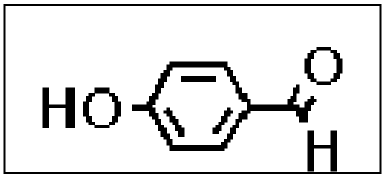

Figure 1.2: 4-Hydroxybenzaldehyde

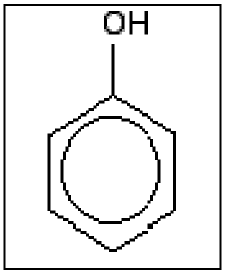

Figure 1.3: Phenol

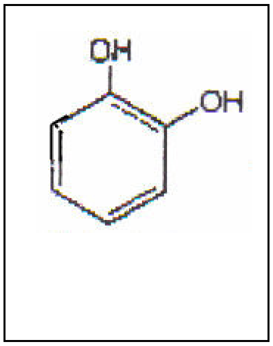

Figure 1.4: Catechol

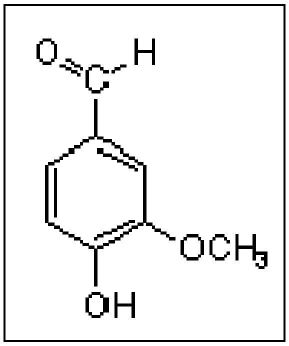

Figure 1.5: Vanillin

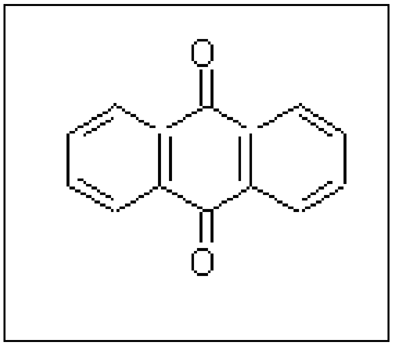

Figure 1.6: Anthraquinone

Understanding the diversity of the papermaking process will provide much insight into the immense variability in the resulting wastewater composition. As all of the samples were collected from alkaline pulping and kraft processing mills, it is important to discuss these background technologies so as to provide a clear understanding of the wastewater composition and nature. Alkaline pulping is the pulping of wood using sodium hydroxide. A solution of sodium sulfide is utilized in the papermaking process along with sodium hydroxide in order to dissolve non-fibrous materials. This sulfide component is believed to be a major contributor to the effluent wastewater color. The kraft or sulfate process is labeled as such given that sodium sulfate is the original compound form involved in the process. Sodium sulfate is then converted to sodium sulfide, which becomes the active ingredient involved in the wood chip cooking process.

Wood is comprised of three main substances: lignin, carbohydrates, and extractives. The intercellular material functioning as fibrous glue called the lamella is highly comprised of lignin. Lignin is an amorphous, highly polymerized substance containing several linked phenyl propane units arranged into a three-dimensional structure (see Figure 1.7).

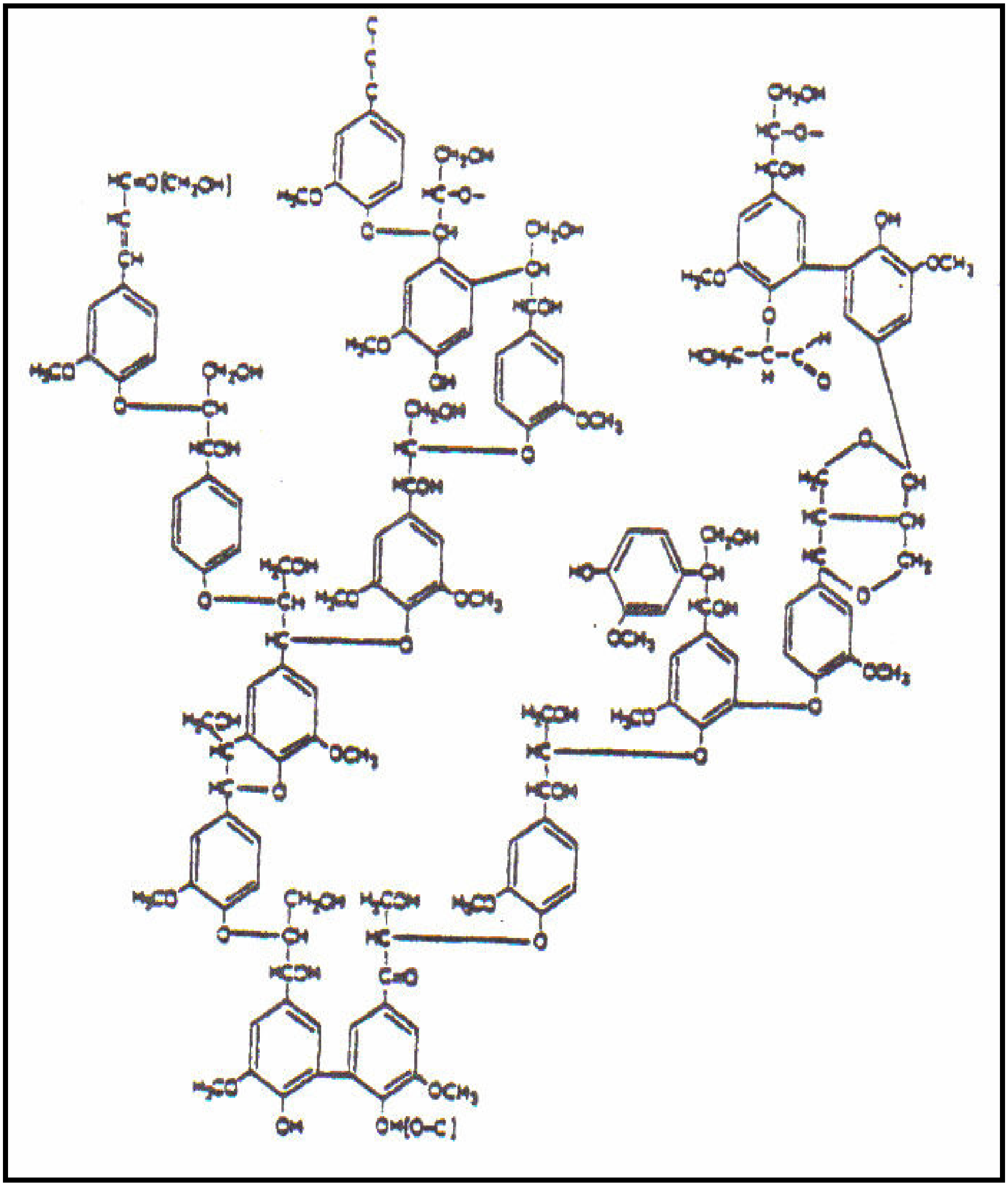

Figure 1.7: Lignin Polymer Segment (Sjöström, 1981)

The amount of color associated with certain wastewaters can actually be traced back to the quantity of lignin discharged into the wastewater. Yet, pulp mill sewers do not produce the most color as would be expected considering the largest amount of lignin is released from this operation. This counterintuitive occurrence is due to the fact that the majority of this colored waste is actually recovered (Joyce and Petke, 1983).

Yet, in examining the next largest lignin distributor, the bleach plant becomes identified as the major source of effluent color. In fact, more than two-thirds of the total color mass contained within the effluent can be attributable to the bleaching process. Moreover, it becomes even more remarkable when considering how concentrated this outlet is since it usually only makes up under half of the total wastewater volume.

Nevertheless, while the amounts and concentrations may vary, the types of lignin derivatives are generally the same. Both humic and fulvic acids are found in wood pulp fibers and derivative components due to its organic composition. Humic acids are dark brown in color, whereas fulvic acids are light yellow to yellow-brown in color (see Figures 1.8 & 1.9).

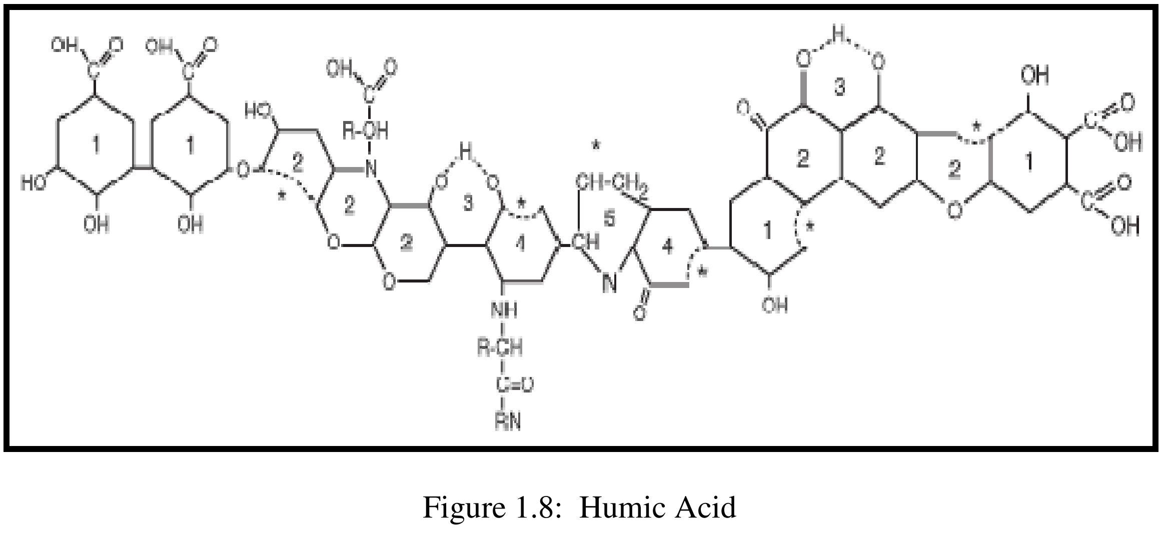

Figure 1.8: Humic Acid

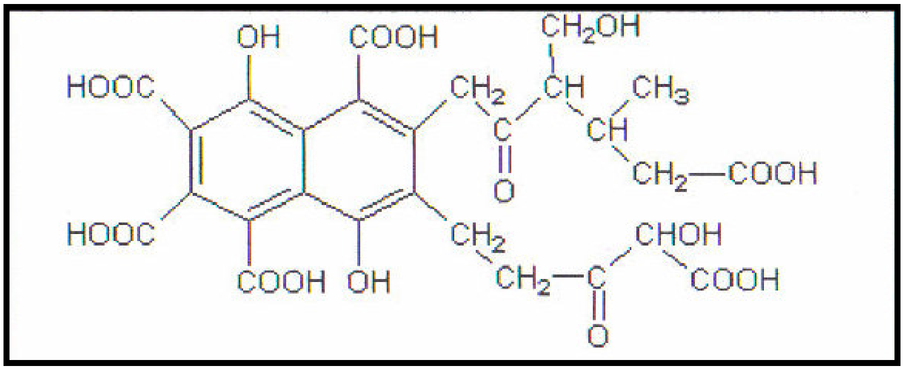

Figure 1.9: Fulvic Acid

Therefore, the hue of wastewater can be dominated by varying combinations of humic substances. The products of lignin transformation, primarily lignin peroxidase (LiP), are the main contributors of effluent color in paper mill wastewaters (Perez *et al*., 1997). Just as ligninase enzymatic competition between 'noncolored lignin' and 'colored lignin' affects decolorization (Yin *et al.* 1989), it would appear that the same should hold for color reversion. This competition affects the rate of color change in wastewater regardless of whether color generation or reduction occurs. The process of lignin transformation and related mechanisms serve as the reasoning behind including the third experimental phase in this thesis, which is discussed later in Chapters 3 & 4.

The results of this research increase the overall understanding of the color reversion phenomenon as affected by sulfide. Various sulfide concentrations, combined aeration effects, and relationships between isolated lignin compounds were explored throughout this investigation and the results are presented herein. Solving the color reversion problem in its entirety and understanding all of the mechanisms and kinetics involved in color generation has only begun. Therefore, by uniting the knowledge obtained from past research, summarized in the following chapter (Chapter 2), and that acquired by conducting this thesis, perceptive familiarity with sulfide color reversion should ensue, and hopefully will spark interest in connected research topics yet to be explored.

CHAPTER 2

LITERATURE REVIEW

Color reversion is the technical term for increases in color that occur during the papermaking process, in wastewater treatment, and/or after release into the environment. While most accounts of color reversion are anecdotal, Lange *et al.* (2005) reported over 30% increase in color across an aerated lagoon system in Grand Prairie, Alberta (Canada), with similar increases replicated in the laboratory. Lange (2005) showed that aerobic color reversion, while occurring under abiotic conditions, appeared to be kinetically controlled by the treatment process microbiology.

While few published accounts are available on the subject of this thesis—color reversion—much research has been conducted on the removal of color (decolorization) in wastewater treatment systems. The ultimate goal for resolving problematic wastewater color is by first understanding the mechanisms involved in color reversion, which is attempted in this thesis, and then by selecting the appropriate means for decolorization, which is discussed thoroughly in this chapter. The following paragraphs seek to provide insight into the available methods and tools that have been identified as successful means for color removal.

General Information

The color problems associated with pulp and paper mill wastewater have become a subject of great importance and research in the last few decades (Dilek and Bese, 2001). High amounts of bio-resistant chlorinated lignin derivatives give kraft mill bleachery plants their highly colored effluents (Tarlan *et al.*, 2002). These brown colored effluents discharged by the pulp and paper industry result in poor water aesthetics as well as cause harm and disturbance to the surrounding environment. For instance, the discharge of colored effluents can result in temperature increases and decrease photosynthesis activity in receiving waters (Kringstad and Lindström, 1984). Therefore, several ecological problems can consequently develop, such as eutrophication.

Yet, despite improved wastewater technology and efficiency over the years, the presence of color bodies has continued to occur in the final effluent of wastewater treatment. As pulp and paper wastewater is treated through various steps involving biological technologies which are geared towards removing biological oxygen demand (BOD), color is at best partially reduced (Pérez *et al.*, 1997). Moreover, the lignin derivative color remains stable and unaltered despite chlorinated organics removal (Tarlan *et al.*, 2002). A study conducted on bleached kraft pulp mills concluded that color originates from residual carbon left in solution after treatment (Kemeny and Banerjee, 1997). Additionally, major contributions to effluent color were determined to ensue from lignin transformation products (Pérez *et al.*, 1997).

Lignin derivatives comprise several aromatic compounds, specifically humic substances. Organic compounds appear to be associated with color in relationship to double bond resonance (Joyce and Petke, 1983). Additionally, along with posing several drinking water problems in terms of taste, another integral part of many colored bodies are phenolic groups.

As a result, several research projects involving the optimization of biological, chemical, and physical treatment techniques have been undertaken in an attempt to solve this persistent color problem. Some of the wastewater compositions explored include wastewaters from the olive oil, the textile, and the pulp & paper (including the following wastewaters: untreated and treated; bleached kraft and bleach plant effluent; chlorine bleaching treatment; sulfide-rich; wood-based; and bio-depurated) industries. In addition, a collaborative research effort summarizing various color removal technologies that were created and researched over a 15-year span prior to 1983 is included in the following paragraphs.

Parameter Optimization

The measurement of color, along with other parameters including trace pollutants, oxygen demand, and particulates, are conservative methods utilized in wastewater treatment systems to characterize OM content (Sonnenberg and Holmes, 1998). Non-mineralized OM was found to be the resulting cause for an increase in color across the lagoon pond (Kemeny and Banerjee, 1997). This phenomenon has been commonly seen across lagoons where a color increase occurs from influent to effluent. The effluent color and COD values provide a consistent correlation: residual carbon remaining in the wastewater that was not removed during treatment can offer conditions sufficient for color generation. Non-mineralized OM becomes converted into smaller, more chromophoric units (Kemeny and Banerjee, 1997), which adds to the color of the wastewater. Therefore, just as occurs with chlorolignin degradation, which can be observed during quinone eradication due to hydrogen peroxide treatment, decolorization can result from the destruction of these chromophores (Chang *et al.*, 1986).

Pulp and paper mill wastewater lagoons and the surrounding forested hardwood wetland areas provide a suitable habitat for woody organic carbon decomposition by bacteria, algae, fungi, and other microbes. Hence, the process characteristics of dissolved organic carbon (DOC) were compared between that found in the lagoon ecosystem and that present in natural aquatic ecosystems (Sonnenberg and Holmes, 1998). It was found that untreated pulp and paper wastewater had similar DOC compounds to naturally occurring DOC; whereas, the treated wastewater consisted of hydrophilic and non-acidic material.

Some relationships have been calculated for the media composition of bench scale analyses. While the results are associated with the related effects of decolorization percentages, these parameters could be considered in analyzing color reversion effects as well. With a glycerol carbon source and low nitrogen and manganese (Mn(II)) levels, decolorization is effectively increased (Pérez *et al.*, 1997). The focus of the subject research of this thesis was not concerned with media nutrient optimization, etc., but these parameters could be considered and analyzed in solving color wastewater problems.

A specific study on eucalyptus pulp explored the pollutants in kraft bleachery effluent using gas chromatographic determination. Phenol and catechol chlorinated derivatives were a few of the compounds detected during analysis of different wastewater treatment sampling points (primarily the chlorination and extraction stage effluents) (Sharma *et al.*, 1999). These compounds have been known to contribute appreciably to color problems as well. The significance of this study was that the concentrations detected were very close to their respective toxicity levels ($^{96}LC_{50}$), and therefore raises the potential concern for environmental effluent noncompliance in the situation of an untreated eucalyptus bleach liquor spill or release.

Other parameters associated with color include the properties of macromolecular organic compounds known as humic substances. The fraction of humic acid in aquatic OM was studied for its relationship to pulp and paper mill effluents. The majority of DOC from stream waters is comprised of humic substances and plays an important role in terms of ionic metal and organic pollutant interactions (Santos and Duarte, 1998). Very little knowledge is known about humic substance composition and influence from pulp and paper wastewater interactions, therefore this investigation sought to provide more information on the subject. The study focused on the difference between two sampling sites—one upstream of a pulp mill effluent discharge outfall and one downstream. As the mill employs the sulfite pulping process, the DOC humic acid portion was characterized by lignosulfonic acid structures, as would be expected, being key sulfite process waste products (Santos and Duarte, 1997). Similarly, the fulvic acids from the samples contained high sulfur contents, suggesting the presence of sulfonic functional groups. The results from this work include the importance of anthropogenic sources of OM, the papermaking process being one of the most significant contributors.

Biological Treatment Techniques

Several biological solutions have been sought and tested related to decolorization, primarily using white-rot fungus (including the strains of *Thiobacillus denitrificans*, *Phanerochaete flavido-alba, Trametes versicolor, Coriolus versicolor, Phanerochaete chrysosporium, Funalia trogii),* although some more recent work using *Trichoderma sp.*, algae, and *Rhizopus oryzae* have been conducted as well. Each of these studies is discussed in detail in the following paragraphs.

One case study delved into the technological aspects of sulfide-rich waters and its effect on microbial treatment (using *Thiobacillus denitrificans*). Substrate inhibition was found to have occurred with the sulfide, but the overall results indicated successful bio-treatment, effective deodorization and detoxification (Sublette *et al.*, 1998).

The white-rot fungus study involving the *Phanerochaete flavido-alba* (*P. flavido-alba*) organism was determined to be very successful as it ultimately reduced olive oil mill wastewater (OMW) color by 70%. As opposed to pulp mill wastewater color growth resulting from lignin and related derivatives, the presence of a polymerized pigment contributes to the dark color associated with OMW (Blánquez *et al.*, 2002). The experiment was conducted using a laboratory-scale bioreactor, but the possibilities for large scale wastewater treatment application using *P. flavido-alba* seem very promising since mill environmental conditions are suitable circumstances for this organism to flourish and carry out its decolorizing activities.

A study on kraft bleach effluents focused on treatment with a urethane prepolymer fluidized bed bioreactor for decolorization and dechlorination evaluation. The white-rot fungi, *Trametes versicolor* (*T. versicolor*), was found to successfully reduce color by 72-80% and adsorbable organic halides (AOX) by 52-59% (Pallerla and Chambers, 1995). Additionally, this study found that decolorization followed first order kinetics and was linearly dependent on glucose co-substrate concentration. Similar ranges of decolorization (70-80%) resulted from straw soda-pulping effluent treatment by *T. versicolor* as well (Martín and Manzanares, 1994).

Another *T. versicolor* study determined that adsorbable organic halogen and color were reduced in conjunction with fungal and ozone combination treatment (Roy-Arcand *et al.*, 1991). Ozone has been found to oxidize pulp and paper mill effluent color. This analysis was performed using samples from the alkaline extraction stage, the most colored and toxic portion of the entire kraft bleaching process. The concentration of ozone was tested in a later study and the results ranged from 90%+ of color destruction at very high doses to 79% at a lower level (210 ppm ozone per 2000 selector control units (scu)), and then to 71% decolorization at an even lower amount (180 ppm ozone per 2000 scu)—a substantial percentage of decolorization, even at the lowest reported level (Amero and Hilleke, 1993). Additionally, another ozone experiment indicated a strong correlation of decolorization to chromophoric lignin concentration (Joyce and Petke, 1983).

One of the Fungi imperfecti, *Trichoderma sp*., was determined to be successful in lignin degradation and decolorization of hardwood extraction-stage bleach plant effluent (Prasad and Joyce, 1991). An 85% reduction in color and a 25% decrease in COD resulted from parameter optimization and a three-day cultivation duration. Additionally, decolorization was found to have been greatly stimulated with glucose as the fungal carbohydrate.

Phanerochaete chrysosporium (P. chrysosporium) was found to effectively remove color from bleach plant effluent when treated in a rotating biological contractor (RBC), typically from 50-60% within one day (averaging 10,000-20,000 PCU removed / day) (Yin *et al.*, 1989). Another study involving *P. chrysosporium* calculated that under optimal conditions, up to 2,000 PCU / L / day of color removal from waste streams could be achievable (Joyce *et al*., 2002).

Another white-rot fungal strain, *Funalia trogii* (from Malatya) showed 31% and 38% decolorization in OMW in static and agitated cultures, respectively (Yesilada *et al*., 1995). Phenol concentrations, a large contributor to wastewater color, were also reduced in this experiment, by 77% in the static culture and by 72% in the agitated culture. However, the major drawback in conducting white-rot fungal research is in the high glucose requirement and need for supplemental trace nutrients (i.e., yeast extract). Therefore, most of the organisms available for use in decolorization tactics do not appear to be economical for plant-scale size operation (Joyce *et al*., 2002).

A zygomycete, *Rhizopus oryzae*, was observed to be more effective than basidiomycetes for bleach plant effluent decolorization, dechlorination, and detoxification as fewer nutrients were required. With one g/L of glucose as the co-substrate, a 92-95% color reduction was reported. Moreover, even without glucose, a 78% reduction in color was calculated (Nagarathnamma and Bajpai, 1998).

When catalyzed by horseradish peroxidase, hydrogen peroxide treatment at a neutral pH was effective in color removal (Paice and Jurasek, 1983). Yet, compared with *Coriolus versicolor* (*C. versicolor*) mycelial color removal (MyCoR), the peroxide/peroxidase system was initially faster, but after two days, the fungal treatment surpassed this rate (suggesting that the fungus used another metabolic route in concurrence with the peroxidase pathway).

A combined culture of white-rot fungi and *C. versicolor* was used in another study for kraft mill wastewater decolorization. In the presence of sucrose, a 60%

reduction in color was observed. Yet, 80% decolorization occurred when immobilizing this same sample in beads of calcium alginate gel (Livernoche *et al.*, 1983). A unique opportunity with this method is that by recycling the beads, an efficient color removal system can be created.

The decolorization potential of algae is being investigated more and more. A 70% reduction in AOX and 80% for color was seen in a wastewater treatment experiment using a mixed algal culture (Dilek *et al.*, 1999). Furthermore, the algae was found to have reduced the color more efficiently when the sample was low in color initially (below 500 PCU) than for samples of a higher initial color (above 500 PCU). Other levels of wastewater constituents, TOC and lignin, were found to have been reduced considerably, indicating the possibility that the color removal mechanism might not be based on the colored-to-non-colored lignin molecular transformation (Dilek *et al.*, 1999).

For a wood-based pulp and paper industrial wastewater study, the treatment was determined to be dominated by some green algae (*Chlorella*) along with some diatom species. The main mechanism of color and organic removal was found to be a combination of basic metabolism processes and metabolic conversion of the colored and chlorinated molecules to non-colored and non-chlorinated products, respectively (Tarlan *et al.*, 2002). Upon parameter optimization of light intensity and wastewater concentration strength, COD and color removal remained stable, but AOX removal rates were significantly affected.

An anaerobic process is currently being developed by Lange *et al.* (2005b), which employs an anaerobic bacterial consortium on fibrous support material to reduce color. The process has been demonstrated to achieve over 85% reductions in highly colored waste streams after 48 hours of treatment. Negligible reversion of color occurred upon reaeration of the anaerobic process effluent. The exact bacterial populations involved in the destruction of color bodies are unknown, but is the subject of ongoing studies.

All of the biological species discussed above resulted in decolorization, though in varying degrees of success. Several factors, such as parameters tested, wastewater compositions, etc., can cause dissimilar results. Additionally, color rates can be affected by ligninase enzymes competition that exists between ‘non-colored lignin’ and ‘colored lignin’ (Yin *et al.,* 1989). Ligninolytic activity of both lignin peroxidase (LiP) and manganese peroxidase (MnP) enzymes were analyzed using *P. flavido-alba* (Pérez *et al.*, 1997). The activity of LiP was determined to play a principal role in paper mill wastewaters, more so than MnP activity. Correspondingly, similar tests were performed on OMW biodegradation by using white-rot fungi. While LiP appears to be the governing mechanism controlling decolorization rates in pulp and paper wastewater, laccase and MnP dominate this aspect in OMW (Pérez *et al.*, 1998).

A comparable study on OMW displayed that by using only concentrated extracellular fluids (MnP) results in unsuccessful removal of OMW pigment (Hamman *et al.*, 1999). This signifies the crucial role mycelium binding plays in the decolorization process. The most efficient OMW decolorization occurred for the *P. flavido-alba* cultures prepared with 40 μg/L Mn(II). Additionally, these results were accompanied by a 90% phenolic content reduction.

Nevertheless, another study explored MnP relationships on pulp mill effluents by using MnP extracted from *P. chrysosporium*. Immobilized lignin and MnP were studied for decolorization effects on Amberlite IRA-400 resin. A 50% color reduction was determined after the completion of a three-hour enzymatic treatment, but it was realized that a considerable fraction of the observed decolorization resulted from resin adsorption (Peralta-Zamora *et al*., 1998).

Physicochemical Treatment Techniques

The chemical methods highlighted during wastewater treatment decolorization research include such chemicals as activated petroleum coke, persulfates, lime and ferrous sulfate, alum and clay combinations, and iron/aluminum chloride/sulfate salts. Turbidity removal techniques, e.g. coagulation and flocculation, were analyzed for modification and improvement possibilities concerning the removal of color along with the main objective of removing colloidal particulates. Additionally, other work related to physical and photolytic techniques were explored as well. The remainder of this section elucidates the details of each of these topics.

The main result of the petroleum coke work comprises the creation of isotherms for more accurate prediction of color removal and AOX (Shawwa *et al.*, 2001). Since biological treatment proved to be ineffective for decolorization in pulp mill wastewater along with the fact that activated carbon is very expensive, a raw carbonaceous material abundant in much of Canada known as petroleum coke is utilized (Çeçen *et al.*, 1992). The experimental results indicated that using petroleum coke is very successful as greater than 90% color and AOX removal was achieved. Additionally, since the petroleum coke treatment oxidized the wastewater, this chemical treatment could serve as a pretreatment step prior to biological wastewater management (Shawwa *et al.*, 2001).

Certain dye decolorization was successful for chlorine-free wet strength paper repulping upon effective treatment with activated alkali metal persulfates. In addition, this analysis was performed under optimal concentration, temperature, and pH conditions (Thorp *et al*., 1995).

Lime and ferrous sulfate comprise another physicochemical treatment technique of color reduction that was researched and documented. This effort incorporated the mechanisms behind some of the color problems associated with cotton textile mill wastewater (Georgiou *et al.*, 2003). The ferrous sulfate was used to stabilize pH for this treatment, which was regulated in the range of 9.0±0.5 (Georgiou *et al.*, 2003). The lime coagulation/flocculation treatment resulted in 70-90% decolorization along with a 50% reduction in COD from the textile wastewater. Specifically for chlorination and extraction pulp and paper wastewaters, the significant groups associated with lime precipitation appeared to be enolic hydroxyl groups (Joyce and Petke, 1983). This conclusion supports the double bond relationship to color: as double bonds were broken through a series of reactions, color was effectively reduced (Figure 2.1).

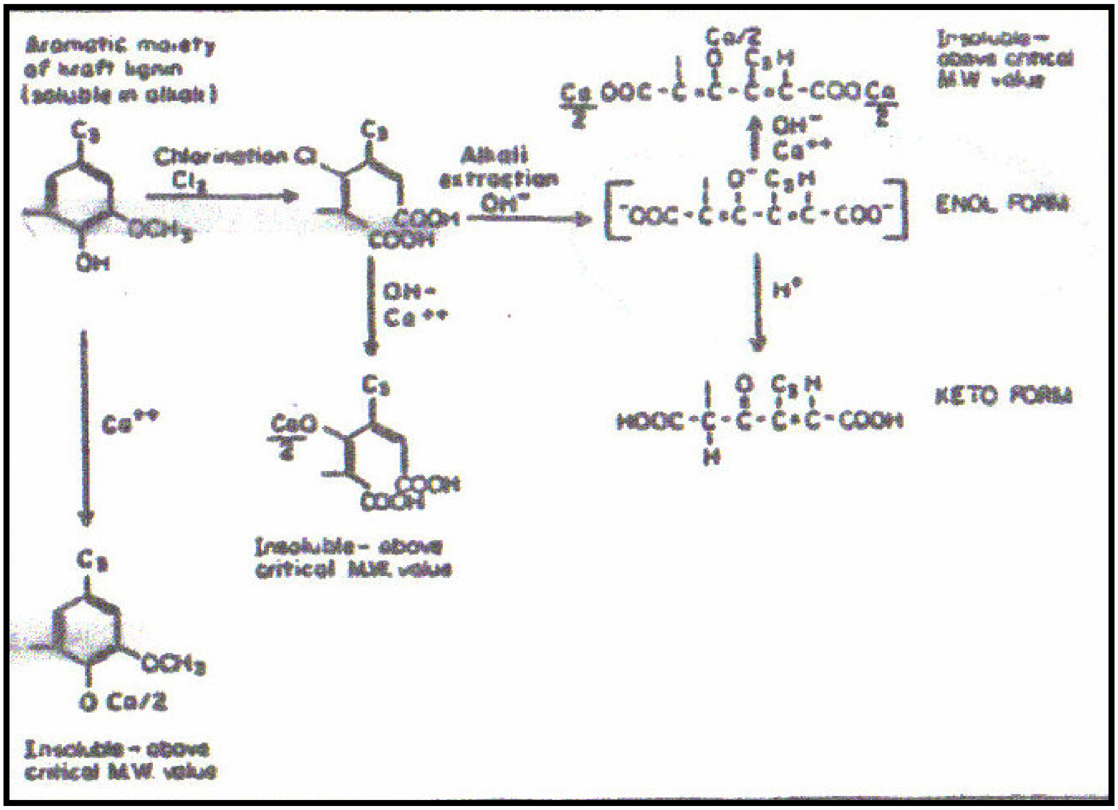

Figure 2.1: Chemical Reactions in the Lime Precipitation Process (Bennett *et al.*, 1971)

Another coagulation/flocculation treatment technique was performed using various alum and clay combinations. While a 88% reduction in color resulted from the most effective coagulation treatment, it yielded poor settling characteristics (Dilek and Bese, 2001). Yet another coagulation and precipitation method was used for analysis on mechanical pulping effluent. This study focused on utilizing both chloride and sulfate salts of iron and aluminum. Decolorization was achieved at 90% while still effectively combating total carbon (TC) and turbidity, with respective reductions at 88% and 98% (Stephenson and Duff, 1996).

During the mid 1970s, decolorization was evaluated for a sulfite, kraft, and thermo-mechanical pulping plant effluent by using ion exchange technology (Fitch, 1982). Yet, up until the turn of the century, no reported ion-exchange study had been performed on elementary chloride free (ECF) bleaching process effluents, commonly used in several mills. Thus, a Sustainable Forest Management Network Project was conducted which integrated ion-exchange resins and reactor design for the effective removal of color and chloride (Ikehata and Buchanan, 2000). This study resulted in effective color removal in all six of the Amberlite® strong base anion exchangers evaluated—each possessing a resin matrix in the hydroxide form, except for one which was in chloride-form. The five hydroxide-form resin exchangers were efficient in chloride removal as well, but the exchanger encompassing the chloride resin form was not successful in this venture. Therefore, in order for this latter resin to be effective in chloride removal, an additional treatment step would be necessary to achieve dechlorination.

Photodegradation of organochlorine and color was investigated specifically for high molecular weight (HWM) bleachery effluent. These HMW fractions are very resistant to microbial degradation, but when subjected to artificial and natural sunlight, the wastewater can be effectively decolorized and dechlorinated (Archibald and Roy-Arcand, 1994). The results of this study indicated that a strong oxygen dependency was present with effective photo-decolorization, while this was not the case for AOX mineralization. In another study, ultraviolet (UV) light, derived from sunlight, catalyzed with oxygen and titanium oxide was tested for decolorization potential; but the results were discouraging as sunlight UV-dependency produced low decolorization rates. Yet, as this photocatalytic approach may not be promising, an electrochemical precipitation process was trialed and consequently provided better results for color removal (Springer and Hand, 1992).

Summary

These decolorization studies aim at creating an understanding of the optimum parameters necessary for selection of the best color removal treatment method. Additionally, the different industrial wastewaters (OMW, textile, and pulp and paper) that were analyzed provide a good foundation for comparison, in terms of varying composition and suitable treatment. Furthermore, whether the appropriate treatment is chemical, physical, or something entirely different, the most important factors to incorporate into the selection process include the projected environmental impact and the financial and practical feasibility. Depending on the decolorization technique chosen, an additional papermaking cost of as much as $20/ton of pulp produced could result (Joyce and Petke, 1983). Nevertheless, before any of these can be implemented with success, the groundwork needs to be laid for appropriate identification and understanding of the underlying mechanisms involved in color generation and growth.

CHAPTER 3

MATERIALS AND METHODS

The rate and degree of color reversion has been hypothesized to be related to four main mechanisms: 1) anaerobic color reduction, 2) anaerobic color generation via sulfide reaction, 3) aerobic color reversion, and 4) aerobic decolorization. The major goal of this thesis is to elucidate the role of sulfide generation during color reversion of treated and untreated paper mill wastewater. The results of this research increase the overall understanding of the color reversion phenomenon, but do not solve the problem of color reversion in its entirety.

To accomplish the goal of this thesis, several representative pulp and paper mill wastewaters were obtained. The pulp and paper plants that served as the source of the test samples included: three Weyerhaeuser mills, one Georgia Pacific mill, and one Rayonier mill. Samples were taken at various points throughout wastewater treatment including: before primary clarification, after primary clarification, and throughout aerobic biological treatment. It was hypothesized that the addition of sulfide, from biogenic generation in anaerobic portions of a pulp mill wastewater treatment process, could increase color intensity. This hypothesis was based on anecdotal information given by various wastewater treatment plant operators. Therefore, to validate this speculation, the wastewater samples were exposed to various concentrations of sulfide through the addition of sodium sulfide crystals, simulating biogenic sulfide production. Resulting changes in color were measured using NCASI method 701. The experimental study approach is outlined in the following section.

Experimental Study Approach

Three aspects of sulfide color reversion were investigated in this research. The first aspect involved adding sulfide to the samples and then measuring changes in color at various time intervals. This simulated the effect of biogenic sulfide production occurring within anoxic regions of sewers and primary clarifiers and also when high organic loadings deplete aeration basin oxygen. Biogenic sulfide production can also occur during lengthy holding periods and during sample shipment if the temperature is above 4°C.

The second aspect of the study implicated aeration effects on the wastewater samples after sulfide color had developed. The purpose of the second phase study was to determine if aeration, occurring subsequent to sulfide generation, could lessen or reverse the impacts of sulfide on wastewater color. This phase would simulate processes occurring in the aerobic portion of the aeration basin, when sulfide is oxidized and stripped off.

During the third aspect, lignin, fulvic acid, and lignin monomer compounds were exposed to sulfide and the resulting color changes were measured. The goal of this study was to determine which compounds contributed to the change in color due to sulfide.

Sulfide Addition Testing

NCASI Method 701

For the color analysis, NCASI Method 701 was followed. Using the Fisher Scientific Platinum Cobalt Color Standard Apha No. 500 Color Standard for Water & Clear Liquids, a calibration curve was calculated (Figure 3.1).

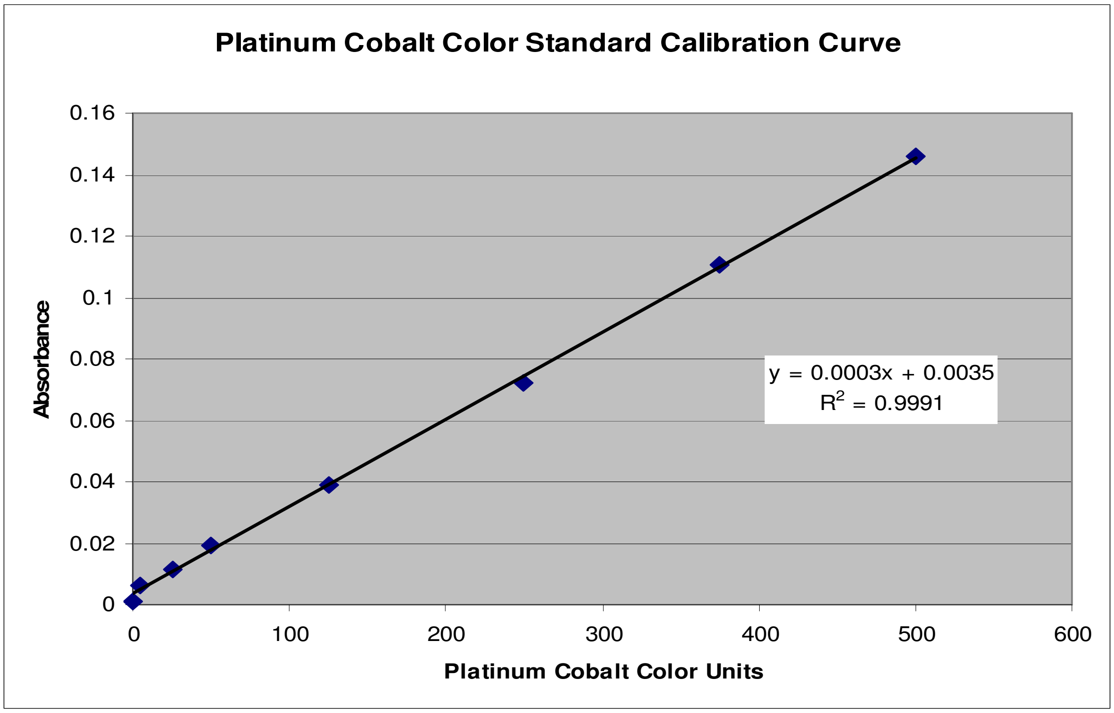

Figure 3.1: Platinum Cobalt Color Standard Calibration Curve

This calibration curve (linear equation) was then applied to the data in order to standardize the results in terms of platinum cobalt color units, PCU. Given the extreme diversity and variability of pulp mill wastewater, the individual color-causing compound concentrations are often very difficult to measure (Ikehata and Buchanan, 2000). Consequently, even though it is not an exact measurement, a color unit of the samples, PCU, is used for conversion so as to represent all of the data on a universal scale for color comparison.

Thirty-milliliter batch solutions were made up by adding increasing amounts of Fisher Scientific sodium sulfide reagent grade crystals. These solutions were made up in 40-mL glass vials with caps. A 10-ppm sodium sulfide solution was created in order to observe the effect of the lower sulfide range extremes. Increasing doses of this solution were administered to the first three sets of samples (which included those from the Grand Prairie, Alberta and Johnsonburg, PA Weyerhaeuser sites along with the sample set from Rayonier). Yet, no more samples were analyzed using this solution in an effort to minimize dosage dilution as well as to explore higher ranges of sulfide exposure. Hence, these samples and the rest of the entire data set were tested using pure crystal doses.

Twenty milligrams of ammonium molybdate (Fisher Scientific lab grade, crystal, tetrahydrate) per liter of sample were added to the first three samples to hinder any color growth unrelated to the sulfide generation. Yet, upon analyzing the results, this chemical treatment was determined to have dramatically inhibited any color reversion increase at all. Therefore, this chemical addition was halted.

Samples were analyzed initially at the time of make-up, but this was stopped after conducting a few experiments in order to ensure complete sodium sulfide crystal dissolution. Therefore, samples were made-up and then analyzed after one hour. Samples were tested at one-hr, four-hr, and 24-hr intervals. Some samples were only measured at the lower and higher end of the doses and/or at the one-hour and 24-hour time intervals, depending upon the volume of sample provided. Ten-milliliter aliquots were extracted at each of the time increments indicated and analyzed.

Using an ATI Orion Expandable Ion Analyzer EA 940 pH meter, the samples were adjusted to a pH value of 7.6 with phosphoric acid and/or sodium hydroxide depending upon the initial pH of the wastewater sample. A few specific instances during pH adjustment, the formation of white colloidal precipitates was observed specifically in the higher sodium sulfide dosage samples (typically in the 330, 660, and 1,650 mg/L doses). Metal hydroxide precipitation is believed to have been the cause for this phenomenon. This event was also observed during the ion-exchange experiments involving color and chloride removal (Ikehata and Buchanan 2000).

After vacuum filtration using Whatman GF/C Circles 47 Diameter Glass Microfibre filters, color determination was accomplished by analyzing sample absorbance at 465 nanometers (nm) using a Hewlett Packard HP 8453 Ultraviolet-Visible Spectrophotometer.

Color Development in Sulfide Blanks

Increasing concentrations of sulfide were added to blank samples of water in order to determine the resulting color change attributed solely from sulfide dissolution (Figure 3.2). Sodium sulfide when dissolved in solution possesses a slightly yellowish tint. Therefore, the purpose of testing blanks was to ensure that the experimental data indicated a color increase as a result of interactions between sulfide and the pulp and paper wastewater and not just the resulting color increase of the sulfide solution alone.

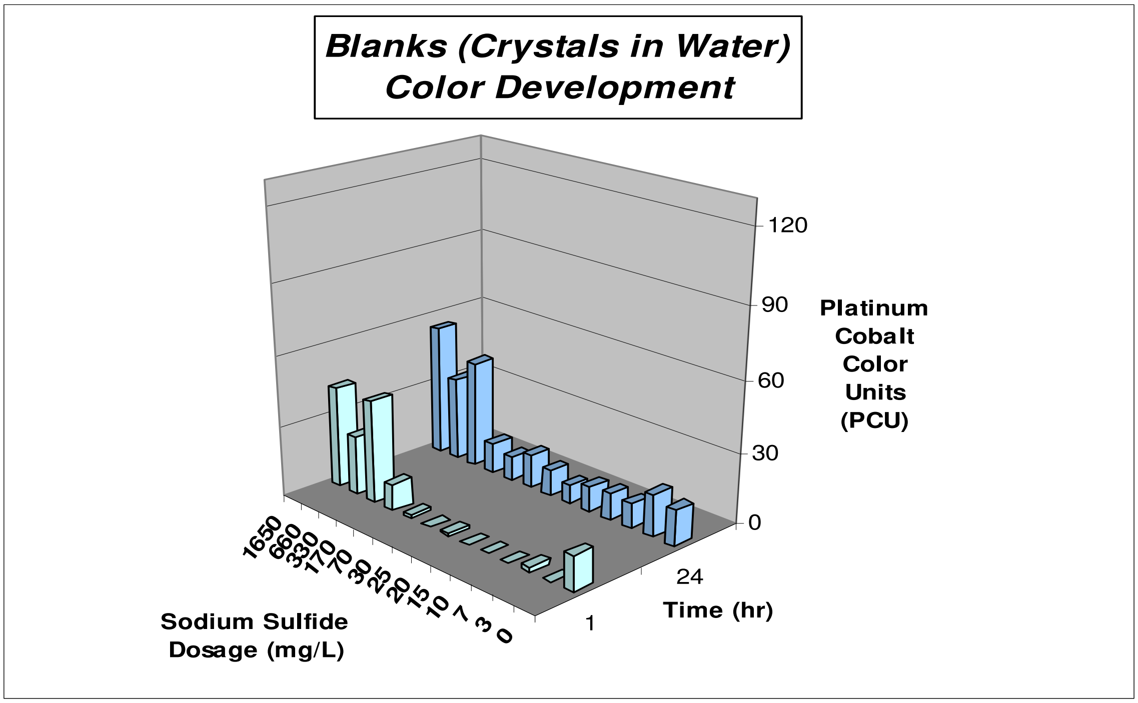

Figure 3.2: Blank Samples Color Results

It is important to note that while color development did occur in these samples, both with increasing doses and over time, the color increase (the highest value being less than 60 PCU) is significantly below the values displayed by the wastewater samples, graphically illustrated throughout Chapter 4. Therefore, the resultant color change of the blank solutions can be considered as negligible.

<u>Colored Wastewater Samples</u>

Wastewater samples were sampled and shipped to Auburn University by the Environmental Departments of Weyerhaeuser (Grand Prairie, Alberta, Canada; Prince Albert, Saskatchewan, Canada; Johnsonburg, PA; and Albany, OR), Rayonier (Jesup, Georgia), and Georgia Pacific (Palatka, Florida) Pulp and Paper Mills. Samples from Weyerhaeuser included the primary clarifier inlet and outlet and secondary effluent sample set from Grand Prairie, Alberta; the primary pond inlet, midpoint, and outlet samples from the Prince Albert, Saskatchewan location; samples collected at the pulp sewer, settling and aeration pond feeds, and final discharge from the Johnsonburg site; and several grab samples from the Albany, OR dual-celled lagoon. Rayonier samples were collected from the primary clarifier, from the “strong pond” influent and effluent, and from the associated effluents from parallel aerated stabilization basins (ASB) #1 and #2. Georgia Pacific provided samples from their lagoon of which is divided into four equivalently-sized ponds (Ponds 1, 2, 3, and 4) and additional grab samples were taken from Pond 2.

Mill Descriptions

Weyerhaeuser

Samples from Weyerhaeuser included sample sets from three separate plants: the Prince Albert mill located in Canada, the Johnsonburg, PA operation, and the Albany, OR business unit.

The Weyerhaeuser Canada Ltd., Alberta, Canada (Prince Albert, Saskatchewan, Canada) plant includes both the Grand Prairie, Alberta and Prince Albert, Saskatchewan mills. The Grand Prairie, Alberta mill is a softwood bleach kraft mill that is currently employing oxygen delignification and chlorine dioxide bleaching. A wastewater discharge of 13.1 million gallons per day is routed through a treatment process consisting of a pair of primary settling ponds, followed by two aeration cells with a total residence time of 25 days. At least half of the first aerated cell has no measurable oxygen concentration and moderate hydrogen sulfide generation (4-6 mg/L). There are two secondary settling cells, followed by discharge into the Wapiti River.

The Weyerhaeuser mill, located in Prince Albert, Saskatchewan, is a bleached kraft pulp mill with a wastewater flow of 19 million gallons per day. The wastewater treatment system consists of a primary clarifier, followed by a highly aerated-three cell aeration lagoon with a five-day residence time and two equally-sized final settling ponds. Final discharge of the effluent is into the Fraser River.

The Johnsonburg, Pennsylvania Weyerhaeuser mill produces specialty paper for book publishing using a bleach kraft process. The wastewater treatment process consists of primary clarification, followed by a 13.8 million gallon per day activated sludge process with an average cell age of 25 days. After secondary clarification, discharge of the treated effluent is into the Clarion River.

The Weyerhaeuser mill in Albany, Oregon is a bleached kraft mill with a wastewater flow of 5.2 million gallons per day. Wastewater treatment consists of a two-cell primary settling pond with a residence time of three days, followed by a two-cell aerated lagoon having an eight-day residence time. Final discharge is into the Willamette River.

Rayonier

The Jesup, GA Rayonier plant operates as a fluff-pulp mill, using an acidic digestion process followed by chlorine bleaching. The wastewater treatment includes a primary clarifier followed by an aerated strong pond where condensate is added to the waste stream. The wastewater is then divided into two aerated lagoons, each having a residence time of eight days. The front of each lagoon is highly aerated while the final half is not aerated or mixed and serves as the settling basin. The final discharge from both lagoons is into the Altamaha River.

Georgia Pacific

Georgia Pacific located in Palatka, FL is a bleached kraft mill that produces specialty grade paper including toilet tissue and paper towels. The wastewater treatment system consists of a 360-foot diameter primary clarifier followed by a 1,000 acre - 900 million gallon aerated treatment lagoon. This lagoon is divided into four equally-sized basins (ponds), each with approximately 15 days of residence time. Ultimate discharge is into the Saint Johns River, which is regarded as sensitive.

Aeration Experimentation

Aeration was tested in order to observe the resulting effect on sulfide color reversion. This environment most closely represents the aerobic portion of the wastewater flow train in a treatment plant (aeration basins, lagoon, etc.); therefore, it was pertinent to incorporate this factor into the analysis.

Two samples were employed in this analysis, one representative lightly colored sample (the Weyerhaeuser Albany, OR composite sample) and one of a darker color (the Georgia Pacific Pond 2 sample). Only the extreme doses of sulfide concentration (one ppm and 500 ppm) were tested during this experimentation.

Aeration testing was conducted in 250-mL Erlenmeyer flasks using a volume of wastewater equal to 150 mL. The flasks were stoppered with foam to minimize evaporation. Aeration was accomplished with the use of aquarium aeration stones, an associated connection apparatus (holding five such stone connection ports), and the inlet and outlet plastic tubing. The manifold tube was then attached to the building air supply and adjusted to permit a slow stream of air to flow into the samples, allowing gentle aeration (approximately 25 mL/L/minute). Ten-milliliter aliquots were extracted at various time intervals and analyzed using NCASI color method 701.

Lignin Components Isolation Analysis

Due to the composition of a variety of color-causing compounds, it is difficult to quantify the individual concentration of each of these wastewater components. As such, it also becomes difficult to ascertain the influence of any one lignin component and/or derivative involved in color reversion. Therefore, several single component solutions were created and analyzed in order to compare the results to that displayed by the wastewater samples. Such common components of lignin including 4-hydroxybenzaldehyde, phenol, vanillin, humic acid, fulvic acid, catechol, and anthraquinone were dissolved in solution, exposed to extreme sulfide concentrations, and analyzed for color. Solutions were created using chemicals from Avocado Research Chemical Ltd. (vanillin, 99% and 4-hydroxybenzaldehyde, 98%), from Fisher Scientific (phenol, reagent A.C.S., loose crystals), from Acros Organics (catechol, 99+%; anthraquinone-2,6-disulfonic, disodium salt; and humic acid, sodium salt.), and from Vital-Earth Minerals, LLC (fulvic mineral complex, ionic mineral supplement, 100% fulvic acid in solution). In addition to the sulfide and time variables, the effects of varying solution strength were also tested (one ppm and 50 ppm).

CHAPTER 4

RESULTS AND DISCUSSION

Three factors affecting color reversion were investigated in this research. In this chapter, the effects of sulfide and subsequent aeration on color growth in wastewaters from various pulp and paper mills are addressed. Additionally, the effect of sulfide on color growth in solutions of humic acid, fulvic acid, and various lignin monomers was quantified.

Sulfide Color Reversion

It was hypothesized that the addition of sulfide, from biogenic generation in anaerobic portions of a pulp mill wastewater treatment process, could increase color intensity. This hypothesis was based on anecdotal information given by various wastewater treatment plant operators. To validate this hypothesis, the addition of sodium sulfide was used as a surrogate for biogenic sulfide production. The results of sulfide addition studies are presented in this section for each mill, and then summarized for all mills.

Weyerhaeuser

The first trends discussed are samples from the primary clarifier inlet/outlet and secondary effluent from the Weyerhaeuser - Grand Prairie, Alberta mill which is approaching its color discharge limits. For the primary clarifier inlet sample, an increase in color was observed immediately after sulfide was added at time zero (Figure 4.1). Higher doses of sulfide resulted in higher increases of color. At the highest dose of five mg/L, over three times as much color was measured in comparison to the zero mg/L control. Minimal increases in color were observed over time, as seen by the one-hour and four-hour time intervals. However, after 24 hours, all samples had significantly lower colors, which may be attributable to stripping of the sulfide or biological anaerobic color removal processes, such as reduction of quinone moieties.

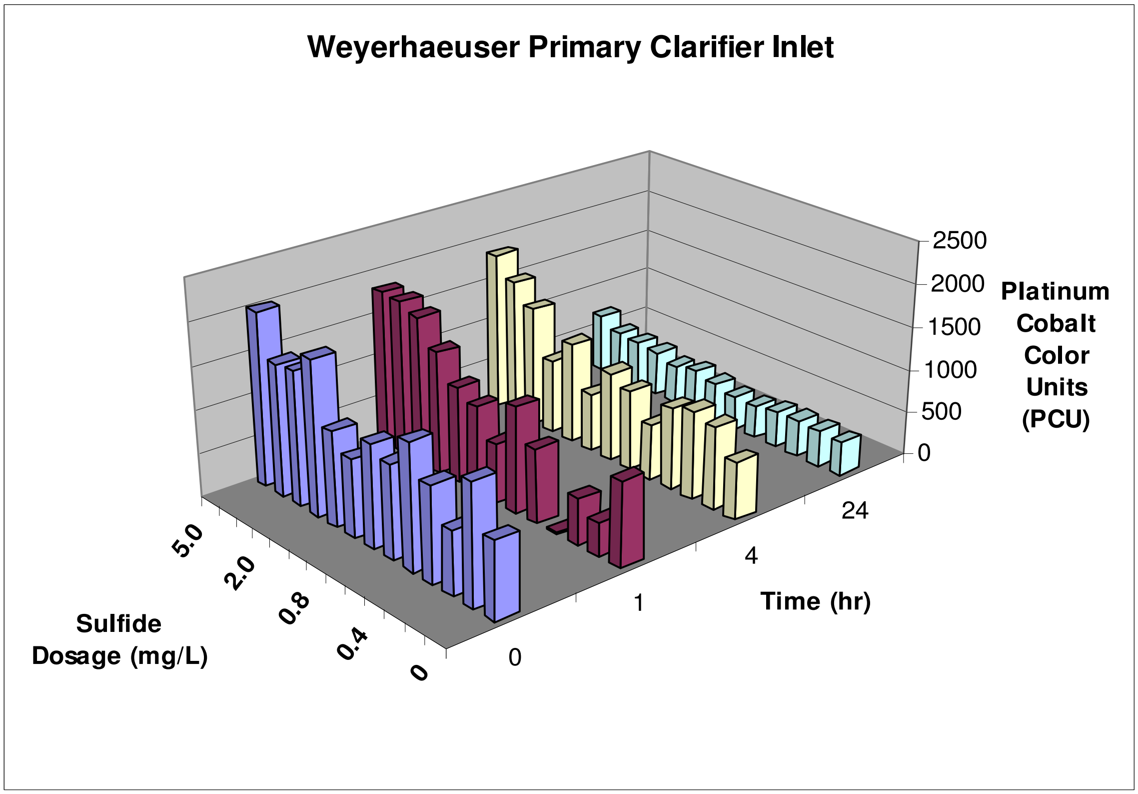

Figure 4.1: Grand Prairie, Alberta Weyerhaeuser Primary Clarifier Inlet Sample Color Results from 10-ppm Sulfide Solution Doses

The clarifier inlet sample was analyzed again, this time being exposed to higher concentrations of sulfide along with ammonium molybdate treatment (Figure 4.2). As this experimentation involved sulfide crystals, instead of the lower 10-ppm concentrations, the expected outcome was postulated to have been proportionally larger in terms of a color increase. Yet, much smaller initial increases in color reversion were observed at all concentrations. This counterintuitive result was believed to have been due to the chemical addition of ammonium molybdate. The samples containing ammonium molybdate demonstrated significantly lower colors at time zero hours and one hour (see Figure 4.2). This indicates that a portion of the rapid color change was inhibited by the presence of the molybdate. Molybdate is an inhibitor of sulfate reducing bacteria, and the reduction of color may be attributable to the decrease of microbial sulfide reduction and accompanying increases in the redox potential of the wastewater solutions. Alternatively, the molybdate could directly compete with sulfide for binding sites on the color bodies and may interfere with the rate and degree of color development. By the four-hour sampling interval, similar degrees of color reversion were observed in the lower sulfide concentration samples, but the color reversion was still much lower at the higher sulfide concentrations.

A second variable appearing to contribute to changes in color was time. Immediately after sulfide addition (at time equaling zero hours), higher colors were measured for higher sulfide doses. These increases were many times the values measured for the sulfide blanks (see Chapter 3) and are likely the result of a rapid reaction between wastewater components and sulfide. Increases in time after sulfide addition resulted in additional increases in color, apparently independent of the ammonium molybdate addition. Thus, color development (color reversion) appears to have both a rapid component and a slower component. The highest percent increase in color occurred at four hours and represented an approximate 280% increase from the original zero-mg/L, zero-hr sample (Figure 4.2).

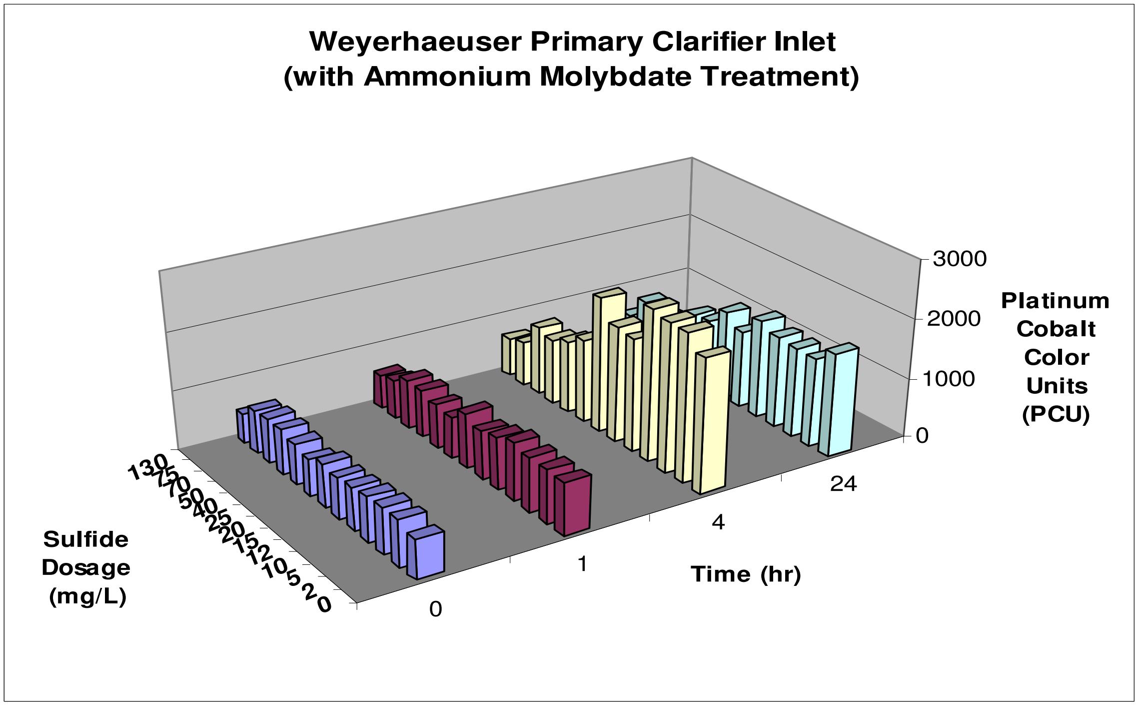

Figure 4.2: Grand Prairie, Alberta Weyerhaeuser Primary Clarifier Inlet Sample Color Results from Crystallized Sulfide and Ammonium Molybdate Treatment

Based on these preliminary results, it was apparent that sulfide had the potential to have a significant effect on color; however, the exact nature of the effect was not clear. Furthermore, the addition of molybdate altered both the rate and the degree of color reversion. Color development can be extremely rapid, with color appearing almost instantly. Additional color development occurs slowly over several hours of time. Color development does not appear to be long-lasting, with colors decreasing after 24 hours.

The outlet sample for the Grand Prairie primary clarifier sample showed similar results to the clarifier inlet samples. The initial color of the primary effluent sample was

400 PCU which was somewhat lower than that of the 500 PCU measured for the primary influent. With increasing doses, color once again became more intense immediately after sulfide addition. Increases in color by 24 hours were similar at all sulfide doses and averaged a 30-40% increase (Figure 4.3). However, the degree of this color increase was somewhat smaller than that observed for the primary influent (Figure 4.1). The color increased slightly with increasing exposure times, but never achieved the colors measured for the primary influent. Since significant biological removal of organics is achieved during the 12-hour residence time in the primary clarifier, it is possible that color precursors are removed by biodegradation and/or settling in the clarifier.

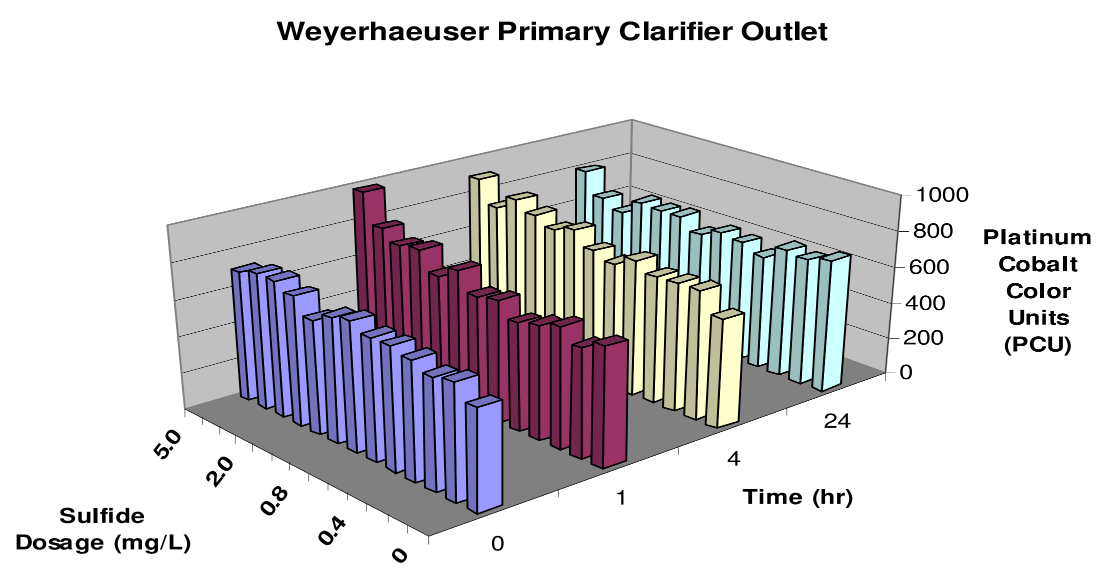

Figure 4.3: Grand Prairie, Alberta Weyerhaeuser Primary Clarifier Outlet Sample Color Results from 10-ppm Sulfide Solution Doses

In Figure 4.4, the results from the ammonium molybdate addition can be seen. This chemical inclusion appeared to cause increased color reversion at lower doses. At higher doses, the color reversion was decreased as was observed for the influent sample.

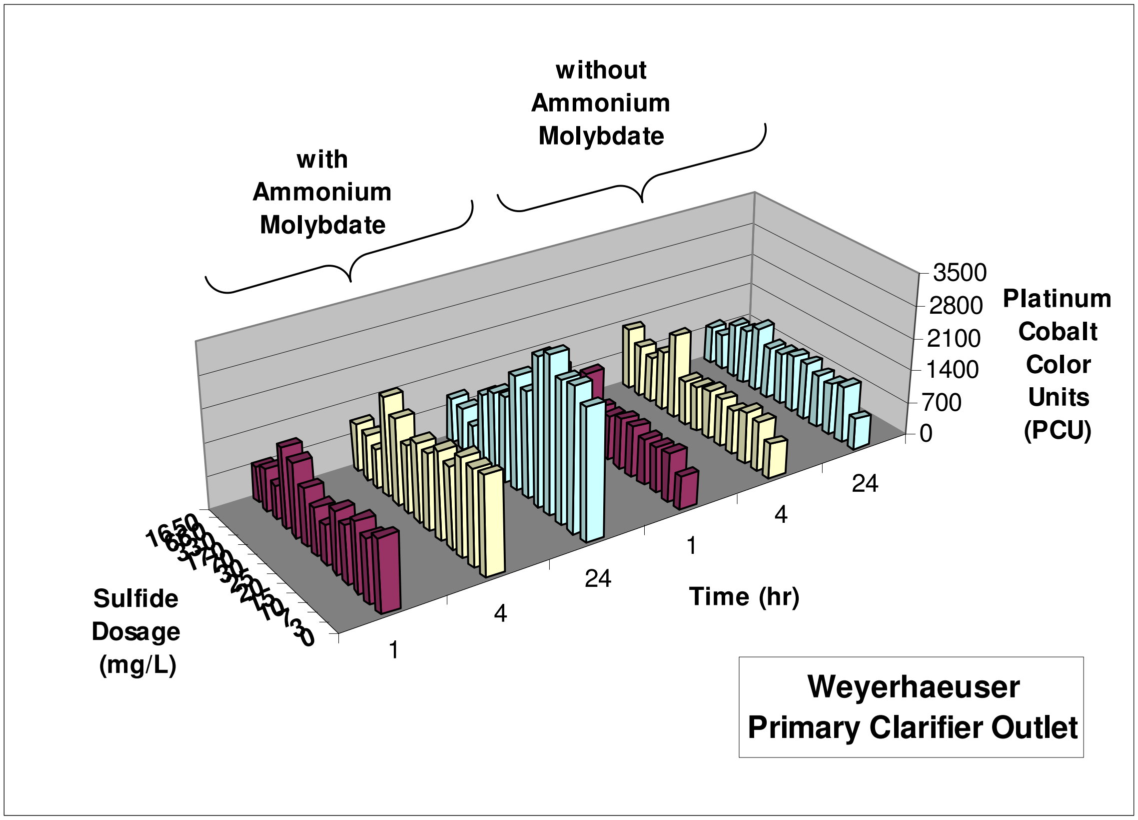

Figure 4.4: Grand Prairie, Alberta Weyerhaeuser Primary Clarifier Outlet Sample Color Results from both Crystallized Sulfide Exposure and with/without Ammonium Molybdate Treatment

The secondary effluent sample had an initial color of less than 300 PCU which is likely reduced from the 400 PCU in the primary effluent due to the 25 days of biological action in the lagoons. For the secondary effluent samples, a color increase was observed immediately after sulfide addition, but was not as prominent as those measured for the primary influent and effluent (Figure 4.5). Additional color reversion was observed as exposure time increased, achieving an approximate 10% increase ultimately after 24 hours. Since discharge permits are written in terms of pounds of color per day, which assumes one PCU is equal to one mg/L, a small increase in the color percentage may represent a significant mass of color in the effluent. In this specific case, based on a 13.1 million gallon per day (gpd) discharge, a 10% increase from 300 PCU of color equates to a color loading increase of 3,280 lbs/day!

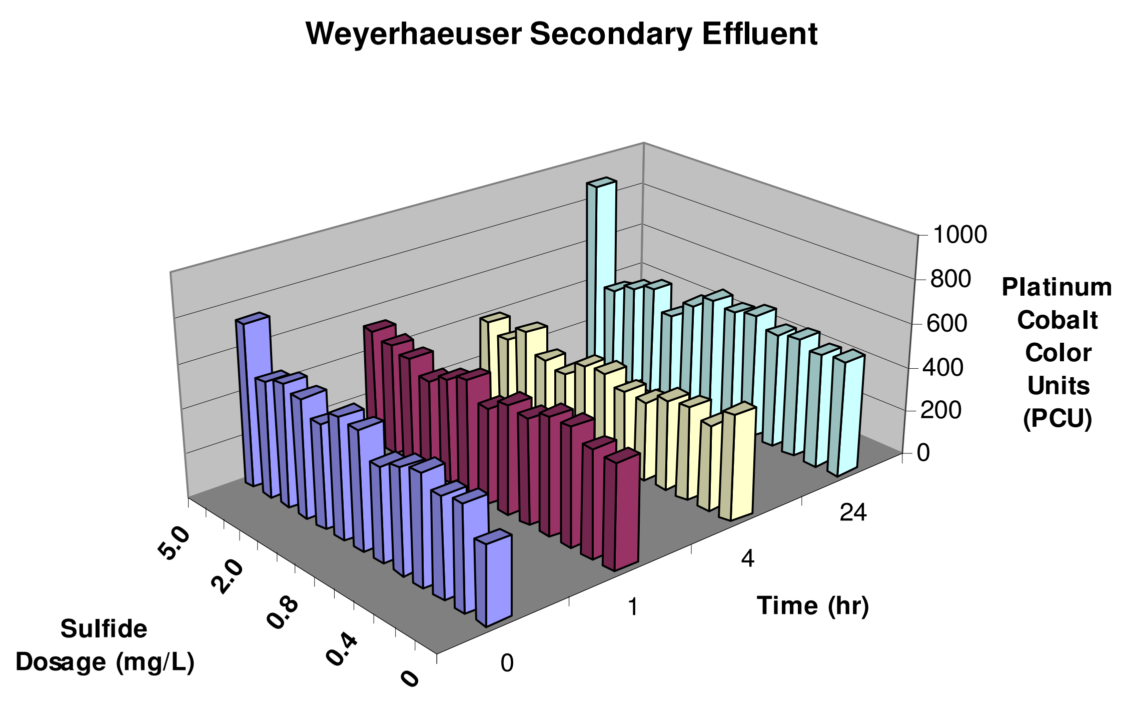

Figure 4.5: Grand Prairie, Alberta Weyerhaeuser Secondary Effluent Sample Color Results from 10-ppm Sulfide Solution Doses

The addition of molybdate had similar effects as was seen for the primary clarifier samples, but color increases were somewhat more variable with increasing sulfide concentrations (Figure 4.6). This variability may be more pronounced in these samples due to the low starting color. Time did not appear to be as significant of a factor for the secondary effluent as it was for the primary clarifier samples. Most of the color increase occurred rapidly and was measured for the zero-hour samples. There was, however, some additional increase from slow development color reversion after one and four hours, though slight, measured at around 25%.

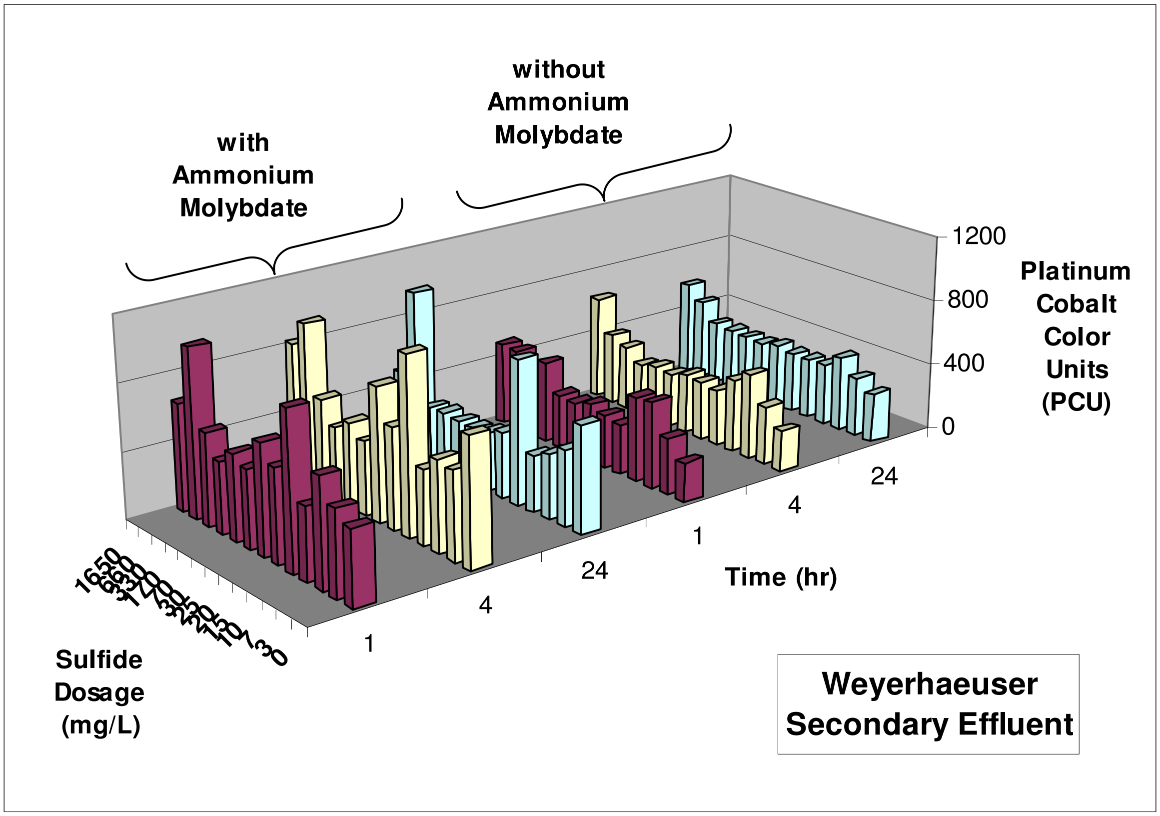

Figure 4.6: Grand Prairie, Alberta Weyerhaeuser Secondary Effluent Sample Color Results from both Crystallized Sulfide and with/without Ammonium Molybdate Treatment

It should be noted that an increase of color occurred in the control samples (zero mg/L of sulfide added) samples. It is likely that biogenic sulfide production may have contributed to these increases. In similar samples from this mill, Lange (2004) measured up to 22 mg/L of sulfide production in a 24-hour period. Therefore, sample data was compared against the related zero-mg/L, zero-hour values for each sampling location to account for any biogenically-created color (refer to Tables 4.1 - 4.3).

Table 4.1: Grand Prairie, Alberta Weyerhaeuser

Color Results Summary (10-ppm Solution)

Weyerhaeuser								
Grand Prairie, Alberta								
Color Results (PCU) from 10-ppm Solution								
Sulfide Dosage	**Primary Clarifier Inlet**			**Primary Clarifier Outlet**			**Primary Clarifier Secondary Effluent**	
(mg/L)	**24 hr**	**% Color Change**		**24 hr**	**% Color Change**		**24 hr**	**% Color Change**
0	392	-56		731	**35**		527	**53**
0.1	416	-53		696	**28**		517	**50**
0.2	434	-51		711	**31**		546	**58**
0.4	418	-53		634	**17**		526	**53**
0.5	387	-56		676	**24**		575	**67**
0.6	393	-56		691	**27**		549	**59**
0.8	442	-50		648	**19**		567	**64**
1.0	495	-44		712	**31**		504	**46**
1.5	456	-49		707	**30**		411	**19**
2.0	523	-41		715	**32**		505	**47**
2.5	553	-38		630	**16**		465	**35**
3.0	564	-36		680	**25**		424	**23**
5.0	697	-21		797	**47**		893	**159**

Table 4.2: Grand Prairie, Alberta Weyerhaeuser Color Results

(Crystallized Sulfide Doses & Ammonium Molybdate)

Weyerhaeuser							
Grand Prairie, Alberta							
Color Results (PCU) with Ammonium Molybdate							
Sulfide Dosage	**Primary Clarifier Inlet**		**Sulfide Dosage**	**Primary Clarifier Outlet**		**Secondary Effluent**	
(mg/L)	**24 hr**	**% Color Change**	**(mg/L)**	**24 hr**	**% Color Change**	**24 hr**	**% Color Change**
0	1719	**159**	**0**	2794	**82**	641	**44**
2	1473	**122**	**3**	3057	**99**	457	2
5	1499	**126**	**7**	3009	**96**	388	-13
10	1525	**130**	**10**	3358	**118**	335	-25
12	1650	**149**	**15**	3159	**106**	862	**93**
15	1307	**97**	**20**	2269	**48**	394	-12
20	1487	**124**	**25**	2423	**58**	357	-20
25	1190	**79**	**30**	1841	**20**	342	-23
40	1143	**72**	**70**	1757	**14**	341	-24
50	881	**33**	**170**	1544	0	354	-21
70	815	**23**	**330**	707	-54	344	-23
75	930	**40**	**660**	924	-40	1008	**126**
130	536	-19	**1650**	974	-37	486	**9**

Table 4.3: Grand Prairie, Alberta Weyerhaeuser Color Results Summary

(Crystallized Sulfide Doses)

Weyerhaeuser						
Grand Prairie, Alberta						
Color Results (PCU) without Ammonium Molybdate						
Sulfide Dosage	Primary Clarifier Inlet		Primary Clarifier Outlet		Secondary Effluent	
(mg/L)	24 hr	% Color Change	24 hr	% Color Change	24 hr	% Color Change
0	880	6	661	-7	237	**25**
3	736	-11	1193	**69**	341	**52**
7	721	-13	1091	**54**	516	**90**
10	735	-11	1116	**58**	507	**56**
15	798	-3	1222	**73**	303	**54**
20	801	-3	1221	**73**	320	**55**
25	824	0	1141	**61**	346	**63**
30	892	**8**	1111	**57**	317	**53**
70	753	-9	1399	**98**	325	**55**
170	757	-8	1182	**67**	492	**57**
330	663	-20	1151	**63**	325	**62**
660	594	-28	779	**10**	489	**108**
1650	749	-9	794	**12**	498	**142**

The next set of data relates to a set of wastewater samples obtained from the Prince Albert, Saskatchewan mill. These samples were taken from the primary pond inlet, midpoint, and outlet where significant sulfidogenic activity was measured, resulting in sulfide increases from 15 ppm to 38 ppm. For the primary pond influent, negligible rapid color increases were observed for sulfide doses at or below 70 mg/L (see Figure 4.7). At sulfide concentrations of 170 mg/L and above, there was an immediate increase in color that approached 200% of the original color. Little additional color change was observed after four hours had passed. However, after 24 hours had elapsed, all of the samples displayed the same color value (averaging 400 PCU). This reduction may be a result of sulfide stripping or biological anaerobic color removal processes, specifically quinone degradation or transformation.

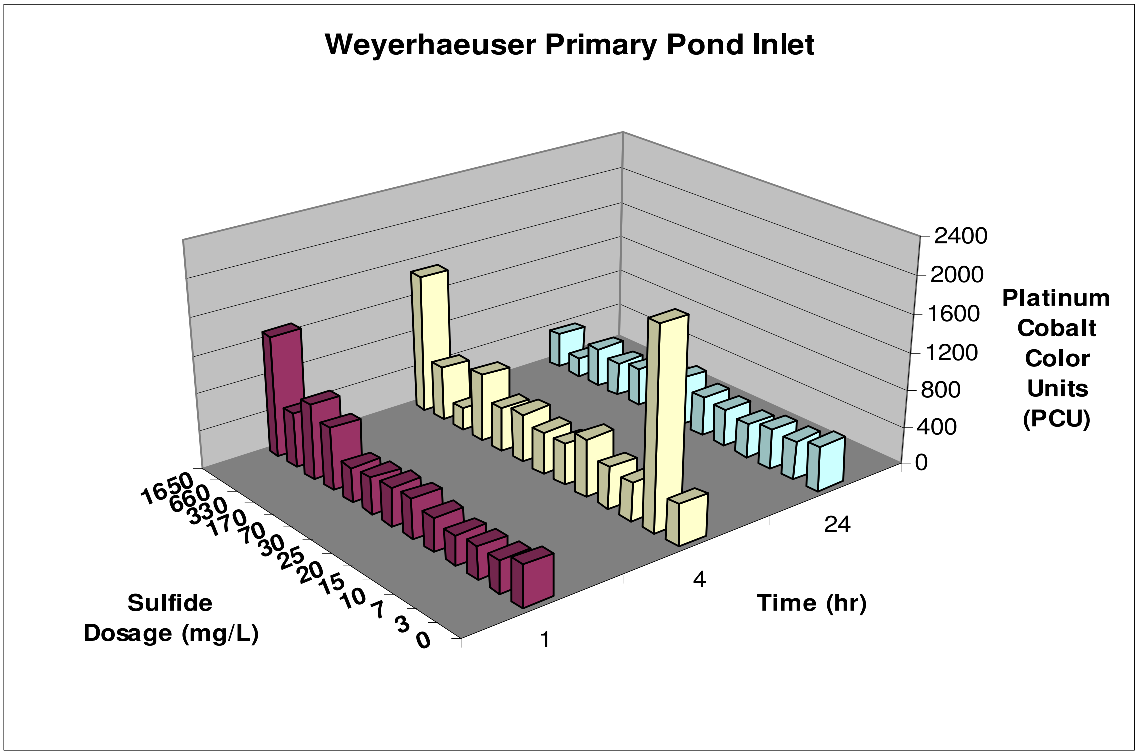

Figure 4.7: Prince Albert, Saskatchewan Weyerhaeuser Primary Pond Inlet Sample Color Results

For the midpoint sampling location of the clarifier, the color increases at one hour were observed for all sulfide doses, being most dramatic at the highest dosage levels (Figure 4.8). At sulfide doses of three mg/L and higher, the color change ranged from 30% to 300%. Once again, very little additional color change was noted after the initial one hour of sulfide exposure. In general, the results for the mid-pond sample were very consistent with the pond influent. However, after 24 hours, color reversion remained prominent (averaging about 40%) for the midpoint sample; whereas, color reduction was observed at 24 hours for the inlet sample (Table 4.4). This later color increase could potentially support the aerobic color reversion mechanism as this pond is a highly aerated lagoon. Furthermore, color increases have been commonly purported to occur across aeration ponds.

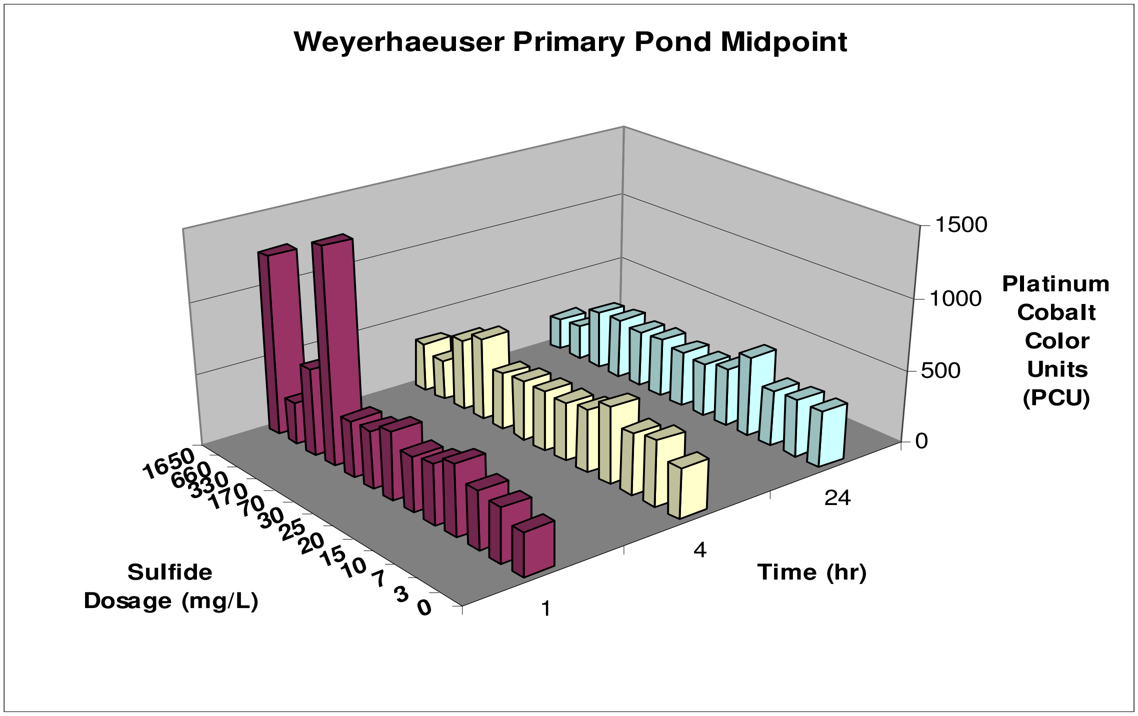

Figure 4.8: Prince Albert, Saskatchewan Weyerhaeuser Primary Pond Midpoint Sample Color Results

The effluent from the primary settling pond showed similar results as given by the influent and mid-pond samples. The one-hour data set displayed a color increase for all sulfide doses: as dose increased, so did resulting color (Figure 4.9). The most significant increases in color occurred for sulfide doses of 330 mg/L and higher. The color change for these sulfide concentrations ranged from 10% to 100% (see Table 4.4). As for the influent and mid-point samples, very little additional color change was noted after the initial one hour of exposure. Therefore, the supposed theory of color reversion becoming intensified as a result of aeration and/or other mechanisms is further deduced by this data set. Table 4.4 clearly shows increasing color percentages from inlet to midpoint to outlet. Though not proven, quinone production is likely to have occurred here.

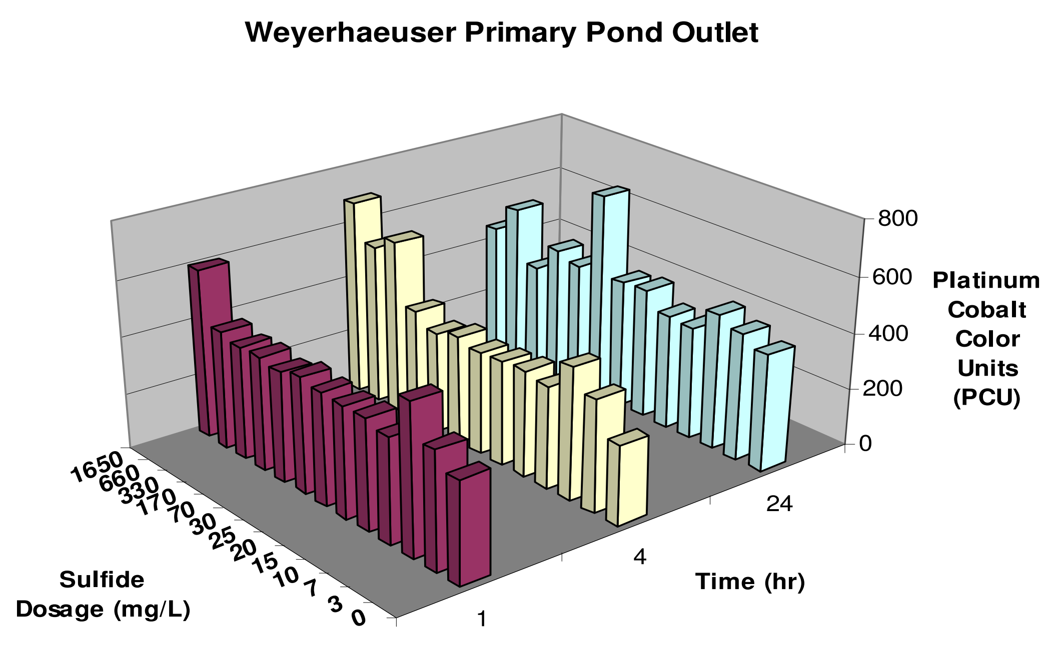

Figure 4.9: Prince Albert, Saskatchewan Weyerhaeuser Primary Pond Outlet Sample Color Results

Table 4.4: Prince Albert, Saskatchewan Weyerhaeuser Results Summary

Weyerhaeuser						
Prince Albert, Saskatchewan						
Color Results (PCU)						
Sulfide Dosage	**Primary Pond Inlet**		**Primary Pond Midpoint**		**Primary Pond Outlet**	
(mg/L)	**24 hr**	**% Color Change**	**24 hr**	**% Color Change**	**24 hr**	**% Color Change**
0	480	**11**	388	**29**	413	**16**
3	418	-3	401	**34**	449	**26**
7	429	-1	386	**29**	481	**35**
10	369	-14	557	**86**	397	**12**
15	408	-5	402	**34**	405	**14**
20	426	-1	372	**24**	464	**31**
25	527	**22**	381	**27**	457	**29**
30	327	-24	409	**36**	733	**106**
70	413	-4	396	**32**	451	**27**
170	368	-15	419	**40**	474	**33**
330	420	-3	408	**36**	379	**7**
660	206	-52	239	-20	564	**59**
1650	383	-11	229	-24	460	**29**

The Johnsonburg samples were collected at the pulp sewer, settling pond feed, aeration pond feed, and the final discharge locations. The initial conditions for the samples are provided below in Table 4.5:

Table 4.5: Johnsonburg, PA Weyerhaeuser Samples—Initial Conditions

Pulp Sewer			**Settling Pond Feed**		
pH	***Cond.***	***Sulfide (ppm)***	***pH***	***Cond.***	***Sulfide (ppm)***
11.4	***3880***	***4***	***11.1***	***2920***	***3***
Aeration Pond Feed			**Final Discharge**		
pH	***Cond.***	***Sulfide (ppm)***	***pH***	***Cond.***	***Sulfide (ppm)***
9	***2400***	***16***	***7.8***	***2500***	***0***

The wastewater samples from the pulp sewer have high BOD, small chlorine residual, highly positive redox, and high pH. Even though a small sulfide residual was reported for this sample, it should not have a long history of sulfide exposure. Because this sample represents wastewater from bleaching, it typically has a low color (approximately 200 PCU) and is believed to be most susceptible to color reversion.

The pulp sewer (often referred to as the alkaline sewer) showed a strong correlation to the mechanistic anaerobic color generation via the sulfide reaction (see Figures 4.10 & 4.11). For the lower ranges of sulfide exposure (Figure 4.10), the initial samples (zero-hour) taken immediately after sulfide addition showed an increase in color. The observed trend provided increasing color with increasing sulfide dose, approaching 400% by the highest dose of five mg/L. Additionally, color reversion was supported by the slower mechanism in that by the 24-hour interval, close to a 1,000% color increase had been reached.

The highest immediate color change for the higher dosage ranges was 180% (Figure 4.11). A further increase in color was observed after four and 24 hours of exposure to sulfide. The highest increases for color ranged from 140% in the 330 mg/L sample to 220% in the 1,650 mg/L sample during the four-hr sampling interval. The high change in color percentage was not unexpected due to the bleached state of the waste and the high potential for non-sulfide reacted color bodies.

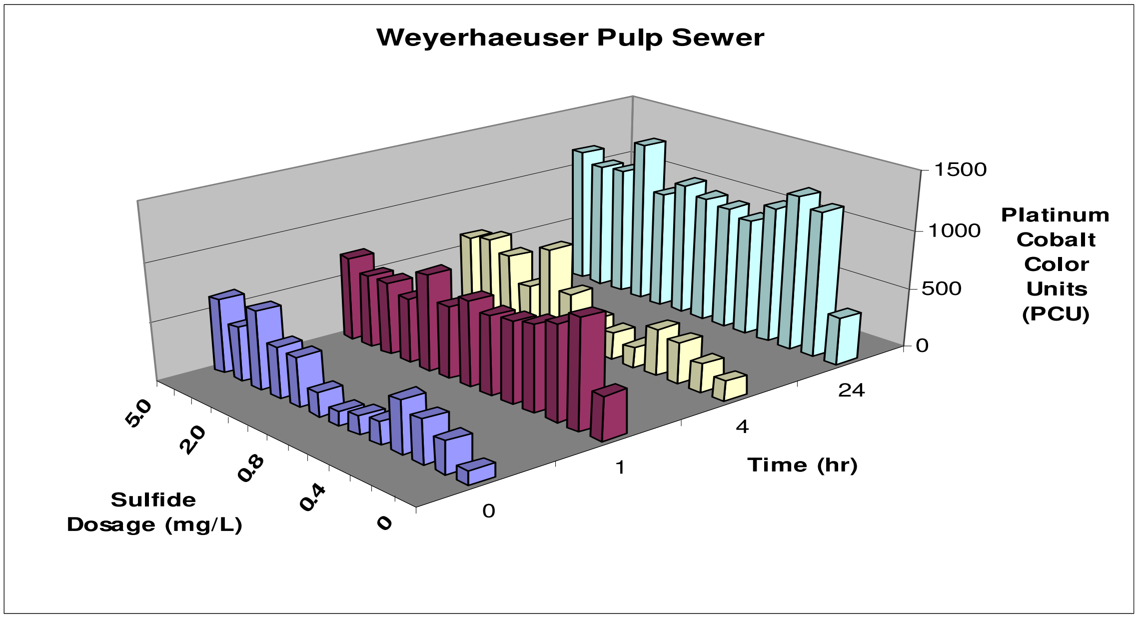

Figure 4.10: Johnsonburg, PA Weyerhaeuser Pulp Sewer Sample

Color Results from 10-ppm Sulfide Solution Doses

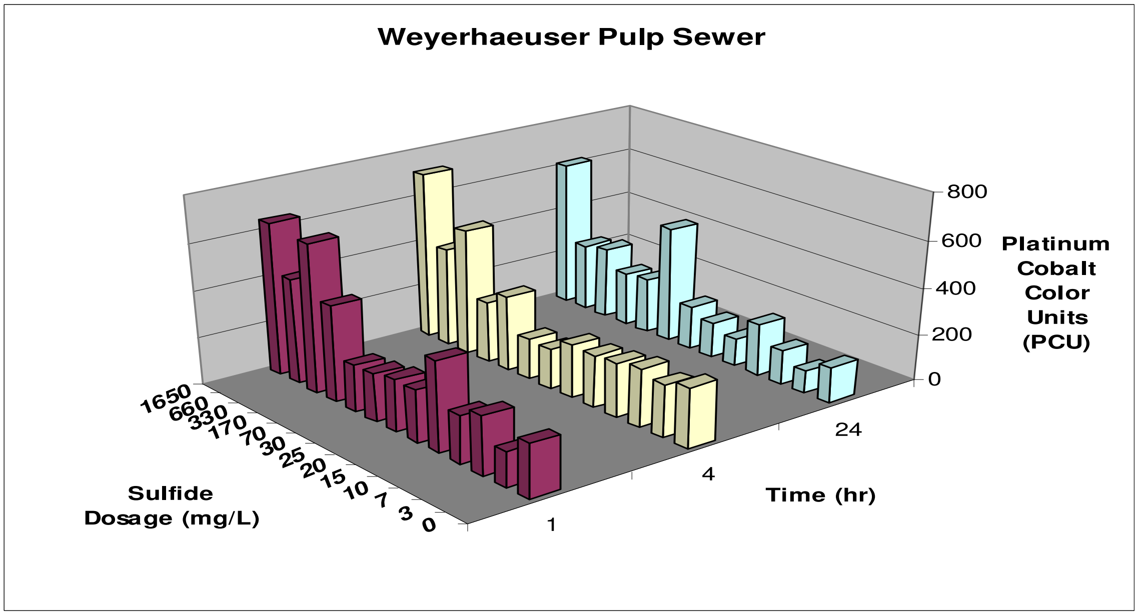

Figure 4.11: Johnsonburg, PA Weyerhaeuser Pulp Sewer Sample

Color Results from Crystallized Sulfide Doses

The feed to the settling pond includes the pulp sewer material, condensate, and other process wastewater from throughout the mill. Higher initial color was noted, as well as similar color reversion trends as seen for the pulp sewer sample (Figure 4.12).

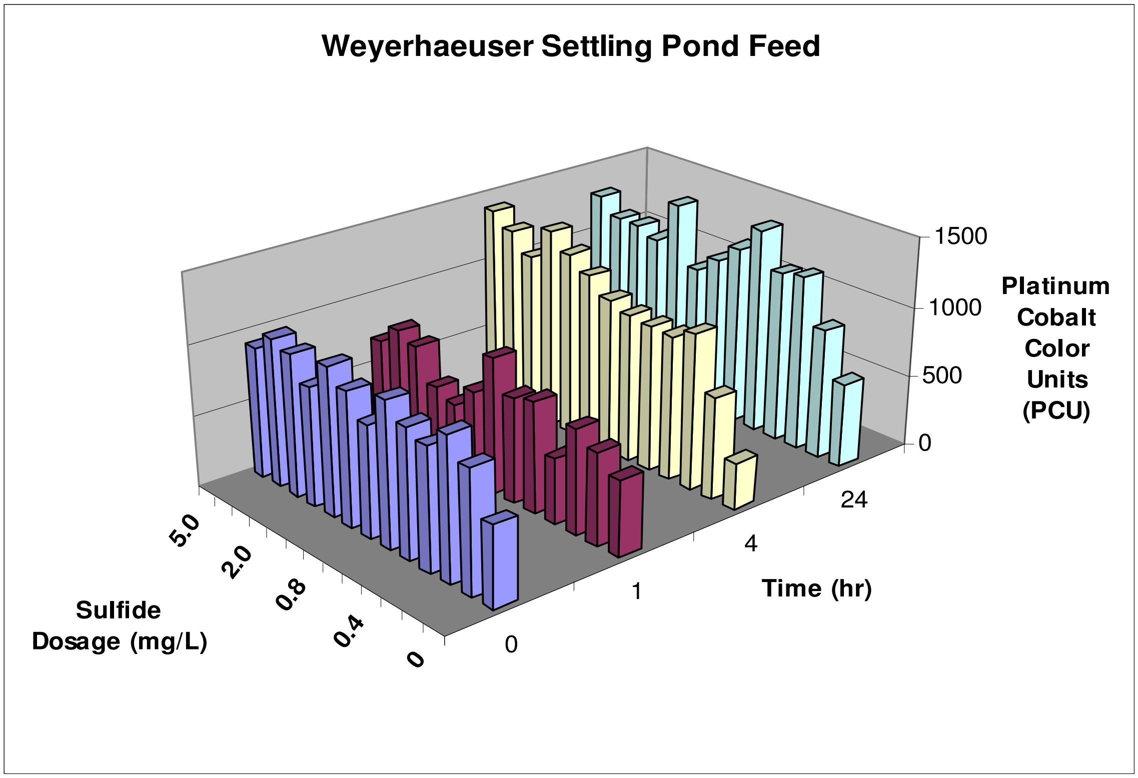

Figure 4.12: Johnsonburg, PA Weyerhaeuser Settling Pond Feed Sample Color Results from 10-ppm Sulfide Solution Doses

The settling pond influent is maintained at a high pH to counter the effects of organic acid production by anaerobic organisms in the pond. The settling pond influent had an initial color of 640 PCU which was somewhat higher than the pulp sewer sample and may be due to some reversion in the pulp sewer wastewater and color contributions from other wastewater streams (Figure 4.13).

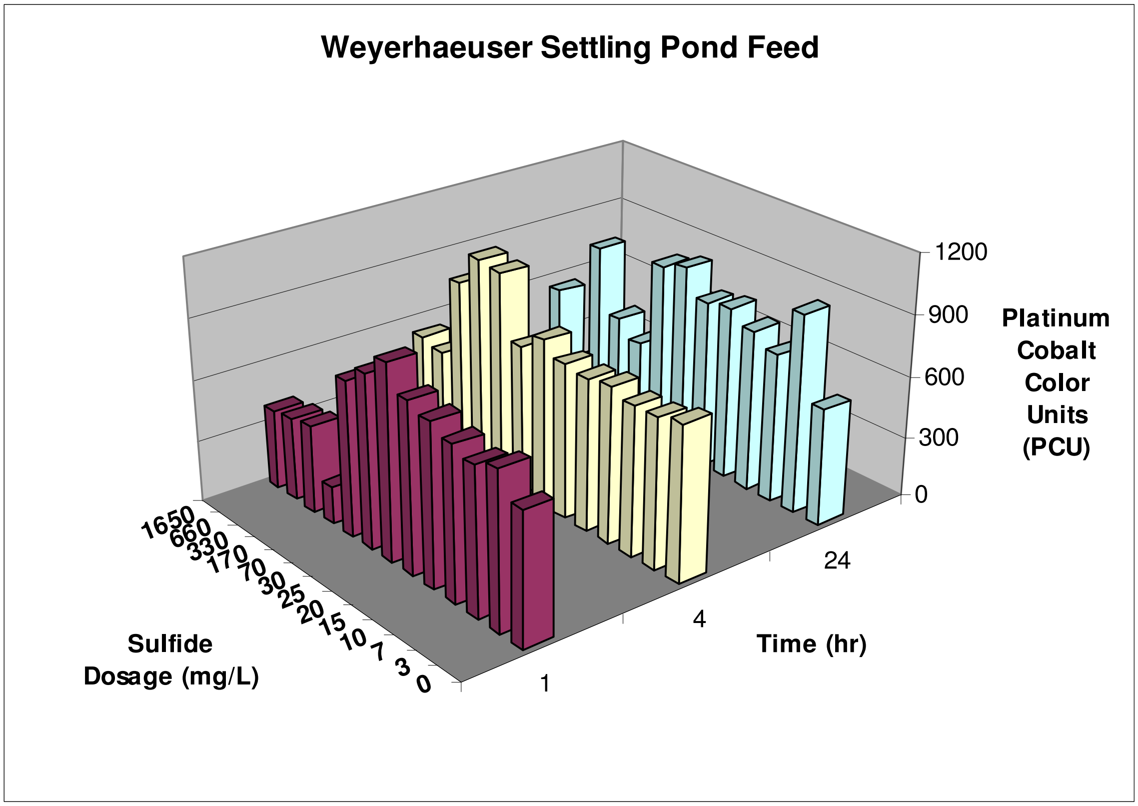

Figure 4.13: Johnsonburg, PA Weyerhaeuser Settling Pond Feed Sample Color Results from Crystallized Sulfide Doses

As shown by Figures 4.12 & 4.13, a rapid increase in color was observed in the settling pond samples immediately after sulfide addition. However, unlike the pulp sewer samples, the increase in color seemed to only rise slightly with increasing sulfide dose. For the higher sulfide exposure doses, the initial increase in color ranged from 30% in the 20 mg/L sample to 50% in the 25 mg/L sample. Additional color reversion was measured after four and 24 hours, reaching final colors that were slightly higher than those observed in the pulp sewer samples. At highest dosage levels, sulfide saturation could have resulted causing color reversion to lessen in value.

Tracking the wastewater further along its treatment path shows that the color in the aeration pond feed stage is similar to the primary settling pond influent (approximately 400 PCU). The aeration basin feed is the effluent from the settling pond that is fed into the aeration basin of the Johnsonburg activated sludge process. Some immediate increases in color were observed in the aeration feed (Figure 4.14). However, these increases were smaller than observed for the upstream samples and did not correlate well to the sulfide dose. Some additional growth was measured after 24 hours, with color growth ranging from four percent in the 0.2-mg/L samples to over 100% in the five-mg/L sample.

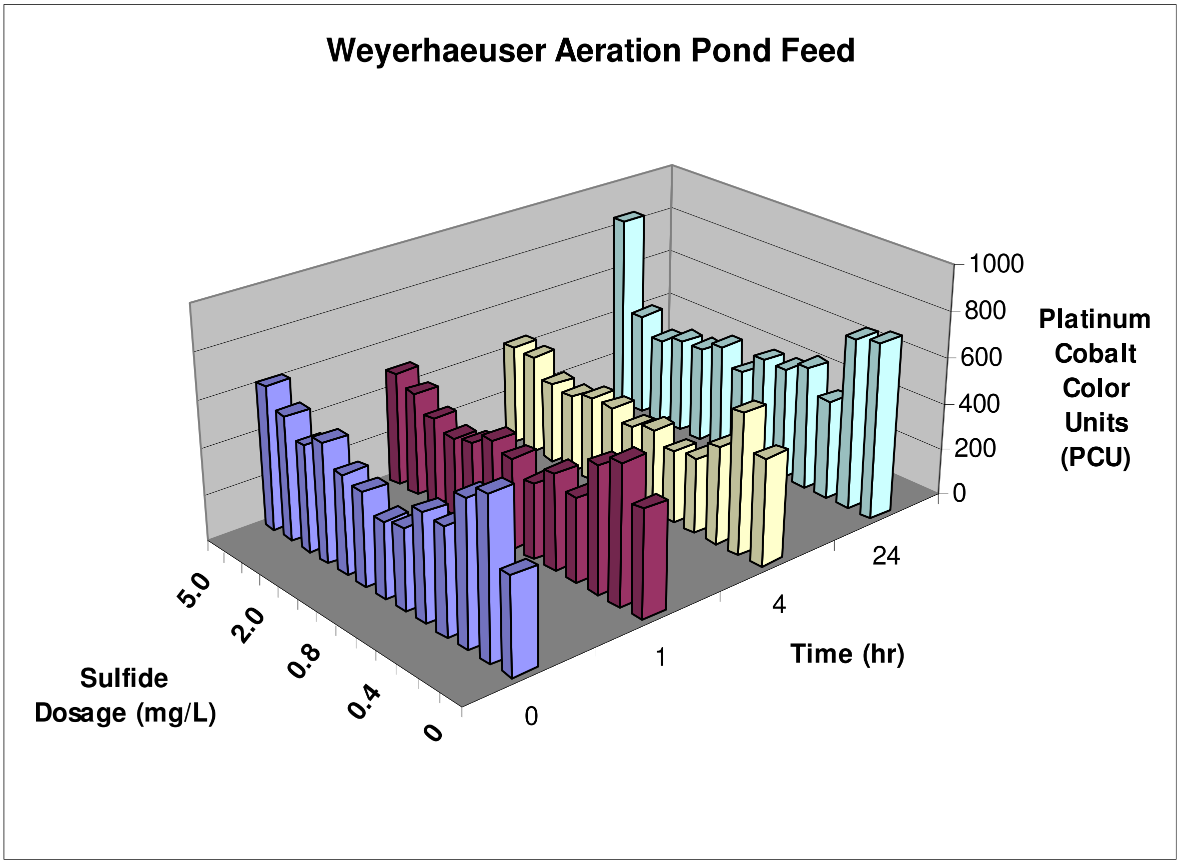

Figure 4.14: Johnsonburg, PA Weyerhaeuser Aeration Pond Feed Sample

Color Results from 10-ppm Sulfide Solution Doses

The final discharge sample represents the wastewater after treatment in the activated sludge process and from final clarification. The color in this discharge was 470 PCU, which is slightly lower than the aeration influent and indicates that some removal of color was accomplished by aerobic treatment. To regulators, this sample would be most important since this is discharged to the environment. Very little immediate color increase was observed in this sample as illustrated by the zero-hour data (Figure 4.15). But then at a concentration of 2.5 mg/L of sulfide and after 24 hours of exposure, the color increased significantly, supporting the slower color development mechanism. While the initial conditions (Table 4.5) suggest that zero ppm of sulfide is characteristic of the final discharge, note that 16-ppm is indicated as a typical concentration seen in the aeration pond feed. As the aeration pond feed wastewater precedes the treatment stage for the final discharge, the potential for color problems seems to be present. Therefore, color reversion seen at these higher levels of five mg/L at the 24-hour interval mark suggests the problematic possibility of color loading upon low sulfide exposure levels.

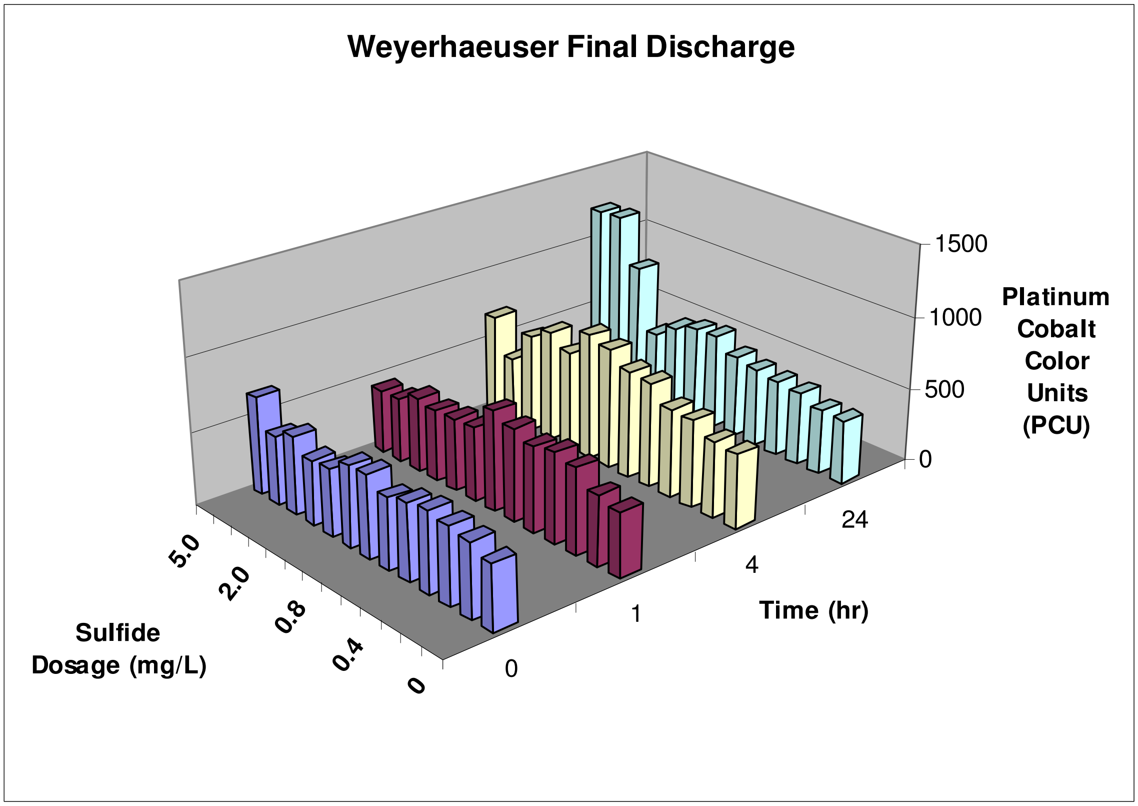

Figure 4.15: Johnsonburg, PA Weyerhaeuser Final Discharge Sample

Color Results from 10-ppm Sulfide Solution Doses

Moreover, color reversion seems to be most sensitive to lower amounts of sulfide doses which are the realistic exposures wastewater would actually encounter. Additionally, the higher sulfide levels achieved through the addition of sulfide crystals resulted in sporadic color increases, suggesting another color mechanism was involved (Figure 4.16). Saturation could be a possible explanation for the sudden decline in color values seen in the highest sulfide levels. Furthermore, color change seemed to suggest an independent relationship to sulfide dosage. Yet, it is important to note the higher color increase seen for the final discharge sample as opposed to the aeration pond feed samples. This observation provides further indication of the possibility of color being augmented across the treatment process train.

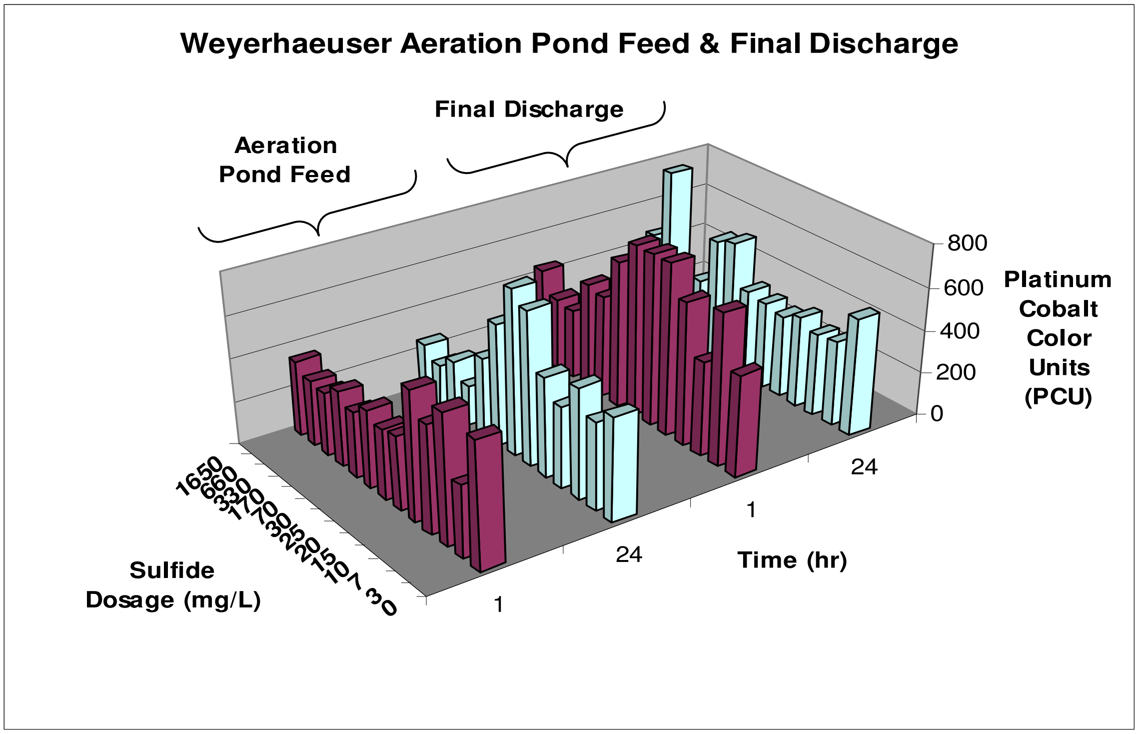

Figure 4.16: Johnsonburg, PA Weyerhaeuser Aeration Pond Feed and Final Discharge Samples Color Results from Crystallized Sulfide Doses

The Johnsonburg, PA mill results propose the importance of the color source: the pulp sewer. Color lessened as the wastewater progressed toward its final discharge location (see Table 4.6). Yet, the residual effects of color reversion from the pulp sewer could still be seen. Therefore, understanding the pulp sewer relationships concerning color reversion should be one of the first steps of any decolorization tactic.

Table 4.6: Johnsonburg, PA Weyerhaeuser Results Summary

Sulfide Dosage	**Pulp Sewer**				**Final Discharge**			
	Color Results (PCU)				**Color Results (PCU)**			
	Sulfide (ppm) =		***4***		***Sulfide (ppm) =***		***0***	
(mg/L)	0 hr	% Color Change	24 hr	% Color Change	0 hr	% Color Change	24 hr	% Color Change
0	115	0	398	246	443	286	437	280
0.1	270	135	1228	969	501	335	440	283
0.2	364	217	1303	1034	527	358	497	332
0.4	443	285	1145	897	545	374	517	350
0.5	192	67	981	753	528	359	538	368
0.6	158	37	1029	795	482	319	565	392
0.8	120	4	1058	821	565	391	658	472
1.0	202	76	1123	877	549	377	646	462
1.5	416	262	984	756	456	296	593	416
2.0	436	279	1363	1086	444	287	489	325
2.5	664	477	1083	843	534	365	918	699
3.0	459	299	1071	832	473	312	1238	977
5.0	625	443	1146	897	665	478	1223	964

The last set of samples from Weyerhaeuser consisted of seven grab samples taken throughout the Albany, OR mill wastewater lagoon. Equal volumes of these samples were combined to form one composite wastewater that was employed in sulfide experimentation as well as in the aeration tests described later in this chapter. These samples appeared to be a suitable representation of lightly colored samples in pulp and paper wastewater treatment. Furthermore, the mill reported problems with increases in both sulfide concentrations and color in this pond system. Due to a series of pulp spills, the front of the lagoon had become anoxic, and sulfide levels had increased from less than one mg/L to over ten mg/L.

The initial color of the composite wastewater sample was just under 200 PCU. After one hour of sulfide exposure, increases in color were apparent, with the highest colors linked to the highest sulfide doses (Figure 4.17). After four and 24 hours of exposure, color increased further resulting in a final increase of about 100%. This substantiates the correlation between sulfide and color reported for this pond.

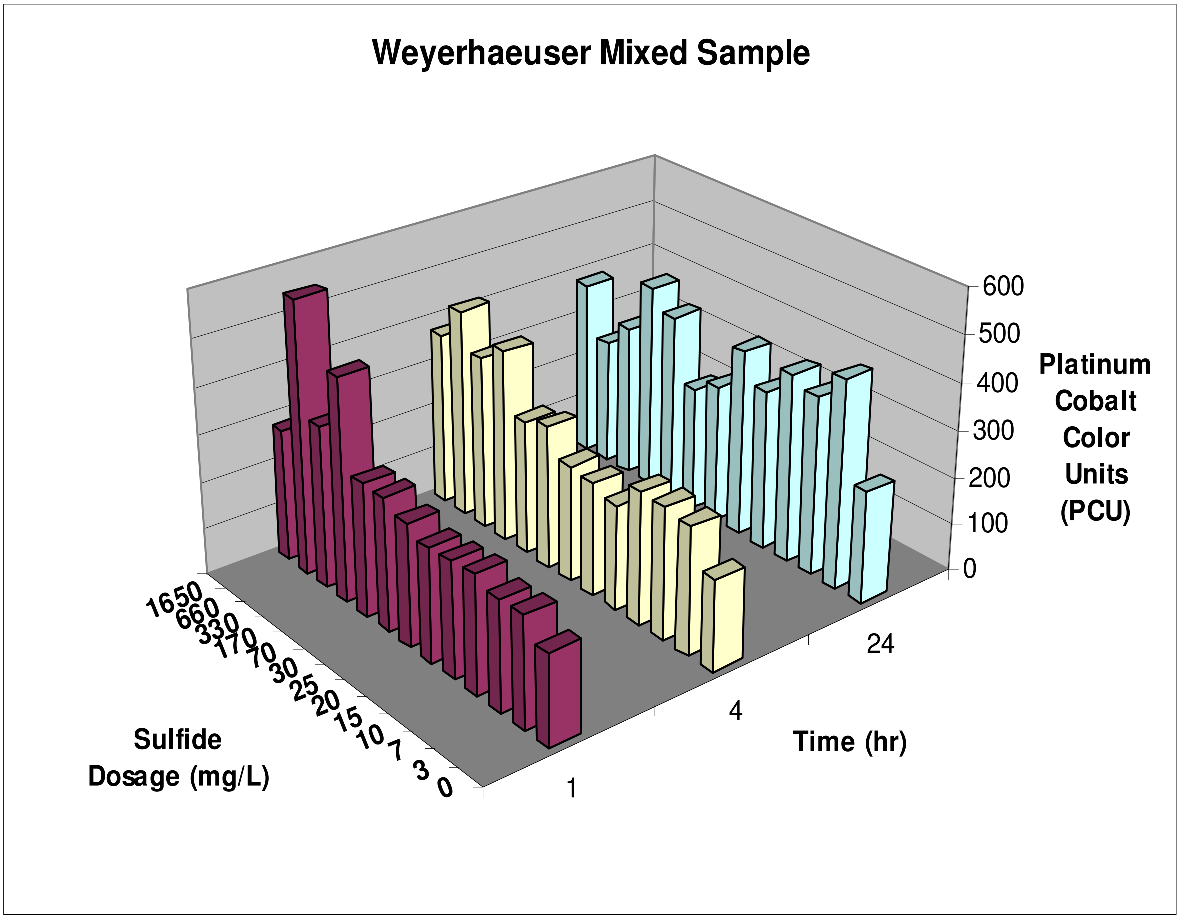

Figure 4.17: Albany, OR Weyerhaeuser Mixed Composite Sample

Color Results with Sulfide Doses

Table 4.7: Albany, OR Weyerhaeuser Results Summary

Weyerhaeuser						
Albany, OR						
Sulfide Dosage	**Mixed Sample Color Results (PCU)**					
	(Composite of seven grab samples from the dual-celled lagoon)					
(mg/L)	**1 hr**	**% Color Change**	**4 hr**	**% Color Change**	**24 hr**	**% Color Change**
0	191	0	192	**1**	239	**25**
3	232	**21**	267	**40**	443	**132**
7	230	**20**	279	**46**	381	**100**
10	248	**30**	280	**46**	401	**110**
15	244	**28**	223	**17**	339	**78**
20	239	**25**	240	**26**	400	**109**
25	258	**35**	248	**30**	297	**56**
30	281	**47**	303	**59**	266	**40**
70	282	**48**	289	**51**	400	**109**
170	473	**148**	412	**116**	442	**131**
330	344	**80**	372	**95**	327	**72**
660	580	**204**	449	**135**	271	**42**
1650	281	**47**	374	**96**	378	**98**

Rayonier

Samples from Rayonier included the primary clarifier inlet, the influent and effluent of an under-aerated “strong pond,” and the effluent from two parallel-configured aerated stabilization basins (ASB #1 & #2). These wastewaters were highly colored (around 1000-2000 PCU), compared to the previously discussed waste streams. This may be due to the high-temperature acid digestion process used to produce cellulose and fluff-pulp at this mill.

There was little immediate change in color in the primary clarifier inlet sample as shown by the zero-hour data of Figure 4.18. There was no measurable increase in color over time for this sample except when exposed to the highest sulfide dosage level of five mg/L. Upon looking at sulfide concentrations above five mg/L (Figure 4.19), color growth continues to occur, though most dramatic at unrealistically high sulfide levels.

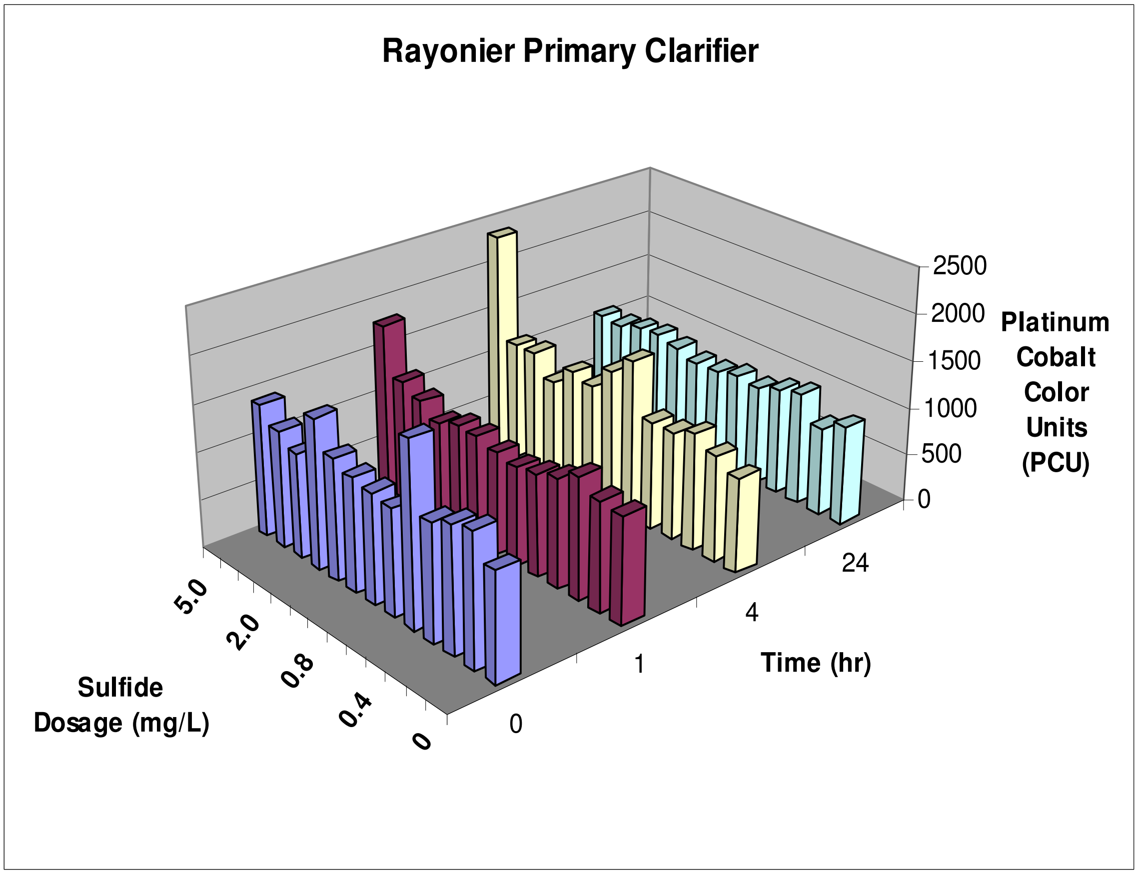

Figure 4.18: Rayonier Primary Clarifier Sample

Color Results from 10-ppm Sulfide Solution Doses

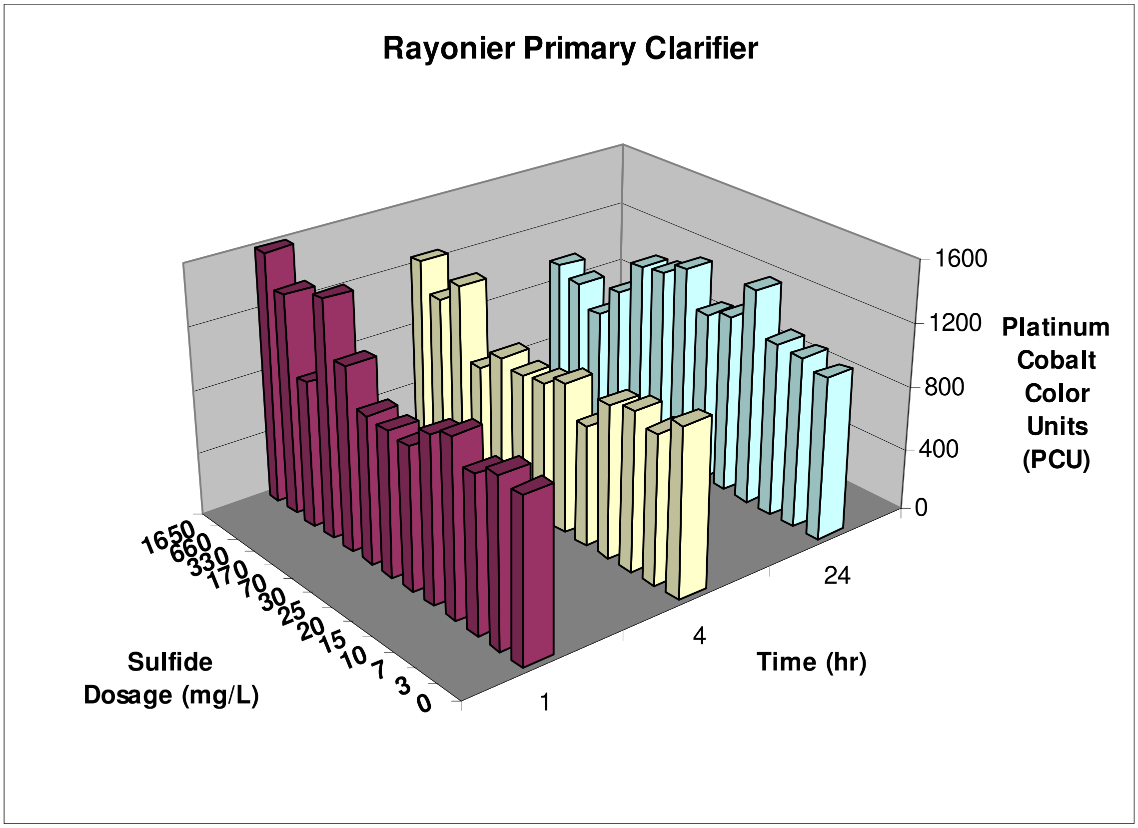

Figure 4.19: Rayonier Primary Clarifier Sample

Color Results from Crystallized Sulfide Doses

The higher initial color of the sample is believed to mask the effects of any sulfide color reversion. The high color of this sample may be indicative of a long history of previous exposure to sulfide. The primary influent has nearly 20 mg/L of sulfide resulting from anaerobic processes in the acid sewer from the hot acid pulping process. Alternatively, the nature of this highly colored wastewater may be variable. The wastewater contains high levels of furfuraldehyde due to the pulping process, which may contribute significantly to color. Furfuraldehyde is not commonly found in bleach kraft processes and is highly colored between 450 and 470 nm.

Due to the high initial color possessed by the combination of primary effluent and bleach plant filtrate of the strong pond influent, little immediate color increase was observed (Figures 4.20 & 4.21). Additionally, little color increase over time due to sulfide was seen. Sulfide exposure even at the highest levels of concentration appeared to be rather negligible. Once again, this higher initial color (above 500 PCU) in comparison to what was seen for the Weyerhaeuser samples seems to overwhelm the color effect that sulfide would be expected to cause. Additionally, a color reduction seen in the higher sulfide doses (Figure 4.21) suggest sulfide saturation as previously discussed.

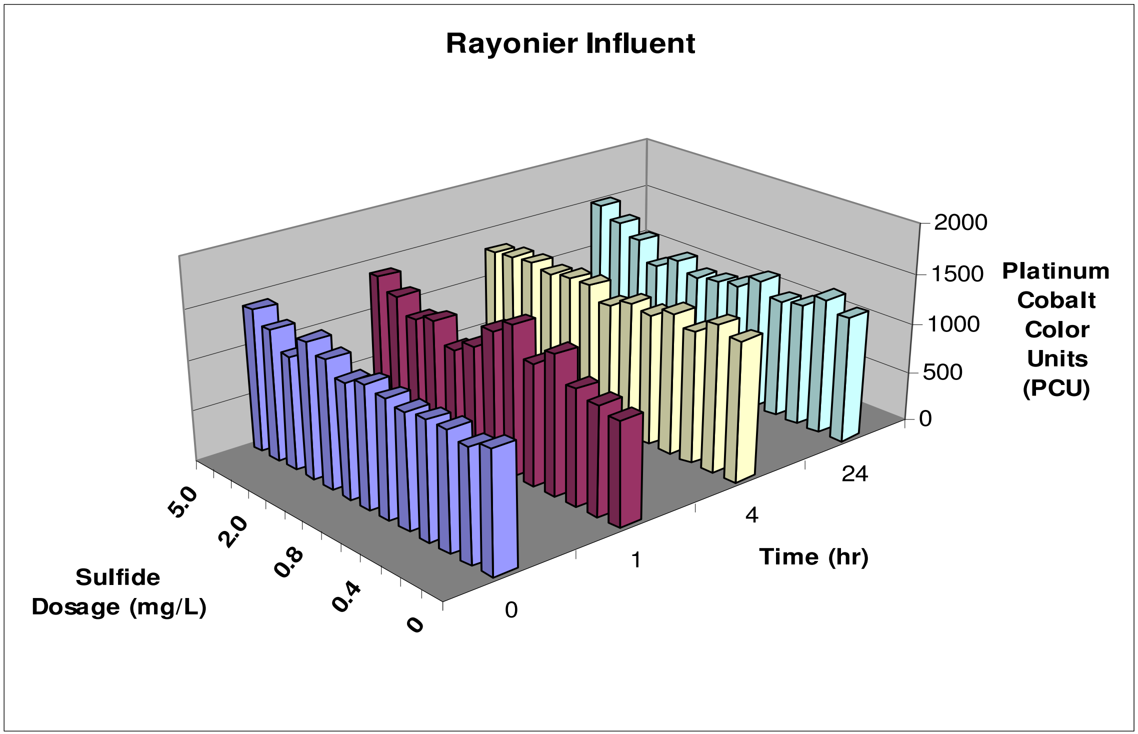

Figure 4.20: Rayonier Influent Sample

Color Results from 10-ppm Sulfide Solution Doses

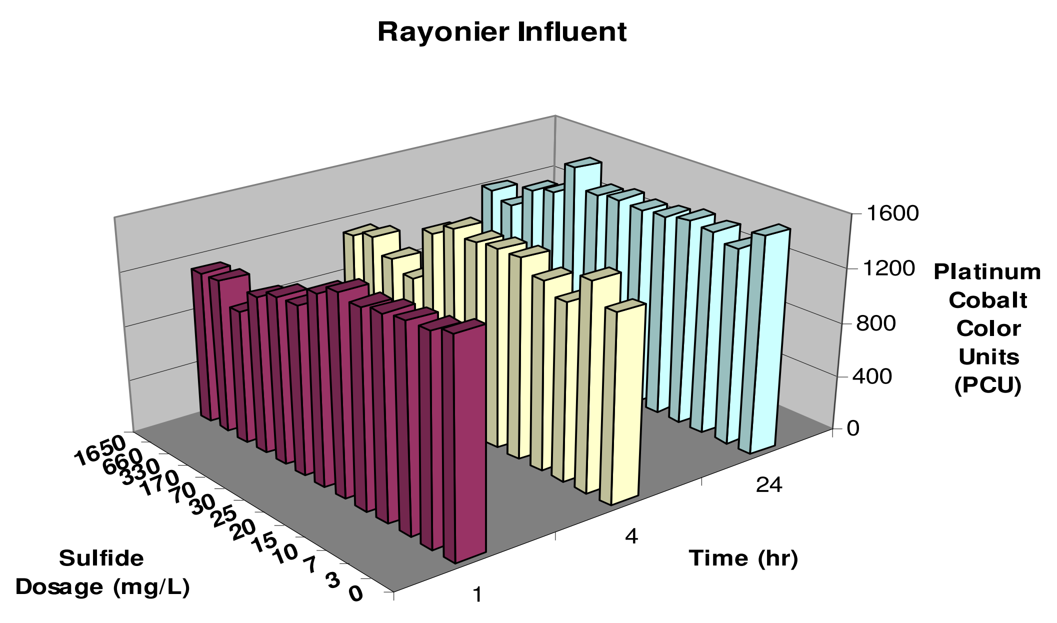

Figure 4.21: Rayonier Influent Sample

Color Results from Crystallized Sulfide Doses

The strong pond effluent was associated with somewhat of a higher color than the influent, but this may be due to color reversion in the pond. Some immediate increase with sulfide dose was seen (Figures 4.22 & 4.23). Significant color growth after 24 hours, seen by an approximate 175% increase in the five-mg/L, 24-hr sample, may indicate formation of color precursors in the pond system. Moreover, sulfide saturation could be a result of the color decrease seen in the highest dosage levels (Figure 4.23).

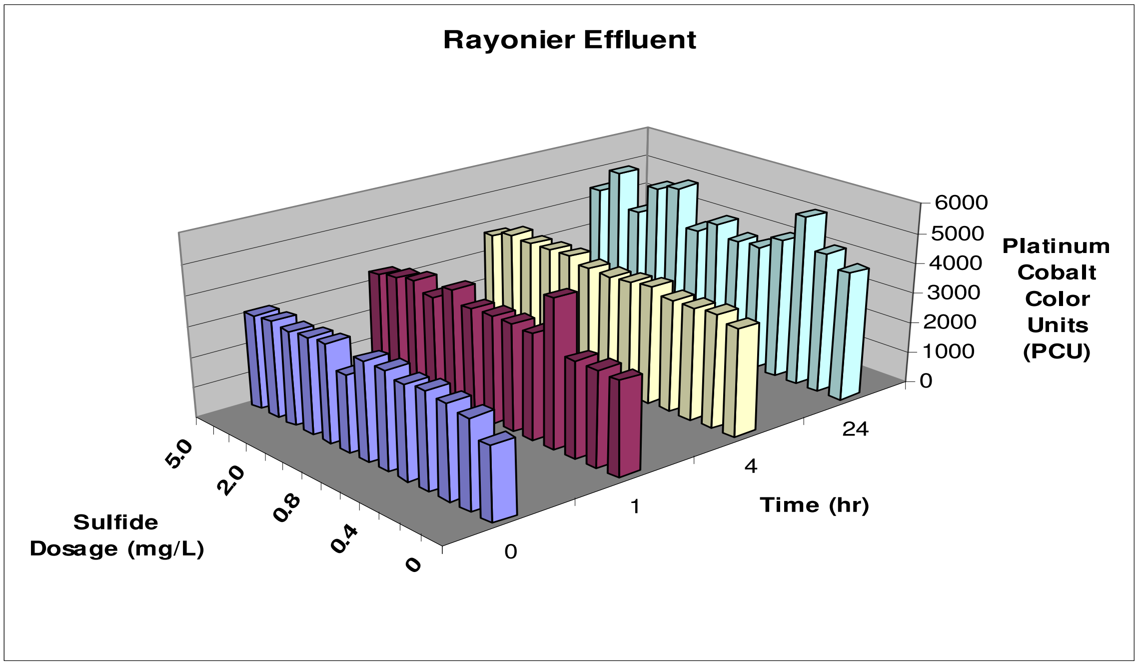

Figure 4.22: Rayonier Effluent Sample

Color Results from 10-ppm Sulfide Solution Doses

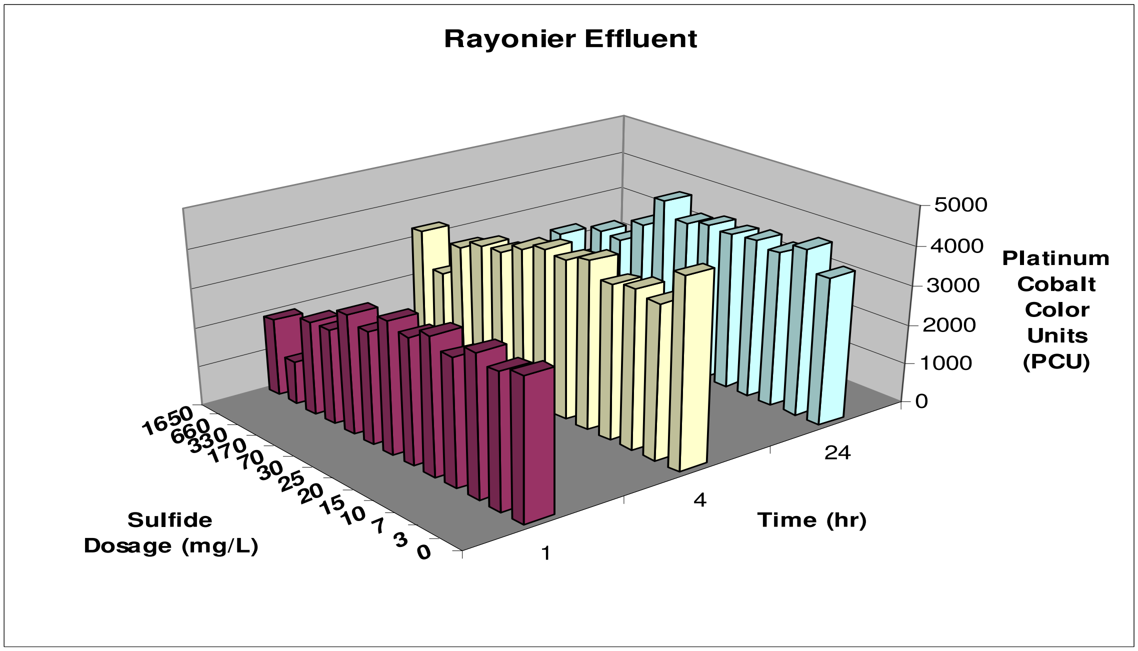

Figure 4.23: Rayonier Effluent Sample

Color Results from Crystallized Sulfide Doses

The two aerated stabilization basins (ASB #1 & #2) were reported to have high effluent color values, but little or no increases in color either immediately or after time resulted from the sulfide experimentation (Figures 4.24 & 4.25). This minimal color change supports the theory that the high degree of initial color appears to be masking any color change due to sulfide.

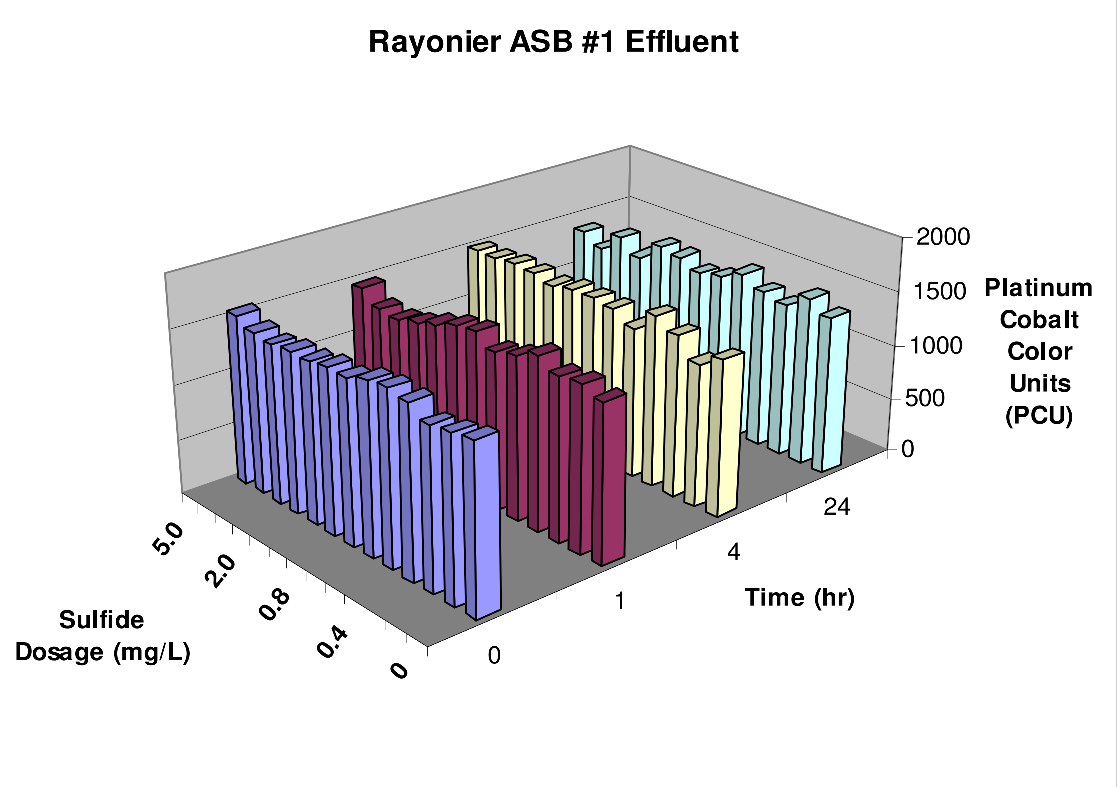

Figure 4.24: Rayonier ASB #1 Effluent Sample

Color Results from 10-ppm Sulfide Solution Doses

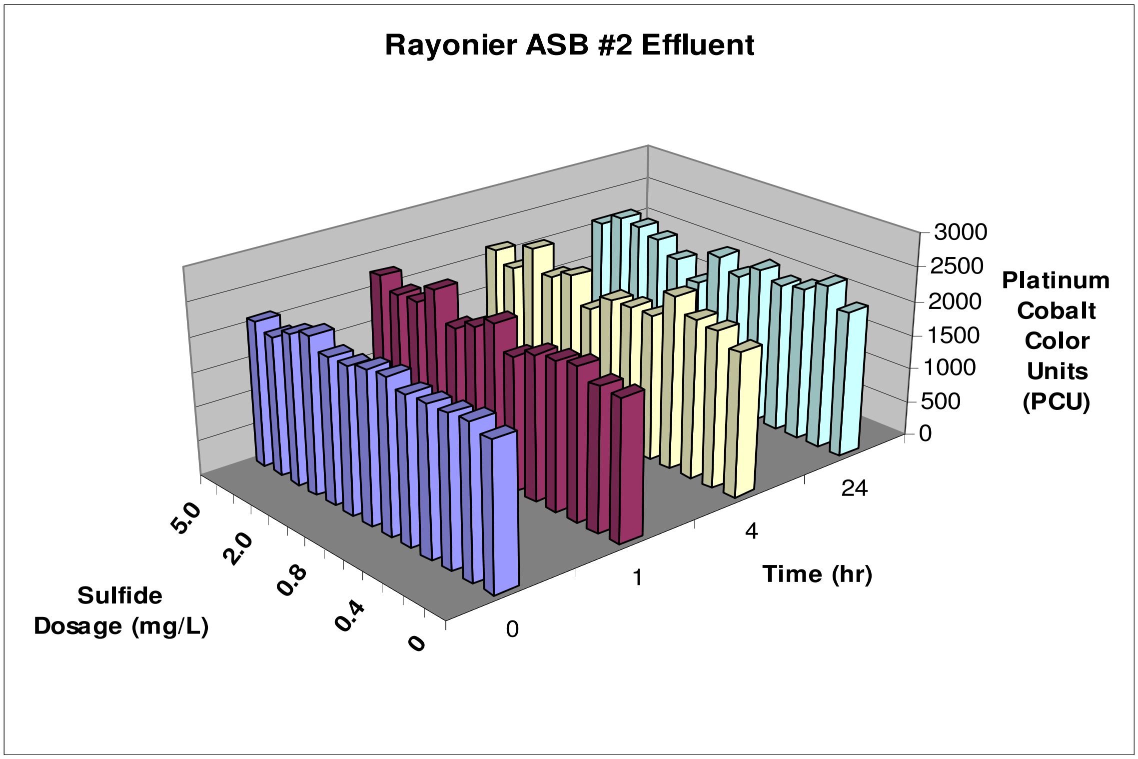

Figure 4.25: Rayonier ASB #2 Effluent Sample

Color Results from 10-ppm Sulfide Solution Doses

The same color decline depicted at the higher sulfide concentrations for the other preceding treatment stages resulted for these two ASB samples as well (Figures 4.26 & 4.27). Once again sulfide saturation appears to be responsible for this trend. Little potential for sulfide reversion appears to be present in these wastewater treatment stages. Yet, it is important to note that the initial color values are appreciably different between the two basins, ABS #2 being around 400 PCU higher. The difference between the initial colors of the two basin samples could be attributable to differences in residence times of the basins, aeration, and other design variations.

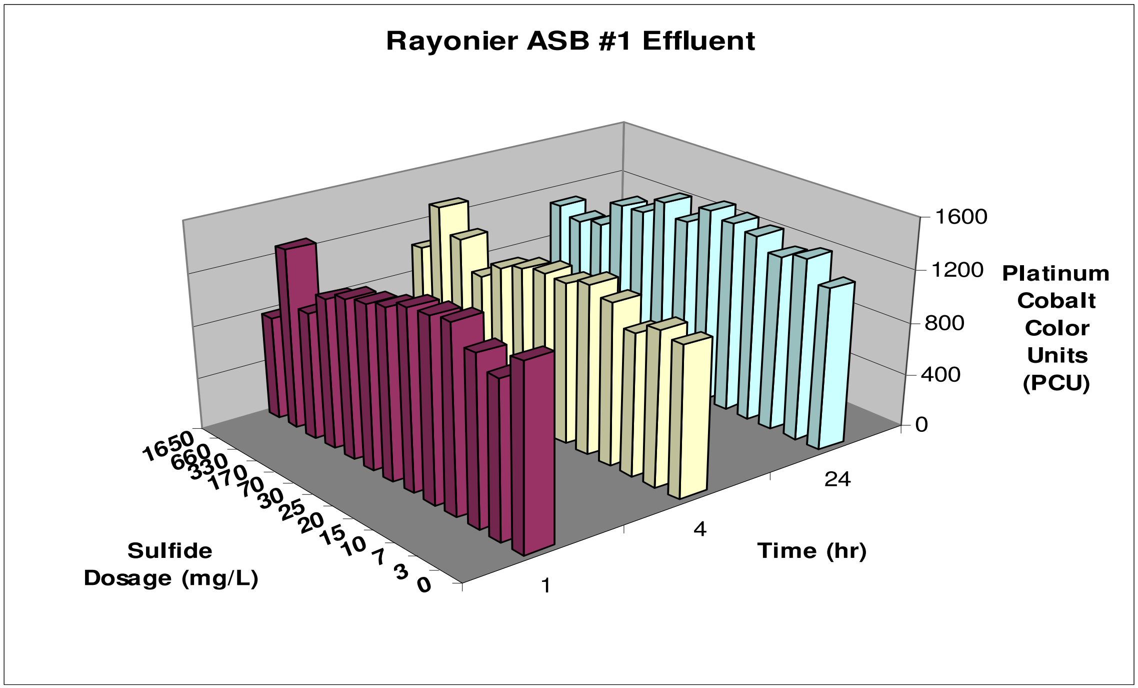

Figure 4.26: Rayonier ASB #1 Effluent Sample

Color Results from Crystallized Sulfide Doses

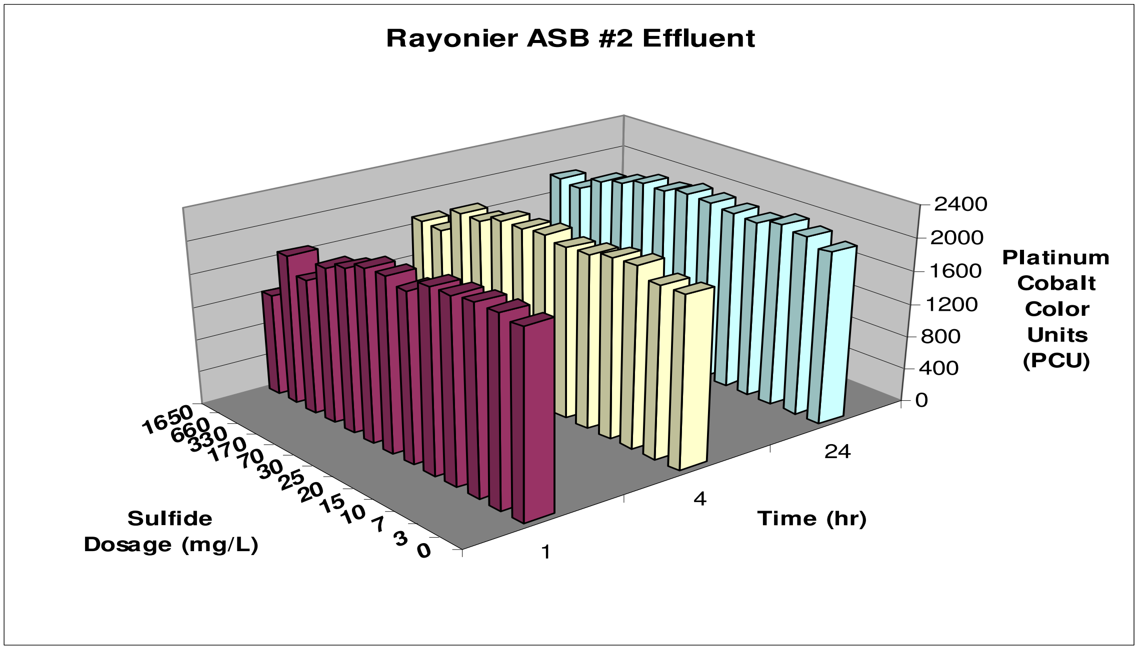

Figure 4.27: Rayonier ASB #2 Effluent Sample

Color Results from Crystallized Sulfide Doses

Georgia Pacific

The samples from Georgia Pacific were collected from each of the lagoon system divides referred to as Ponds 1, 2, 3, and 4. One effluent sample from each pond was collected and sent for participation in this experiment. The initial color of the wastewater increased slightly as the water passed through the series of ponds, indicating that color reversion was occurring in this system. In Pond 1, the initial color was 1,160 PCU, and after treatment through all four ponds, was discharged at almost 3,000 PCU, a 150% increase. According to Georgia Pacific personnel, significant hydrogen sulfide (H_2S) generation occurs in this lagoon, ranging from 12 ppm in Pond 1 to 20 ppm in Pond 4.

For Pond 1, increases in color were observed with increasing sulfide dose after one hour of exposure (see Figure 4.28). The color growth trend observed as sulfide doses were increased was apparent for this sample, especially at higher sulfide doses. There was no significant change in color between the one and 24-hour color readings. The results for Pond 2 were similar to those for Pond 1, the most prominent color change occurring at the highest sulfide doses.

For Ponds 3 and 4, there was little change in color except at the 2,500 mg/L sulfide dose (Figure 4.29), which is unrealistically high for an actual treatment process scenario.

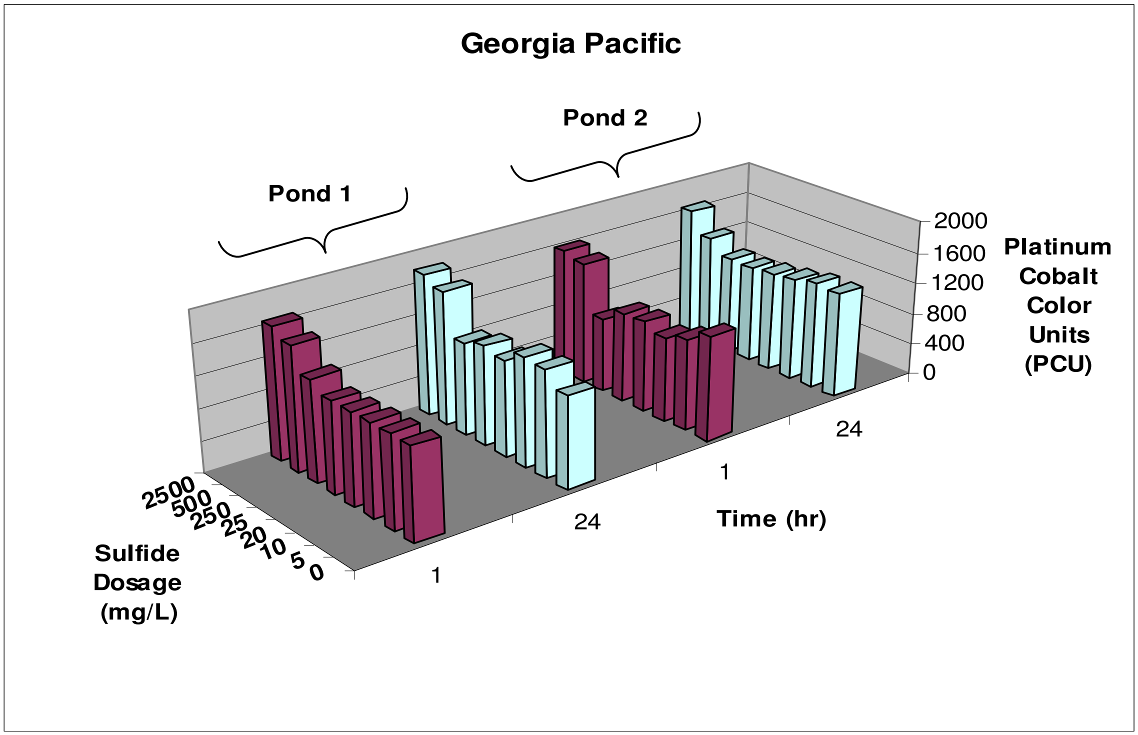

Figure 4.28: Georgia Pacific Ponds 1 & 2 Samples Color Results

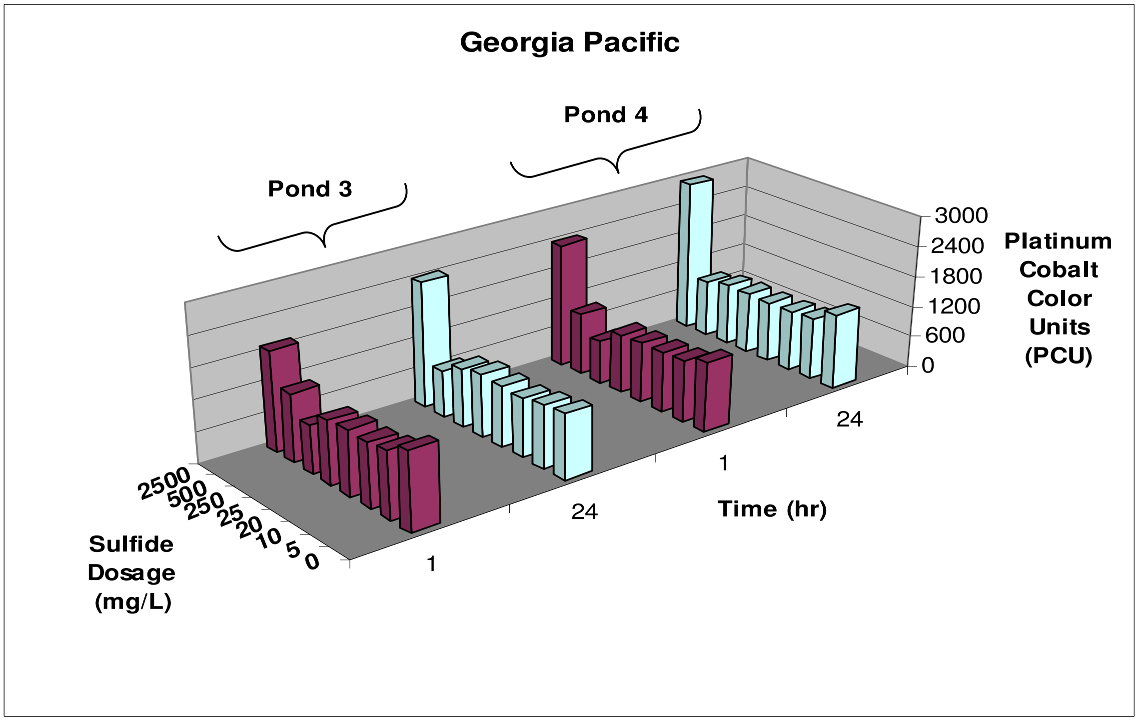

Figure 4.29: Georgia Pacific Ponds 3 & 4 Samples Color Results

Also, while the results indicate color growth across the ponds, color reversion was minimal when the samples were exposed to concentrations up to 250 mg/L (Table 4.8).

Table 4.8: Georgia Pacific Results Summary

Georgia Pacific Color Results (PCU)								
Sulfide Dosage	**Pond 1**		**Pond 2**		**Pond 3**		**Pond 4**	
(mg/L)	**24 hr**	**% Color Δ**	**24 hr**	**% Color Δ**	**24 hr**	**% Color Δ**	**24 hr**	**% Color Δ**
0	1165	0	1342	**1**	1240	-17	1456	**8**
5	1347	**16**	1355	**2**	1199	-20	1207	-11
10	1370	**18**	1298	-2	1132	-24	1178	-13
20	1205	**4**	1259	-5	1157	-22	1175	-13
25	1259	**9**	1237	-7	1200	-19	1193	-12
250	1173	**1**	1244	-6	1119	-25	1187	-12
500	1700	**46**	1412	**7**	890	-40	1083	-20
2500	1798	**55**	1677	**27**	2418	**62**	2933	**117**

The conclusion from this observation is that color reversion that results from the sulfide mechanism appears to be affected at extreme levels of sulfide. Lower values of sulfide have a minimal affect on color generation. One of these ponds (Pond 2) was sampled again at a later date (nearly two months later) and provided dissimilar results than those previously presented for this pond. The second sample set (four grab samples from Pond 2) reflected a previous exposure history of 40-50 ppm of sulfide. Thus, any reversion would have already occurred. The underlying difference was that the second sample set exhibited the effects of having no primary clarifying treatment as it had been previously taken offline. Therefore, the resulting effect on color was actually expected given the treatment conditions. Therefore, to test this theory, the four grab samples from the same pond were analyzed individually. As with any grab sample, including every sample used throughout this entire experiment, they represent a “snapshot” of the current wastewater characteristics present upon sample collection. Any spills, releases, upsets, etc. can therefore cause sample variation. Therefore, to ensure that variation was not caused by experimental variation, one of the grab samples (Grab 1) was analyzed in triplicates for a reproducibility analysis (Figure 4.30).

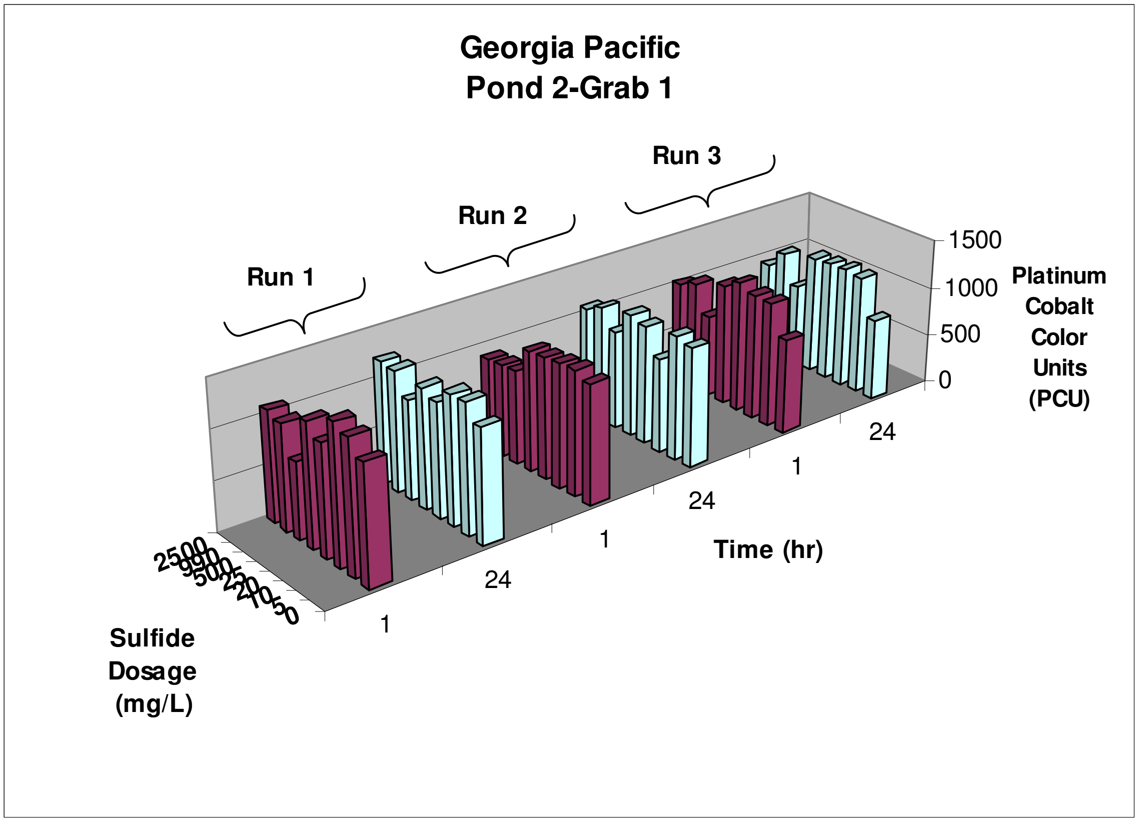

Figure 4.30: Georgia Pacific Pond 2—Grab 1 Reproducibility Color Results

Furthermore, the resulting error bars calculated on the three samples did not indicate dramatic variation and illustrated consistent color trends (Figure 4.31). Hence, it was concluded that the data for an individual sample was reproducible and the discrepancy seen in the color results between two samples from the same source was due to process modifications.

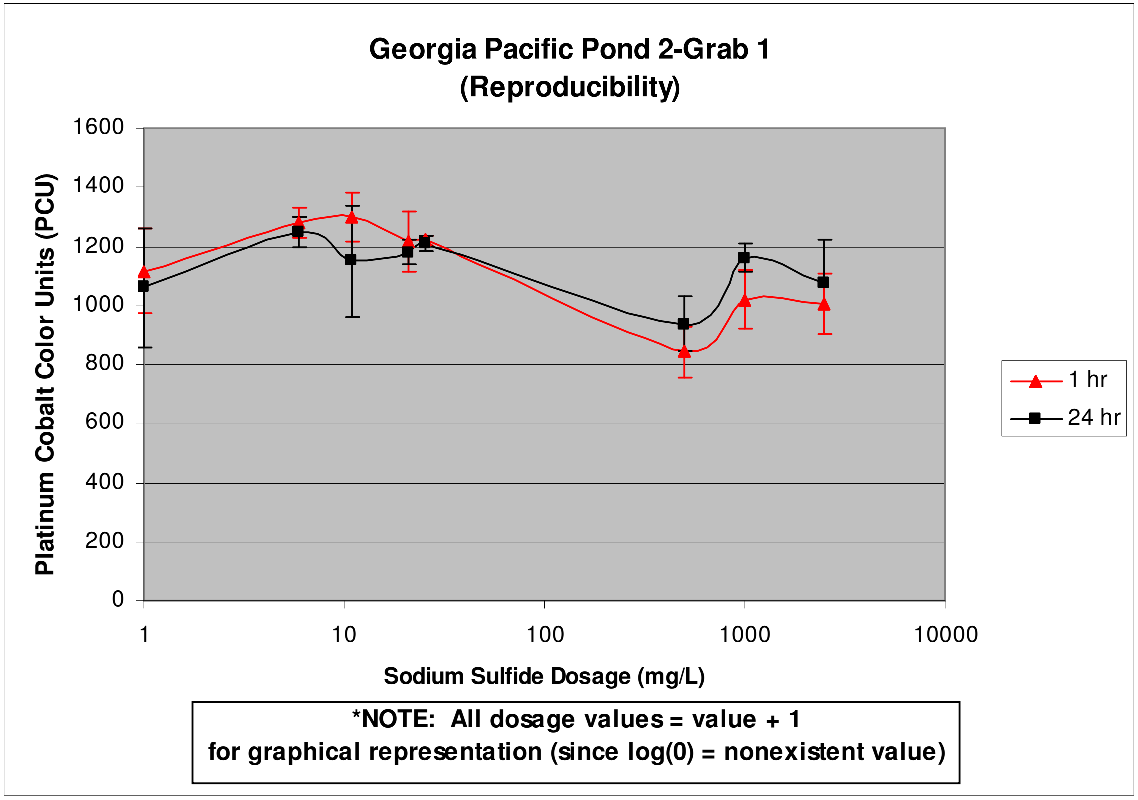

Figure 4.31: Georgia Pacific Pond 2—Grab 1 Averaged Color Results

Color appeared to remain relatively stable for Grabs 2 and 3, while slight color growth was seen in Grabs 1 and 4 (Figures 4.32 & 4.33). The data from Run 1 was used for the Grab 1 sample set plotted in Figure 4.32.

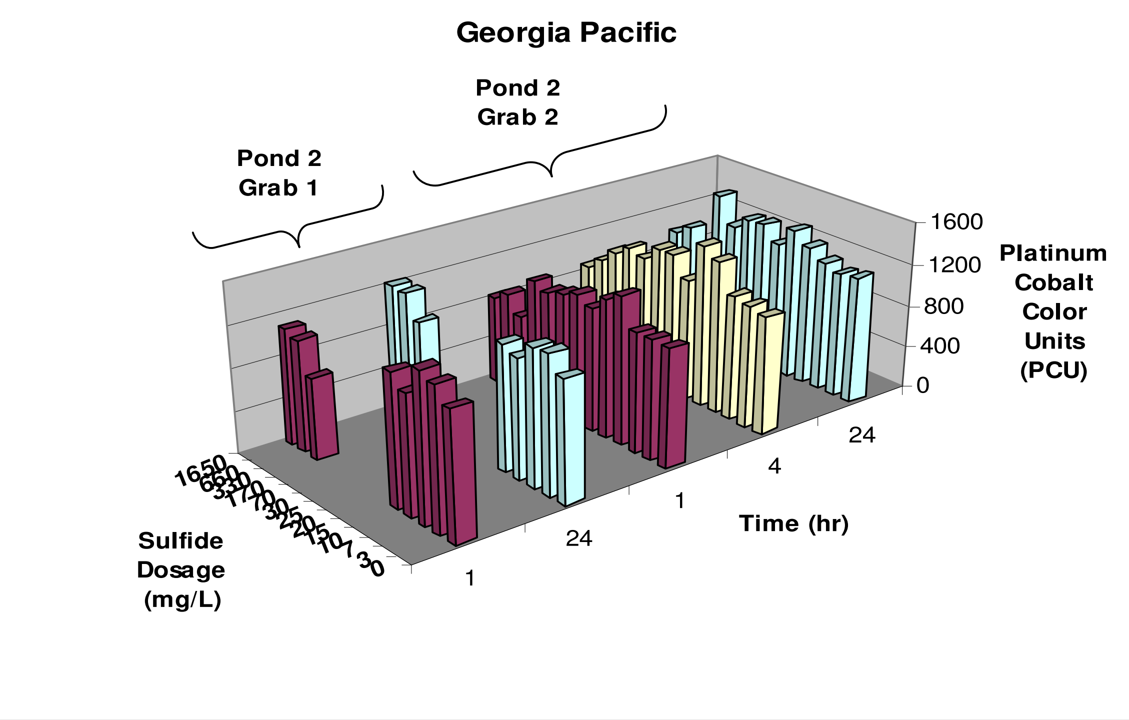

Figure 4.32: Georgia Pacific Pond 2—Grabs 1 & 2 Samples Color Results

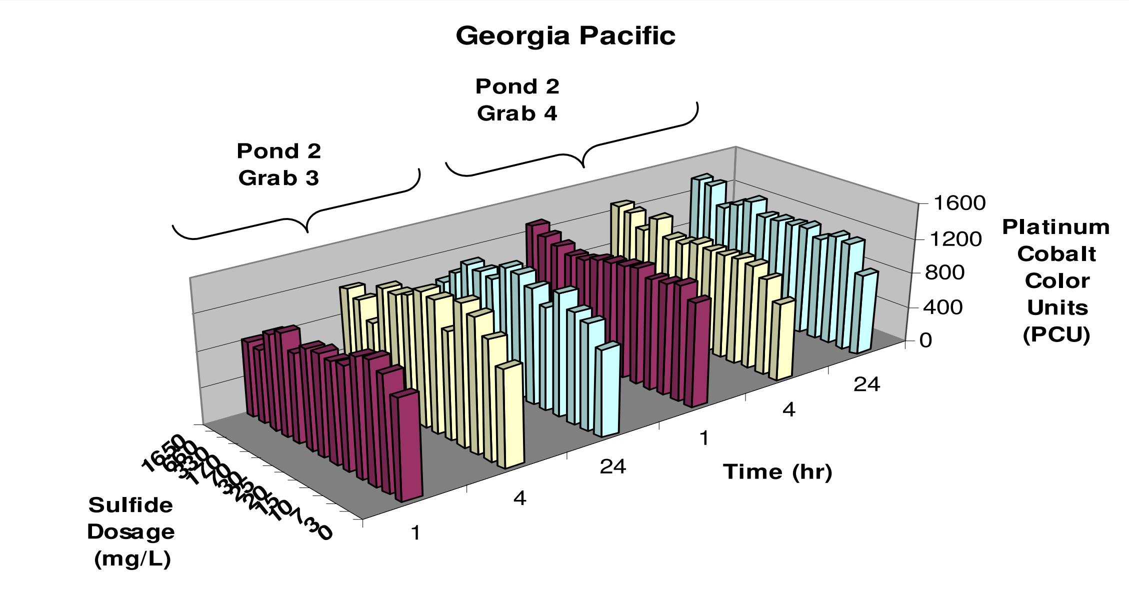

Figure 4.33: Georgia Pacific Pond 2—Grabs 3 & 4 Samples Color Results

As previously shown for the other Georgia Pacific samples, time was not apparently an important factor on color development. Additionally, color reduction was evident at the highest dosages, reflecting sulfide saturation. Sulfide saturation seems to be dependent on initial wastewater color. For the lighter samples, as sulfide dosages increased, so did the resulting degree of color reversion; yet, for the darker samples, a decline or saturation point was reached when exposed to the highest sulfide concentrations.

Aeration Experimentation

The aforementioned Georgia Pacific Pond 2 sample (the latter sample set of four grabs from Pond 2) was selected as the representative darkly colored sample. Therefore, this darkly colored sample along with the representative lightly colored sample previously discussed as the Weyerhaeuser-Albany, OR composite sample were used in a bench scale aeration study. The goal of this study was to ascertain if color increases due to sulfide were reversible by stripping and/or oxidation of the sulfide by aeration.

Samples were first analyzed based on the effects of aeration on prior color generation (Figure 4.34). Only the higher sulfide doses of 330-ppm, 660-ppm, and 1,650-ppm were tested in this aeration experiment based on the hypothesis that the greatest color generation occurs at these higher sulfide levels. Color was measured at one- hour and four-hour intervals in the same manner as previously described for the sulfide experimentation (seen by the first two points of each line on the plot in Figure 4.34). Then the samples were aerated overnight and analyzed the following day for any resulting color change. Color was reverted in both sample sets as shown by the upward trend for each line in Figure 4.34. It is likely that aeration was not sufficient to reduce the sulfide concentration during the 24-hour aeration period, since these sulfide doses are much higher than would be expected in actual treatment systems. Therefore, it was deemed necessary to examine the affects of aeration on lower sulfide doses as well.

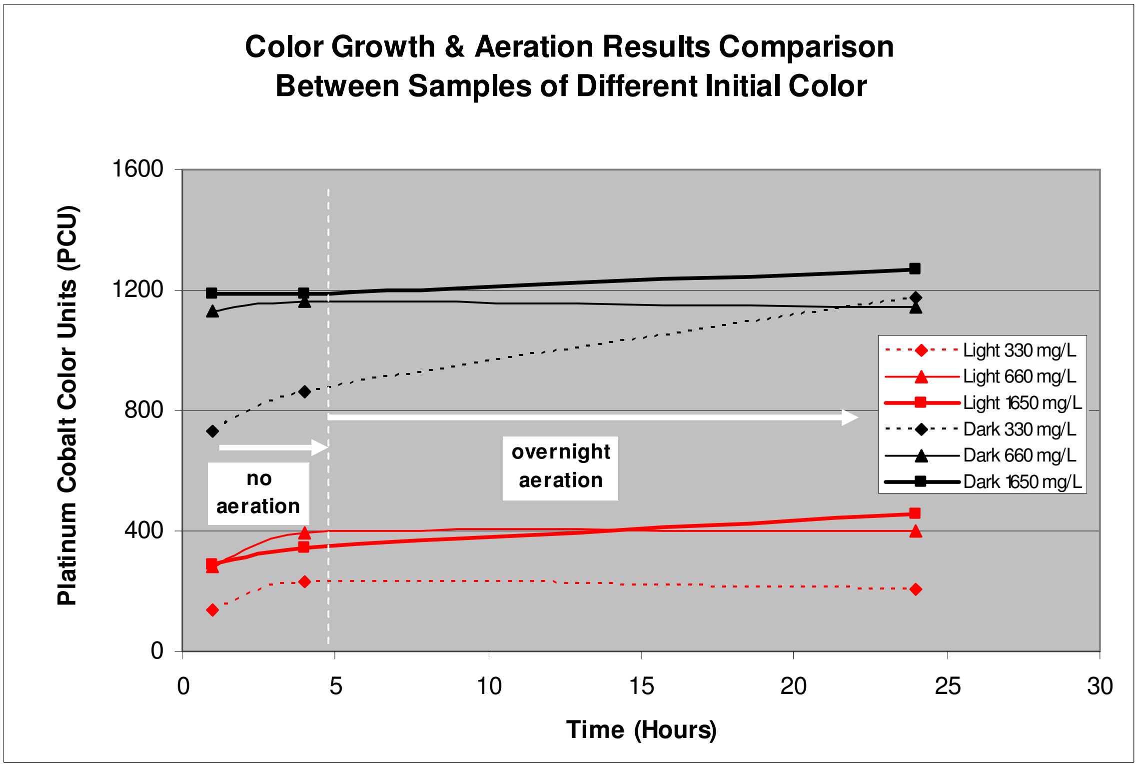

Figure 4.34: Albany, OR Weyerhaeuser and Georgia Pacific Pond 2—Grab 4 Color Reversion / Aeration Results Comparison

Additional aeration tests were performed on these representative samples (the lighter colored sample from the Albany, OR Weyerhaeuser mill (less than 500 PCU) and the darker one from Georgia Pacific (greater than 500 PCU)) in two duplicate trials. For the first run, one-mg/L and 500-mg/L sulfide doses were added to each of the two sample sets (100-mL batches). One hour was allowed to pass before beginning aeration to ensure complete sodium sulfide crystal dissolution and rapid phase color formation.

Aeration was then begun and 10-mL aliquots were taken and tested at the following times (after one, four, and twenty-four hours of aeration and then on each additional day of aeration, ending on the fourth day). The sample with one mg/L of sulfide showed a significant decrease in color during the first 10 hours of aeration. The color increased slightly over the remainder of the aeration period. The 500-mg/L sulfide-treated sample showed a small decrease in color during the first 10 hours of aeration, but thereafter an increase during the remainder of the 4-day aeration experiment (Figure 4.35).

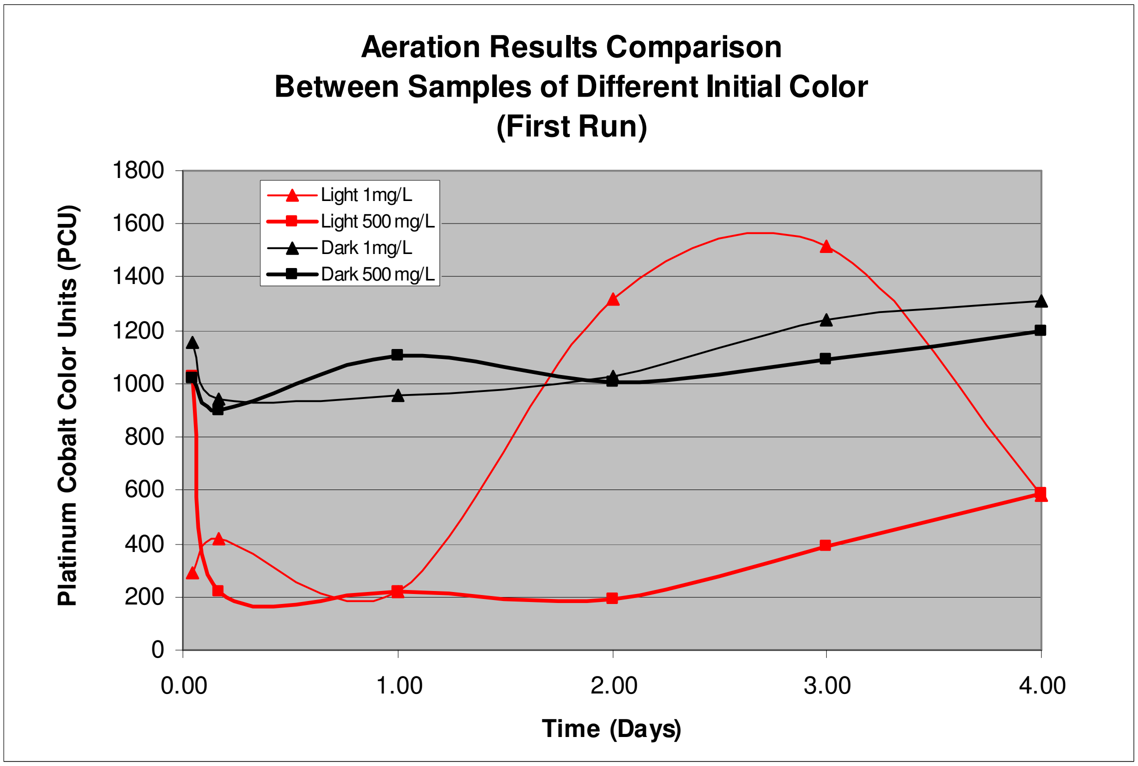

Figure 4.35: Albany, OR Weyerhaeuser and Georgia Pacific Pond 2—Grab 3 Color Reversion / Aeration Results Comparison

It is possible, but unproven, that the aerobic increase of color observed during the experiment reflects aerobic color formation of quinones resulting from catechol compound precursors. The large degree of color growth seen in the one-mg/L dosage for the lighter sample was believed to have been primarily attributable to high turbidity. Over the duration of the experiment it was noted that the sample was increasing in turbidity visibly, and these conspicuous particles were not effectively removed during the vacuum filtration step of analysis. Therefore, the large PCU values for this data set (associated with the one-mg/L light sample) in particular could be influenced by turbidity and not accurately reflect the true color value. Nevertheless, the overall development of color for the samples is noteworthy (Table 4.9).

Table 4.9: Georgia Pacific Aeration—Run 1 Results Summary

ALL VALUES X TIME AFTER AERATION					
Weyerhaeuser (Albany, OR)					
Light Sample*					
Color Results (PCU)					
Sulfide Dosage (mg/L)	**1 hr**	**% Color Change**		**4-day**	**% Color Change**
1	292	0		581	**99**
500	1027	**252**		590	**102**
Georgia Pacific, Pond 2 Grab 3					
Dark Sample					
Color Results (PCU)					
1	1155	0		1309	**13**
500	1023	-11		1200	**4**
Notes:	**High Turbidity, even after filtration for the lighter sample at 1 mg/L of sulfide exposure; it appeared as though precipitation was occurring throughout the aeration duration, specifically at the 2 and 3-day time periods.*				

This experiment was run for comparison purposes, but this time each sample set included a control sample (containing zero sodium sulfide crystals), and also a more frequent sampling schedule was followed during the first day of aeration. Furthermore, the sulfide concentration was measured using gas chromatography (GC) / flame photometric detector (FPD) to establish the actual corresponding sulfide concentration for each color measurement. Aeration was again started after one hour of time was allowed to pass to promote rapid phase color development; thereafter, samples were taken at the start of aeration (at zero hours), at the one-hour mark, after two hours had elapsed, and then on increments of two hours up until 10 hours of aeration had been reached. Subsequent samples were drawn from the aeration batch as before on each successive day up until the fourth day had been attained. During the first 10 hours of aeration, color decreased by the following percentages: 13% for the zero-mg/L sample, 36% for the one-mg/L, and 26% for the 330-mg/L samples (Figure 4.36).

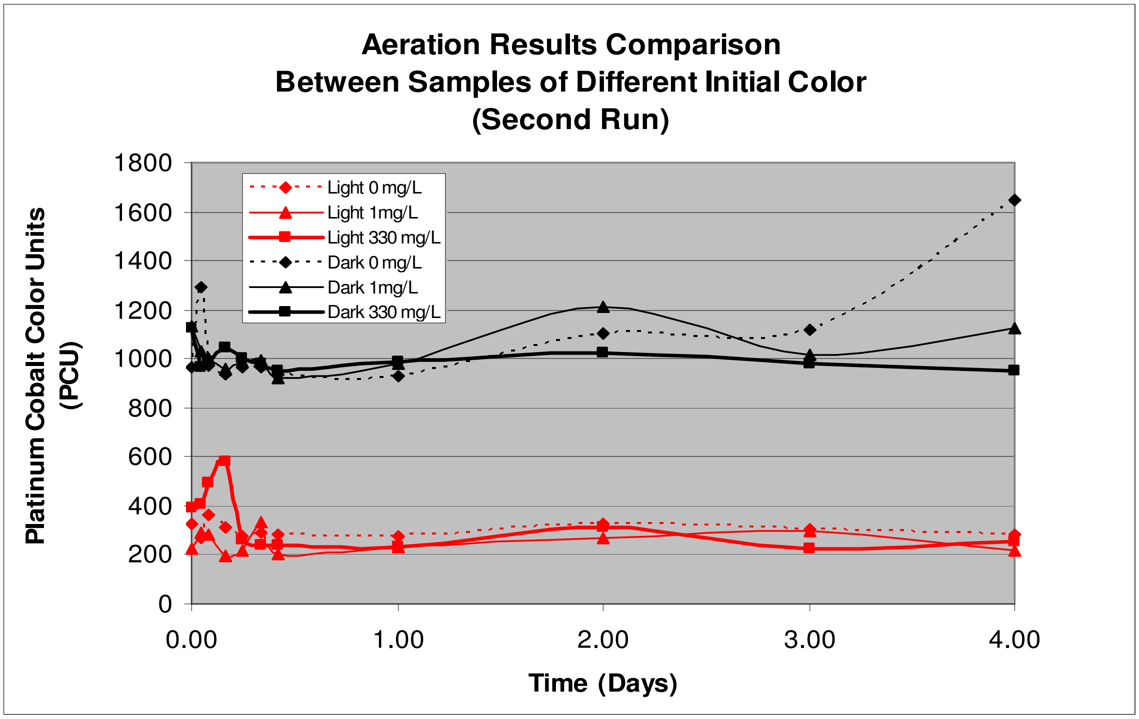

Figure 4.36: Albany, OR Weyerhaeuser and Georgia Pacific Pond 2—Grab 2 Color Reversion / Aeration Results Comparison

These color reductions corresponded to the decreasing sulfide concentration detected by (GC) / (FP) (Table 4.10). Therefore, removal of sulfide by stripping and/or oxidation can reverse the affects of sulfide. Table 4.10 supports this as it displays how after only one day of aeration, all of the sulfide had been removed. Also, note the presence of a small amount of sulfide (2-3 ppm) in the "zero" mg/L samples (no sulfide was added to these samples during experimentation). This suggests the presence of sulfide in both samples initially and further validates the reasoning behind comparing the resulting color changes against the zero-mg/L, zero-hour sample.

Table 4.10: Georgia Pacific Aeration—Run 2 GC/FPD Results Summary

Sample I.D. / Time	Light (0 mg/L)	Light (1 mg/L)	Light (330 mg/L)	Dark (0 mg/L)	Dark (1 mg/L)	Dark (330 mg/L)
0 hr	2.1	3.4	479	3.0	4.7	349
1 hr	1.6	2.5	341	2.2	3.1	290
2 hr	0.4	0.6	138	0.3	0.8	16
4 hr	0.1	0.2	56	0.2	0.3	2.5
6 hr	0	0.1	8.5	0	0.2	0.9
8 hr	0	0	0.7	0	0	0.2
10 hr	0	0	0.3	0	0	0
1 day	0	0	0	0	0	0
2 day	0	0	0	0	0	0

The remaining duration of aeration demonstrated that after sulfide was depleted, color was again reverted. This is likely due to mechanistic aerobic oxidation of catechols to quinones and the oxidation of reduced quinones to more colored oxidized forms as reported by Lange *et al.* (2005) (see Figure 4.37).

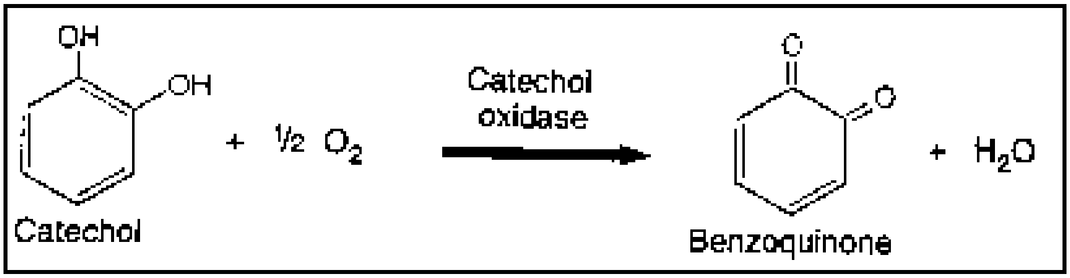

Figure 4.37: Catechol—Quinone Color-Producing Reaction

Therefore, aeration did in fact reverse the effects of sulfide color reversion, but color growth became consequential of other dominant mechanisms. Table 4.11 provides the initial and final color values from the four-day aeration test (second trial). Overall, it appears that aeration has negligible effect on color reversion for the lighter sample, but provided a significant outcome for the darker sample. However, in looking closely at the aforementioned aeration spectrum of color reversion (Figures 4.36 & 4.37), the results were characteristically cyclical in nature and suggested other color mechanisms were at work.

Table 4.11: Georgia Pacific Aeration—Run 2 Results Summary

ALL VALUES X TIME AFTER AERATION				
Weyerhaeuser (Albany, OR)				
Light Sample **Color Results (PCU)**				
Sulfide Dosage (mg/L)	**0 hr**	**% Color Change**	**4-day**	**% Color Change**
0	324	0	283	-13
10	228	-30	220	-32
330	390	**21**	254	-22
Georgia Pacific, Pond 2 Grab 2				
Dark Sample **Color Results (PCU)**				
0	966	0	1645	**70**
10	1130	**17**	1128	**17**
330	1127	**17**	953	-1

Lignin Components Isolation Analysis

As explained in the previous chapters of this thesis, lignin degradation products have been known to highly contribute to color reversion. In order to provide some additional analysis of color reversion regarding the subject sulfide reaction, several solutions were created for color analysis using the same experimental variables as before: sodium sulfide crystal dosages and time, while adding a third factor—solution strength (one-ppm and 50-ppm). Compounds were selected based on their relationship with humic functional groups and included 4-hydroxybenzaldehyde, phenol, vanillin, humic and fulvic acid, catechol, and anthraquinone (as a surrogate for the array of quinones found in color bodies).

The color increases observed for phenol and 4–hydroxybenzaldehyde are close in magnitude to those reported earlier for the sulfide blanks (see Chapter 3) and may not be a result of color development due to sulfide-lignin derivative interactions (Figures 4.38 & 4.39).

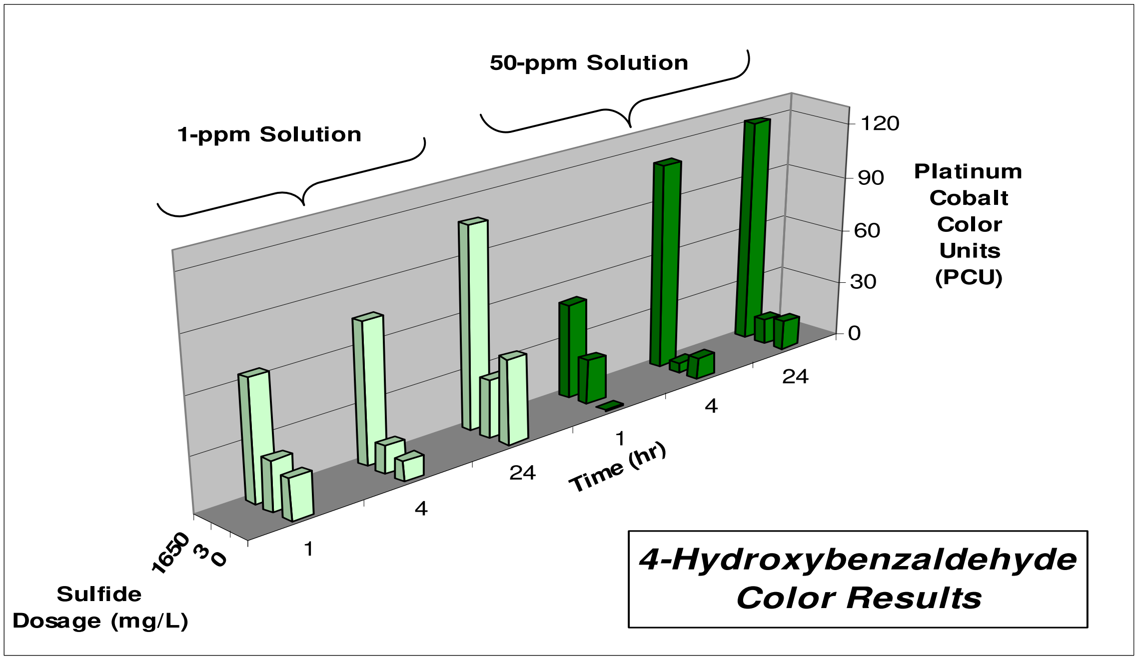

Figure 4.38: 4-Hydroxybenzaldehyde Color Results

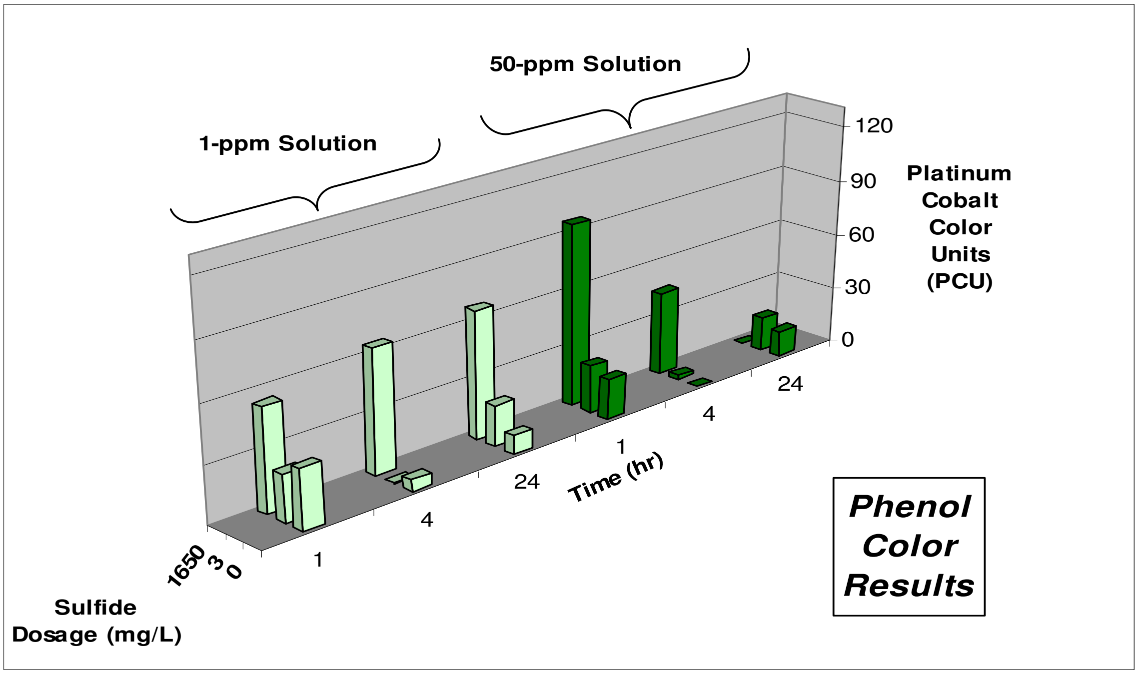

Figure 4.39: Phenol Color Results

Vanillin showed intriguing results. In these samples, as time elapsed, the solutions actually resulted in reduced color (Figure 4.40). The highest color associated with vanillin was its initial hue resulting from the 1,650-mg/L dosage in the 50-ppm solution. Therefore, color mechanisms independent of sulfide appear to be controlling this particular outcome. As a result, no significant connection between vanillin and sulfide color reversion appears to be present.

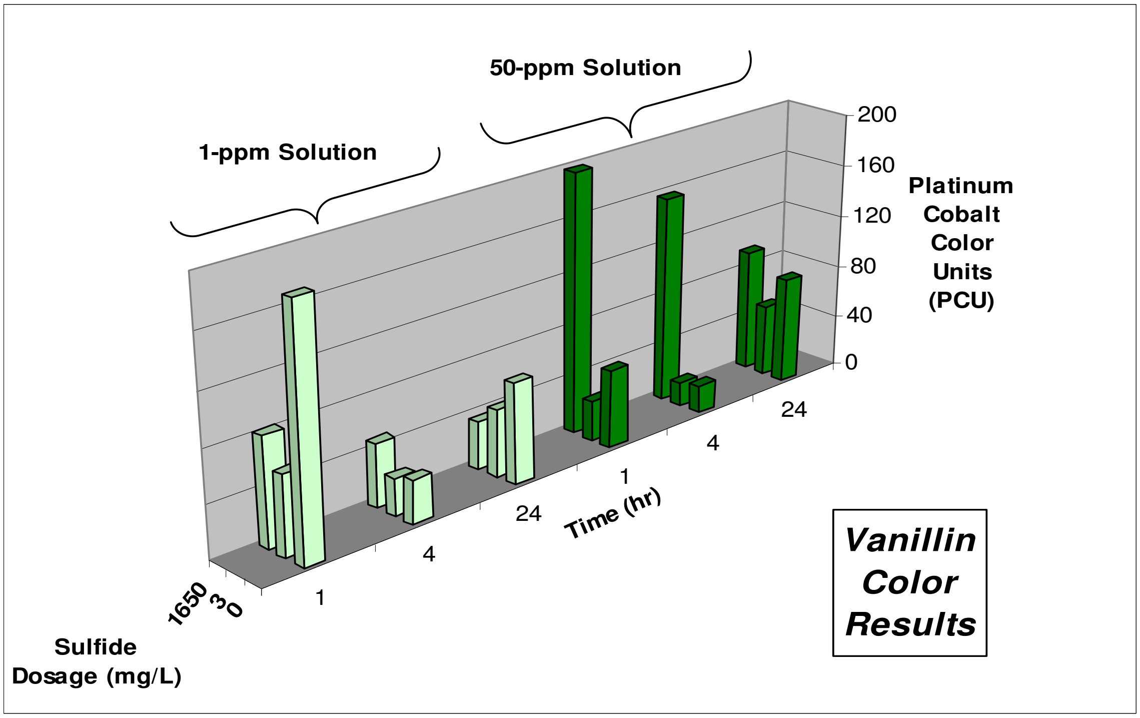

Figure 4.40: Vanillin Color Results

Since humic acids and fulvic acids are the likely products of lignin degradation and have been implicated as chief sources of color in pulp mill wastewater, sulfide studies were conducted on humic and fulvic acid solutions.

Humic acid, being the darker colored humic substance in comparison to fulvic acid, resulted in a greater color effect in the one-ppm solution than for the solution having a 50-ppm concentration. This latter solution strength had such high initial color that it would have been difficult to observe even moderate magnitudes of color change (as was true for highly colored wastewaters) (Figure 4.41). As the amounts of sodium sulfide crystals were increased in the one-ppm solution, the color correspondingly rose. Additionally, for the one-ppm solution, color increased over time as well. The 50-ppm solution reflected a relatively stable color effect with respect to the sulfide doses and time increments. The high initial color present in the 50-ppm solution is believed to have masked any sulfide color reversion.

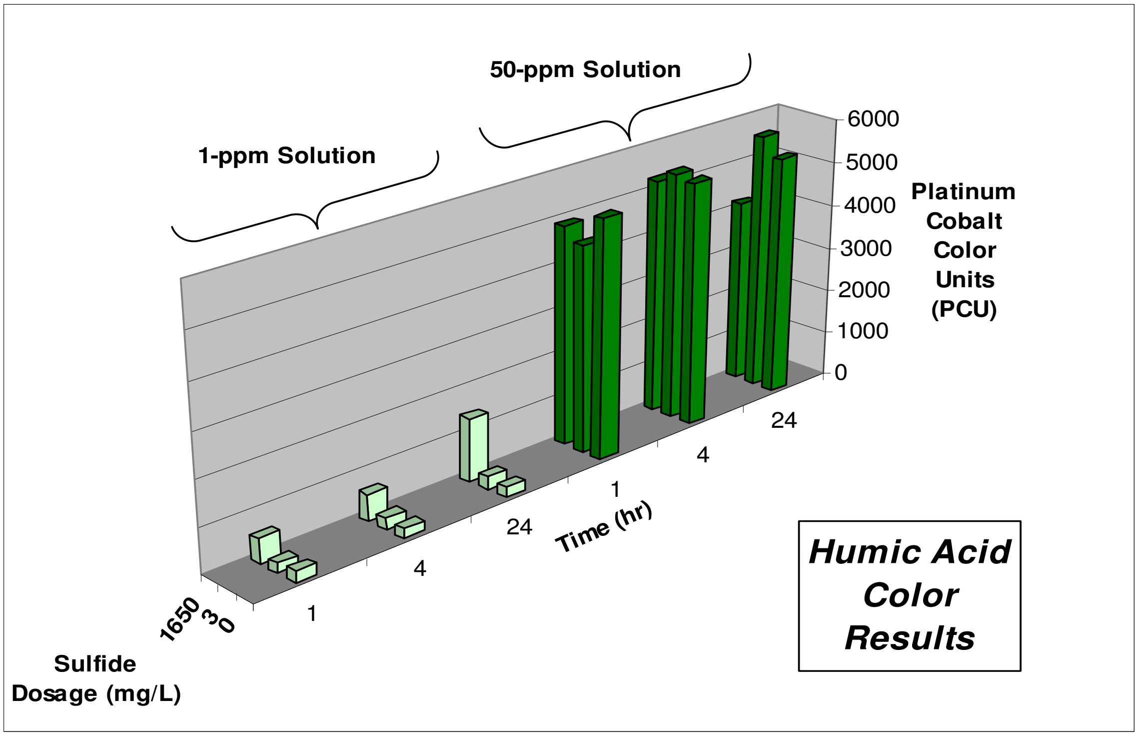

Figure 4.41: Humic Acid Color Results

Fulvic acid yielded a much lower colored solution than the humic acid. For the fulvic acid solution, the experiment resulted in a somewhat different outcome than was given in the analysis of its associated humic substance complement (humic acid). Sulfide contributed to color development with rapid increases of color of 400% being observed for the one percent solution, 60% for the 20% solution, and 30% for the 50% solution (Figure 4.42). Unlike humic acid, for which color development occurred slowly, no additional color increase was observed for fulvic acid after the initial one hour. Trends were proportionally related for the three fulvic acid concentrations.

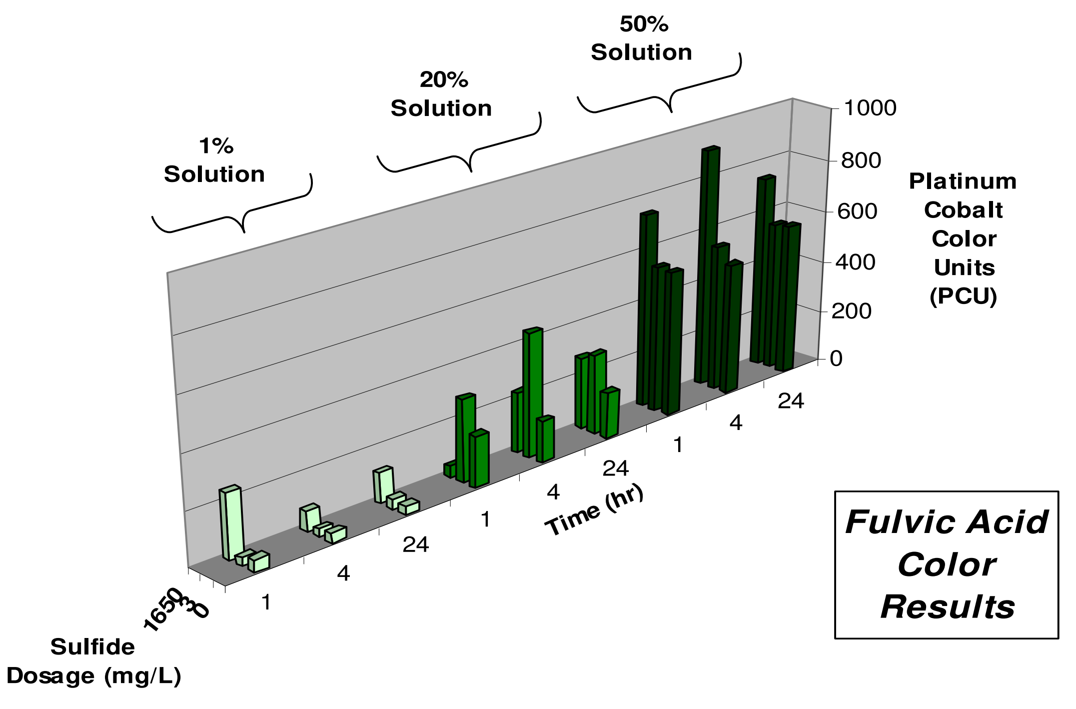

Figure 4.42: Fulvic Acid Color Results

It is imperative to note that both humic and fulvic acids are reported as having large numbers of catechol and quinone functional groups. And as these compounds have been known to contribute significantly to wastewater color, concentrated solutions of catechol and anthraquinone were subsequently tested in order to further isolate the related sulfide color effects.

For the compound catechol, time appeared to be the greatest factor involved in the ultimate development of color. For both catechol concentrations, sulfide addition resulted in minimal rapid color increase, but yielded some slow development color growth. The solution strength did not appear to result in any major differences, except when time was factored in. For the 1650-mg/L, 24-hr, 50-ppm solution, a 20-fold increase of color production resulted, denoted by practically 3,000 PCU in value (Figure 4.43). Additionally, an intense yellow color became visible upon adjusting the pH to 7.6.

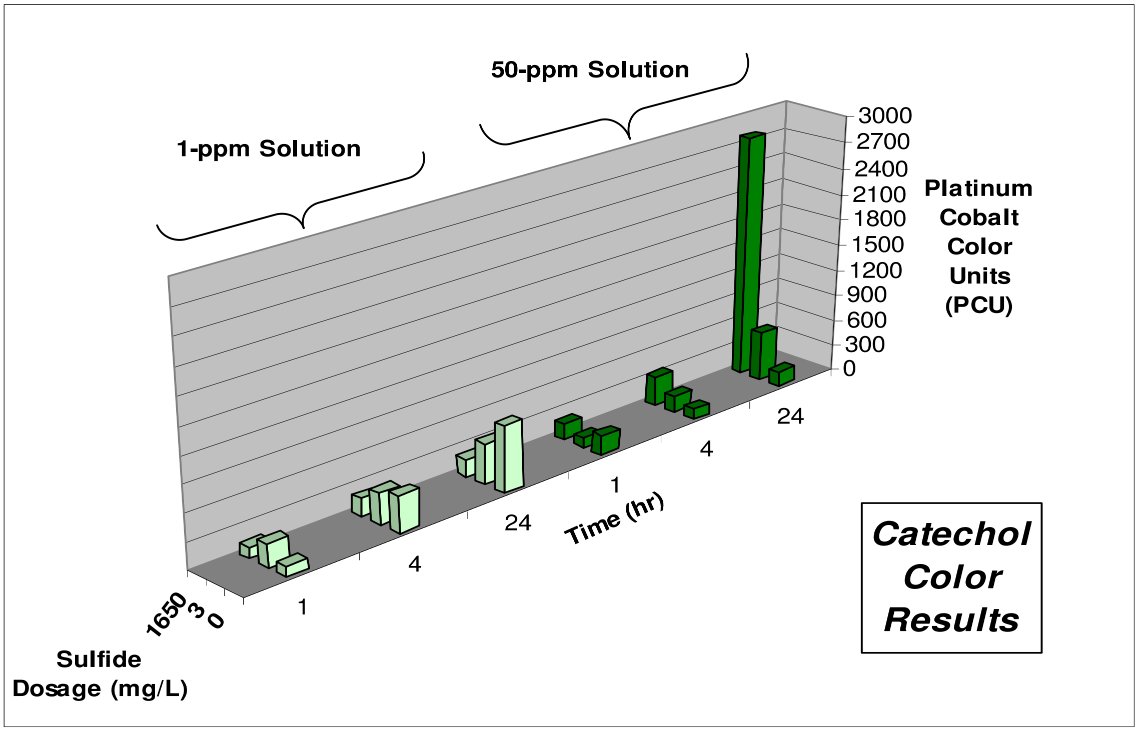

Figure 4.43: Catechol Color Results

Anthraquinone yielded undoubtedly the most extraordinary results of all of the compounds tested during this experimental phase. Time was the key factor in these results as was true for the catechol solutions. Likewise, sulfide interactions and solution strength contributed to the color generation (as the amount of sulfide and anthraquinone went up, so did color) (Figure 4.44). Visually, these solutions actually took on a very different hue than any of the other samples analyzed throughout this thesis. As color grew during this experiment, the solution took on a slightly pinkish color followed by a bright pinkish orange hue and finally to a deep shade of wine red, respective with the time intervals. As shown in Figure 4.44, the presence of sulfide and anthraquinone led to the development of extremely high color in the solution. The measured PCU values of all of the results throughout this investigation only represent the yellow band of color present in these solutions as this wavelength (color) is characteristic of pulp and paper wastewater. Therefore being as high as 2,000 PCU initially for the 1,650-mg/L and then as high as 9,000 PCU after four and 24 hours had elapsed is quite remarkable, considering only a partial color value is thus reported.

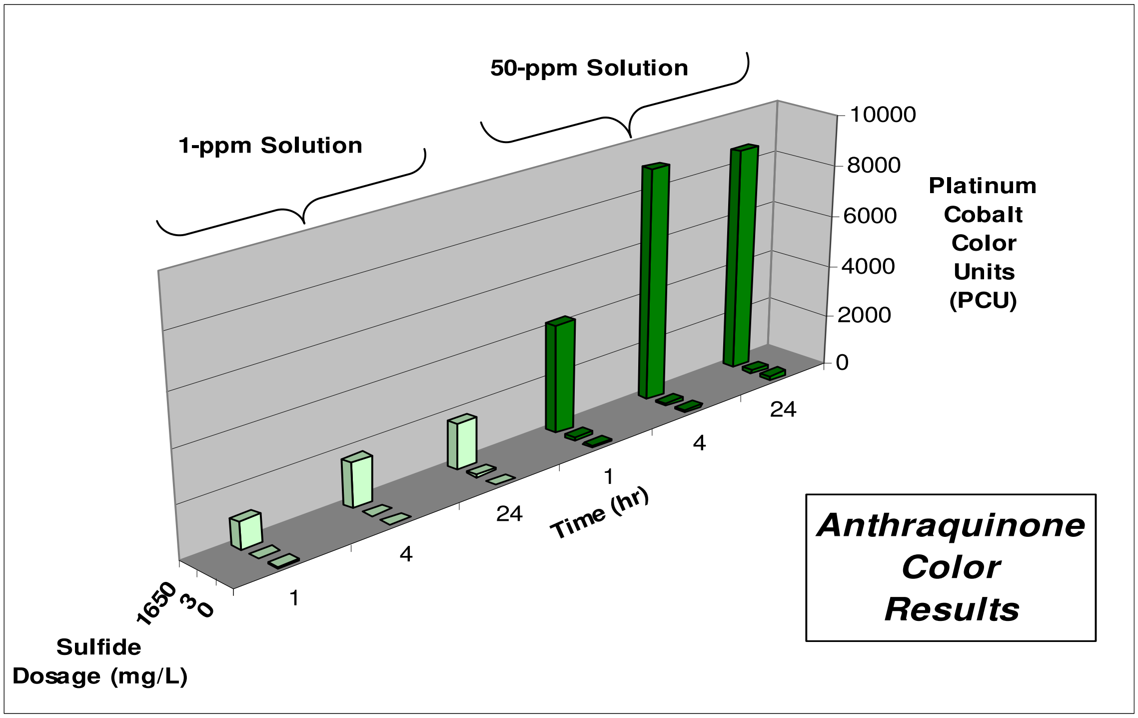

Figure 4.44: Anthraquinone Color Results

Based on the results of the lignin monomer studies, it is apparent that quinones and catechols are the two moieties that are most affected by sulfide color reversion. Therefore, wastewaters containing these compounds have the potential to cause large changes in color upon sulfide exposure (Table 4.12).

Table 4.12: Catechol and Anthraquinone Results Summary

Solution Strength	**Sulfide Dosage**	**Catechol Color Results (PCU)**	
	(mg/L)	**24 hr**	**% Color Change**
1 ppm	**0**	745	**523**
	3	463	**287**
	1650	198	**65**
50 ppm	**0**	177	**48**
	3	565	**373**
	1650	2785	**2229**

Solution Strength	**Sulfide Dosage**	**Anthraquinone Color Results (PCU)**	
	(mg/L)	**24 hr**	**% Color Change**
1 ppm	**0**	11	**-69**
	3	92	**168**
	1650	1726	**4917**
50 ppm	**0**	163	**373**
	3	147	**326**
	1650	8731	**25274**

CHAPTER 5

SUMMARY AND RECOMMENDATIONS

The research presented in this thesis supports the hypothesis that sulfide plays a role in color reversion observed in pulp and paper mill wastewater treatment processes. Color reversion does not appear to be a common subject for research and the mechanisms are poorly understood. The results of this thesis will contribute to the understanding of one aspect of this phenomenon. In this chapter, a summary of the findings along with overall conclusions and recommendations for further work are presented.

Summary

Given the extreme diversity of wastewater, sample-based, specific case-based results need to be sought for accurate inference. The role of sulfide generation in color reversion of treated and untreated paper mill wastewater appears to be important but highly variable. Color reversion was observed to be mediated by sulfide. While some ranges of increases were considerable, sometimes being quadruple of the initial color, other samples showed no increase at all. As such, the degree of sulfide effects differs due to highly variable conditions and wastewaters from mill to mill. The initial color of wastewater appears to have a direct relationship with sulfide color reversion: the lighter the initial wastewater color, the greater the resulting color generation. Additionally, while samples can be variable from process to process, the most significant treatment stages appear to occur earlier on in the wastewater process train (i.e., sewers, primary clarifiers, and ponds).

Additionally, sample color as well as related conditions can be variable with time for the same process – as was seen with the Georgia Pacific samples that were both from Pond 2, but from different collection timeframes. This was attributable to process/equipment changes which therefore needed to be incorporated into the analytical conclusions.

From the other two experimentation results, the aeration and lignin solution color tests, the results successfully provided some insight into these color relationships. Sulfide color reversion appears to be reversible when sulfide is removed by aeration. Quinones and catechols are groups causing color reversion when sulfide is added. This coincides with sulfide addition to humic acid and fulvic acids which also can result in large color increases. Other lignin degradation products that were tested – specifically phenols, vanillin, and 4-hydroxybenzaldehyde – do not contribute much to color and are not significantly affected by sulfide.

As demonstrated by the lignin components isolation analysis, the degradation of lignin can contribute significantly to color depending on the amount at which the derivatives are present in a certain wastewater, the degree of double bond resonance, and the types of related functional groups linked to such compounds. While aeration can reverse the effects of sulfide color reversion, subsequent aerobic mechanisms take over and cause a relapse of color reversion to ensue. In exploring initial color relationships, if a lighter sample is characterized by fulvic acid and a darker sample by humic acid, color growth might only be notable in the lighter sample, as demonstrated by the previously depicted tests results involving synthesized solutions. Yet, as observed, aeration can reverse the effects and cause a recurrence of color in the darker sample. Therefore, many variables need to be considered and factored in when considering color reversion mechanisms. The objective of this thesis seeks to provide meaningful information to aid in the understanding and eventual solution of color reversion. The effects of sulfide on pulp and paper wastewater color reversion are deemed significant, but need to be combined with the other key pieces of the wastewater color puzzle in order to accurately and effectively recognize color generation and eradicate its progression.

In relation to wastewater treatment plants in general, these findings are significant in that they can supplement the understanding of color reversion and the search for its ultimate solution for removal (decolorization). Pinpointing the optimal conditions and environments for color reversion can result in more effective and efficient means for developing and implementing color reduction technologies. Color generation in sewers, primary clarifiers, and anoxic portions of the biological treatment processes can lead to color formation if sulfidogenic activity is present. Additionally, some color decreases in aerobic wastewater treatment processes may be due to stripping/oxidation of sulfide. Furthermore, in shipping/storage of color samples, care should be taken to prevent sulfide generation conditions so that representative and accurate results can be obtained and reported.

Based on the Weyerhaeuser (Albany, OR) color results (refer back to Figure 4.17 and Table 4.7), specific color loadings can be calculated. Based on an initial color value of 200 PCU and a 5.2-mgd flow rate, percentage increases can be linked to consequent color loads (Table 5.1). For every five percent increase in color, close to 200 lbs/day of color would be discharged into nearby receiving water. For a worst case scenario, consequential to spills or equipment failure for example, a 100% color increase could develop which equates to more than 4,000 lbs/day of color that would be discharged into a particular water body, in this case Willamette River.

Table 5.1: Weyerhaeuser—Albany, OR Color Loadings

Color Increase	Color Loading	Δ Color Loading
(%)	(lbs/day)	(lbs/day)
1	8765	87
3	8939	174
5	9112	174
10	9546	434
15	9980	434
20	10414	434
25	10848	434
50	13017	2170
100	17357	4339

Recommendations

In order to solve pulp and paper wastewater color reversion problems, the mechanisms underlying color formation need to be identified and understood. Whether the dominant cause of the color generation is deemed aerobic, anaerobic, and/or sulfide-driven, these factors need to be recognized in order for effective removal applications to be performed. Therefore, it is recommended that several factors undergo testing and analysis to determine and provide more information regarding color reversion.

More knowledge of the sulfur cycle in pulp mill wastewater treatment processes needs to be obtained in order to fully solve the color reversion problem and understand this phenomenon. Additionally, more samples, including mills with sulfite process, coated fiber board processes should be tested for comparison to these results. This request also coincides with the need for temporal studies to be conducted with the purpose of observing color reversion changes as affected by certain seasonal conditions.

Throughout the course of this thesis, better redox control and sulfide measurements during studies was recognized as a potential area for improvement and therefore, should be obtained in further studies. For instance, it should be determined if sulfide decreases over longer time periods can lead to lower color in the 24-hour samples. Moreover, similarities and differences need to be verified for biogenic sulfide production versus sodium sulfide addition. The dissociation of sodium sulfide in water should produce similar ions as observed for biogenic sulfide production, but more support on this topic should be sought.

The time factor needs to be tested more in relation to color change also, including sample shipping time. Additionally, reproducibility studies should be performed numerous times (10-20 trials) to achieve true statistical significance. This could provide more insight into the influence of sample holding time as well.

More kinetic studies should be included in this research topic in order to establish instant or immediate color change–rate models. Additionally, relationships involving nutrient concentrations and compositions should be explored.

Moreover, the results of a study using *P. Flavido-alba* displayed that the highest color reduction occurred when the culture media was low in nitrogen and manganese (Mn (II)) and contained a sufficient amount of glycerol (Pérez *et al.*, 1997). These conditions could be tested for color reversion to determine if the opposite set of parameters holds in the case of color growth. Similarly, additional tests utilizing isolated LiP and MnP could be tested to determine relationships to color growth as was performed for decolorization.

More work with aeration and lignin solutions could be very beneficial work as well. More aeration tests could be conducted to observe optimal parameters and describe more of the role between aeration and sulfide color generation. Another suggested study would be to test various combinations of catechol and anthraquinone with humic substances, as well as with other solutions, in order to further implicate the color relationship to individual lignin components.

Numerous topics could serve as research topics regarding color reversion. In fact, as color generation continues to pose problems, understanding the root cause and identifying a solution could soon become mandatory.

REFERENCES

Amero, B. and Hilleke, J. (1993), Advancement in Effluent Decolorization Using Ozone, 1993 Environmental Conference Proceedings.

Archibald, F. and Roy-Arcand, L. (1995), Photodegradation of High Molecular Weight Kraft Bleachery Effluent Organochlorine and Color. *Wat. Res.*, Vol. 29, No. 2, pp. 661-669, 1995

Bennett, D. J., Dence, C. W., Kung, F.-L., Luner, P., Ota, M., The Mechanism of Color Removal in the Treatment of Spent Bleaching Liquors with Lime, TAPPI, Vol. 54, No. 12, p. 2019, 1971.

Blánquez, P., Caminal, M. Sarra, M., Vicent, M. T., and Gabarrell, X. (2002), Olive Oil Mill Waste Waters Decoloration and Detoxification in a Bioreactor by the White Rot Fungus *Phanerochaete flavido-alba*. *Biotechnol. Prog*. 2002, *18*, 660-662.

Davies, J. S., and Wilson, M. A. (1990), Biological Treatment and Color Reduction in Alberta Bleached Kraft Effluents, 1990 TAPPI Environmental Conference Proceedings.

Dilek, F. B. and Bese, S. (2001), Treatment of Pulping Effluents by Using Alum and Clay – Colour Removal and Sludge Characteristics. *Water SA,* Vol. 27, No. 3, July 2001.

Dilek, F. B., Taplamacioglu, H. M., Tarlan, E. (1999), Colour and AOX removal from pulping effluents by algae. Appl. Microbial. Biotechnol (1999) 52: 585-591.

Georgiou, D., Aivazidis, A., Hatirras, J., Gimouhopoulos, K. (2003), Treatment of Cotton Textile Wastewater Using Lime and Ferrous Sulfate. Water Research 37 (2003) 2248-2250.

Hamman, O. B., Rubia, T. De La, Martínez, J. (1999), Decolorization of Olive Oil Mill Wastewaters by Phanerochaete Flavido-alba. Environmental Toxicology and Chemistry, Vol. 18, Issue. 11, pp. 2410-2415.

Ikehata, K. and Buchanan, I. D. (2000), Colour and Chloride Removal from Pulp Mill Effluent Using Ion-Exchange Resins. Sustainable Forest Management Network Project.

Joyce, T. W., Chang, H.-M., Campbell, Jr., A.G., Gerrard, E. D., and Kirk, T. K. (2002), A Continuous Biological Process to Decolorize Bleach Plant Effluents.

Joyce, T.W. and Petke, W.H. (1983), Effluent Decolorization Technologies for the Pulp and Paper Industry, Water Resource Research Institute of the University of North Carolina

Kemeny, T. E. and Banerjee, S. (1997), Relationships Among Effluent Constituents in Bleached Kraft Pulp Mills. *Wat. Res.* 31(7), 1589-1594.

Lange, C.R. (2004). Aerobic Color Reversion in the Grand Prairie Lagoon System: Final-Report, submitted to Weyerhaeuser, Environmental Technology Center, Federal Way, Washington, December, 2004.

Lange, C. “Color Reversion at the Grand Prairie Mill – Final Report” submitted to Weyerhaeuser, Inc., Federal Way, Washington. January 2005.

Lange, C., Christiansen, J, Rogers, D., and DeWitt, G. “Development of a Biological Color Removal Process for Selected Pulp and Paper Mill Waste Streams. NCASI Effluent Color Management Workshop, Baltimore, Md., March 21, 2005.

Lange, C., Pagoria, P, Lincoln, D, McIlveen, L, “Weyerhaeuser - Grand Prairie Effluent Color Growth”, NCASI Effluent Color Management Workshop, Baltimore, Md., March 21, 2005.

Livernoche, D., Jurasek, L., Desrochers, M., Dorica, J., and Veliky, A. (1983), Removal of color from kraft mill wastewaters with cultured of white-rot fungal and with immobilized mycelium of *Coriolus versicolor*. *Biotechnology and Bioengineering.*

Martín, C. and Manzanares, P. (1994), A Study of the Decolourization of Straw Soda-Pulping Effluents by *Rametes versicolor*. *Bioresource Technology*, Vol. 47, Issue 3, 1994, pp. 209-214.

Nagarathnamma, R. and Bajpai, P. (1999), Decolorization and Detoxification of Extraction-Stage Effluent from Chlorine Bleaching of Kraft Pulp by Rhizopus oryzae. Applied and Environmental microbiology, March 1999, pp. 1078-1082, Vol. 65, No. 3.

National Council for Air and Stream Improvement, Inc. (NCASI). 2000. Methods Manual – NCASI Method Color 253: Color Measurement in Pulp Mill Wastewaters by Spectrophotometry. Research Triangle Park, NC:

National Council for Air and Stream Improvement, Inc.

Paice, M. G. and Jurasek, L. (1983), Peroxidase-catalyzed color removal from bleach effluent.

Pallerla, S. and Chambers, R. P. (1995), New Urethane Prepolymer Immobilized Fungal Bioreactor for Decolorization and Dechlorination of Kraft Bleach Effluents. Vol. 79: No. 5 TAPPI Journal.

Peralta-Zamora, P., de Moraes S. G., Esposito, E., Antunes, R., Reyes, J., Durán, N. (1998), Decolorization of Pulp Mill Effluents with Immobilized Lignin and Manganese Peroxidase from *Phanerochaete chrysoporium*. *Environmental Technology,* Vol. 19, No. 5, 1998, pp. 521-528(8).

Pérez, J., Saez, L., Rubia, T. De La, and Martínez, J. (1998), *Phanerochaete Flavido-alba* Laccase Induction and Modification of Manganese Peroxidase Isoenzyme Pattern in Decolorized Olive Oil Mill Wastewaters. Applied and Environmental Microbiology, July 1998, pp. 2726-2729.

Pérez, J., Saez, L., Rubia, T. De La, and Martínez, J. (1997), *Phanerochaete Flavido-alba* Ligninolytic Activities and Decolorization of Partially Bio-Depurated Paper Mill Wastes. Wat. Res. 31(3), 495-502.

Prasad, D. Y. and Joyce, T. W. (1991), Color Removal from Kraft Bleach-Plant Effluents by *Trichoderma sp.* January 1991 TAPPI Journal.

Roy-Arcand, L., Archibalc, F. S., and Briere, F. (1991), Comparison and Combination of Ozone and Fungal Treatments of a Kraft Bleachery Effluent. September 1991 TAPPI Journal.

Santos, E. B. H. and Duarte, A. C. (1998), The Influence of Pulp and Paper Mill

Effluents on the Composition of the Humic Fraction of Aquatic Matter. *Wat. Res.* Vol. 32, No. 3, pp. 597-608, 1998.

Sharma, C., Mohanty, S. K., and Rao, N. J. (1999), Gas Chromatographic Determination of Pollutants in Kraft Bleachery Effluent from the Eucalyptus Pulp. *Analytical Sciences*, November 1999, Vol. 15, 1115-1121.

Shawwa, A. R., Smith, D. W., Sego, D. C. (2001), Color and Chlorinated Organics Removal from Pulp Mills Wastewater Using Activated Petroleum Coke. *Wat. Res*. Vol. 35, No. 3, pp. 745-749, 2001.

Sjöström, Eero, Wood Chemistry – Fundamentals and Applications, Academic Press: New York, 1981.

Sonnenberg, L.B. and Holmes, J.C. (1998), Physicochemical Characteristics of Dissolved Organic Matter in Untreated and Treated Pulp and Paper Mill Wastewaters. Proceedings 1998 TAPPI International Environmental Conference, Vancouver, BC, April 1998.

Springer, A. M. and Hand, V. C. (1992), Analysis of the Potential of Photochemical and Electrochemical Techniques for Decolorization of Bleached Kraft Mill Effluent, 1992 Environmental Conference Proceedings.

Stephenson, R. J. and Duff, S. J. B. (1996), Coagulation and Precipitation of a Mechanical Pulping Effluent—I. Removal of Carbon, Colour and Turbidity. *Wat. Res*. Vol. 30, No. 4, pp. 781-792, 1996.

Sublette, K. L., Kolhatkar, R., and Raterman, K. (1998), Technological Aspects of the Microbial Treatment of Sulfide-rich Wastewaters: A Case Study. *Biodegradation* **9**: 259-271, 1998

Tarlan, E., Dilek, F. B., and Yetis, U. (2002), Effectiveness of Algae in the Treatment of a Wood-bases Pulp and Paper Industry Wastewater. *Bioresource Technology* 84 (2002), 1-5.

Thorp, D. S., Tieckelmann, R. H., Millar, D. J., and West, G. E. (1995), Chlorine-Free Wet Strength Paper Repulping and Decolorizing with Activated Persulfates, 1995 Papermakers Conference Proceedings.

Yesilada, Ö, Fiskin K., and Yesilada, E. (1995), The Use of White Rot Fungus *Funalia trogii* (Malatya) for the Decolourization and Phenol Removal from Olive Mill Wastewater. *Environmental Technology*, Vol. 16, No. 1, 1995, pp. 95-100(6).

Yin, C.-F., Joyce, T.W., and Chang, H.-M. (1989) Kinetics of Bleach Plant Effluent Decolorization by *Phanerochaete chrysosporium*. *Journal of Biotechnology,* 10, 67-76.

APPENDIX

EXPERIMENTAL DATA

Table A.1: Weyerhaeuser - Grand Prairie, Alberta Results Summary (from 10-ppm Sulfide Solution Doses)

	Weyerhaeuser - Grand Prairie, Alberta											
	Color Results (PCU) from 10-ppm Sulfide Solution Doses											
Sulfide Dosage	**Primary Clarifier Inlet**				**Primary Clarifier Outlet**				**Secondary Effluent**			
(mg/L)	**0 hr**	**1 hr**	**4 hr**	**24 hr**	**0 hr**	**1 hr**	**4 hr**	**24 hr**	**0 hr**	**1 hr**	**4 hr**	**24 hr**
0	886	981	672	392	543	648	597	731	345	474	478	527
0.1	1383	396	954	416	619	593	707	696	461	482	388	517
0.2	728	535	1019	434	601	662	704	711	448	532	423	546
0.4	1100	20	946	418	640	620	697	634	495	529	407	526
0.5	1442	862	636	387	664	593	746	676	467	478	358	575
0.6	1084	1226	922	393	663	668	688	691	425	491	361	549
0.8	1188	683	1033	442	705	648	722	648	534	433	405	567
1.0	905	1006	673	495	675	745	797	712	542	513	395	504
1.5	1104	1121	1169	456	622	676	759	707	471	475	313	411
2.0	1795	1419	872	523	705	780	806	715	537	427	341	505
2.5	1558	1726	1395	553	744	762	855	630	554	484	432	465
3.0	1529	1807	1618	564	740	819	773	680	521	503	354	424
5.0	2017	1824	1858	697	708	984	904	797	736	533	397	893

Table A.2: Weyerhaeuser - Grand Prairie, Alberta Results Summary

(from Crystallized Sulfide and Ammonium Molybdate Treatment)

	Weyerhaeuser - Grand Prairie, Alberta												
	Color Results (PCU) with Ammonium Molybdate												
Sulfide Dosage	**Primary Clarifier Inlet**				**Sulfide Dosage**	**Primary Clarifier Outlet**			**Sulfide Dosage**	**Secondary Effluent**			
(mg/L)	**0 hr**	**1 hr**	**4 hr**	**24 hr**	**(mg/L)**	**1 hr**	**4 hr**	**24 hr**	**(mg/L)**	**1 hr**	**4 hr**	**24 hr**	
0	663	872	2237	1719	**0**	1537	2084	2794	**0**	446	765	641	
2	770	890	2475	1473	**3**	1339	2041	3057	**3**	510	527	457	
5	776	908	2486	1499	**7**	1480	2093	3009	**7**	643	548	388	
10	748	971	2550	1525	**10**	1210	1727	3358	**10**	432	445	335	
12	711	876	1898	1650	**15**	1316	1860	3159	**15**	931	1065	862	
15	680	795	1943	1307	**20**	834	1625	2269	**20**	562	612	394	
20	724	926	2277	1487	**25**	1011	1670	2423	**25**	661	800	357	
25	604	692	1416	1190	**30**	1223	1453	1841	**30**	471	444	342	
40	690	727	1229	1143	**70**	1574	1827	1757	**70**	517	510	341	
50	756	808	1099	881	**170**	1689	2095	1544	**170**	423	442	354	
70	766	816	1165	815	**330**	725	832	707	**330**	553	572	344	
75	723	638	743	930	**660**	906	970	924	**660**	1007	981	1008	
130	482	575	657	536	**1650**	760	1018	974	**1650**	639	824	486	

Table A.3: Weyerhaeuser - Grand Prairie, Alberta Results Summary

(without Ammonium Molybdate, only Crystallized Sulfide Doses)

	Weyerhaeuser - Grand Prairie, Alberta								
	Color Results (PCU) without Ammonium Molybdate								
Sulfide Dosage	**Primary Clarifier Inlet**			**Primary Clarifier Outlet**			**Secondary Effluent**		
(mg/L)	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**
0	872	2237	1719	1537	2084	2794	446	765	641
3	890	2475	1473	1339	2041	3057	510	527	457
7	908	2486	1499	1480	2093	3009	643	548	388
10	971	2550	1525	1210	1727	3358	432	445	335
15	876	1898	1650	1316	1860	3159	931	1065	862
20	795	1943	1307	834	1625	2269	562	612	394
25	926	2277	1487	1011	1670	2423	661	800	357
30	692	1416	1190	1223	1453	1841	471	444	342
70	727	1229	1143	1574	1827	1757	517	510	341
170	808	1099	881	1689	2095	1544	423	442	354
330	816	1165	815	725	832	707	553	572	344
660	638	743	930	906	970	924	1007	981	1008
1650	575	657	536	760	1018	974	639	824	486

Table A.4: Weyerhaeuser – Prince Albert, Saskatchewan Results Summary

	Weyerhaeuser – Prince Albert, Saskatchewan								
	Color Results (PCU)								
Sulfide Dosage	**Primary Pond Inlet**			**Primary Pond Midpoint**			**Primary Pond Outlet**		
(mg/L)	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**
0	432	438	480	300	351	388	355	279	413
3	339	2127	418	378	459	401	408	395	449
7	339	405	429	405	428	386	526	463	481
10	317	442	369	495	535	557	369	359	397
15	361	615	408	416	438	402	391	375	405
20	428	449	426	389	414	372	390	372	464
25	417	449	527	475	417	381	397	364	457
30	387	526	327	402	425	409	410	382	733
70	368	475	413	393	402	396	389	358	451
170	673	728	368	1501	584	419	402	403	474
330	800	253	420	606	503	408	401	616	379
660	584	587	206	294	284	239	416	568	564
1650	1303	1487	383	1251	339	229	599	692	460

Table A.5: Weyerhaeuser – Johnsonburg, PA Results Summary (from 10-ppm Sulfide Solution Doses)

Weyerhaeuser - Johnsonburg, PA

Color Results (PCU) from 10-ppm Sulfide Solution Doses

Sulfide Dosage	**Pulp Sewer**				**Settling Pond Feed**				**Aeration Pond Feed**				**Final Discharge**			
(mg/L)	**0 hr**	**1 hr**	**4 hr**	**24 hr**	**0 hr**	**1 hr**	**4 hr**	**24 hr**	**0 hr**	**1 hr**	**4 hr**	**24 hr**	**0 hr**	**1 hr**	**4 hr**	**24 hr**
0	115	369	167	398	560	533	331	593	407	455	460	752	443	438	506	437
0.1	270	925	243	1228	855	647	719	913	673	593	603	731	501	471	520	440
0.2	364	802	350	1303	994	733	1089	1227	611	536	415	423	527	582	599	497
0.4	443	731	395	1145	851	456	1015	1197	448	357	323	529	545	611	607	517
0.5	192	689	167	981	906	778	1025	1451	455	409	310	480	528	582	722	538
0.6	158	666	224	1029	1014	740	1041	1263	348	322	357	484	482	634	735	565
0.8	120	724	273	1058	783	948	1090	1127	324	385	328	389	565	685	829	658
1.0	202	612	433	1123	941	648	1206	1003	398	415	370	465	549	505	865	646
1.5	416	812	754	984	1045	495	1297	1419	422	361	370	413	456	499	679	593
2.0	436	547	372	1363	836	553	1410	1120	509	339	334	412	444	489	760	489
2.5	664	616	578	1083	998	779	1172	1173	454	377	349	375	534	508	671	918
3.0	459	608	668	1071	1044	833	1303	1172	532	447	432	450	473	436	449	1238
5.0	625	705	626	1146	916	700	1399	1286	614	492	436	853	665	435	694	1223

Table A.6: Weyerhaeuser – Johnsonburg, PA Results Summary (from Crystallized Sulfide Doses)

	Weyerhaeuser - Johnsonburg, PA									
	Color Results (PCU)									
Sulfide Dosage	**Pulp Sewer**			**Settling Pond Feed**			**Aeration Pond Feed**		**Final Discharge**	
(mg/L)	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**24 hr**	**1 hr**	**24 hr**
0	224	253	153	640	759	572	580	480	470	548
3	145	222	98	762	731	977	333	408	707	396
7	246	248	147	719	727	729	599	511	437	385
10	202	231	224	752	767	793	492	379	666	424
15	381	221	121	798	748	853	599	464	906	386
20	219	227	153	834	761	834	343	719	819	404
25	220	170	187	953	826	957	324	769	871	421
30	203	177	496	850	740	917	363	569	683	613
70	198	321	236	765	1048	472	302	366	477	580
170	408	261	228	186	1066	552	351	186	495	352
330	632	535	305	431	903	869	297	259	325	244
660	449	421	288	407	502	213	306	194	340	1016
1650	650	714	621	393	532	551	351	252	443	458

Table A.7: Weyerhaeuser – Albany, OR Results Summary

Weyerhaeuser (Albany, OR) Color Results (PCU)			
Sulfide Dosage	**Mixed Sample (different grab points)**		
(mg/L)	**1 hr**	**4 hr**	**24 hr**
0	191	192	239
3	232	267	443
7	230	279	381
10	248	280	401
15	244	223	339
20	239	240	400
25	258	248	297
30	281	303	266
70	282	289	400
170	473	412	442
330	344	372	327
660	580	449	271
1650	281	374	378

Table A.8: Rayonier Results Summary (from 10-ppm Sulfide Solution Doses)

	Rayonier																			
	Color Results (PCU) from 10-ppm Sulfide Solution Doses																			
Sulfide Dosage	(Before) Primary Clarifier				Strong Pond Influent				Strong Pond Effluent				ASB #1 Effluent				ASB #2 Effluent			
(mg/L)	0 hr	1 hr	4 hr	24 hr	0 hr	1 hr	4 hr	24 hr	0 hr	1 hr	4 hr	24 hr	0 hr	1 hr	4 hr	24 hr	0 hr	1 hr	4 hr	24 hr
0	1119	1121	997	1048	1181	1021	1383	1252	2404	3091	3546	4236	1507	1436	1419	1443	2081	2031	2087	2103
0.1	1373	1145	1114	925	1099	1075	1454	1349	2909	3138	3742	4622	1475	1500	1299	1539	2172	2051	2261	2375
0.2	1322	1277	1225	1191	1163	1135	1306	1209	3080	3141	3691	5589	1446	1477	1477	1396	2141	2197	2293	2205
0.4	1218	1148	1130	1128	1154	1373	1398	1172	3143	4835	3696	4609	1553	1574	1568	1443	2127	2143	2500	2154
0.5	1914	1078	1132	1043	1132	1199	1303	1304	3083	3469	3875	4161	1583	1481	1372	1529	2119	2093	2107	2267
0.6	1115	1031	1674	1077	1167	1479	1332	1174	3238	3520	3787	4139	1558	1436	1474	1433	2226	1945	2104	2060
0.8	1159	1074	1463	1024	1208	1340	1237	1134	3232	3528	3734	4494	1493	1534	1490	1392	2200	2286	2084	2242
1.0	1196	1133	1203	1026	1139	1104	1360	1109	2539	3501	3770	4064	1499	1507	1492	1472	2107	2114	1850	1738
1.5	1277	1134	1256	1096	1269	990	1354	1200	3249	3855	3942	5294	1466	1436	1452	1506	2110	1972	2221	1971
2.0	1572	1050	1043	1153	1350	1195	1323	1068	3177	3381	3932	5044	1469	1370	1493	1328	2282	2408	2089	2167
2.5	1104	1183	1270	1127	1119	1125	1358	1270	3104	3687	3915	4022	1444	1320	1510	1449	2167	2116	2397	2254
3.0	1225	1287	1255	1063	1292	1276	1345	1392	3179	3534	3979	5195	1476	1340	1491	1263	2005	2097	1997	2294
5.0	1389	1789	2351	1084	1412	1394	1323	1505	3117	3393	3722	4367	1546	1461	1487	1372	2105	2259	2143	2107

Table A.9: Rayonier Results Summary (from Crystallized Sulfide Doses)

	Rayonier														
	Color Results (PCU) from Crystallized Sulfide Doses														
Sulfide Dosage	**(Before) Primary Clarifier**			**Influent (Pond)**			**Effluent (Pond)**			**Effluent ASB #1 (Pond)**			**Effluent ASB #2 (Pond)**		
(mg/L) (or ppm)	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**
0	1018	1069	1028	1368	1143	1230	2198	2058	2074	1552	1371	1595	3519	4747	3718
3	1054	946	1080	1177	1175	1381	2232	2054	2158	1499	1516	1440	3351	3871	4223
7	978	1008	1104	1272	1079	1328	2236	2178	2197	1491	1303	1496	3533	3988	3911
10	1121	966	1372	1412	1229	1423	2206	2155	2126	1470	1380	1512	3198	3866	4006
15	1051	767	1140	1385	1290	1451	2187	2102	2147	1441	1471	1481	3456	4237	3950
20	906	957	1087	1369	1230	1484	2042	2077	2181	1470	1468	1466	3183	4037	3980
25	920	888	1312	1301	1243	1338	2108	2130	2201	1392	1448	1482	3318	4091	3840
30	939	863	1228	1247	1203	1429	2090	2106	2140	1243	1479	1457	2830	3904	4227
70	1174	909	1204	1218	1144	1287	1977	2098	2148	1226	1383	1711	3026	3602	3407
170	1507	772	969	1143	1014	1277	1881	2000	2052	1155	992	1354	2396	3565	2800
330	925	1236	760	969	1238	1069	1629	2000	1985	977	1066	1308	2377	3319	2852
660	1401	1087	905	1378	1419	1034	1819	1700	1814	1137	1169	1140	1105	2422	1886
1650	1618	1273	965	792	1035	1101	1230	1718	1857	1124	1118	1200	1968	3315	2362

Table A.10: Georgia Pacific Results Summary (First Sample Set)

Georgia Pacific								
Color Results (PCU)								
Sulfide Dosage	Pond 1		Pond 2		Pond 3		Pond 4	
(mg/L)	1 hr	24 hr	1 hr	24 hr	1 hr	24 hr	1 hr	24 hr
0	1160	1165	1324	1342	1490	1240	1348	1456
5	1173	1347	1164	1355	1283	1199	1187	1207
10	1167	1370	1067	1298	1221	1132	1169	1178
20	1155	1205	1149	1259	1246	1157	1165	1175
25	1151	1259	1134	1237	1213	1200	1141	1193
250	1286	1173	947	1244	910	1119	830	1187
500	1574	1700	1558	1412	1308	890	1201	1083
2500	1672	1798	1618	1677	1923	2418	2397	2933

Table A.11: Georgia Pacific Results Summary (Second Sample Set)

	Georgia Pacific					
	Color Results (PCU)					
Sulfide Dosage	**Pond 2 Grab 1-Run 1**		**Pond 2 Grab 1-Run 2**		**Pond 2 Grab 1-Run 3**	
(mg/L) (or ppm)	**1 hr**	**24 hr**	**1 hr**	**24 hr**	**1 hr**	**24 hr**
0	1197	1150	1198	1203	948	828
5	1336	1298	1252	1244	1247	1200
10	1393	1289	1240	936	1259	1222
20	1119	1131	1214	1194	1320	1213
25	1239	1189	1206	1240	1216	1203
500	767	995	937	986	822	831
990	1050	1208	912	1164	1099	1112
2500	1094	1219	896	1089	1025	927

Table A.12: Georgia Pacific Results Summary (Second Sample Set-continued)

	Georgia Pacific								
	Color Results (PCU)								
Sulfide Dosage	**Pond 2 Grab 2**			**Pond 2 Grab 3**			**Pond 2 Grab 4**		
(mg/L) (or ppm)	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**
0	1115	1120	1211	1089	1065	959	1174	872	925
3	1127	1159	1186	1256	1300	1178	1301	1088	1225
7	1127	1181	1240	1332	1470	1221	1258	1177	1246
10	1403	1450	1326	1287	1546	1369	1238	1195	1163
15	1311	1542	1435	1133	1180	1151	1300	1177	1236
20	1169	1150	1244	1105	1457	1300	1269	1176	1215
25	1229	1343	1385	1120	1482	1390	1240	1195	1206
30	1170	1337	1371	1098	1370	1400	1211	1137	1190
70	1121	1193	1258	981	1310	1206	1152	1133	1319
170	1174	1234	1503	1133	1326	1232	1140	1302	1225
330	779	1136	793	1043	884	1248	1190	1124	1139
660	924	1002	1080	819	1066	1092	1244	1262	1352
1650	832	883	977	835	1126	936	1311	1293	1370

Table A.13: Aeration Analysis (24-hour)

	Aeration Analysis					
	Color Results (PCU)					
Sulfide Dosage	**"Light" Sample**			**"Dark" Sample**		
(mg/L) (or ppm)	**1 hr**	**4 hr**	**24 hr (overnight aeration)**	**1 hr**	**4 hr**	**24 hr (overnight aeration)**
330	135	229	204	732	861	1173
660	284	393	402	1132	1161	1146
1650	288	343	458	1185	1190	1270

Table A.14: Aeration Analysis (4-day, Run 1)

	ALL VALUES X TIME AFTER AERATION					
	Weyerhaeuser (Albany, OR)					
	Light Sample					
Sulfide Dosage	**Mixed Sample (different grab points)**					
(mg/L) (or ppm)	**1 hr**	**4 hr**	**24 hr**	**2 day**	**3 day**	**4 day**
1	292	420	217	1317	1520	581
500	1027	217	221	194	391	590
	Georgia Pacific, Pond 2 Grab 3					
	Dark Sample					
1	1155	945	957	1025	1240	1309
500	1023	900	1103	1006	1088	1200

Table A.15: Aeration Analysis (4-day, Run 2)

	ALL VALUES X TIME AFTER AERATION										
	Weyerhaeuser (Albany, OR)										
	Light Sample										
Sulfide Dosage	**Mixed Sample (different grab points)**										
(mg/L) (or ppm)	**0 hr**	**1 hr**	**2 hr**	**4 hr**	**6 hr**	**8 hr**	**10 hr**	**1 day**	**2 day**	**3 day**	**4 day**
0	324	269	363	314	278	289	281	277	325	304	283
1	228	289	287	196	219	334	205	231	271	294	220
330	390	403	496	579	262	237	238	231	314	228	254
	Georgia Pacific, Pond 2 Grab 2										
	Dark Sample										
0	966	1290	972	939	967	967	936	926	1104	1119	1645
1	1130	1033	1004	959	991	991	925	980	1210	1017	1128
330	1127	964	986	1046	1005	982	950	987	1025	982	953

Table A.16: Lignin Components Isolation Analysis

	Lignin Components Isolation Analysis									
	Color Results (PCU)									
Solution Strength	**Sulfide Dosage**	**4-Hydroxybenzaldehyde**			**Phenol**			**Vanillin**		
	(mg/L) (or ppm)	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**
1 ppm	**0**	22	11	46	32	6	10	187	33	77
	3	26	15	31	25	0	22	61	28	51
	1650	64	75	108	54	65	68	82	48	36
50 ppm	**0**	1	12	16	22	-3	14	59	21	81
	3	24	5	14	25	3	18	31	19	55
	1650	51	112	122	96	45	-6	198	158	94

Table A.17: Lignin Components Isolation Analysis (continued)

	Lignin Components Isolation Analysis									
	Color Results (PCU)									
Solution Strength	**Sulfide Dosage (mg/L) (or ppm)**	**Catechol**			**Anthraquinone**			**Humic Acid**		
		1 hr	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**	**1 hr**	**4 hr**	**24 hr**
1 ppm	**0**	120	414	745	34	9	11	239	222	232
	3	259	353	463	35	10	92	213	266	294
	1650	126	198	198	1025	1712	1726	543	591	1410
50 ppm	**0**	225	121	177	86	112	163	5335	5463	5394
	3	113	197	565	102	79	147	4617	5546	5786
	1650	193	338	2785	4181	9008	8731	4918	5258	4132

Table A.18: Lignin Components Isolation Analysis (continued)

Lignin Components Isolation Analysis				
Color Results (PCU)				
Solution Strength	**Sulfide Dosage**	**Fulvic Acid**		
	(mg/L) (or ppm)	**1 hr**	**4 hr**	**24 hr**
1%	**0**	46	38	32
	3	30	29	37
	1650	241	74	114
20%	**0**	194	157	174
	3	312	470	301
	1650	44	225	272
50%	**0**	552	504	579
	3	556	556	574
	1650	738	911	738