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Optimization and Dynamic Control

of the Coagulation Process

in Water Treatment

by

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TECHNICAL COMPLETION REPORT

Water Resource Research Center University of New Hampshire Durham, New Hampshire

May, 1983

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CHAPTER 1

INTRODUCTION

Surface waters commonly serve as a community's water supply. One characteristic of such waters is the presence of sediment and small suspended particles, as well as natural organic materials called humic substances. A more critical characteristic, as far as the treatment of such waters is concerned, is the dynamic quality of their concentrations. Figures 1 and 2 depict the nature of the time dependence of color and turbidity. One major portion of this research work is to describe the development of a control strategy for treatment of waters with dynamic characteristics such as displayed here. The other major portion describes the characteristics for obtaining maximum color and turbidity removal from water. The effects of chemical dose, pH, temperature, and mixing were investigated.

The treatment process of coagulation-flocculation, sedimentation, and filtration are relied upon for removal of both particulate material and humic substances. Coagulation-flocculation refers to the destabilization of individual particles and subsequent aggregation to a degree whereupon gravitational settling may occur. Filtration serves as a final polishing step.

The occurrence of natural color in surface waters is prevalent throughout New England. When these surface waters, mostly lakes and impounded reservoirs, are used as water supplies, coagulation of color and turbidity becomes a concern to the treatment plant operator. This system was chosen as a topic for research for several reasons: the operational complexity associated with treatment of waters containing color should be better understood, there is a need for a simple cost effective control strategy for treating surface waters, and there is a widespread regional relevance of this problem to New England because there are many small New England communities that operate facilities that treat surface water displaying the temporal variations as shown in Figures 1 and 2.

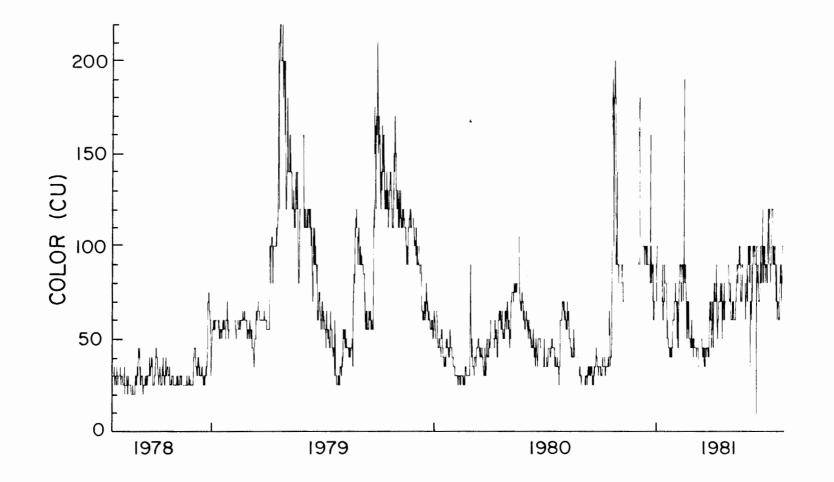
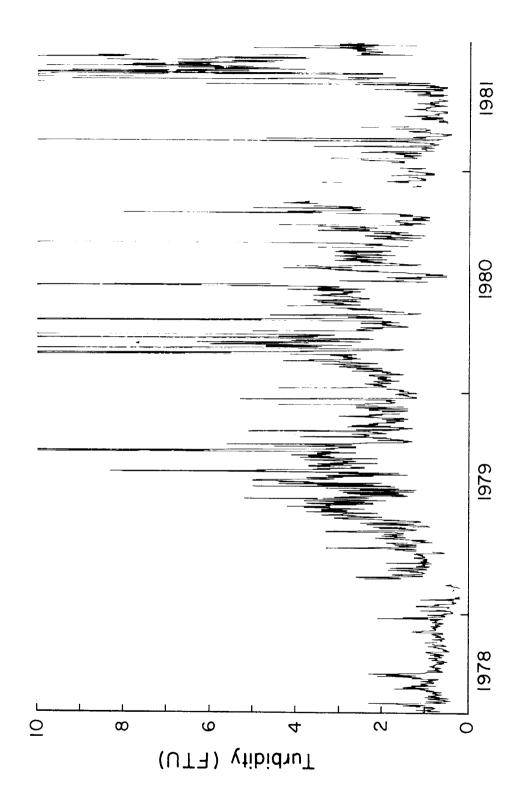
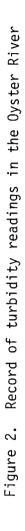


Figure 1. Record of apparent color readings in the Oyster River

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Coagulation is utilized for the removal of both inorganic particulate material as well as humic substances. However, the physical-chemical mechanisms by which these contaminants are removed by coagulation and subsequent processes are quite different. The work reported herein considered the removal of natural mixtures of humic substances and turbidity with aluminum sulfate or alum, $Al_2(SO_4)_3 \cdot 18H_2O$, used as a coagulant chemical. In addition, time series analysis is used to identify the mathematicalmodel that describes the temporal behavior of the data. This model will be incorporated into a control strategy for achieving maximum color and turbidity. The effectiveness of the dynamic control strategy is reported in terms of cost of treatment and the likelihood the method will improperly forecast the proper chemical dose for effective particulant and color removal, or in other words the risk of underdosing.

A case study of the Oyster River in Durham, New Hampshire was undertaken. The dynamic characteristics and water quality of this river is typical of the surface waters serving many communities in New England. The water from the Oyster River is treated at Arthur Rollins Treatment plant, which serves the population of approximately 8000 permanent residents and a student population of 10,500 who attend the University of New Hampshire. The methods and procedures described in this report, however, are applicable to other areas using surface water as a water supply.

CHAPTER 2

RESEARCH OBJECTIVES

The purpose of this research is two fold: to improve the operation of the coagulation process in water treatment and to reduce the chemical costs associated with this process while assuring safe drinking water is supplied to the public.

The primary reason for conducting this research is economic. It has recently been demonstrated that close operational control of the coagulation process results in cost savings because of more efficient use of chemicals (Manning, 1977). The practice of overdosing of coagulants to insure finished water quality is all to often a result of a lack of operator training and good operational procedures and practices. The major objective is to provide a basis for closer operational control. The features of simplicity for the operator and the assurance that finished water quality control is being delivered at all times are inherit in the dynamic control strategy presented herein.

The present method of control of the coagulation process is based upon the use of the jar test in which varying amounts of treatment chemicals are added to samples of raw water. The resultant settling action and treatment efficiency are noted and serve as a starting point for adjustment of actual plant dosages. The jar test is a laboratory model for the coagulation, flocculation, and sedimentation processes and its limitations are well recognized (Litwin, 1974). The hydraulic conditions occurring within the plant and those in the jar test are usually very dissimilar. This can easily explain the often poor prediction of plant treatment performance by jar tests.

The method of control of coagulation proposed herein is intended to drastically reduce the need for reliance on jar tests for operational control.

Instead, routine water quality tests, pH, alkalinity, color, turbidity, and temperature become the basis for operational control. Our experimental results show that raw water color is the leading indicator for the dynamic control strategy. The time required for analytical work necessary for operational control is reduced and simplified, and the operator need not understand either the intricacies of the coagulation process or the statistical techniques upon which the control strategy is based.

The frequency at which water quality tests and chemical dosage is adjusted will have bearing upon the risk of underdosing and economics. The potential for adaptation to automatic control is immediately obvious and should not be overlooked. However, our work is directed at smaller treatment plants, where funds for automatic control equipment are assumed to be unavailable. The training and abilities of water treatment plant operators is often seriously lacking. The Community Water Supply Survey (U.S. Public Health Service, 1970) noted that two thirds of all operators had no formal training. This research would not increase the training of operators but would significantly simplify the operational control of the coagulation process especially in smaller plants. The majority of communities in New England rely on smaller water utilities for their water. In New Hampshire, there are a total of 107 water treatment plants with 53 plants treating surface waters. Of the surface water treatment plants, 42 serve communities with less than 10,000 people and only two have populations greater than 60,000. It can be seen that most of the systems are very small and operation in these plants may be intermittent and probably substandard. Similar situations certainly exist throughout many sections of New England.

Humic substances derive from the natural degradation of lignins and other organic material and include a broad class of chemical compounds, many of which have yet to be identified. Fulvic acid is a generic term for the low molecular

weight, acid soluble fraction of humic substances and has been shown to be the major fraction of humic substances in water. These compounds give rise to the yellow brown color of many natural waters. Aesthetics and public health regulations require the effective removal of color and turbidity. There is no evidence to suggest that either color or turbidity alone cause a health hazard; however, bacteria and viruses are a health hazard and may be protected from the disinfection process when caught in the interstices of turbid material.

The research does have a related health impact in that application of chlorine to waters containing particulate or soluble organic matter, especially fulvic acid, which results in the formation of a class of compounds called trihalomethanes, mostly chloroform. These compounds are suspected human carcinogens whose health effects are currently being assessed by health and regulatory agencies. The optimization of the coagulation process under all conditions is a key ingredient in the strategy for control of the formation of these compounds (Stevens, et al, 1976). The most practical means of reducing these hazards is to remove as much color and turbidity from the water as possible prior to chlorination or disinfection.

CHAPTER 3

AN OVERVIEW

A schematic diagram of a typical water treatment plant is presented in Figure 3. Chemicals for coagulation are usually added in a rapid mix tank and the water continuously flows through the remaining treatment tanks. The typical operation of the coagulation process involves the addition of a chemical coagulant, usually aluminum and ferric salts. Aluminum sulfate or alum, $Al_2(SO_4) \cdot 18H_2O$, is used in our studies. The plant is assumed to utilize surface water as its raw water supply and to employ the treatment processes of coagulation, sedimentation, and filtration for color and turbidity removal. The raw water from the Oyster River entering the Arthur Rollins Treatment plant was monitored for a three year period at twelve hour intervals. These data are typical of the low turbidity surface waters found in New England. See Figure 1 and 2. The watershed is a rural area with a small population containing fields for apple farming and woods for recreation.

The coagulation process is quite complex and not easily amendable to theoretical formulation. For instance, researchers have found that the control of pH is important in the color removal process. In a typical plant however, operators do not usually control pH carefully. The time variant properties of raw water, as depicted in Figures 1 and 2, make close control difficult. Jar tests are normally used to determine chemical dosages at most treatment plants. They are time consuming and require the presence of an operator. As a result, many believe that overdosing of treatment chemicals occurs for substantial periods of plant operation. The practice of overdosing results in greater operating costs. Obviously, overdosing is a costly practice; however, it does avoid the risk of possibly underdosing. However it may not assure the delivery of water of good quality. Recent research

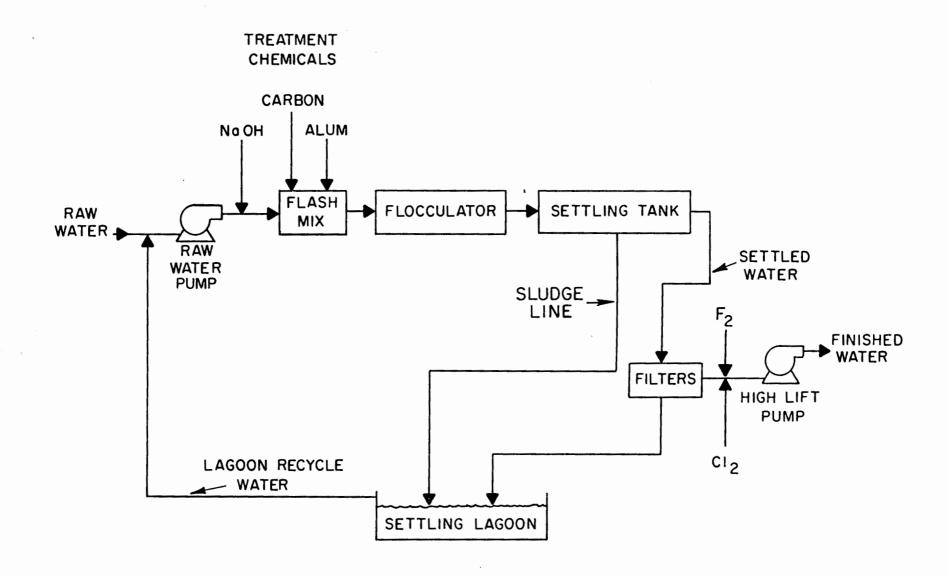


Figure 3. Schematic diagram of a typical water treatment plant

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links high levels of aluminum to several medical disorders, including osteomalacia, a mineral deposit in the joints causing severe pain, dialysis encephalopathy syndrome (DES), a neuropathological syndrome which can lead to death, Alzheimer's disease, a form of premature senility, and renal failure (Sung, et al, 1983). It is our policy to avoid these risks by minimizing the amount of alum and other chemicals used in the treatment process.

The Development of the Dynamic Control Strategy

By use of control theory, the dynamic nature of water treatment can be better understood and strategies for reducing chemical costs can be implemented. It is proposed in this research to more closely regulate pH and coagulant dosages in a treatment plant. Extensive investigation has shown the importance of pH for effective utilization of chemicals. Since alum is an acid, a base may be needed to maintain proper pH for effective coagulation. Sodium hydroxide and sulfuric acid will be the base and acid compounds for controlling pH. The alkalinity of the water will determine the dosage to maintain the desired pH upon addition of a given amount of coagulant. Thus, the major objective of this research is to optimally control the dosages of alum, sodium hydroxide, and sulfuric acid for conditions changing over time.

Jar tests of over 100 samples of natural and stock water samples of mixtures of color (humic substances) and turbidity (kaolinite) were observed. These tests reveal that the initial color is the controlling factor in establishing the critical coagulant dose of alum, $Al_2(SO_4)_3 \cdot 18H_2O$. This is a significant finding because it greatly reduces the complexity of the treatment strategy. Only color will be required to determine the optimum dosage of alum. This funding will be discussed in greater detail in this report.

The following steps were used in this development of the dynamic control strategy.

 determine a predictive equation for alum dose as a function of raw water color,

2. determine the effects of temperature and mixing conditions on the color and turbidity removal processes,

 determine the dynamic relationship among color with the use of time series analysis methods,

4. combine the results from 1, 2, and 3 to develop a strategy to be easily implemented by plant operators at surface water treatment facilities, and

 evaluate the dynamic control strategy for the risk of underdosing and cost.

Literature Review

There are a considerable number of articles on the coagulation of color compounds and on the coagulation of turbidity; however, few articles appear on the treatment of natural waters, water consisting of both color compounds and turbidity. The information that exists is insufficient to establish a quantitiable relationship between raw water quality and the dosage to achieve efficient removal of these materials from natural water. This relationship is necessary in order to achieve optimum water treatment plant operation. In this report the "critical" coagulant dose is defined to be the minimum coagulant dose of aluminum sulfate to achieve maximum color and turbidity removal.

Since the removal of color compounds and turbidity occur by different mechanisms, the contol of pH and the concentration of aluminum salts are critical variables in determining the efficiency of the coagulation process. It has been found that optimum turbidity removal occurs in the sweep coagulation and

adsorption-destabilization zones. See Figure 4. In the restabilization zone, coagulation efficiency of dilute colloidal solutions is improved. Most raw waters used as drinking waters meet this criterion at a dilute colloidal solution. Intense rapid mixing has been found to improve turbidity removal efficiency in the restabilization zone (Amirtharajah and Mills, 1982). The most efficient removal of color compounds is characterized by treatment with pH and alum concentrations that lie within the restabilization zone. Restabilization has been observed in studies of the removal organic color with ferric chloride (Hall and Packham, 1965). These observations stimulated our interests in determining if mixing conditions in the rapid mix and flocculation stages of treatment affect the removal efficiency of color and turbidity of natural waters. The factors that may achieve optimum water treatment performance are reported.

<u>Color</u>: Color, found in most surface waters, is obtained from the extraction of decomposed vegetation by-products. Natural waters containing color are assumed to be obtained by aqueous extraction of living woody substances, decaying wood, and soil organic matter. The extent of color extraction is a function of pH, temperature, contact period, and type and quantity of material available (Christman, et al., 1966). The mixture of these extracted products are called humic substances.

The overall chemical and physical properties of humic substances help to explain its removal from water by coagulation and aluminum chemistry. It is known that the molecular weight of the humic substances range from less than 800 to greater than 50,000 atomic mass units (Cohen and Hannah, 1971). The lower molecular weight substances exhibit properties of a true solution while those of the higher molecular weights exhibit properties similar to colloidal particles.

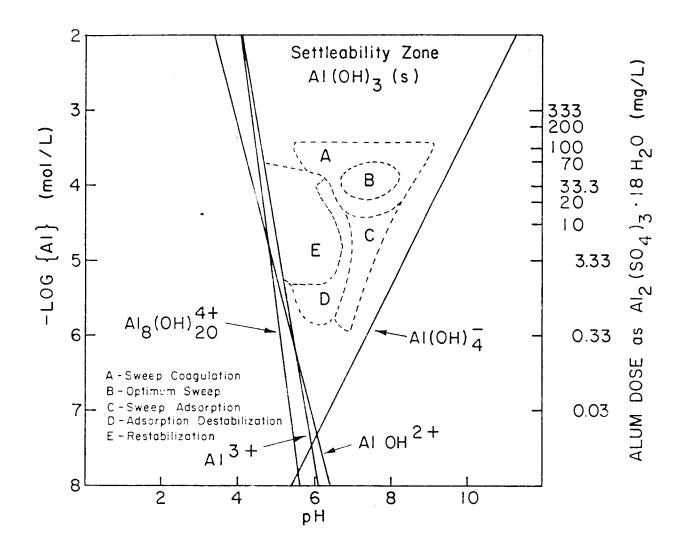


Figure 4. pAl-pH diagram showing the predominant hydrolysis products assuming that solid $Al(OH_3)$ is present

Cohen and Hannah's study (1971) report that 90% of the color particles were greater than 3.5nm in size and about 10% were greater than 10nm. Midwood & Felbeck (1968) observed that some color particles are as large as clay particles which are of the order of lu in size.

The humic substances may be classified by its proportion of fulvic, hymatomelanic, and humic acid. Fulvic acid is the most predominate form of humic substance in water (Black and Christman, 1961; Wilson, 1959) because it is the most soluble of the three acids in water. On a unit weight basis, fulvic acid produces the most color followed by hymatomelanic acid and humic acid (Black and Christman, 1963). In one of our studies of the removal of color and turbidity of natural waters, fulvic acid is used as an independent variable to predict coagulant dose.

There has been much discussion regarding the chemical groups which comprise the color molecules. The color molecules have been shown to be dibasic polyhydroxy aliphatic acids (Shapiro, 1957). It has also been shown that the humic and fulvic acid fractions are aliphatic unsaturated polyhydroxy dicarboxylic acids (Shapiro, 1964). It has been found that the fulvic acid fraction of the color molecule is an aromatic polyhydroxy methoxy carboxylic acid (Black and Christman, 1963; Christman and Ghassemi, 1966). Other investigators have suggested that the humic substances are formed in the soil by a polymerization of polyphenolic units derived from either bacterial synthesis or the breakdown if lignin residues. Alcholic OH⁻, phenolic OH⁻, carboxyl, methoxyl, and quinoid groupings have been found in addition to variable proportions of nitrogenous compounds such as amino acids and polypeptides (Hall and Packham, 1965). Christman and Ghassemi (1964) were able to find the following phenolic compounds in natural water: vanillin, vanillic acid, syringic acid, catechol, resorcinol, protocatechuic acid, and 3,5 dihydroxybenzoic

acid. Since these color compounds have a net negative charge in waters of neutral pH, the control of pH is considered an important factor for maximum color removal and is carefully controlled in our studies to a pH of 5.7. The range of pH reported for maximum color removal is reported as follows:

TABLE 1

Reported pH ranges for maximum color removal

Range	Source	
5.2-5.7	Black and Willems (1961)	
5.5-6.0	Gaunlet and Packham (1973)	
5.5-6.5	Moore (1979)	
5.4-6.0	Hall and Packham (1965)	

The chemistry of aluminum sulfate may be used to explain why the pH of 5.7 is chosen for our determination of a prediction equation. Aluminum sulfate releases aluminum ions upon dissolution in water. The aluminum ions then enter into hydrolysis reactions. The major hydrolysis products are: Al^{3+} , $Al0H^{2+}$, $Al_8(0H)_{20}^{4+}$, and $Al(0H)_4^{-}$. These species may be in equilibrium with the solid $Al(0H)_3(s)$ (Rubin and Kovac, 1974). The concentration of the major species of aluminum in water is a function of pH. A pAl - pH diagram, without ionic strength considerations and for 25°C, is presented in Figure 4, a modified version of figures taken from Amiritharajah and Mills (1982). The settleable zone boundary differs because our calculations show $*K_4 = 10^{-13.35}$ instead of $10^{-12.35}$ and the Al^{3+} line is shown to be part of the boundary of the settleable zone. From this figure it can be seen that at a pH below about 6.0 the major species in equilibrium with the $Al(0H)_3(s)$ precipitate are the positively charged aqueous aluminum species and above a pH of about 6.0 the major species in equilibrium with $Al(0H)_3(s)$ is the negatively charged aqueous aluminum species. It has been suggested by Hall and Packham (1965) that the color molecule reacts with an aluminum species of empirical formula $Al_x(OH)_{2.5x}$ to form an insoluble aluminum-hydroxy-humic precipitate. $Al_8(OH)_{20}^{4+}$ fits this model. Since the color molecule has a net negative change, humic substances may be removed by enmeshment within the $Al(OH)_3(s)$ and/or reacting with the positively charged aqueous aluminum species to form an aluminum-hydroxy-humic precipitate.

Turbidity: Colloidal particles are generally characterized as having a high surface area to mass ratio and usually possess a negative electrical charge in waters of neutral pH. Colloidal particles do not readily settle of out suspension because of Brownian motion and the electrostatic repulsion of charged particles. To remove turbidity, the stable dispersion of particles may be destabilized by adding coagulant chemicals so that the colloidal particles agglomerate and settle out of suspension by gravitational means. Rubin and Kovac (1973) report pH control is a primary factor in alum coagulation. With the use of experimental data for the removal of colloid species from water and equilibrium chemistry considerations, they have developed a pAl-pH diagram similar to the one shown in Figure 4. Thev also indicate that in addition to pH that alum concentration is important in efficient coagulation. At low pH and alum concentrations, restabilization and inefficient turbidity removal was observed for certain colloids (Rubin and Kovac, 1974). Thus, special attention was given to the treatment of natural waters and stock solutions of color-turbidity mixtures that fall within the restabilization region.

<u>Color-Turbidity Mixtures</u>: Natural surface water contain various mixtures of color compounds and turbidity and not all color molecules have the same chemical structure. Furthermore, the chemical composition of the color in the natural

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water tends to be similar to the humic substances in the surrounding soil and the plant life surrounding the water source. Owing to the variability of the proportions of color compounds and turbidity it might appear that the goal of achieving a prediction equation of alum coagulant dose as a function of raw water quality as impractical. However, Hall and Packham (1965) performed coagulation studies using aluminum and ferric salts as a coagulant agent on water containing a mixture of humic and fulvic acids and colloidal particles of kaolinite. They found that suspensions of kaolinite had no effect humic and fulvic acid removal. The coagulant dose for the coagulation of turbidity and humic substances is independent of initial concentration of turbidity and dependent upon the initial concentration of fulvic and humic acids. Water mixtures of kaolinite and fulvic acid, using aluminum sulfate as a coagulant, that kaolinite is removed concurrently with fulvic acid (Moore, 1979). Van Breeman et. al., (1979) report that a stochiometric or empirical relationship exists between the initial fulvic acid concentration and alum dose to achieve maximum color removal in their coagulation studies using aluminum slats. Narkis and Rebhun (1977) report a nonlinear relationship between initial concentration of humic acid and alum and report a linear relationship when a cationic polyelectrolyte is used as a coagulant.

Time Series Forecasting

The major objective of utilizing the control strategy is to determine the chemical dosages necessary to maximize the removal of color and turbidity as the raw water entering the plant changes over time. At any given instant of time, the quality of water entering the plant can be monitored. Unfortunately, continuous monitoring is not economically feasible for this study and for most water treatment

plant operations. Water samples were drawn twice daily from the Oyster River from September 1978 to September 1981. Color, turbidity and temperature were recorded. High frequency variations were observed for both color and turbidity. See Figures 1 and 2. Since turbidity is effectively removed with color, investigation of the temporal properties of color was only undertaken. Our jar tests show that turbidity is effectively removed when the maximum amount of color is removed. Through monitoring, the finished water quality and the present level of chemical dosages, are known at this instant of time. Since there is a lag time between treatment at the rapid mix stage and outlet of plant, forecasts must be made to determine the future water quality. These forecasts will be used in controlling the present level of treatment.

Since the raw water quality is measured as the water enters the plant and this information is used to forecast finished water quality, they are called leading indicators. Obviously, the use of leading indicators are important to the overall success of the control strategy and must be selected carefully. Raw water color and temperature are believed to be important leading indicators. Owing to low cycle variation in temperature, temperature can be tracked. The temperature effect can be easily incorporated in the dynamic control strategy. In the work that follows, the majority of the discussion deals with the development of prediction equation for alum dose as a function of raw water color and the development of the dynamic control strategy with time series analysis. Temperature is an important factor in the establishment of an effective control strategy. A prediction for raw water color - alum dose was developed for 20°C. Treatment of raw water below 20°C was undertaken and methods to incorporate into the dynamic control strategy are presented. The effects of the settling behavior were studied in detail. The effect of mixing in the rapid mix and flocculation stages of treatment were also investigated.

CHAPTER 4

THE "CRITICAL" COAGULANT DOSE

The results of Hall and Packham (1965), Moore (1979) and Van Breeman et al. (1979) were used as a premise that natural surface waters will exhibit the same characteristics if treated under similar conditions. Consequently, the "critical" coagulant dose d* is assumed to be dependent upon initial fulvic concentration, a surrogate measure of initial raw water color, and independent of raw water turbidity. A empirical relationship to forecast d* as a function of initial apparent fulvic acid concentration x'_0 and, in a separate analysis, initial apparent color x_0 is sought. Since natural surface samples were used, the results of those experiments will give an indication of the sensitivity to treatment of various proportions of color and turbidity mixtures and the practicality of using these assumptions is actual practice.

In our experiments twenty three samples were randomly drawn from the Oyster River in Durham, N.H. These samples had a color range of 30 to 320 CU and a turbidity range of 0.5 to 5.0 NTU. In order to achieve a wide range of raw water conditions, some samples were spiked with fulvic acid. An independent sampling of raw water quality of this site taken at twelve hour intervals from August 1978 to December 1981 show a range of color from 20 to 220 CU. with approximately 65% falling between 60 and 90 CU. The average turbidity was 2.3 NTU with approximately 65% falling between 1.0 and 4.0 NTU. Thus, the samples used in the study are representative of the conditions that must be treated at the plant at this location.

The Prediction Equation

Prior to performing the jar tests on these samples, an Jar Test Procedures: alum stock solution containing 17.77 grams per liter of reagent grade aluminum sulfate with 18 waters of hydration were prepared on the day the tests were performed. Daily preparation was used because the solutions precipitated after two days storage. During these tests, the pH was adjusted with sodium hydroxide and hydrochloric acid solutions. The same procedure was used for each sample. A one liter beaker containing an 800 ml aliquot of water was placed on a magnetic jar stirrer. The pH of the water was adjusted to 5.7 with additions of hydrochloric acid. The required alum and sodium hydroxide were added simultaneously to maintain the pH near 5.7. Within the first minute any deviations from the desired pH were adjusted. After 2 minutes of rapid mixing, the beaker was transferred to a standard jar stirring apparatus set at 20 rpm. Following a 20 minute flocculation period, the samples were allowed to settle for 30 minutes. After this approximately 400 ml were decanted off and an aliquot of supernatent was passed through a glass fiber filter. The apparent color, apparent fulvic acid concentration, turbidity, and pH of the raw, settled, and filtered waters were measured. The apparent fulvic acid concentration was measured by comparing the solutions absorbance at 350 nm with a standard calibration curve. Apparent color is the color of the color-turbidity mixture measured by visually comparing the sample to a platinum-cobalt standard. The other parameters were determined with procedures in Standard Methods. See Gallot (1980) for details.

<u>Jar Test Results</u>: Residual apparent color-dosage and residual turbidity-dosage curves were prepared for each sample. The same piece-wise linear residual color-

dosage form was observed for each sample, whether the residual color is assigned to be a filtered apparent color reading or a settled color reading. The results are typified by the curve shown in Figure 5 for an initial water color or $x_0 = 65$ CU. It shows that the residual fulvic acid q is a piece-wise linear function of the alum coagulant dose q or

$$q = \alpha_0 + \alpha_1 d \tag{1}$$

where α_0 and α_1 are the intercept and slope terms, respectivefully. For dosages below d*, both terms α_0 and α_1 were found to be nonzero values. For dosages above d*, the slope α_1 term is observed to be equal to zero and α_0 equal to a constant and equal to the average of residual color readings above d*.

For maximum color and turbidity removal, color is found to be the controlling factor in determining d*. This conclusion is drawn for all experiments performed on natural water samples and other studies of stock solutions of humic acid and kaolinite mixtures described in the following sections. Dosages below the critical d* are considered to be underdoses because maximum color removal is not achieved. A dosage above d* is considered to be an overdose and cost inefficient because these dosages do not improve the quality of the finished water. Thus, there is no advantage of overdosing.

A stoichiometric relationship between alum dosage and apparent fulvic acid exists. The prediction equation where d* is the critical alum dose d* in mg/ ℓ and x'_0 is the apparent fulvic acid concentration in mg/ ℓ is

$$i^* = 13.3 + 2.2 x_0^2$$
 (2)

with a correlation coefficient of 0.94 and a standard error of 6.2. Similarly, linear relationships between optimum alum dose d* and apparent color x_0 , measured in apparent color units, is

$$d^* = 13.9 + 0.23 x_0 \tag{3}$$

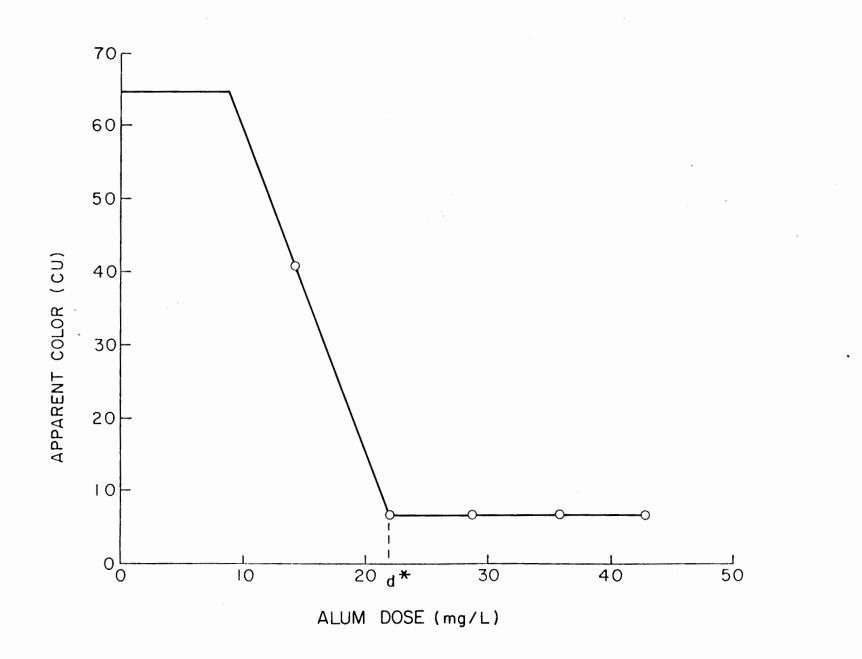


Figure 5. Filtered color-alum relationship for a river sample with an initial raw water color of 65 CU

with a correlation coefficient of 0.94 and a standard error of 6.5. Apparent color is the color of a color-turbidity mixture measured by visually comparing the sample to a platinum-cobalt standard.

The results observed in these studies on natural waters agree with the results of Beaurivage (1979); Davis and Steinhurst (1960); Moore (1979); and Van Breeman, et. al. (1979), who used synthetic stock solution samples. All alum doses as recommended by these researchers are within a 95% confidence interval. See Figures 6 and 7. These results give confidence that stock water samples, using fulvic acid, humic acid, and kaolinite, are representative of natural water samples. Equation (3) is used in the dynamic control strategy for raw waters of 20°C.

The Effects of Temperature

Since the treatment of natural water and stock solutions of humic substances and kaolinite exhibit the same behavior, another series of 34 jar tests of stock solution samples of 130 CU were performed at 4°C and 20°C. The primary purpose of these tests is to determine effect of temperature upon removal efficiency of color.

<u>Jar Test Procedure</u>: A $10g/\ell$ stock $A1_2(S0_4)_3 \cdot 18 H_20$, solution was used to keep sample dilution to a minimum. The stock solution was made daily to avoid aging. A 0.20N NaOH solution was used to adjust the pH to a specified value. While the sample was being stirred, the appropriate volume of stock alum was added, followed by NaOH titration until the desired pH was reached. Four beakers were used in each jar test. Each beaker was filled with the recalculated volume of batch water and put in the temperature bath. Four paddles from a Phipps and Bird gang stirrer, each with dimensions 1 in x 3 in, were placed in the beakers. The appropriate volumes of NaOH and stock alum were added, followed immediately by rapid mixing.

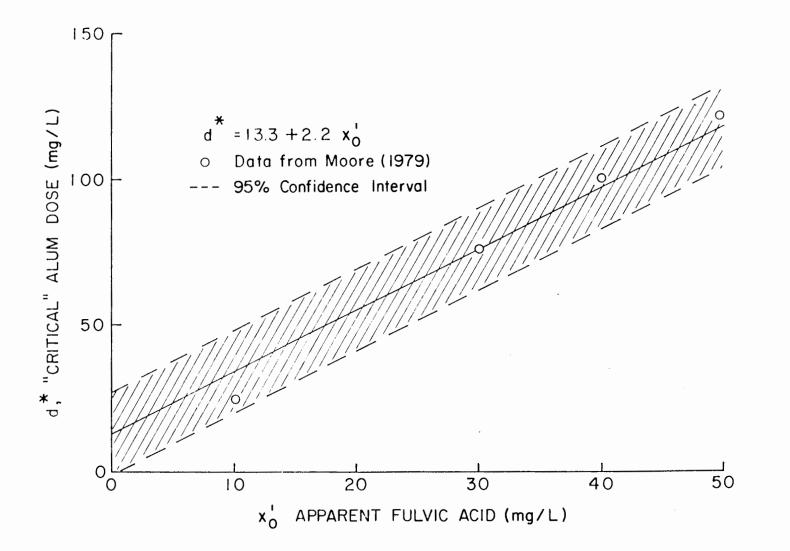


Figure 6. "Critical" alum dose-initial apparent fulvic acid relationship for river water

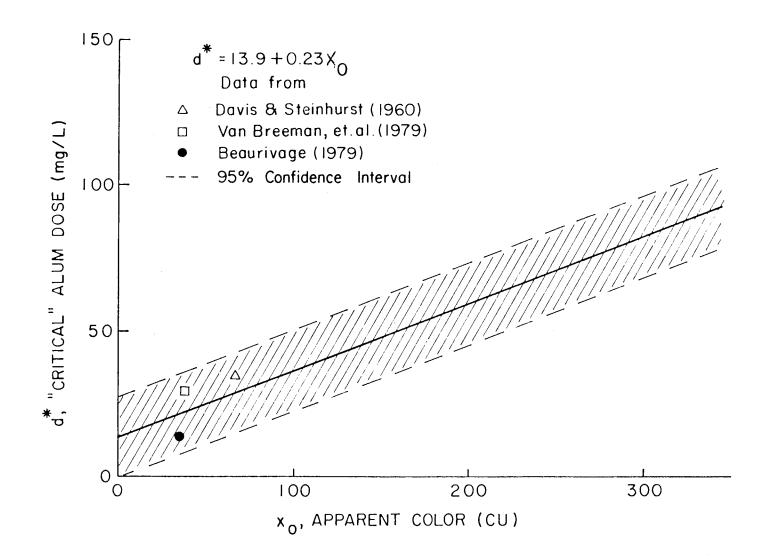


Figure 7. "Critical" alum dose-initial apparent color relationship for river water

The rapid mix step occurred for 2 minutes at 150 rpm. Fifteen minutes of flocculation at 15 rpm then occurred. A 15 minute settling period was allowed before sampling. Two types of samples were taken from each jar after settling. The first one consisted of a 25 ml aliquot that was used for absorbence readings of the settled water sample. The second type consists of centrifuged aliquots. Two 50 ml centrifuge tubes were filled and centrifuged at 10,000 rpm for 10 minutes on a Damon/IEC Division centrifuge. A 25 ml aliquot was taken from one tube of each jar. This was used for absorbence reading of the centrifuged water sample. Three 10 ml aliquots were taken from each of the remaining tubes and used for residual aluminum measurements. The absorbence reading reported here were transformed to color reading in color units (CU) by multiplying the absorbence reading taken at a wavelength of 267 nm by 127.8.

<u>Centrifuged Samples</u>: The results obtained in the series of jar tests are summarized in Table 2. These tests were performed in the same as described.

TABLE 2

Optimum conditions for maximum color removal of color-turbidity mixtures with an initial color of 130 CU. Readings taken after centriguging

Temperature (°C)	Optimum alum dose range (mg/l)	Optimum pH range	Mean residual color (CU)
5	30-140	5.5-7.4	9
20	30-140	5.8-7.4	9

These results validate the alum dose prediction equation, equation 3, for both temperatures 5°C and 20°C. For raw water samples of 130 Cu, the "critical" alum dose from the jar tests is found to be 30 mg/l, a value within the lower boundary of the 95% confidence interval shown in Figure 7.

For temperatures of 5°C and 20°C, the optimum pH range differs from the pH ranges reported by other researchers for samples containing color only. Our results indicate that higher pH values will give better results.

<u>Settled Samples</u>: In order to achieve optimum performance in the settling tank, readings were taken after settling and prior to centrifuging. The results are summarized in Table 3.

TABLE 3

Optimum conditions for maximum color removal at color-turbidity mixtures with an initial color of 130 CU. Readings taken after settling.

Temperature (°C)	Optimum alum dose range (mg/l)	Optimum pH range	Mean residual color (CU)
5	75-140	6.4-7.4	29
20	45-140	6.0-7.4	19

Compare these results with the results of Table 2. For 20° C the "critical" alum dose of 45 mg/l is greater than the one reported in Table 2 of 30 mg/l and is approximatley equal to d* = 44 mg/l from equation 3. The optimum pH range for 20° C is very similar. For the colder temperature of 5°C, the "critical" alum dose is found to be 75 mg/l and the optimum pH range is between 6.4 and 7.4. Thus, temperature has an influence upon the alum dosage and pH range. In these tests, the settling time for the 5°C and 20°C samples is the same 15 minutes. Improved color removal as measured by the mean residual color may be achieved by increasing the settling time. The effect of settling time was not investigated in this study.

Figures 8 and 9 show the effect of pH and temperature upon color removal. These samples were both treated with an alum dose of 80 mg/l, an overdose for both temperatures. Recall that overdosing does not result in increased color removal, thus pH and temperature are considered to be the only controlling factors in this series of experiments. Greater variability of the residual color is observed for pH less and of 6.4. Whereas, the variance for values between 6.4 and 7.4 appear to equal, indicating pH has a significant effect upon color removal process. A method of least squares was used to fit a nonlinear relationship for residual color, pH and temperature. The lines of best fit are shown in Figures 8 and 9. See

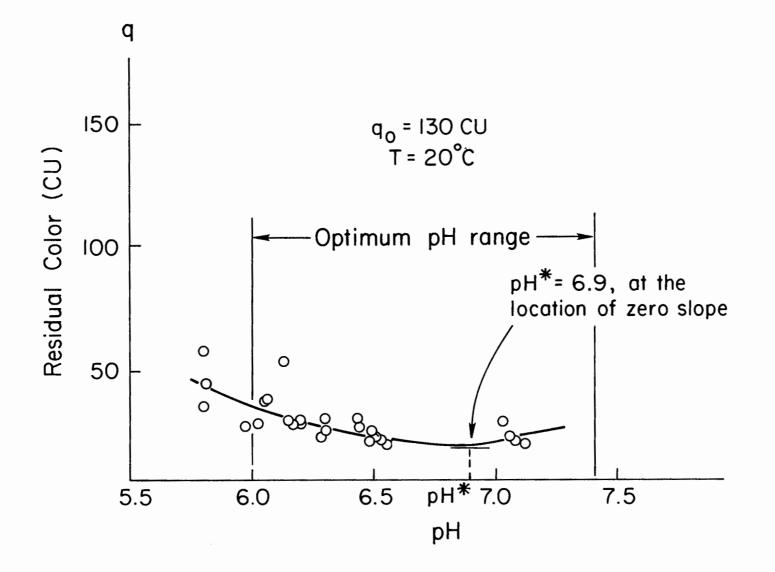


Figure 8. Residual color-pH relationship, after settling. T = 20°C

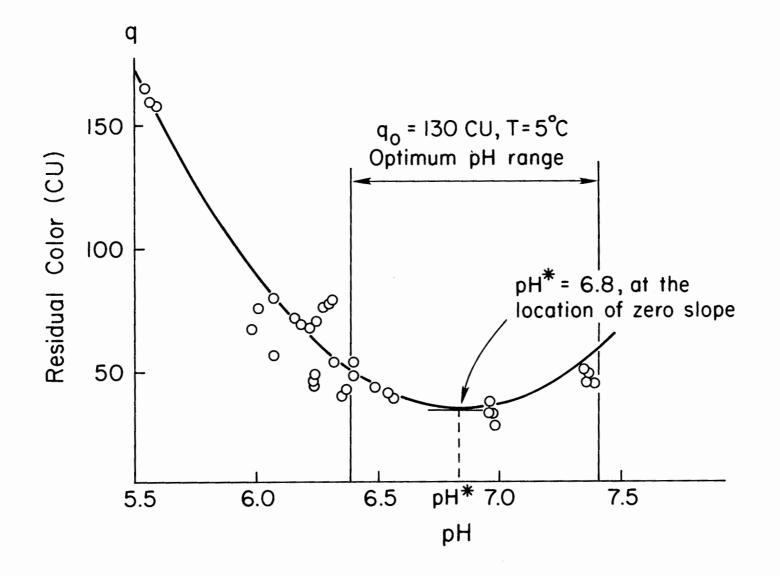


Figure 9. Residual color-pH relationship after settling. T = $5^{\circ}C$

Viscardi (1983) for details. Using this relationship for pH for maximum color removal is found to be 6.79 at 20°C and 6.86 at 4°C. Further analysis of the data tests shows there are no significant difference in maximum color removal for the ranges shown in Table 3. Thus, for optimum performance in the settling stage of the water treatment process, it is recommended that the pH be adjusted to within these ranges in order to achieve better performance in the settling tank. These recommended ranges of pH fall within the sweep coagulation zone shown in Figure 3.

Since colder temperatures impair the removal process, a series of jar tests at temperature 5, 9, 14 and 20°C were performed. These tests were performed at pH levels that fall within the optimum pH range reported in Table 3. The results are shown in Table 4.

TABLE 4

Alum dose for color-turbidity mixtures with an initial color of 130 CU.

Temperature (°C)	Alum dose d*,(mg/l)	Mean residual color (CU)	
5	80	29	
9	66	25	
14	56	28	
20	50	27	

Reading taken after settling

The dosages used in these tests are slight overdoses for the 5°C and 20°C. Note the performance, as measured by the mean residual color at 20°C, is not as good as reported in the Table 3, for the same tests. Thus, one should not conclude that better settling performance is achieved at higher temperatures as implied in Table 3.

The alum dosages at 9°C and 14°C have similar mean residual color readings after settling, thus giving confidence that these alum doses are effectively removing the color and turbidity. These results indicate that a linear relationship between alum dose and temperature exists. It is expected that similar results will occur for initial raw water colors other than 130 CU.

Residual Aluminum

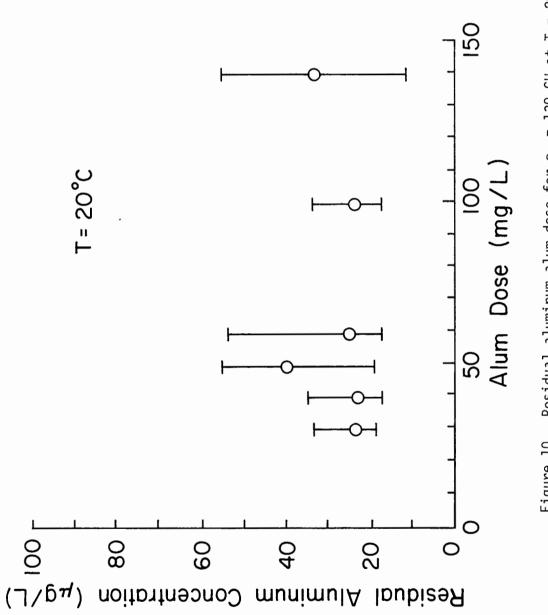
A series of jar tests were performed to determine the effect of temperature upon residual aluminum concentration. As previously mentioned, aluminum may cause health problems. Secondly, high residual aluminum concentrations may indicate overdosing, which results in higher operational costs without a substantial increase in color or turbidity removal.

The studies of residual aluminum utilized a relatively new method of measuring aluminum with fluorescense with Morin (2', 3, 4', 5, 7 pentahydroxy-flauone) as the chelate agent. Details are presented in Viscardi (1983). The results of these tests show that a range of observations between 15 μ g/ ℓ and 100 μ g/ ℓ . See Figures 10 and 11. These figures show a higher median and a broader range of residual aluminum readings at all alum dosage levels for 5°C as compared to 20°C. Although the National Drinking Water Standards do not yet limit the amount of residual aluminum leaving a plant, it is anticipated that Standard Methods will recommend a maximum limit of 50 μ g/ ℓ (Sung, et al. 1983).

Mechanical Mixing Effects

The effects of mechanical mixing, mixing intensity and mixing duration, in the rapid mix and flocculation stages on the color and turbidity removal process was investigated. In these jar test studies various combinations of mixing conditions were investigated, while alum coagulant dose was held constant for a given initial water color.

<u>Velocity Gradient</u>: In water treatment facilities, a rapid mix unit is used to uniformly disperse the coagulant chemicals in the water; and a flocculator unit is used to promote particle contact and to promote the formation of larger





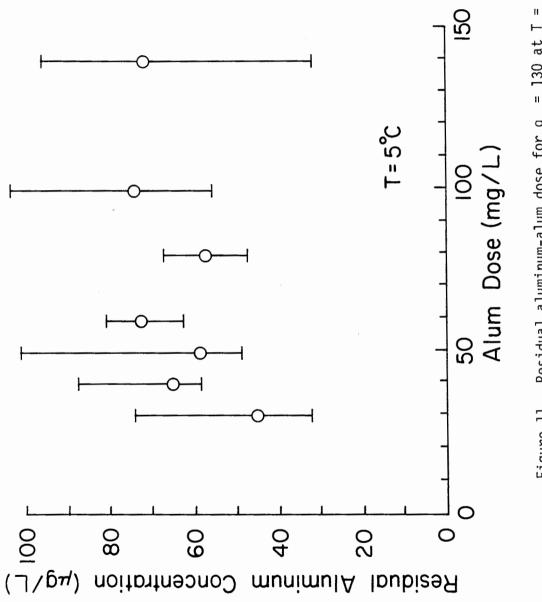


Figure 11. Residual aluminum-alum dose for $q_0 = 130$ at $T = 5^{\circ}C$

particles. Mechanical mixing is suspected to have a significant impact upon performance and the sand filter, which is used to remove material not removed by settling in the settling tank. The mixing intensities used in the rapid mix and flocculator units may be measured with the velocity gradient G. It is a measure of the total work performed at a point or on a unit volume of fluid over a unit time.

G =
$$\left(\frac{W}{t\mu V}\right)^{1/2} = \left(\frac{\bar{p}}{\mu V}\right)^{1/2}$$
 (4)

where W is the work input per unit volume, t is the mixing duration time, V is the volume of liquid, μ is the absolute viscosity, and P = W/t is the power per unit volume. Camp and Stein (1973) defined the average velocity gradient \overline{G} as

$$\overline{G} = \left(\frac{\overline{P}}{V\mu}\right)^{1/2}$$
(5)

where \bar{P} is the average power transmitted into the liquid, V is the volume of the liquid and μ is absolute viscosity. Since \bar{P} can be easily measured, the average velocity gradient \bar{G} is used in our studies. The measurement of the velocity gradient was determined through the use of a precalibrated motor. Based on the measurements of motor amperage, impeller speed, volume of water, temperature and torque, the average velocity gradient, \bar{G} , can be determined. See Gottlieb (1982) for details.

It should be recognized that the configuration of the mixing basin and the shape of the impellers used for mixing can yield different results, even though the same \overline{G} was used. The turbidity removal experiments conducted by Letterman, et. al. (1973) using cylindrical jars with baffled chambers showed that turbine impellers produced slightly lower residual turbidities than propeller impellers. They also reported that square chambers produced residual turbidities slightly lower than when using cylindrical chambers when either impeller type was used.

<u>Jar Test Procedures</u>: The results and conclusions presented in this portion of the paper are a result of the investigation of 80 jar tests of stock solutions of color and turbidity mixtures. For each jar test investigation the experiment was repeated four times for the same initial water color and turbidity concentrations under identical treatment conditions. Thus, a total of 320 samples were analyzed. Water colors of 142, 80, and 20 CU are used to represent high, medium, and low water colors, respectively. These colors of 142, 80, and 20 CU were produced by adding 11.94, 6.7, and 1.7 mg/l of Aldrich brand humic acid, respectively. For the mechanical mixing tests, kaolinite was added to the samples giving an average turbidity of 3.7 NTU and standard deviation of 1.2 NTU.

All jar tests were performed at 25°C and at a constant pH of 5.7 in 2 liter Gator jars, square chambers, with 3 in x 1 in flat impellers. The rapid mix tests were performed first. The selected alum dose and 0.1N NaOH were added simultaneously in the rapid mix phase to maintain a pH of 5.7. Any deviations from a pH of 5.7 were adjusted within one minute with either 0.1N NaOH or 0.1N HC1. Rapid mix detention times and velocity gradients were varied among jar tests. The velocity gradients that were investigated are $\bar{G} = 100$, 300, and 500 sec⁻¹. Flocculation occurred for 20 minutes at 15 rpm or approximately $\bar{G} = 15$ sec⁻¹ and sedimentation occurred for 15 minutes at which point residual turbidity, settled color, and residual humic acid were measured.

The turbidity was measured with a Hach model 2100 turbidimeter. The settled color was measured by visually comparing the water in a 100 ml Nessler tube to a platinum cobalt standard in the same type of tube. Humic acid was measured by a Bausch & Lomb Spectronic 2000 spectrophotometer at 267nm. Since the remaining turbidity in the sample can account for some of the absorbance, the sample was centrifuged for 30 minutes at 18,000g. Because centrifuging can change the pH of the sample, which in turn can cause a color change (Christman and Ghassemi, 1966), the sample was buffered with an equal volume of 0.1M K₂HPO₄.

The flocculation tests were performed exactly as the rapid mix tests, except that the rapid mix conditions were held to a constant, $\bar{G} = 500 \text{ sec}^{-1}$, and detention time t = 30 seconds, giving a $\bar{G}t$ of 15,000, while the flocculation velocity gradients and detention times were varied among jar tests. Velcoity gradients of 20, 50, and 90 sec⁻¹ were investigated at different levels of mixing duration.

The same alum dosages were used for the rapid mix and flocculation tests. Alum doses of 50mg/l, 40mg/l, and 30mg/l were used for initial water colors of 142, 80, and 20 CU, respectively. These doses may be considered to be slight overdoses. Using equation (3), the critical alum dose for these initial color waters are 46, 32, and 19 mg/l of alum for these initial water colors, respectively.

<u>Statistical Methods</u>: In order to determine the effects of mechanical mixing upon color removal, a series of experiments were performed with fixed levels of alum dosages at various levels of \overline{G} and t, the mixing duration time is in seconds. The purpose of this investigation is to infer a cause-effect relationship between the residual color of the finish water q, \overline{G} , and t for a given dosage d. A linear model will be used to explain this investigation.

$$q = \beta_0 + \beta_1 \bar{G} + \beta_2 t + \beta_3 \bar{G} t$$
 (6)

The dependent variable q represents the apparent color reading of the water after settling or equivalent color reading after centrifuging. The coefficient, β_0 represents the intercept, β_1 , β_2 , and β_3 are slope terms which represent the average change in response to a unit change in \overline{G} , t, and \overline{G} t, respectively. The terms $\beta_1\overline{G}$ and β_2 t are called the main factors and $\beta_3\overline{G}$ t is called the interaction factor. The effect of interaction may be seen more clearly by rewriting the linear model as

$$q = \beta_0 + \beta_1 \overline{G} + (\beta_2 + \beta_3 \overline{G})t$$
(7)

The magnitude and signs of the parameters β_0 , β_1 , β_2 , and β_3 may be determined by the method of least squares and hypothesis testing to determine if these estimates are significantly different than zero (Mendenhall, 1968).

In order to show the significance of the main and interaction factors, assume that experiments have been conducted, the linear models have been fitted, and hypothesis tests have been performed. Suppose that the interaction factor is shown to be statistically insignificant. The linear model reduces to

$$q = \beta_0 + \beta_1 \bar{G} + \beta_2 t \tag{8}$$

If $\beta_1 < 0$ and $\beta_2 < 0$, increasing either \overline{G} or t or both will reduce the residual color in the finish water. Contrast this result with the model

$$G = \beta_0 + \beta_3 \bar{G}t$$
 (9)

Here, the main factors are statistically insignificant. If $\beta_3 < 0$, then changing \bar{G} and t such the product $\bar{G}t$ is increased will reduce the residual color in the finish water. This result implies that there will be no difference in residual color for one sample treated at a $\bar{G} = 300$ per second and t = 100 seconds and for a second sample treated at a $\bar{G} = 500$ per second and t = 60 seconds because the two samples have the same $\bar{G}t$ value of 30,000. If the main and interaction factors play no part in the color removal process, then the model is

$$q = \beta_0 \tag{10}$$

 $\boldsymbol{\beta}_0$ may be estimated by averaging all observations of the residual color readings.

Analysis of variance, ANOVAII tests were used to determine the statistical significance of the main and interaction factors. All statistical testing were performed at 5% level of significance. In order to detect interaction relationship, tests were performed for a broad range of combinations of \tilde{G} and t. Scattergrams were used to investigate the variability in the data and to determine trends.

<u>Rapid Mix Test Results</u>: The same conclusions were drawn for all rapid mix tests performed for settled sample. ANOVAII tests indicate that $\overline{G}t$ is statistically significant and that \overline{G} and t are statistically insignificant. The model describing this behavior is

$$q = \beta_0 + \beta_3 \,\overline{G}t \tag{11}$$

The parameters of β_0 and β_3 were estimated by use of the method of least squares and hypothesis testing for 20, 80, and 142 CU. The estimates of β_3 are 1.14 x 10⁻⁴, 0.59 x 10⁻⁴, and 0.66 x 10⁻⁴ for the respective raw water colors All these terms are statistically significant. Since the estimate of the slope parameter is small and the estimated error s_e^2 is relatively large, Tukey's method of multiple comparisons (Box, Hunter, and Hunter 1978) were employed. This statistical method helps identify the range of $\bar{G}t$ where the average residual color of the finish water is statistically the same value. The mathemtical model describing this condition is

$$q = \beta_0 \tag{12}$$

The results of the analysis are tabulated in Table 5.

TABLE 5

Gt range for maximum color removal of color-turbidity mixtures

Raw Water Color	Alum dose	Settled Samples	Centrifuged Samples
20 CU	30 mg/l	9000-36000	-
80 CU	40 mg/£	3000-36000	3000-72,000
142 CU	50 mg/£	9000-30000	9000-120,000

In other words, for 142 CU raw water there is no statistically significant difference among the average values of residual color in the interval of Gt between 3000 and 36,000. Similar conclusions were observed for water samples with initial color of 20 and 80 CU. This is in good agreement with the range of Gt for the removal of turbidity recommended in standard practice.

Absorbance readings of the settled finished water were taken after the samples were centrifuged. The analyses shows that color removal is independent of \overline{G} , t and $\overline{G}t$. The model describing this finding is $q = \beta_0$. Comparing the $\overline{G}t$ ranges for settled apparent color and centrifuged absorbance samples Table 5 shows the expected result that a broader range of $\overline{G}t$ for maximum color removal exists for the centrifuged samples.

<u>Flocculation Test Results</u>: ANOVAII tests show that \bar{G} and t for raw water colors of 40, 80, and 142 are statistically significant and the interaction term $\bar{G}t$ is statistically insignificant. Thus, q residual color is assumed to be a function of \bar{G} and t or

$$q = \beta_0 + \beta_1 t + \beta_2 \bar{G}$$
(13)

Data analysis of residual color of q and mixing time t with the data for \overline{G} of 20, 50, and 90 per second identified, shows the effect of average velocity gradient upon settling. The velocity gradient \overline{G} is a primary factor to efficient settling \overline{G} of 20 per second is the most effective in achieving the best results. Thus, attention is focused upon the relationship between q and t for $\overline{G} = 20$ per second. Tukey's mean comparison tests were performed and the range of mixing times for maximum color removal were determined. For the data obtained in our studies, the optimum values of t are shown in Table 6.

TABLE 6

Detention time for maximum color removal of color-turbidity mixtures for $\tilde{\rm G}$ = 20 per second

Raw water color	Settled Samples	Centrifuged Sample
20 CU	900-1800	300-1800
80 CU	600-1800	600-1800
142 CU	600-2400	600-2400

For $\bar{G} = 50$ and 90 per second, shearing forces damage the floc or deter floc formation. Visual observation of flocs at higher \bar{G} values indicate that they were weaker and not as dense as flocs at the \bar{G} value of 20 per second. Flocs at $\bar{G} = 90$ per second were approximated to have an average diameter of 3mm (1/6 inch); whereas, flocs at $\bar{G} = 20$ per second had an average diameter of 6mm (1/8 inch).

For higher \overline{G} values, residual turbidity readings were also greater than for the lower \overline{G} readings. Maximum turbidity removal is achieved at $\overline{G} = 20$ per second. It has been found that the higher the velocity gradient the denser the floc; however, if \overline{G} is too high, shear forces will break up the floc (Cohen and Hannah, 1971). Other investigators (Lagvanker and Gemmel, 1973; Tambo and Watanbe, 1979) have also reported as the density of the floc decreases, the floc size increases. Further details may be obtained in Ossenbruggen, et al. (1983).

CHAPTER 5

TIME SERIES MODELLING

Jar tests of over 100 samples of natural and stock water samples of mixtures of color (humic substances) and turbidity (kaolinite) were observed. These tests reveal that the initial color of the sample and its temperature are leading indicators in establishing the "critical" coagulant dose of alum. The relationship for determining the dosage is given in equation (3) and rewritten here as

$$d = 13.9 + 0.23 x_0$$
(14)

where x_0 is apparent color of the raw water measured in color units at 20°C. This equation appears to give good results for investigations of samples after settling and after centrifuging. As previously discussed, the critical dose for temperatures below 20°C require additional alum above the predicted dose of equation (14) if maximum color removal is to be achieved after settling. Color-turbidity samples of 30, 80, and 130 CU conducted at 4°C were found to require additional alum of 16, 24, and 30 mg/ ℓ above the predicted value. In the quantitative results presented in this section, the effects of temperature are not considered.

Time series modelling provides a method to forecast over a period of time called the lead time. The accuracy of the forecast depends upon many factors including temporal variation of the signal and the autocorrelative relationship among the data. By investigating an historical record of the data, causal relationship can be identified and incorporated into a forecast model. This process is known as model identification. If a high degree of autocorrelation exists, an autoregressive model can be developed which is extremely useful in forecasting events with present and past observations. The forecast may be \hat{x}_{t+1} for future period t+l estimated with the following model

$$x_{t+1} = \phi_0 x_t + \phi_1 x_{t-1} + \dots + \phi_p x_{t-p} + a_t$$
 (15)

where x_t , x_{t-1} , \dots x_{t-p} are observations taken at the present time t, and at past time periods, t-1, \dots t-p. The terms ϕ_0 , ϕ_1 , \dots , ϕ_p are nonzero weights and a_t is an error term. This model and all times series models developed under the general heading of Box-Jenkins models (1970) are assumed to be linear filter models. These models are stochastic models that are dependent upon a series of successive observations of correlated values. Furthermore, these models are assumed to possess the property of stationary and to be generated from a series of independent shocks, or in other words, a_t has the properties of white noise. Utilizing these assumptions allows one to identify a model and test the model's validity with statistical methods.

Model Identification

Time series analysis were performed upon the color data shown in Figure 1. The monitoring time interval T or time between observations is twelve hours. The temporal color variation is found to be represented by a linear filter model

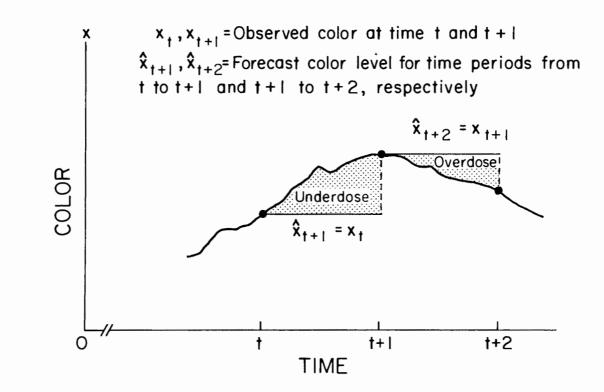
$$x_t - x_{t-1} = a_t$$
 (16)

where $x_t - x_{t-1}$ represents the first difference between an apparent color observation taken at time periods t and t-1. The random variable a_t is assumed to be normally distributed with a mean equal to zero and a standard deviation of σ_a . Furthermore, a_t , a_{t-1} , a_{t-2} ,... are assumed to be uncorrelated random variables. Run and chi square tests were performed to validate the assumptions for the model represented by equation (16). Equation (16) is a simplified version of the model shown in equation(15) with p = 1 and $\phi_0 = 1$.

The model may be rewritten as:

$$x_{t} = x_{t-1} + a_{t}$$
 (17)

Utilizing this form, the observed value of x_t may be interpreted as the sum of the observed value x_{t-1} plus a random "shock" a_t . This model is sometimes called a random walk model. The model may be used to forecast future events.



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Figure 12. A simple dynamic control strategy

$$\hat{x}_{t+1} = x_t + a_{t+1}$$
 (18)

where x_{t+1} is the forecast of color for the upcoming period t+1. The lead time interval for forecasting is equal to the monitoring time interval T. Thus, the selection of the monitoring time T is an important decision in establishing an effective dynamic control strategy. The forecast is based upon the observation of color taken at present time t, x_t and a "shock", a_{t+1} . Since a_{t+1} is assumed to be normally distributed with zero mean, the expected value of color is simply equal to x_t .

$$E[x_{t+1}] = x_t \text{ or } x_{t+1} = x_t$$
 (19)

Let x_{t+1} equal the expected apparent raw water quality for treatment period between t and t+1.

Using x_{t+1} , the critical alum dose from equation (19) with $x_0 = x_{t+1}$, a simple dynamic control strategy is established. Using expected value theory, it can be anticipated that the water will be underdosed approximately 50% of the time. An underdose is defined as the event where the \hat{x}_{t+1} or less than the observed value x_{t+1}^{r} or

$$x_{t+1} < x_{t+1}$$
 (20)

The concepts of underdosing and overdosing are depicted in Figure 12. Clearly, this simple dynamic control strategy is an unsatisfactory method because of the frequent occurrence of underdosing.

During an underdose, it is possible that the water will be aesthetically unpleasing and the chances of a health hazard are also increased. If chlorine is used as a disinfectant, the possibility of forming trihalomethane, a suspect carcinogen is present. Overdosing avoids these problems; however, excessive overdosing does not improve water quality only adds to the cost of treatment and possibly results high levels of residual alum in the finish water. Thus, the goal is to find a method that eliminates the occurrence of underdosing and at the same time avoids excessive overdosing.

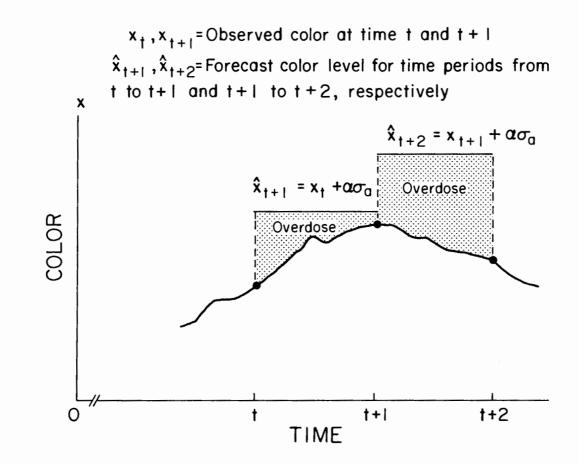


Figure 13. A dynamic control strategy with overdosing

The frequency of underdosing will be reduced if the forecast relationship, equation (19) of the simple control strategy, is modified to:

$$x_{t+1} = x_t + \alpha s_a$$
 (21)

where α is a positive value called the overdose factor and s_a is the estimate of σ_a . The magnitudes of α and s_a will determine the frequency of underdose occurrences. Figure 13 shows the addition of αs_a to x_t is sufficient to eliminate the underdose for the period between t and t+1 shown in Figure 12. The effects of α and s_a upon the occurrence of underdosing and the cost of treatment are important considerations in establishing an effective control strategy, and consequently, their relationship will be studied in greater detail.

The magnitude of s_a will be dependent upon the monitoring time interval T. Since the standard deviation is equal to the square root, of the variance, s_a = $(s_a^2)^{1/2}$, the standard deviation s_a may easily be calculated from the estimate of variance s_a^2 where

$$s_a^2 = \frac{1}{(N-1)} \sum_{t} (x_t - x_{t-1})^2$$
 (22)

The effect of the sampling interval on s_a is shown in the following table for the Oyster River data shown in Figure 1.

TABLE 7

Standard deviation estimates of the random shock,

Monitoring interval T (hours)	Sample size N	Standard deviation s _a (CU)
12	2015	10.8
24	995	13.3
36	658	14.8
48	478	14.9
60	391	16.2
72	319	16.1

term a_t for various monitoring intervals

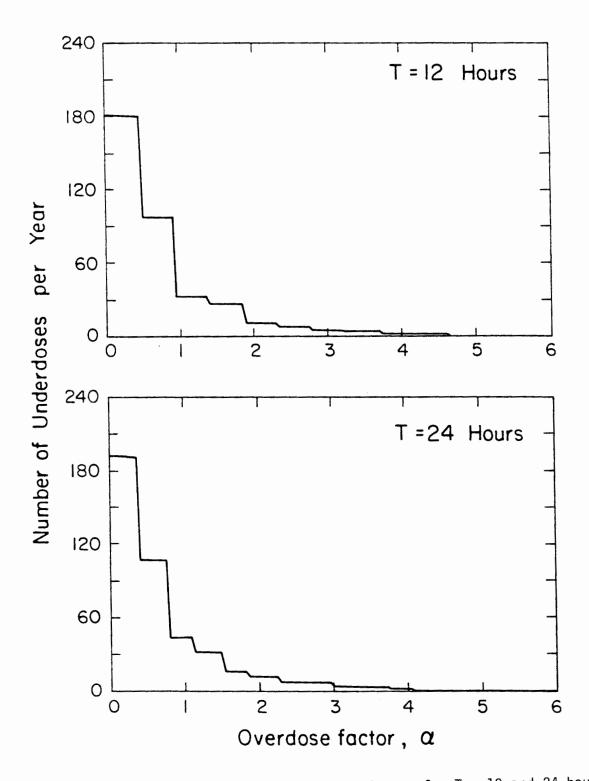


Figure 14. Underdoses per year - overdose factor for T = 12 and 24 hours

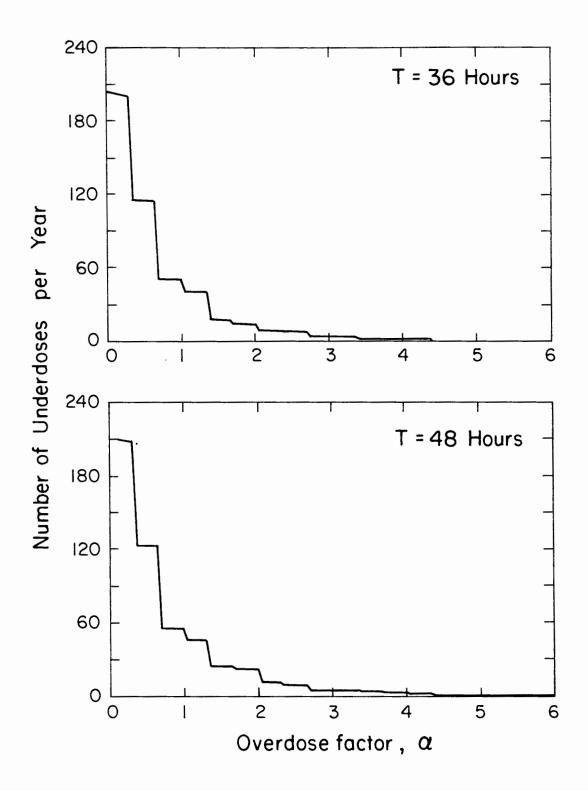


Figure 15. Underdoses per year - overdose factor for T = 36 and 48 hours

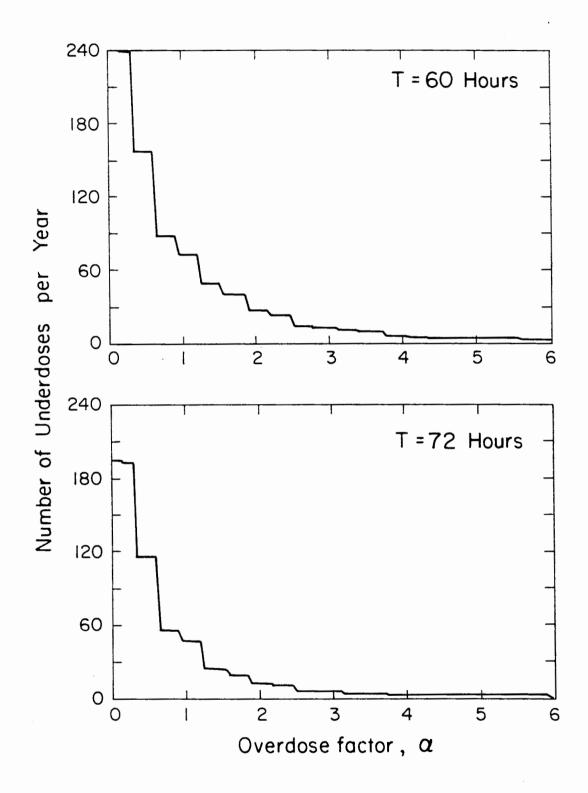


Figure 16. Underdoses per year - overdose factor for T = 60 and 72 hours

The same time series data was used to calculate each value tabulated in Table 7. For T=12 hours, all observations were used. For T>12 hours, appropriate values were selected to simulate that given monitoring time interval. For example for T=24, every other observation was used to establish a new data set. There were time periods where data was not recorded. The most common causes for missing data were a frozen water line leading from the reservoir to the sampler and pump failure. As a result, there are gaps in the time series which in turn is reflected in the sample size N and standard deviation s_a shown in Table 7.

The steps for calibrating a dynamic control strategy forecast model are:

 monitor the water supply source at a fixed time frame T. A record of a mininum of one year is recommended; and

2. calculate s_a by use of equation (22).

Once the model is calibrated, the underdose factor α must be selected. The alum is determined with equations (14) and (21). Let $x_0 = \hat{x}_{t+1}$. Thus, the dosage for the treatment period between t and t+l is

$$d_{t+1} = 13.9 + 0.23 x_{t+1}$$
(23a)

or

$$d_{t+1} = 13.9 + 0.23 (x_t + \alpha s_a)$$
(23b)

where x_t is the observed color reading at time period t. It should be evident from this equation that the effectiveness of the dynamic control strategy will be dependent on how well the forecast of \hat{x}_{t+1} is made. In order to evaluate its various combinations of α and T were taken and the number of underdoses per year were counted. The results of our studies are summarized in Figures 14 through 16.

The following observations are made:

- 1. the α is the primary factor for determining the number of underdoses
- the monitoring interval T is a secondary factor for determining the number of underdoses.

From Figures 14 through 16 an overdose factor of 3 appears to be a reasonable choice to minimize the number of underdoses per year.

The cost of treatment is another measure of how effective the dynamic control strategy is. In order to evaluate it, the total amount of alum required per year to treat a flow of 1 million gallons per day was investigated. An analysis of the yearly averages of color shows that these data are normally distributed with mean, $\bar{x}_t = 74.2$ CU and standard deviation $s_x = 10.5$ CU. The expected annual amount of alum may be estimated by taking the expected value of equation (23b) and multiplying it by an appropriate factor (1.523) to convert the dosage from grams to tons, the expected annual alum in tons per year is

$$z = E[1.523\{13.9 + 0.23 (x_{+} + \alpha s_{-})\}]$$

or

$$\bar{z} = 21.2 + 0.35 (E[x_t] + \alpha s_a)$$
 (24)

In a similar manner, the standard deviation may be evaluated. It is simply equal to $s_z = (1.523)(0.23)s_x = 3.7$ tons. This shows the variation in the annual dosage of alum is expected to be small. The estimated annual chemical dose for a flow of 1 million gallons per day is tabulated in Table 8.

TABLE 8

Number of underdoses per year and yearly alum dose estimates for a dynamic control strategy with overdosing. Overdose factor, α =3.

Monitoring Interval T (hours)	Annual alum dosage _ Mean z (tons/yr)	Number of underdoses per year m	
12	58.5	5	
24	61.1	7	
36	62.7	4	
48	62.8	5	
60	64.2	13	
72	64.1	8	

Flow, 1 million gallons per day

These results show there is a slight penalty in cost for larger monitoring intervals of T. The overdose factor, $\alpha=3$, gives a good assurance that higher quality will be delivered.

Tracking is a control strategy where continuous monitoring, T=0, is conducted. Since the incoming raw water is monitored at every instant, there is no need to overdose, α =0. Since sophisticated equipment is required, it is deemed economically impractical for most communities, especially smaller ones. In order to evaluate the penalty cost for monitoring intervals and overdose factors other than zero, T=0 and α =0, compare the values shown in Table 8 to 47.2, the annual average alum dose amount for tracking. This comparison shows a percentage increase of alum ranges from 23.3 to 36.0 percent for T between 12 and 60 hours.

An investigation of overdose factors greater than three, $\alpha>3$, shows that there is little benefit in reducing the underdose frequency. See Figures 14 through 16. The dynamic control strategy is unable to predict spike events. A spike event is defined as one that has a large increase in color over the time interval T. Our studies of the three year time series record indicates that spike events occur after snow melt, ground thaw, and heavy rains. The operator may utilize this monitor at a higher frequency during these periods or may elect to increase α for a temporary period until the critical period is considered to be past.

Our economic study did not consider the effect of temperature. In order to improve settling efficiency, additional alum is required. This will add to the total cost of treatment. Labor, backwash, and sludge disposal costs are considered major cost factors in the total cost of the water treatment process. These costs are related to the alum dosage; unfortunately they are not simple ratios and cannot be simply introduced in our economic analysis. For example, the time between backwash and disposing of sludge will depend on the alum dosage. The higher the alum dosage the more frequently backwashing and sludge disposal must occur. The net result is a more costly plant operation.

It is recommended that the overdose factor be minimized in order to reduce the level of residual alum in the finish water. Thus, overdose factors between 1.5 and 3.0 should be investigated. An investigation of Figure 1 shows that there are reasonably long periods, weeks and months, when the raw water color does not vary significantly. During these periods it might be possible to utilize a different overdose factor then during other parts of the year. These studies should be performed before they are introduced into the plant. Our recommendation is to utilize the dynamic control strategy with α =3 with T=12 hours.

CHAPTER 6

CONCLUSIONS

- A simple dynamic control strategy was developed based upon observations of water quality measures of color and temperature.
 - a) Predictive models for specifying the "critical" alum dosage as a function of raw water color are developed. For centrifuged samples these equations are an effective forecasting tool for all temperatures investigated. This implies that the critical alum dose is independent of temperature.
 - b) A dynamic control strategy model for forecasting color was derived from a time series record of color. This model may be calibrated by obtaining a one year time series record of the water entering the plant. The overdose factor and monitoring time interval were shown to be the principle factors in reducing the risk of underdosing and the cost of operation.
 - c) For good performance, pH should be carefully controlled. The pH ranges for maximum color removal after settling are narrower than the pH range for maximum color removal after centrifuging.
 - d) For temperatures below 20°C, the amount of alum required for maximum color and turbidity removal after settling is greater than the predicted "critical" alum dose given by the prediction equation. The amount of this addition is dependent upon raw water color and water temperature.
- 2. The dynamic control strategy appears to be cost effective. The major factor of chemical treatment cost is a function of raw water color and temperature. Overdosing at moderate levels to reduce the risk of underdosing is relatively small fraction of the overall chemical cost.

- 3. Results from jar tests indicate
 - a) raw water color, not turbidity is the controlling factor for predicting the "critical" alum dose. Both color and turbidity are effectively removed at the "critical" alum dosage level.
 - b) for a given alum dose, additional color removal may be achieved by proper adjustment of the mixing conditions in the rapid mix and flocuclator units. For rapid mixing, the controlling factor in operation is the interaction Gt and for flocculation, G and t are controlling factors.
 - c) the amount of residual aluminum in the finish water is shown to be a function of temperature.

The effectiveness of this treatment strategy has not been tested in actual practice. A pilot plant, 2400 gallons per day, has been constructed at the Arthur Rollins Treatment Plant in Durham, N.H., a 1.7 Mgal/day facility. The pilot plant operates in parallel with the actual plant, thus it permits direct comparison between treatment strategies. A few tests have been run in this facility. The results have been encouraging, thus giving confidence that the predictive equation for "critical" alum dose is a useful tool in practice.

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NOMENCLATURE

at	=	random shock term, CU
d	=	alum coagulant dose, mg/l
d*	=	"critical" alum coagulant dose, mg/l
e _t	=	forecast error
G	=	velocity gradient, second ⁻¹
Ğ	=	average velocity gradient, second ⁻¹
N	=	number of observations in the time series record
m	=	number of underdoses, number per year
₹ _t	=	yearly annual average of color, CU
×o	=	apparent raw water color, CU
×o	=	apparent raw water fulvic acid concentration, mg/l
×t	=	color reading, CU
ž	=	annual average dosage of alum, tons/year
q	=	residual color, CU
sa	=	estimate of σ_{a} , CU
^s e	=	estimate of σ_{e}
s z	=	estimated standard deviation of annual dosage
t	=	mixing duration time, seconds
т	=	sampling time interval between observations x_{t-1} and x_t hours and the lead time interval for the forecast for the treatment period between t and t+1.
σ_{a}	=	standard deviation of random shock term, a _t , CU
σ _e	=	standard deviation of forecast error e _t , CU