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Trihalomethane Precursor Reduction Using Magnesium Coagulation

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TRIHALOMETHANE PRECURSOR REDUCTION USING MAGNESIUM COAGULATION

BY

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ABSTRACT

This study investigated the effectiveness of the magnesium coagulation process in reduction of trihalomethane (THM) precursors. The water was obtained from Lake Washington, a highly colored potable water supply which is used by the City of Melbourne, Florida. The THM concentrations in the finished water at Melbourne currently exceed the THM standard of 0.1 mg/l.

For Lake Washington water, treatment varies according to seasonal changes in water quality. During the dry period, the recycle magnesium does not perform effectively as a coagulant for THM precursor removal. This is because of the high levels of magnesium in the lake water at this time. During the wet period, when magnesium concentrations are very low, it is much more effective. Magnesium sulfate was found to be effective in reducing THM precursors for both types of water. There was a direct correlation observed between THMFP, TOC and color observed in treated water samples. The lack of effectiveness in THMFP, TOC and color removals by recycle magnesium was not found to be due to a lack of magnesium precipitation. Variations in rapid and slow mixing times had no effect on THM precursor removal, but did affect settling of the floc. Addition of alum as a polymer at high pH values was also very effective in reducing the THMFP, TOC and color, and increasing floc sedimentation.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Disinfection by Chlorination

In the United States, chlorination of public water supplies has been practiced since the early 1900's for the purpose of biological disinfection. Disinfection is necessary because of the number of diseases for which the principal means of transmission is water. In 1849, Dr. John Snow first theorized that water was the mode of transmission for cholera. He later demonstrated his theory in the Broad Street pump episode in London in 1854. By removing a pump handle he stopped an epidemic of cholera which had already claimed 500 lives. The source of the epidemic was a broken sewer line contaminating the water drawn from the Broad Street Pump (White 1972). More recently there was an outbreak of typhoid fever in South Florida in 1973 due to an interuption in the disinfection process (Craun 1981).

Chlorine is very effective in killing pathogens associated with many waterborne diseases. Typhoid, cholera, amoebic dysentery, gastroenteritis, and even viral diseases are effectively eliminated by proper chlorination (White 1972). Besides providing security from waterborne diseases, chlorination is also responsible for destroying other nuisance organisms which cause

taste and odor problems, foul the filter media, and degrade the quality of water in the distribution system.

Trihalomethanes (THM's)

Recently it has been shown that the chlorination process is responsible for the chemical formation of a group of organic compounds known as trihalomethanes (THM's). The general reaction for THM formation is:

$$\text{Organic precursor} + Cl_2 \rightarrow \text{THM's} \qquad (1)$$

The four commonly occurring THM's are chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Naturally occurring organics in water, such as those resulting from decaying vegetation are one of the important precursors for THM formation (Rook 1976). These natural organics often impart a brownish color to the water when they are present.

The widespread occurrence of THM's in the United States was identified by the National Organics Reconnaissance Survey (Symons, et al. 1975). In this survey 80 water supplies were examined for the presence of several chlorinated organic compounds, including THM's. The THM's found were chloroform, bromodichloromethane, dibromochloromethane, and bromoform, present in almost all waters investigated. These findings were supported by a later, more intensive study, the National Organics Monitoring Survey involving over 100 public utilities (U.S. EPA 1977).

The presence of THM's in drinking water supplies has generated concern for public health. Laboratory studies conducted on animals have indicated chloroform may be carcinogenic to humans (U.S. NCI 1976). There have been conflicting reports where statistical correlations have been made between water containing THM's and cancer incidence (Cantor 1975). There is also suspicion that the brominated THM's found may also be toxic to humans.

Due to the evidence of the widespread occurrence of THM's and their potentially harmful effects, the United States Environmental Protection Agency (U.S. EPA) has promulgated a minimum contaminant level of 0.1 mg/l for total THM's. Many utilities currently exceed this level and must take steps to reduce their THM levels or seek an extension to the November 19, 1981 deadline.

The Magnesium Process

The use of magnesium salts for coagulation was not practiced until recently because of chemical cost. Magnesium sulfate ($MgSO_4 \cdot 7\ H_2O$), the least expensive commercial source of magnesium, costs \$0.22/lb compared to \$0.18/lb for $Al_2(SO_4)_3 \cdot 14\ H_2O$, alum The additional cost of lime, \$72/ton, also increases the chemical cost of magnesium coagulation. If no additional alkalinity is required for alum coagulation an approximate chemical cost of \$8.00 per mg/l Al^{+3} dosed per million gallons, using $Al_2(SO_4)_3 \cdot 14\ H_2O$ is incurred compared to \$29.50 per mg/l Mg^{+2} dosed per

million gallons using $MgSO_4 \cdot 7\ H_2O$ and lime, CaO at pH 11 for typical raw waters.

In recent years, a potable water treatment process was developed in which magnesium carbonate and lime are used as the treatment chemicals and then recovered for reuse. This process is advantageous due to reduction in sludge disposal problems and chemical cost.

Magnesium coagulation involves addition of lime slurry and magnesium carbonate to the water causing precipitation of magnesium hydroxide and calcium carbonate. This is accomplished at a pH of approximately 11. Both color and turbidity are effectively reduced by magnesium coagulation (Thompson, et al. 1972a). After settling, the water is stabilized by recarbonation, filtered, and then chlorinated before distribution.

The sludge from coagulation contains magnesium hydroxide and calcium carbonate. Carbonation of this sludge selectively solubilizes the magnesium in the bicarbonate form. The magnesium is then separated from the calcium carbonate by sedimentation and recycled to the coagulation tank as supernatant. There is a significant amount of soluble organics which are also recycled in the supernatant if the water is taken from a highly naturally colored source. The calcium carbonate remains in the solid form and is thickened, vacuum filtered, and calcined producing calcium oxide, which is also reused. This ability to separate and

recycle the components of the sludge makes this process cost effective because of the high costs associated with sludge disposal (Thompson 1972a).

The City of Melbourne, Florida utilizes the magnesium process to treat raw water from Lake Washington. The average color and total organic carbon (TOC) concentration is 80 cpu and 27 mg/l in Lake Washington (Mason and Belanger 1977). Seasonal changes in water quality of the lake occur due to rainfall occurrence. Melbourne was one of the cities chosen for evaluation in the National Organics Monitoring Survey. Of all utilities examined, Melbourne had the highest concentrations of THM's, an average of 550 µg/l (U.S. EPA 1977), in the finished water. The problem of complying with the standard is substantial, in view of their highly organic raw water supply and the organics recycled with the recovered magnesium to the coagulation tank in the magnesium process.

Purpose

The primary objective of this study was to optimize the removal of Trihalomethane Formation Potential (THMFP) in the coagulation unit operation in the magnesium process. Color and TOC removals were also documented and correlated to THMFP removal during the study. The effect of differing mixing energies during coagulation and flocculation on THMFP, TOC and color removal and floc sedimentation were also investigated. Finally, the ability

of aluminum to act as a polymer at high pH for floc, color, TOC and THMFP removal was evaluated.

This study is part of a grant from the Environmental Protection Agency to investigate methods for reducing the THMFP in the drinking water of Melbourne, Florida. This study is of most interest to anyone interested in using the magnesium process to reduce THMFP, TOC and color from a highly colored surface water source, especially when different treatment variations may be necessary for different seasons. It is also of interest to anyone using any lime softening process who is concerned with the effects of precipitation, mixing energies and alum polymer additions on floc settling and THMFP, TOC and color reduction during precipitation.

CHAPTER II

LITERATURE REVIEW

Trihalomethanes in Drinking Water

Discovery and Occurrence

In 1974, numerous chlorinated organic compounds were identified in drinking water derived from the lower Mississippi River (Dowty, et al. 1975). Predominant among the chlorinated organics present was a group of organic compounds known as trihalomethanes (THM's). Chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$) were the THM's identified. The presence of these contaminants prompted the U.S. EPA to conduct a study to determine the occurrence of THM's in drinking water supplies from various regions of the United States.

The National Organics Reconnaissance Survey examined 80 drinking water supplies from a variety of locations (Symons, et al. 1975). Chloroform was the THM observed most frequently, being present in all supplies investigated. Due to the absence or extremely low concentrations of these compounds in the raw water source it was concluded that THM's were formed during the chlorination process in water treatment. These findings were

supported by a later, more intensive study, the National Organic Monitoring Survey involving over 100 public utilities (U.S. EPA 1977).

Public Health and Law

Disinfection of potable water is an essential part of water treatment. Many waterborne diseases such as cholera, typhoid, amoebic dysentery, gastroenteritis and some viral invections can be transmitted in drinking water. The organisms which produce these diseases must be destroyed to protect the health of the public. In addition, there are other organisms which cause problems in water treatment processes, contributing to taste and odor problems, and fouling filter media (White 1972).

The use of chlorine has been proven very effective in achieving biological disinfection. Since the 1900's, chlorination has been an integral part of water treatment practice. The recent findings that chlorination is responsible for the chemical formation of THM's is significant, due to reports that chloroform, one of the THM's, may be carcinogenic to humans.

In 1976, the United States National Cancer Institute (U.S. NCI) disclosed that chloroform had been found to cause cancer in rats and mice when administered orally. The potential risk to humans has been questioned by some investigators. Stokinger (1977) suggested that biological responses to a toxic agent are not identical at low and high doses, and extrapolation of data

from animals to humans is questionable. Tardiff (1977) defended the data from the U.S. NCI and stated that there may be a risk to bottle-fed infants. The kidney and liver were the major organs affected by chloroform (U.S. NCI 1976). The risk of cancer in these organs has been estimated by Tardiff to be between no risk and 1.6 per million population per year.

To avoid problems with extrapolating data from animal studies to human populations, epidemiologic studies have been conducted relating cancer incidence to drinking waters containing chloroform. One such study of Massachusetts communities supplied with water containing chloroform indicated that THM's and other by-products of chlorination were not significantly associated with cancer incidence (Tuthill and Moore 1980). Investigations of this type are difficult to substantiate due to limitations including the long latent period for most cancers, difficulties in estimating dose, the definition of at-risk populations and the relatively low exposure to carcinogenic agents (Cantor 1975).

Because of the widespread occurrence of THM's and their potentially harmful effects the U.S. EPA has promulgated a minimum contaminant level of 0.1 mg/l for total THM's (U.S. EPA 1978). For many water utilities this standard means modifications or alterations of present treatment processes are necessary. By understanding conditions favorable to THM formation or THM precursor removal, it may be possible to limit their production to acceptable levels.

Factors Affecting Formation

Trihalomethanes (THM's) are formed by the reaction of chlorine with organic compounds present in the water during treatment (Bellar, et al. 1974). A general reaction describing THM formation is:

$$\text{Organic precursor} + Cl_2 \rightarrow \text{THM's} \qquad (2)$$

Although some THM's are formed immediately, this reaction is not instantaneous and typically continues for several days until either chlorine or organic precursors are exhausted (Rook 1976). The rate of formation of THM's as well as the particular THM species formed have been shown to depend upon many factors including concentration and type of organic precursor, pH, temperature, presence of inorganic species such as bromide, chlorine contact time and chlorine dose.

Higher concentrations of THM's have been detected in drinking waters derived from surface waters than in those derived from groundwaters (Bellar, et al. 1974; Symons, et al. 1975). Because the potential for contamination of surface waters is somewhat greater than for groundwaters, higher levels of organic precursors are usually found. However, groundwater contamination is currently a major national concern.

There have been many investigations concerning the identification of THM precursors and the mechanisms of THM formation. The classical haloform reaction described in organic chemistry

texts involves the combination of methyl ketones with halogens and a base to form THM's as shown in equations 3 and 4 (March 1968).

$$\mathrm{H\text{-}\overset{H}{\overset{|}{C}}\text{-}\overset{}{\overset{||}{C}}\text{-}R + Cl_2 \xrightarrow[OH^-]{H^+ \text{ or}} Cl\text{-}\overset{Cl}{\overset{|}{C}}\text{-}\overset{}{\overset{||}{C}}\text{-}R} \qquad (3)$$

$$\mathrm{Cl\text{-}\overset{Cl}{\overset{|}{C}}\text{-}\overset{}{\overset{||}{C}}\text{-}R + OH^- \rightarrow Cl\text{-}\overset{Cl\ OH}{\overset{|\quad|}{C\text{-}C}}\text{-}R \rightarrow CCl_3^- + RCOOH \rightarrow CHCl_3 + RCOO^-} \qquad (4)$$

Bellar, et al. (1974) theorized ethanol as the compound with oxidation by hypochlorite (OCl^-) ion to acetaldehyde, followed by the classic haloform reaction to be the mechanism of formation, as shown in equation 5.

$$\mathrm{CH_3\text{-}CH_2OH + OCl^- \rightarrow CH_3\text{-}\overset{}{\overset{||}{C}}\text{-}H \rightarrow \text{Haloform reaction}} \qquad (5)$$

Rook (1976) proposed that natural humic substances present in water supplies were largely responsible for THM production. He observed that m-dihydroxyaromatic compounds, common building blocks of humic materials, produce high levels of chloroform when chlorinated. Although algae (Hoehn 1979) has been shown to produce THM's upon chlorination, in most instances humic materials appear to be the primary THM precursor (Oliver and Lawrence 1979; Oliver and Visser 1980).

Surface waters are frequently brownish colored due to the presence of humic substances. These natural organic compounds

result from decay of vegetation, leaching of soil organic matter, and extraction of soluble substances from wood tissues. There are three types of compounds comprising humic substances. Fulvic acids are the predominant compounds found, followed by humic acid and hyatomelanic acid (Rook 1977). Furthermore, the relative amounts of each fraction observed in natural waters are fairly constant (Black and Christman 1968).

There are several theories as to which fraction of the humic substances is most important as precursors in the THM reaction. Babcock and Singer (1979) found that chlorination of humic acids results in greater yields of chloroform than fulvic acids. Peters, et al. (1980) also determined that humic acids produce higher yields of chloroform due possibly to a greater number of active sites present on larger humic acid molecules. Other studies indicate humic and fulvic acids produce equal quantities of chloroform upon chlorination (Oliver and Lawrence 1979). Kavanaugh, et al. (1979) proposed that the TOC concentration is the determining factor affecting THM formation rather than the type of organic precursor present.

The pH of the water during chlorination is directly proportional to the THMFP of a given water if adequate chlorine and organics are present. In Figure 1 it can be seen that as the pH increases, the corresponding level of THM's formed also increases (Stevens, et al. 1975). From the shape of the curves one can

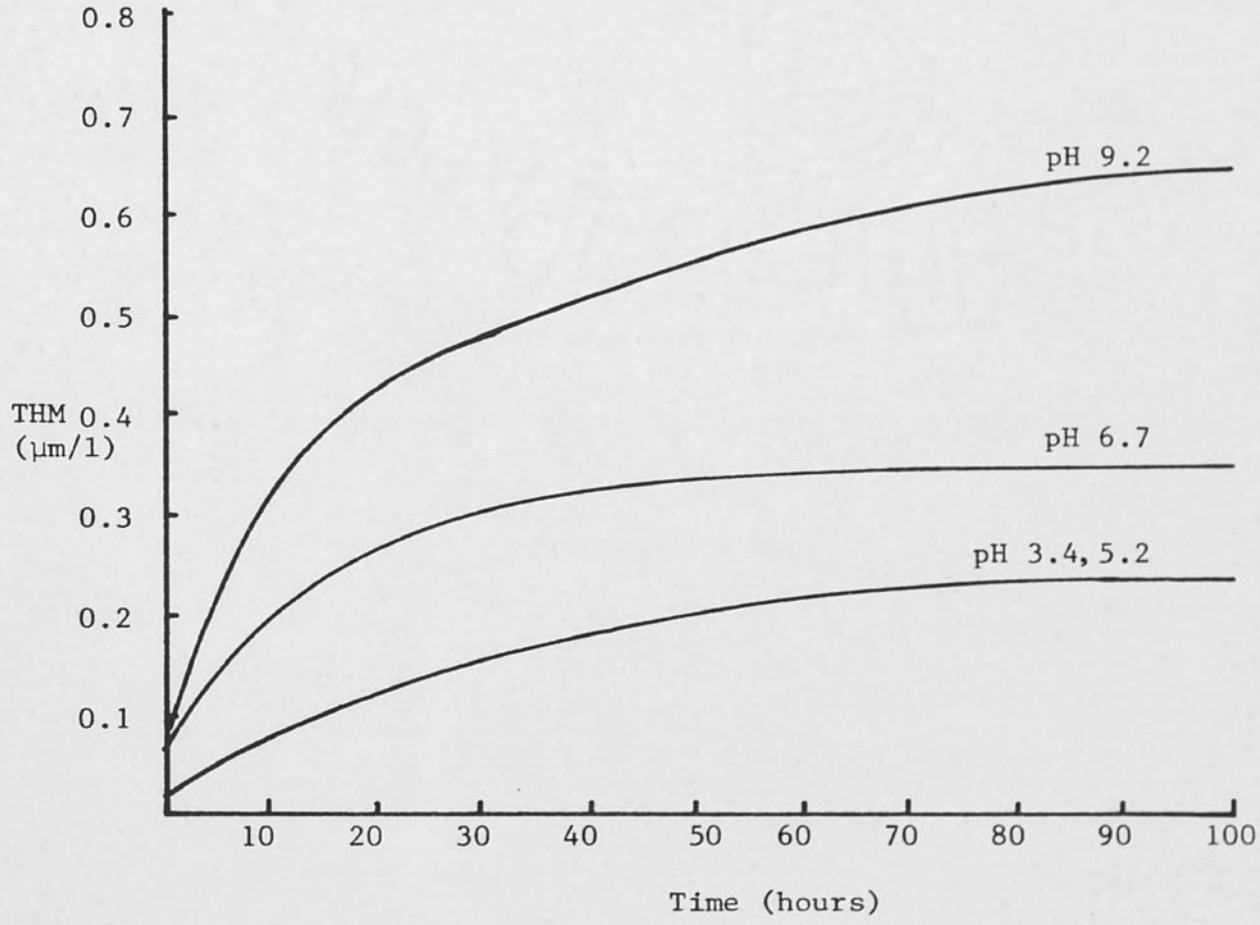


Fig. 1. Effect of pH on THM production from humic acid, 1 mg/1. Conditions:chlorine dose, 10 mg/1; 25° C.

SOURCE: Stevens, et al. 1976.

assume that at pH 6.7 the reaction was nearly complete or proceeding at a very slow rate relative to the initial rate. At pH 9.2there is almost a two-fold increase in final product concentration. This is explained by the presence of certain reactive sites on the humic acid molecule that react at insignificant rates at the lower pH but are reactive at higher pH values. This effect could also be partially due to base hydrolysis. Peters, et al. (1980) indicates that pH may be a parameter which affects the particular route which is taken to chloroform production.

Temperature of the water has been shown to have a direct effect on the levels of THM's formed, shown in Figure 2 (Stevens, et al. 1975). As the temperature was increased, the concentrations of THM's formed also increased. This trend was also observed by Arguello, et al. (1979) in a study on variations in THM levels for a water treatment plant over a period of one year. Lower levels of THM's were formed during the colder months than the warmer summer months, although lower precursor levels might also occur during colder months.

The presence of bromide salts in the water has been shown to cause the formation of brominated THM's (Rook 1977). It has been proposed that the chlorine reacts with bromide to form bromine, which is then able to react with organic precursors forming brominated THM's (Arguello, et al. 1979). A strong correlation existed between the concentration of inorganic bromide in

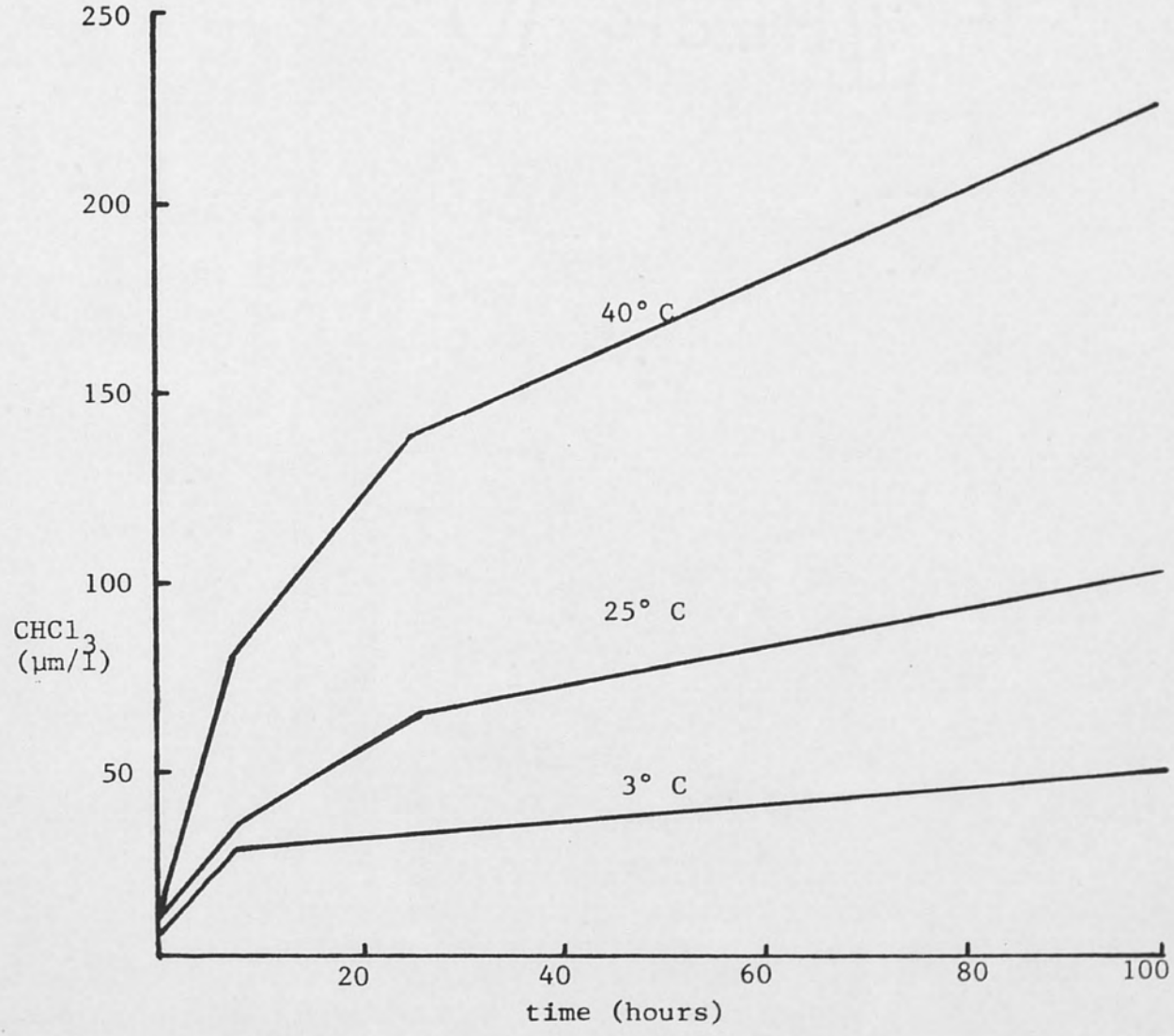


Fig. 2. Effect of temperature on chloroform production from raw water. Conditions: chlorine dose, 10 mg/l; pH 7.

SOURCE: Stevens, et al. 1976.

the raw water and the amount of brominated THM's present in the finished water. Stevens and Symons (1977) found that the ratio of chloroform to other THM's is highly dependent on the bromide content of the water. Kimes (1979) demonstrated that increasing doses of ozone to a high TOC water prior to chlorination significantly increased the bromide containing THM compounds.

Chlorine contact time is important in the reaction of chlorine with organic precursors. Trihalomethanes continue to be produced until one of the reactants is exhausted. For this reason concentrations of THM's are greater at the consumer's tap than at the water treatment plant. The chlorine dose which is applied has been shown by Kimes (1979) and Kavanaugh, et al. (1979) to strongly influence THM formation. The addition of large amounts of chlorine was believed to cause compounds resistant to attack to become precursors for THM formation.

Methods of Reduction

By applying knowledge of the conditions favorable to THM formation it may be feasible to alter present water treatment practices to produce substantially lower levels of these compounds in the finished water. There are three principle strategies for control of THM's. These are:

1. to reduce the potential for THM formation prior to chlorination
2. to remove THM's after formation

3. to use an alternate disinfectant

There are many methods of reducing the potential for THM formation before chlorination. Changes in the location of chlorination, optimization of coagulation and flocculation, and adsorption of organic precursors are all important modifications in water treatment which can lower the THM levels in the finished water.

Changes in the location of chlorination in the process train have been shown to be very effective in producing lower THM levels. Elimination of pre-chlorination practices can reduce levels formed by up to 76% (Blanck 1979). A move from pre-chlorination to chlorination of the effluent from the settling basin produced this reduction in formation. Tifft, et al. (1979) achieved a 67% reduction in THM formation by changing the location of chlorination in an alum flocculation process. It is important to add chlorine to water with the lowest possible organic content. To prevent problems from arising in the plant from discontinuation of pre-chlorination an alternate pre-treatment disinfectant such as potassium permanganate may be used (Blanck 1979). In lime softening treatment plants it is advisable to delay chlorination until the effluent of the recarbonation basin since chlorination at the high pH encountered in lime softening will cause significantly higher levels of THM's to be formed (Harms and Looyenga 1980).

The optimization of coagulation and flocculation processes for organics removal has been studied by some investigators. Stevens, et al. (1975) observed that alum coagulation removed

most organic precursors from Ohio River water. In coagulation of humic materials, Babcock and Singer (1979) achieved a 70% reduction in chloroform concentrations. Hall and Packham (1965) found there was a stoichiometric relationship between dose and 50% removal of organics using alum and iron as coagulants. There have been studies indicating that lower pH levels and higher coagulant doses are necessary for efficient organics removal when alum or iron is used as the coagulant (Stevens, et al. 1975; Semmens and Field 1980).

Studies conducted to determine the influence of operating variables on coagulation for organics removal indicate rapid mix time had no effect on organics removal. In an investigation by Albert (1979) neither the speed of addition of coagulant nor the method of mixing had a significant effect on removal of humic acid. He used rapid mix times from a few seconds to 10 minutes. Semmens and Field (1980) found that in coagulation of Mississippi River Water mixing conditions were very important in turbidity removal but organics removal was unaffected. They also observed that the order of chemical addition was not significant in removal of organics. Flocculation times also seem not to affect precursor reduction. Semmens and Field (1979) obtained no additional benefit in soluble organics removal by ferric sulfate if the flocculation time was extended to 10 hours.

Efficient removal of organic compounds by coagulation processes is important also if activated carbon is to be used

to further reduce the organic carbon content of the finished water. By optimizing coagulation processes the reduced load on the activated carbon bed will extend its useful life. Adsorption by activated carbon is effective for removing organic precursors when it is fresh, but typically after about one month, its effectiveness is limited to removal of only the larger organic compounds, necessitating frequent regeneration (Symons 1976).

Adsorption of precursors on weak base anion exchange resins was found to be effective but expensive (Rook 1976). Rook and Evans (1979) determined weak base resins in conjunction with coagulation, flocculation and filtration reduced the chloroform potential of Meuse River water by 75%. The corresponding reduction in total THM's was approximately 65%.

It is more difficult to remove THM's after their formation than it is to reduce their potential before chlorination (Rook and Evans 1979). Aeration of chlorinated water was not feasible due to the high air-water ratio necessary for THM removal for the water studied by Duke, et al. (1980). This high air-water ratio also leads to algal growth problems. However, aeration is being used to remove some volatile organics from groundwater in Miami, Florida at the Dade County Water Treatment Plant. Granular activated carbon has been investigated for THM removal but its effectiveness only lasts for a few weeks (Blanck 1979). The use of alternate disinfectants is a promising solution to the THM

problem. Ozone, chlorine dioxide and chloramines are being evaluated for use in disinfection both alone and in combination (Vogt and Regli 1981).

Ozone does not produce THM's but it also does not produce a disinfectant residual to be carried throughout the distribution system (Symons 1976). The health hazard, if any, of the by-products of the reaction of ozone with organic matter is not known at this time (Greenberg 1981). Ozonation of water for disinfection is common in Europe, accompanied by small dosages of chlorine, chlorine dioxide or chloramines to prevent bacterial re-growth in the distribution system (Rice, et al. 1981).

Chlorine dioxide has been used often for control of taste and odor problems. In Europe, it too is commonly used as a disinfectant in drinking water treatment. Although chlorine dioxide does not produce THM's, it produces other compounds which could be harmful. Chlorite and chlorate ions are inorganic reaction products of ClO_2 which may be toxic to humans (Greenberg 1981). Oxidation of hemoglobin in the blood to methemoglobin, which has a reduced capacity for oxygen transfer is one of the more striking effects (Symons 1976).

The use of chloramines in place of chlorine also reduced THM formation but its use requires a longer contact time for adequate biological control (Schull 1981). The greatest application for chloramines has been as a secondary disinfectant, providing

maintenance of a residual in the distribution system (Rice, et al. 1981).

The Magnesium Process

Magnesium Coagulation

When lime-soda softening treatment is applied to a water with high levels of magnesium, magnesium hydroxide is precipitated in addition to calcium carbonate. The presence of magnesium hydroxide, because of its voluminous nature, hindered sludge handling operations for many years. In studies conducted by Nelson (1944) and Black and Eidsness (1957) it was demonstrated that by bubbling CO_2 gas through the lime softening sludge the magnesium hydroxide could be selectively dissolved, increasing sludge settleability and lowering sludge volume. Because of the reduced magnesium content of the sludge, recalcination of the lime became a feasible process.

Stumm and O'Melia (1968) demonstrated that aluminum, magnesium and calcium perform effectively as coagulants. Because magnesium, in either the sulfate or chloride form is more expensive than alum, its potential use as a coagulant was often overlooked. The discovery that the magnesium hydroxide and calcium carbonate in lime-soda sludges could be separated generated interest in the use of magnesium as a coagulant.

In 1972, a new potable water treatment process was proposed combining lime softening and conventional coagulation (Thompson,

et al. 1972a). Magnesium was used as the primary coagulant and lime was used to raise the pH for magnesium hydroxide precipitation. Important reactions taking place in the process are shown in equations 6 through 9.

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \quad (6)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \quad (7)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + 2H_2O \quad (8)$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCO_3 \quad (9)$$

The resulting sludge was carbonated and magnesium was recovered for reuse. Lime could then be recovered by recalcination from the remaining solids. This ability to recycle magnesium and lime greatly reduces sludge handling problems and treatment chemical costs (Thompson, et al. 1972 b). In addition, the high pH of coagulation, usually above 11, should:

1. provide complete disinfection when adequate contact time is provided
2. eliminate the need for pre-chlorination in many plants
3. provide essentially complete removal of iron and manganese, where present (Thompson, et al. 1972b)

A flow diagram of the magnesium process is depicted in Figure 3.

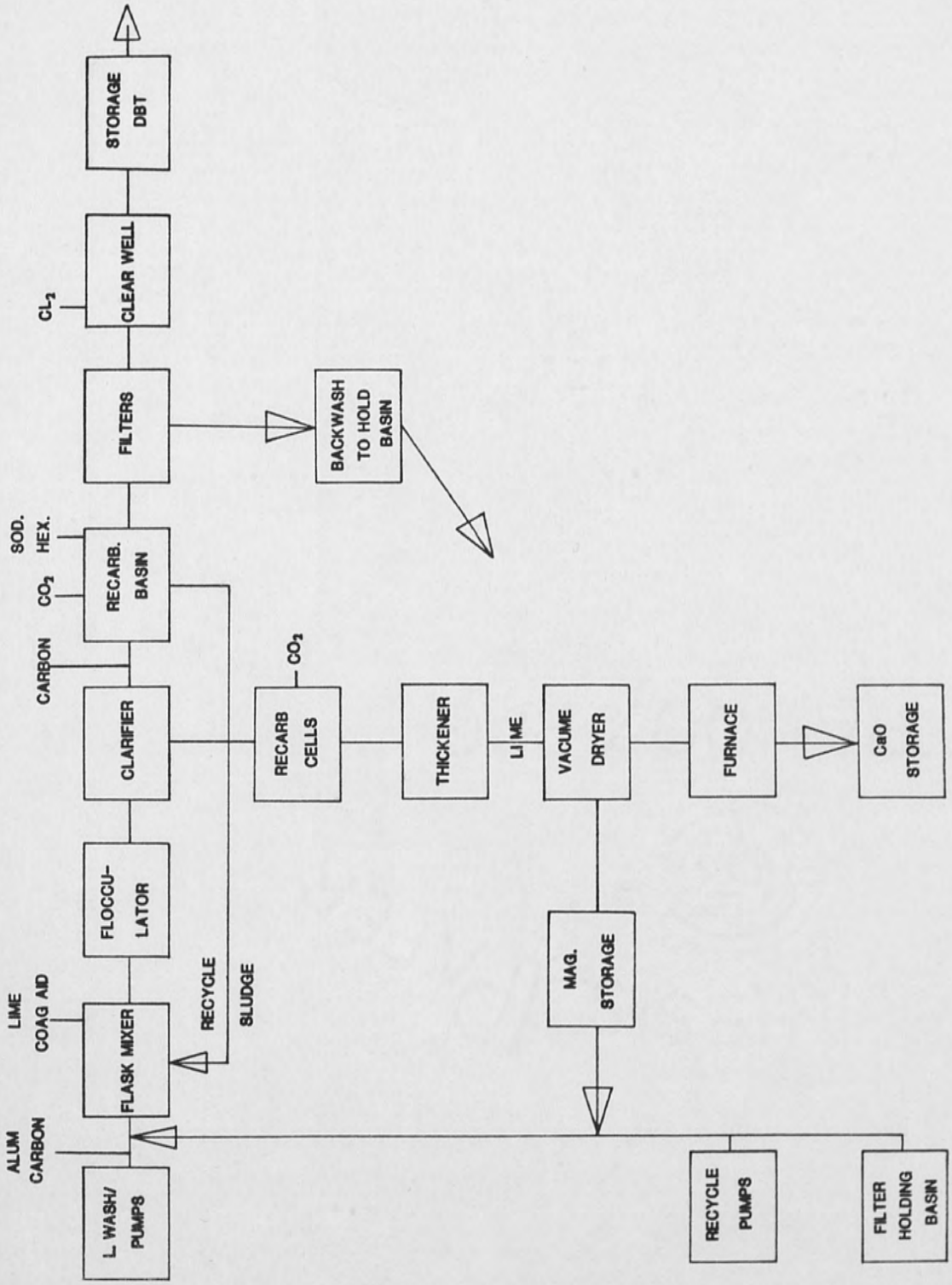


Fig. 3. Flow diagram for Melbourne Water Treatment Plant.

Magnesium and Lime Recovery

In the carbonation process it is important to know the quantity of magnesium which will be recovered, especially if this magnesium is to be recycled as a coagulant. The concentration of CO_2 is the main factor determining the solubility of magnesium in the sludge (Black and Eidsness 1957). Important reactions taking place during sludge carbonation are:

$$Mg(OH)_2 + 2CO_2 \rightarrow Mg(HCO_3)_2 \qquad \text{pK: } -4.19 \qquad (10)$$

$$Mg(OH)_2 + CO_2 + 2H_2O \rightarrow MgCO_3 \cdot 3H_2O \qquad -8.15 \qquad (11)$$

$$MgCO_3 \cdot 3H_2O + CO_2 \rightleftarrows Mg(HCO_3)_2 + 2H_2O \qquad 3.95 \qquad (12)$$

$$Mg(OH)_2 + Mg(HCO_3)_2 + 4H_2O \rightarrow 2MgCO_3 \cdot 3H_2O \qquad -12.12 \qquad (13)$$

Reaction 10 is the overall reaction taking place. Reactions 11 and 12 are consecutive and represent two steps in the overall reaction. Reaction 13 shows that as carbonation progresses, there will be an increasing tendency for undissolved $Mg(OH)_2$ to react with the dissolved $Mg(HCO_3)_2$, resulting in the precipitation of nesquehonite ($MgCO_3 \cdot 3H_2O$)(Black, et al. 1971).

Principles of equilibrium chemistry can be used to predict the quantity of magnesium which will sobulize upon carbonation. Peplin (1977) investigated this and found that nesquehonite was the controlling solid phase for the system considering only Mg, CO_2 and H_2O. By considering the following reaction, the magnesium available can be determined.

$$MgCO_3 \cdot 3H_2O + CO_2 = Mg^{+2} + 2HCO_3^- + 2H_2O \quad pK=2.91 \quad (14)$$

The electroneutrality condition is shown in reaction 15.

$$2[Mg^{+2}] + [H^+] = 2[CO_3^{-2}] + [HCO_3^-] + [OH^-] \quad (15)$$

From equation 14, one finds the following relationships:

$$K = \frac{[Mg^{+2}][HCO_3^{-2}]}{[CO_2]_{aq}} \quad (16)$$

For a 100% CO_2 solution:

$$[Mg^{+2}][HCO_3^-]^2 = 10^{-2.91} \quad (17)$$

From the proton condition:

$$2[Mg^{+2}] \tilde{=} [HCO_3^-] \quad (18)$$

and

$$4[Mg^{+2}]^3 = 10^{-2.91} \quad (19)$$

Peplin found that the equilibrium pH for this sytem was 7.34 and using a 100% CO_2, a saturation magnesium concentration of 6850 mg/1 as $CaCO_3$ was determined. Using a 25/75 CO_2:air gas mixture, a theoretical saturation concentration of 4320 mg/1 as $CaCO_3$ was determined. An equilibrium diagram for magnesium in a 100% CO_2 system is shown in Figure 4. These values are considerably less than the saturation concentrations actually recovered in carbonation. Black, et al. (1971) found that with pure CO_2 a saturation concentration of 25,000 mg/1 as $CaCO_3$ was achieved, and with a 25/75 CO_2:air gas mixture, a concentration

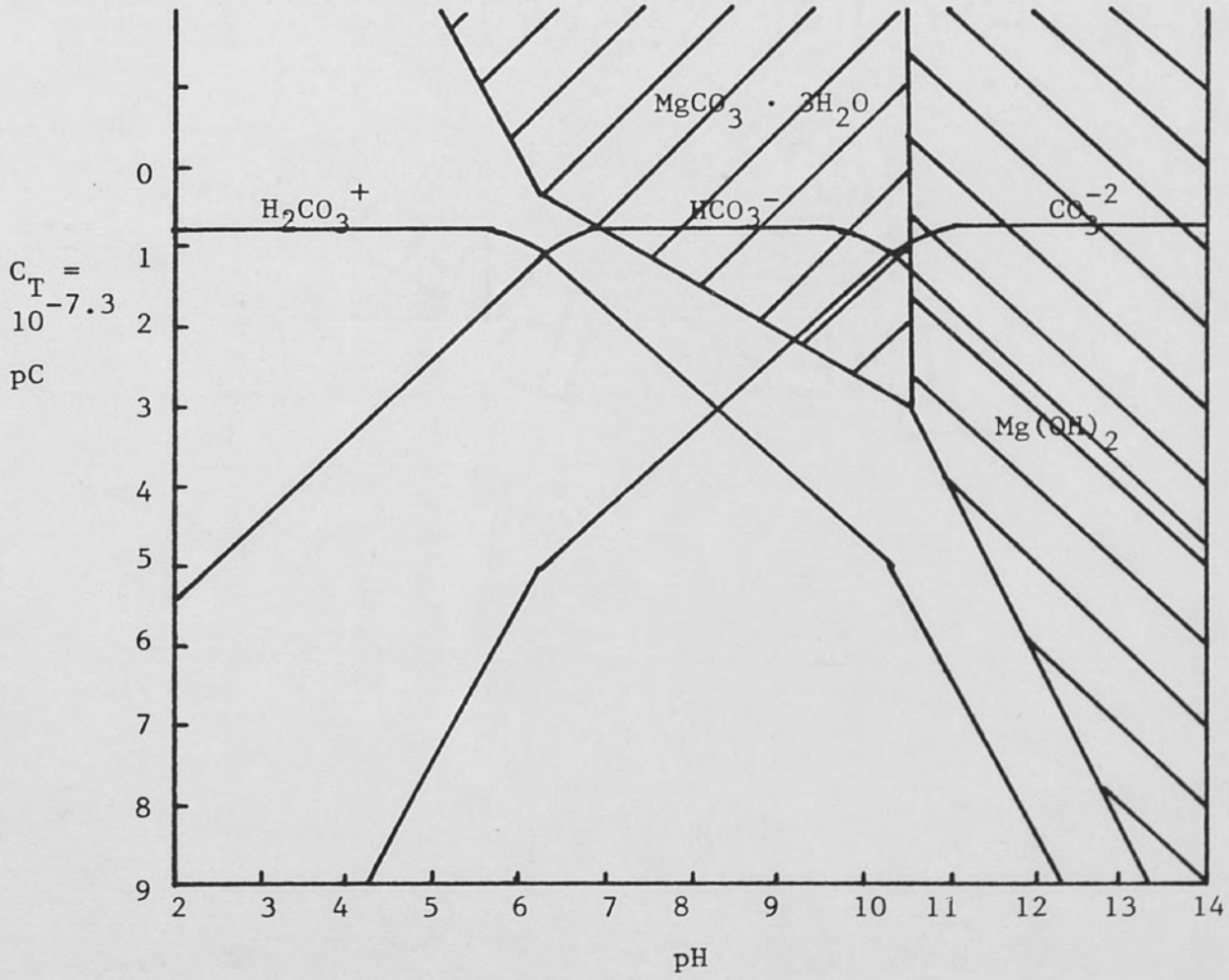


Fig. 4. Equilibrium diagram for a carbonation system using 100% CO_2.

of 16,500 mg/l as $CaCO_3$ was obtained. This is illustrated in Figure 5. Burris, et al. (1976) and Peplin (1977) obtained slightly lower concentrations. The discrepancy between predicted and actual values is considerable. The theoretical calculations do not typically consider complexation due to the many naturally occurring organic compounds and the corresponding lack of thermodynamic data for these compounds. The formation of ion pairs and complexes with both organic and inorganic ligands will increase the solubility of magnesium (Black, et al. 1971).

The recovery of quicklime from the calcium carbonate is accomplished by the burning of the material at a temperature of 1600-2200° F (871-1204° C). This process produces a high quality chemical lime containing as high as 92-93% calcium oxide (Black, et al. 1971). In pilot plant studies conducted by Burris, et al. (1976), 86% purity was obtained with recalcination. Other benefits derived from lime recovery include:

1. cost of water treatment has been reduced
2. lime values present in the raw water are recovered along with lime used in treatment
3. considerable CO_2 is produced for use in carbonating the treated water and for use in carbonating the magnesium hydroxide - calcium carbonate sludge (recovered in concentrations of 25% by volume)
4. a continuous in-plant supply of lime is available
5. land is not required for lime storage (Black, et al. 1971)

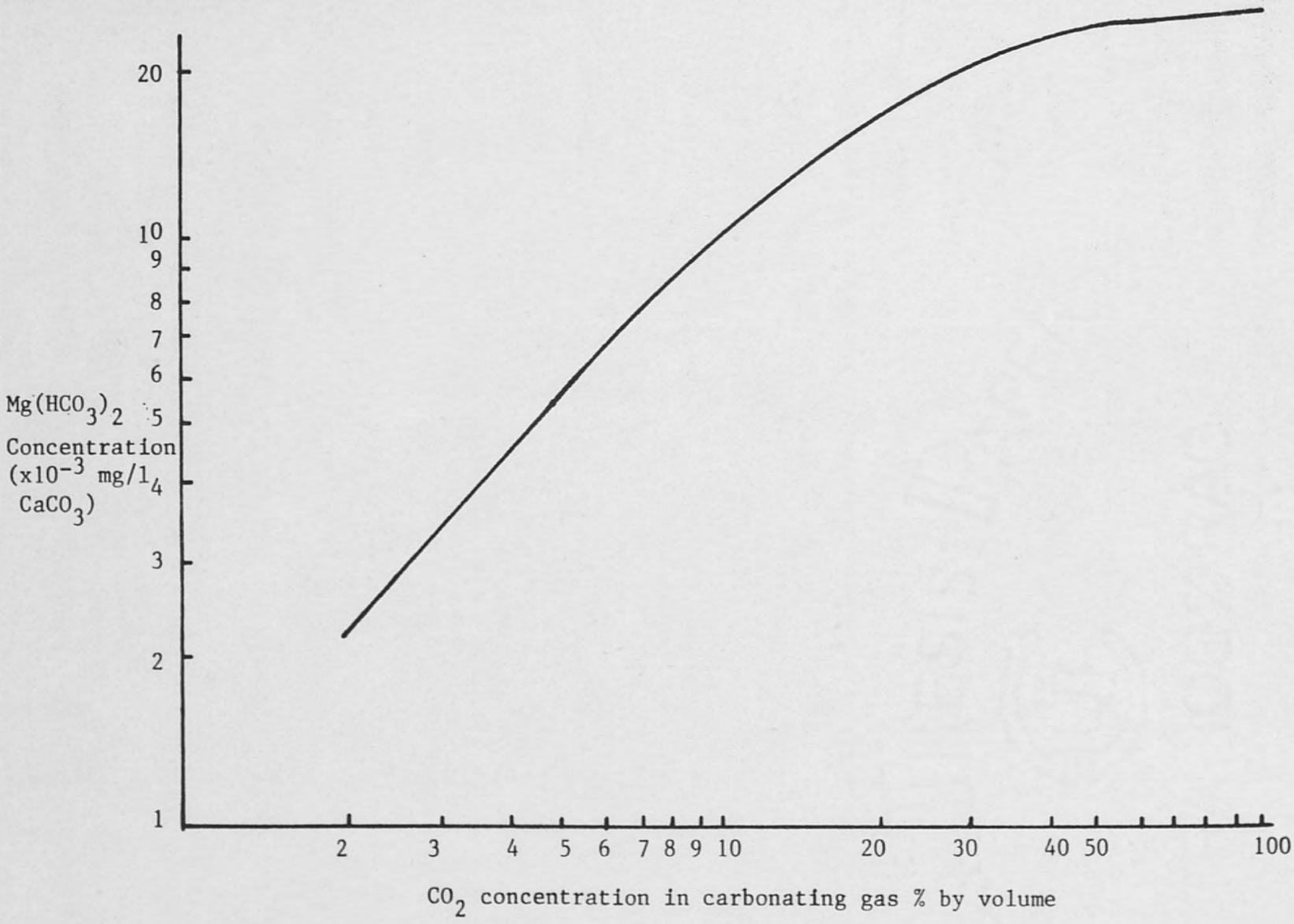


Fig. 5. $Mg(HCO_3)_2$ solubility vs. CO_2 concentration in gas.

SOURCE: Black, et al. 1971.

Effectiveness of Magnesium as a Coagulant

Comparisons of the turbidity and color removal obtained by use of alum and magnesium carbonate have been made. Thompson, et al. (1972a) studied seventeen natural waters from various locations and in every case, coagulation by magnesium carbonate produced reductions in color and turbidity comparable to alum treatment. In this investigation, the effectiveness of the recycle magnesium as a coagulant was also evaluated. Twice recovered magnesium performed as well as fresh magnesium carbonate.

In 1975, Black and Thompson compared magnesium and alum treatment on soft turbid water at Montgomery, Alabama, and on highly colored, moderately hard waters in Melbourne, Florida. In both plants, full scale studies were conducted with parallel treatment by alum and magnesium occurring simultaneously. The results showed that the magnesium coagulation was as effective in color and turbidity reductions as alum treatment. There was a problem encountered in reducing the organic content of the finished water in the Melbourne plant. It seems that neither the alum process nor the magnesium process removed more than 50% of the total organic carbon (TOC) even though color removal was occurring.

Hatcher (1979) compared the effectiveness of ferric sulfate, alum and magnesium sulfate for THMFP removal from a high TOC water. He found the optimum coagulation pH for the aluminum, iron and magnesium salts to be 5.0, 5.5, and 11.5, respectively.

Although ferric ion was the most effective coagulant in THMFP removed/mmole coagulant dose, there was no significant difference in the final THMFP reduction from the raw water with each coagulant achieving approximately 50% reduction.

Taylor (1976) demonstrated that in the lime-magnesium process, magnesium is responsible for color removal. This may be due to larger floc being produced in coagulation, providing more sites for interaction between magnesium and color. When highly colored waters have been treated with this process, problems have been encountered. When the sludge is carbonated, color molecules also solubilize, causing color buildup in the recycled magnesium. Taflin, et al. (1975) in Minneapolis was forced to discontinue recycling magnesium because the potable water produced was too colored to be acceptable. Burris, et al. (1976) found that the concentration of color is directly proportional to the quantity of magnesium dissolved in the supernatant, represented by alkalinity. This relationship is shown in Figure 6. Black and Thompson (1975) demonstrated in pilot plant studies that by treating the magnesium bicarbonate with either chlorine or activated carbon, followed by flotation, color was removed. Another method of removing color from the magnesium liquor is to incinerate the sludge before the magnesium is carbonated. This would cause the color bodies to be oxidized to CO_2 or removed as other gaseous products of incineration (Taylor 1976).

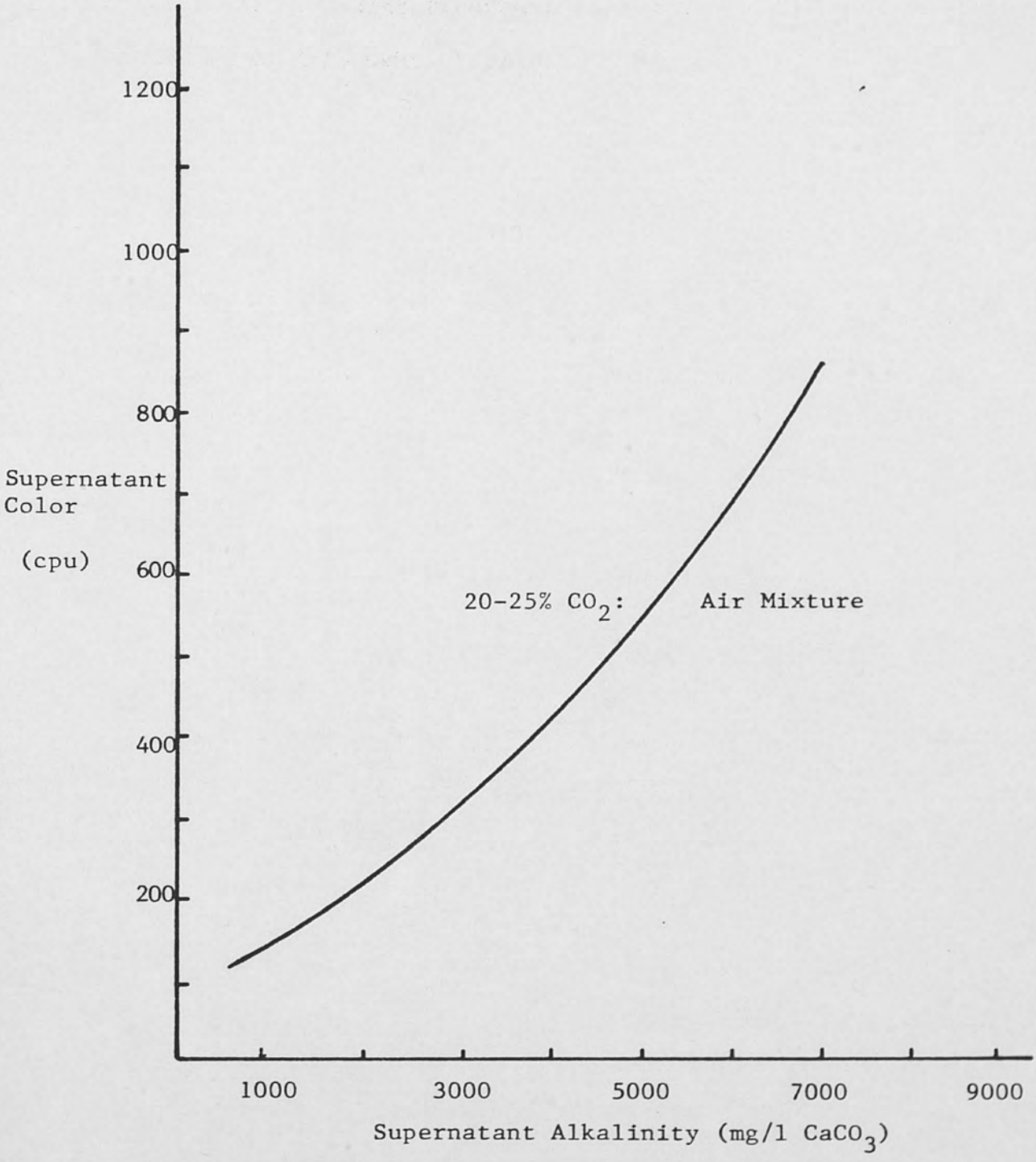


Fig. 6. Carbonated sludge supernatant color vs. supernatant alkalinity.

SOURCE: Burris, et al. 1976.

Presently, there are two water treatment plants using the magnesium process. These are Melbourne, Florida and Montgomery, Alabama.

CHAPTER III

EXPERIMENTAL METHODS

Introduction

This chapter describes the methods of sample collection, laboratory experimentation, and data evaluation used in this study. All testing was conducted in the Environmental Engineering laboratories at the University of Central Florida (UCF). The experimental procedures used in this study are in accord with Standard Methods or accepted engineering practice.

Sample Collection

Lake Washington water was collected from the raw water intake to the Melbourne water treatment plant. Each week, 55 gallon plastic-lined drums were filled with water and returned to the UCF laboratory. Before use, the water was mixed for approximately one hour to ensure homogeneity of the sample. Recycle magnesium supernatant was also collected in 55 gallon plastic-lined drums on a biweekly basis from the plant recovery cell. The recycled magnesium samples were sealed in order to prevent precipitation due to the absence of 100% CO_2 gas used to recover $Mg(HCO_3)_2$ from the $Mg(OH)_2$ sludge.

Jar Test Procedure

A Phipps and Byrd jar testing apparatus was used for all jar testing experiments. For the experiments optimizing coagulation dose and pH, magnesium sulfate or recycled magnesium bicarbonate was used as the coagulant. Because the magnesium content in the lake water was relatively high during the dry period, approximately 20 mg/l, coagulation was also evaluated with no magnesium addition. Reagent, commercial or recalcined lime was used for pH control. Reagent lime refers to pure reagent grade calcium hydroxide. Commercial lime is lime bought by the Melbourne plant from a commercial source, and recalcined lime is calcium oxide, recovered by the lime kiln at the plant. The sequence of chemical addition was lime followed by magnesium during rapid mix. Standard mixing conditions were 140 rpm for 45 seconds, then 35 rpm for 19 minutes. These are the mixing conditions which most closely resemble actual mixing conditions in the Melbourne plant. These conditions correspond to velocity gradients (G) of 126 sec^{-1} and 16 sec^{-1}. The equation used to determine G values was (Weber 1972):

$$G = (P/CU)^{1/2} \qquad (20)$$

where:

P = useful power, ft-lb/sec

C = fluid volume, ft^3

U = proportionality factor, $lbf\text{-}sec/ft^2$

After settling for 30 minutes, the samples were filtered through a 0.4 micron Nucleopore filter, then adjusted to pH 7.6 with

sulfuric acid. The maximum dilution of the samples was always kept below 2%.

The mixing study was conducted under various rapid and slow mixing conditions. Rapid mix conditions were 140 rpm with times varied from 0 to 15 minutes. Slow mix conditions were 35 rpm with times varied from 0 to 60 minutes. Values of velocity gradient (G) and conjunction opportunity (Gtd) are shown in Table 1 for the conditions evaluated. Recycled magnesium was used as the coagulant and recalcined lime was used for pH control. As in the optimization of dose and pH, jar tests involving only lime addition were also evaluated for all the mixing conditions. Because residual turbidity was measured in samples during settling, two liter beakers were used with sampling ports 10 cm below the water surface. After settling 30 minutes, samples were filtered, adjusted to pH 7.6 with sulfuric acid and evaluated for removal of THM precursors.

When alum was investigated as a polymer at high pH, it was done with lime addition only because of the high magnesium content of the raw water. The sequence of chemical addition was lime, followed by alum during the rapid mix period. Standard mixing conditions were used as in the optimization of coagulant dose and pH. Two liter beakers were used to facilitate sampling for turbidity measurement during settling. Turbidity was measured to determine settling velocity distribution curves for various alum doses.

TABLE 1

VALUES OF VELOCITY GRADIENT, G, AND CONJUNCTION OPPORTUNITY FOR JAR TESTS (WITH A PHIPPS AND BYRD JAR TEST MACHINE) TO DETERMINE THE EFFECT OF MIXING ON THMFP, TOC AND COLOR REDUCTION DURING MAGNESIUM COAGULATION

Rapid Mix				Slow Mix			
Time (min)	W (rpm)	G (sec^{-1})	Gt_d	Time (min)	W (rpm)	G (sec^{-1})	Gt_d
0.75	140	126	5,674	5.	35	16	4,725
3.	140	126	22,698	19.	35	16	12,955
5.	140	126	37,830	30.	35	16	28,350
10.	140	126	75,600	60.	35	16	56,700
15.	140	126	113,490				

pH was monitored with a research grade Corning Model # 12 pH meter with a sliding glass sleeve reference electrode for faster response.

Measurement of Trihalomethane Formation Potential (THMFP)

Finished water from the jar tests and raw filtered lake water were chlorinated, then analyzed for THMFP to determine the efficiency of precursor removal attributable to different treat-

ment variations. Samples were chlorinated with 60 mg/1 of free chlorine for a period of 48 hours. This dose was necessary to provide a free chlorine residual in the raw lake water. Because the THMFP is influenced by chlorine dose, the finished water samples were also dosed with 60 mg/1 of free chlorine. A contact time of 48 hours is the approximate detention time in the Melbourne distribution system before the water reaches the consumer. The pH of chlorination was 8.0 corresponding to Melbourne finished water quality (pH 7.5 to 8.5). To prevent contamination by organic matter, sample bottles and pipettes were prepared by washing and heating for 1 hour at 350° C. After 48 hours, all remaining free chlorine was reduced to chlorides by 0.1 N sodium thiosulfate.

Samples for extraction were prepared by addition of 10 ml of sample and 2 ml of hexane into an extraction vial. The samples were carefully shaken for 30 seconds by hand, then allowed 1 minute for separation of the phases. A 30 µl sample was taken from the upper hexane layer and injected into the gas chromatograph. Chlorinated samples of distilled water, filtered distilled water and quenched (with sodium thiosulfate) distilled water were analyzed to enable detection of possible contamination problems. Between injections the syringe was thoroughly rinsed with methanol, then hexane to prevent error in results.

The samples were analyzed on a Hewlett Packard model 5750 research gas chromatograph. A six foot glass column with an inside diameter of 1/8 inch was used in conjunction with an electron capture detector. The column, manufactured by Supelco, Inc., was packed with 3% SP-1000 on a Supelco 100/120 mesh. The nickel 63 electron capture detector was used with a pulse interval of 150 microseconds. A mixture of 95% argon and 5% methane was used as the carrier gas. Table 2 lists operating conditions for the gas chromatograph.

TABLE 2

OPERATIONAL CONDITIONS FOR GAS CHROMATOGRAPH

Parameter	Condition
Carrier gas pressure	40 psi
Carrier gas flow rate	30 ml/min
Injection port	275° C
Electron capture detector	210° C
Column oven	70° C

Each time the gas chromatograph was used, a standard curve was prepared by dilution of a stock standard THM mixture purchased from Supelco, Inc. A blank sample of hexane and distilled + deionized water was analyzed to detect possible contamination of the hexane. To prevent differences due to extraction efficiency, the standard samples were prepared in an identical manner

to the experimental samples, using chloroform-free distilled and deionized water. By comparing peak heights of the samples to that of the standards, the concentration of the different THM's were determined. An example standard curve is shown in Figure 7.

Total Organic Carbon (TOC) Determination

Total Organic Carbon (TOC) levels were analyzed with a Dohrmann Envirotech DC-54 TOC analyzer. When the TOC analyzer was operated it was calibrated to a standard of known concentration. This standard was prepared each day from a stock reagent solution of potassium acid phthalate ($KHC_8H_4O_4$), where:

$$1 \text{ mg/l C} = 2.125 \text{ mg/l } KHC_8H_4O_4 \qquad (21)$$

Following calibration, 50 ml samples were prepared for analysis. The samples were acidified by addition of 1 ml of a reagent solution of phosphoric acid and potassium permanganate. Each run uses a 10 ml aliquot of sample, 2 runs were performed for each sample, then the values were averaged together.

The process of freeing carbon from the water sample for subsequent measurement is divided into two sequential steps: The Purgeable Organic Carbon (POC) Step, and the Non-Purgeable Organic Carbon (NPOC) Step. In the POC step, helium gas flows through the sample in the POC sparger at 100 ml/min to purge CO_2 well as purgeable organics from the sample. These gases next pass through a CO_2 scrubber where CO_2 is quantitatively removed, allowing the POC to be carried on to the Totalizer/Reaction model.

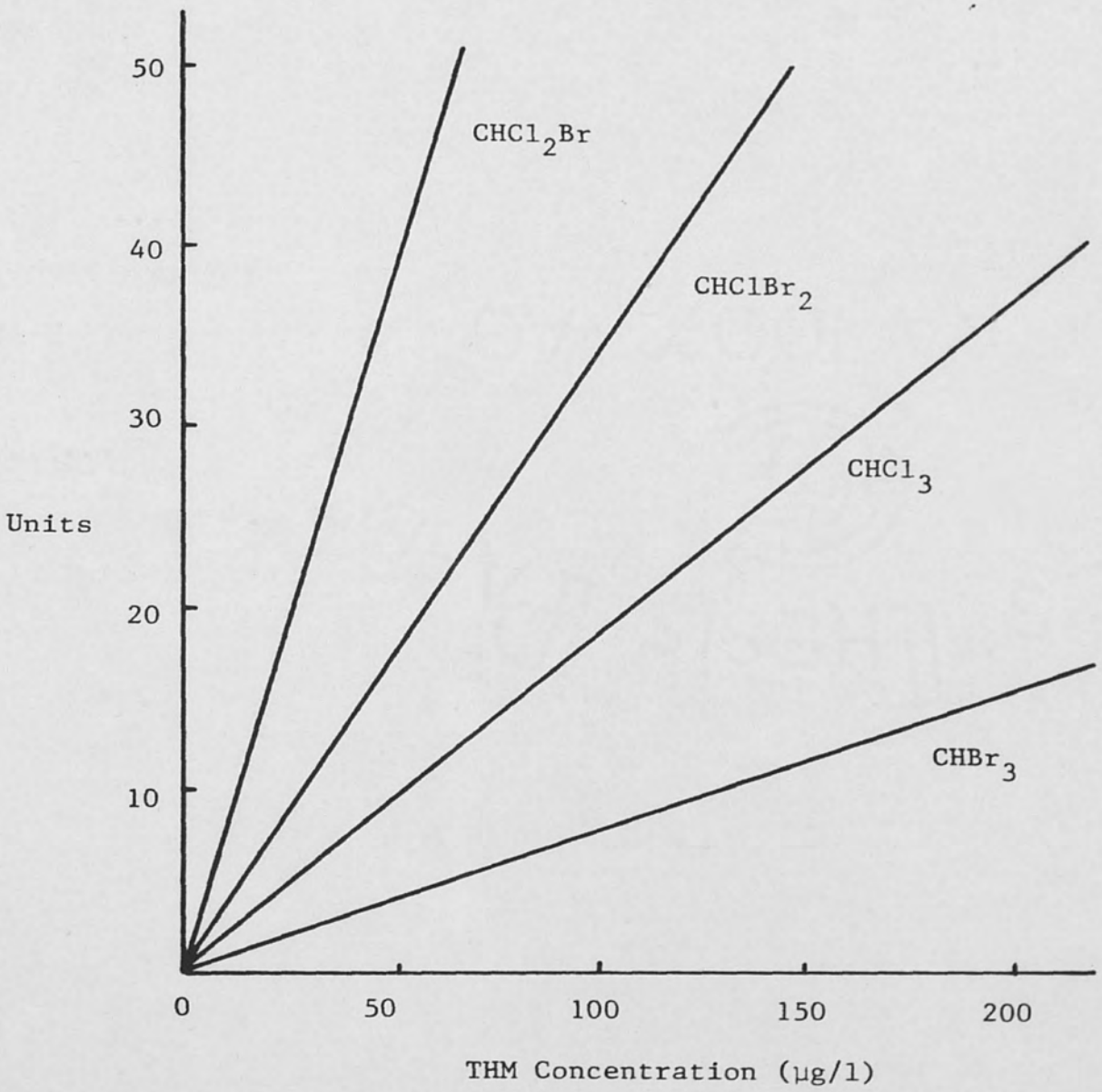


Fig. 7. Standard curve for THM determination.

In the Totalizer/Reaction Module the gas stream is joined by hydrogen and passes over a nickel catalyst at 350° C where the POC is converted to methane (CH_4). The gases then flow to the flame ionization detector (FID) which responds linearly to CH_4. The detector signal is integrated and the integrated value is displayed in mg/l. After measurement of POC, the sample is transferred to the NPOC sparger by helium gas. During this transfer the sample passes through the UV reactor coil where it is exposed to intense ultraviolet radiation which, aided by the persulfate reagent added, oxidizes all remaining organic carbon to CO_2. In the sparger helium gas removes the CO_2 from solution and into the Totalizer/Reaction Module. In the Totalizer/Reaction Module the CO_2 is converted to CH_4 and detected. The detector signal continues to be integrated and the integrated value displayed is composed of the POC and NPOC and represents the TOC of the sample. Operating conditions for the TOC analyzer are shown in Table 3.

TABLE 3

OPERATIONAL CONDITIONS FOR TOC ANALYZER

Parameter	Condition
Hydrogen Pressure	20 psi
Helium Pressure	20 psi
Air Pressure	30 psi
Furnace Temperature	800° C
Cooling Water Flow	500 ml/min

Color Determination

Color was determined by use of a double beam spectrophotometer, Beckman model DB-GT, at a wavelength of 460 nm using a 5 cm cell. A standard curve of chloroplatinate solutions was constructed with each use. By comparing absorbance of samples to that of standards, color levels were determined. An example standard curve for color determination is shown in Figure 8.

Each sample was analyzed at pH 7.6, since color is known to be pH dependent. Because color values of the water samples were low, dilution was not necessary. The recycle magnesium liquor was diluted when color measurements were performed.

Metals Determination

Metal concentrations were measured with a plasma emission spectrophotometer, a Spectraspan III, produced by Spectrametrics, Inc. Samples were acidified to a pH of 1 with nitric acid, then analyzed for dissolved metals concentrations following Standard Methods Procedure for Total Metals Analysis, Section 301A.

When analyzing the recycle liquor for magnesium content, dilutions of 250:1 were necessary because of the high magnesium content, approximately 2500 mg/1 Mg^{++}. An average value was determined for this reason.

Turbidity Measurement

Turbidity was measured by use of a Hach model #2100A turbidimeter. Using Formazin standards acquired from Hach Company, the

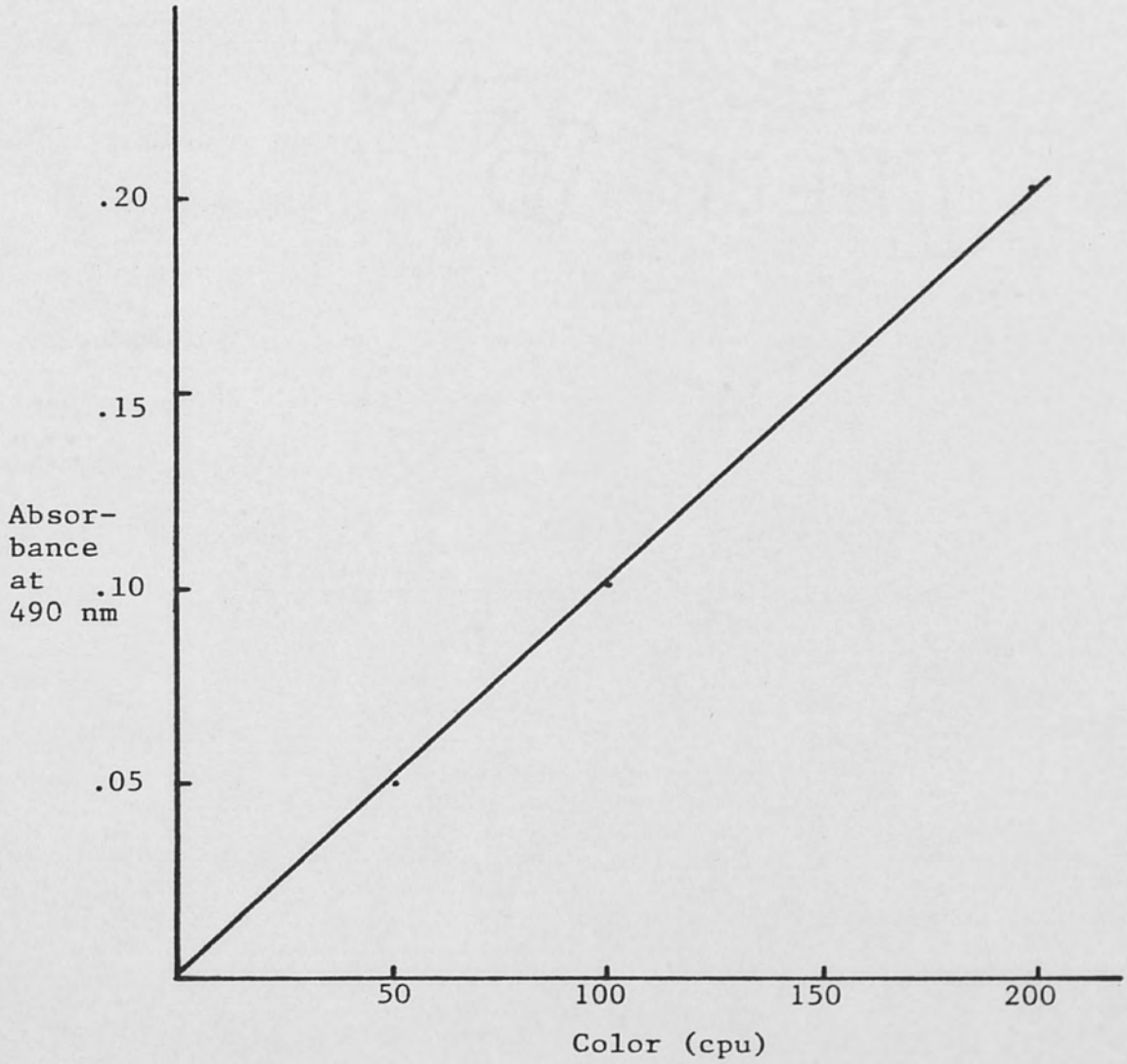


Fig. 8. Standard curve for color determination.

turbidimeter was calibrated. Turbidity was measured during settling of alum jar tests to determine settling velocity distribution of the floc.

Quality Assurance

To ensure precision and accuracy of the data for THMFP, TOC and metals determinations, either a duplicate sample or a spiked sample was run for every 6 experimental samples. For color determinations, duplicate samples were analyzed every 10 samples. In addition, unknown quality control samples for THM's and TOC were obtained from the U.S. EPA and analyzed to further ensure accuracy of the data. Precision and accuracy sample analyses for THMFP, TOC and metals determinations are shown in Tables 4 through 9.

TABLE 4

SAMPLE ANALYSIS FOR THMFP PRECISION
FOR DUPLICATE ANALYSIS

Analysis 1	Analysis 2	% Difference
870	840	3.4
800	760	5.0
660	650	1.5
749	797	-6.4
1244	1234	0.8
1527	1537	0.7
1180	1 204	-2.0
1298	1374	-5.8
1188	1212	-2.0
1119	1158	-3.5
2636	2721	-3.2
1488	1442	3.1
943	952	-1.0
1125	1127	-0.2
1006	1019	-1.3
1008	954	5.4
1039	1044	-0.5
1039	1064	-2.4
1009	1031	-2.2
904	975	-7.9
851	872	-2.5

TABLE 5

SAMPLE ANALYSIS FOR TOC PRECISION
FOR DUPLICATE ANALYSIS

Analysis 1	Analysis 2	% Difference
10.35	10.63	-2.7
28.63	29.32	-2.4
33.26	33.46	0.6
18.57	18.77	-1.1
24.40	24.22	0.7
13.36	13.32	0.3
17.62	17.80	-1.0
17.25	17.32	-0.4
18.57	18.69	-0.6
24.48	24.85	-1.5
12.50	12.70	-1.6
12.6	12.7	-0.8
18.46	18.39	3.8
22.13	20.19	8.8

TABLE 6

ACCURACY MEASUREMENTS FOR THM'S

Sample	Measurement	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
1	True Value	30.0	7.5	7.6	1.4
	Reported Value	27.5	8.6	8.4	1.3
	Acceptance Limit	15.8-41.2	3.0-11.9	3.5-11.9	0.4-2.4
2	True Value	76.6	91.2	71.1	98.7
	Reported Value	74.6	88.1	75.1	106.3
	Acceptance Limit	61-92.0	73-110.	57-85	79-120
3	True Value	10.2	22.8	11.8	32.9
	Reported Value	10.7	25.5	13.65	37.5
	Acceptance Limit	8.2-12.0	18.-27	9.4-14.	26-39

TABLE 7

ACCURACY MEASUREMENTS FOR TOC

Sample	True Value	Reported Value	95% Confidence Limit
1	6.1 mg/l	6.12 mg/l	4.0 - 9.4
2	91.8 mg/l	91.40 mg/l	74.6 - 107

TABLE 8

SAMPLE ANALYSIS METALS PRECISION
FOR DUPLICATE ANALYSIS

Metal	Analysis 1	Analysis 2	% Difference
Magnesium	51.2	49.4	2.5
	23.7	23.0	1.3
	7.51	7.31	2.7
	12.5	12.6	-0.8
	.485	.479	1.2
	3.075	3.149	-2.3
	41.3	38.3	7.3
	30.9	30.8	0.3
	8.6	9.19	-6.4
	2.58	2.57	0.4
Calcium	42.4	41.8	1.4
	36.1	35.6	1.4
	48.2	48.5	0.6

TABLE 9

SAMPLE ANALYSIS METALS ACCURACY
FOR SPIKED SAMPLES

Metal	Expected Value	Analyzed Value	% Difference
Magnesium	71.4	71.4	0.0
	80.2	78.2	2.5
	2.485	2.563	-3.1
	0.932	0.926	0.6
	54.0	51.1	5.4
	3.38	3.45	-2.1
	0.583	0.611	-4.8
	1.23	1.25	-1.6
	0.567	0.584	-3.0
	34.2	35.1	-2.6
Calcium	37.4	38.1	-1.9
	59.0	62.9	0.2
	39.2	39.0	0.5

CHAPTER IV

RESULTS AND DISCUSSION

Lake Washington Water Quality

Lake Washington serves as the source of potable water for the City of Melbourne, Florida. It is fed by the St. John's River, which flows through a region utilized for cattle grazing. In Figure 9, water quality parameters for the lake are shown for the years 1974-1981, obtained from the operating reports of the plant. Water quality was averaged over 3 month periods, and rainfall was expressed as a cumulative value over the 3 month periods. Although the author did not analyze the chemical data presented in Figure 9, this data was taken from three different sources and represents an original attempt to correlate water quality variations between high and low rainfall periods. This is obviously significant to the magnesium process because of magnesium recovery and lime recalcination and is presented here for this reason.

The water quality of Lake Washington varies, depending on the season of the year. During the months of January through June, when there is little rainfall occurring, color levels are relatively low, approximately 60 cpu and magnesium, calcium and alkalinity levels are relatively high, approximately 50 mg/l, 140 mg/l, and 90 mg/l, all as $CaCO_3$. During this period, groundwater

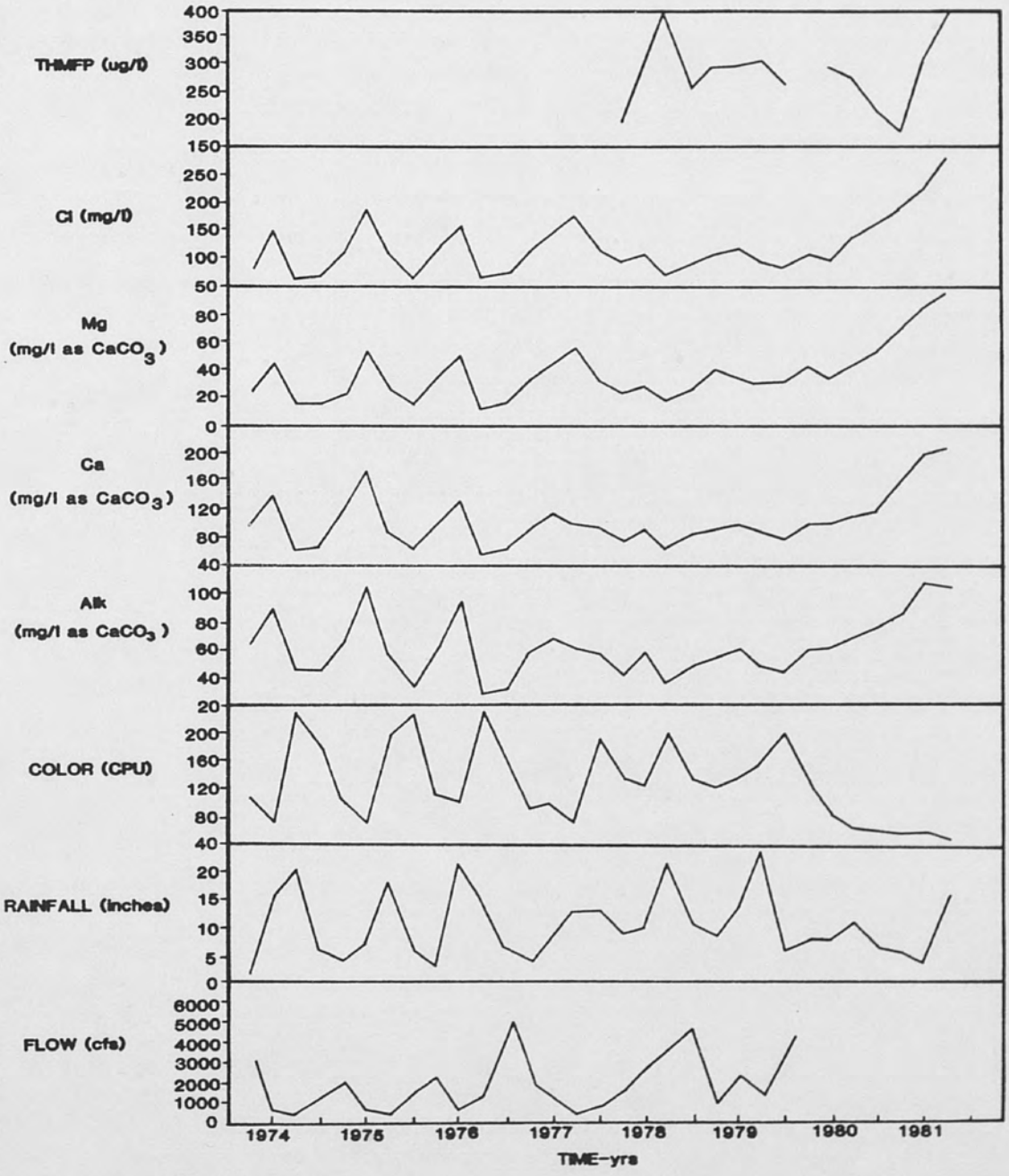


Fig. 9. Lake Washington seasonal water quality.

seepage seems to exert an important influence on lake water quality. During the latter half of the year, there is considerably more rainfall occurring and this increase in rainfall probably causes a significant change in water quality. Color levels are much higher, often over 200 cpu, and magnesium, calcium and alkalinity levels are much lower, approximately 20 mg/1, 60 mg/1 and 40 mg/1, all as $CaCO_3$. An increase in surface runoff from the surrounding land is responsible for this shift in water quality. From the Figure, one can see there is a lag period between rainfall and increased flow through the lake, corresponding to the change in water quality. Values of flow through the lake were obtained from U.S.G.S. records and also averaged over 3 month periods.

During 1980, this seasonal change in lake water quality did not occur, due to the corresponding lack of rainfall during this year, a maximum of only 11 inches during the peak color period as opposed to 20 inches seen in other years. Color levels remained low, approximately 55 cpu until October 1981, but levels of magnesium, calcium and alkalinity were very high, 100 mg/1, 200 mg/1 and 120 mg/1, all as $CaCO_3$. In October, color levels rose to over 300 cpu following a period of increased rainfall. Corresponding levels of magnesium, calcium and alkalinity dropped at this time to 10 mg/1, 120 mg/1, 85 mg/1, all as $CaCO_3$.

Chlorides, as seen from the figure, follow the same trend as magnesium, calcium and alkalinity and have been steadily increasing

in the lake during 1980 and 1981 due to intrusion of salt water into the groundwater table, and then seepage of this mineralized groundwater into the St. John's River and Lake Washington. The presence of canals constructed to drain the surrounding marshy land promotes seepage into the river and lake.

Even when color levels in the lake are relatively low, the concentration of organic matter present is still significant. The TOC in the lake averages approximately 20 mg/l during this period, indicating the presence of organic compounds which do not produce much color. During the period when color levels are high, TOC levels are often over 40 mg/l. The presence of these high levels of organic compounds makes it difficult to produce a high quality potable water. In particular, there is a problem with THM levels in the finished water for the Melbourne water treatment plant. As shown in the figure, the level of THM's in the finished water significantly exceed the standard of 0.1 mg/l, often as high as 0.4 mg/l.

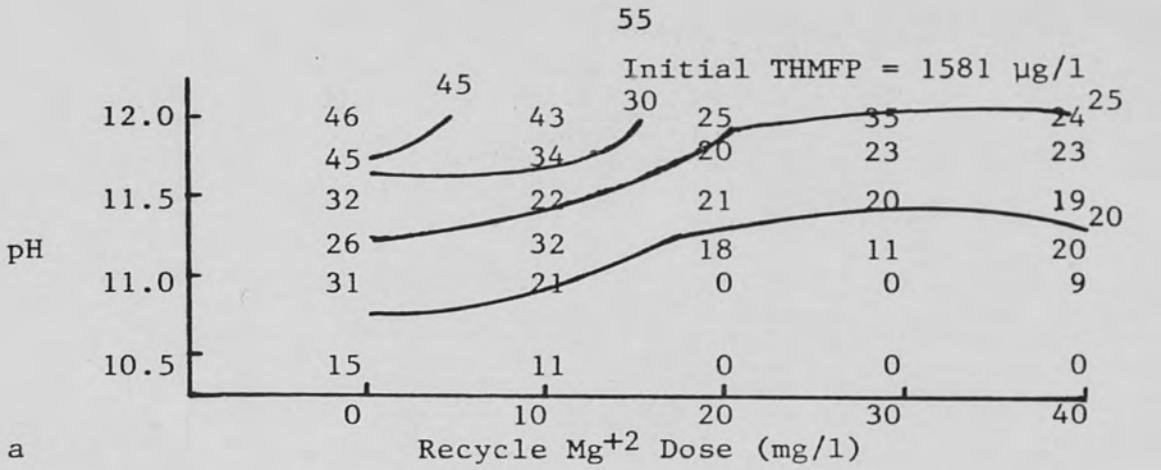
Coagulation with Recycle Magnesium

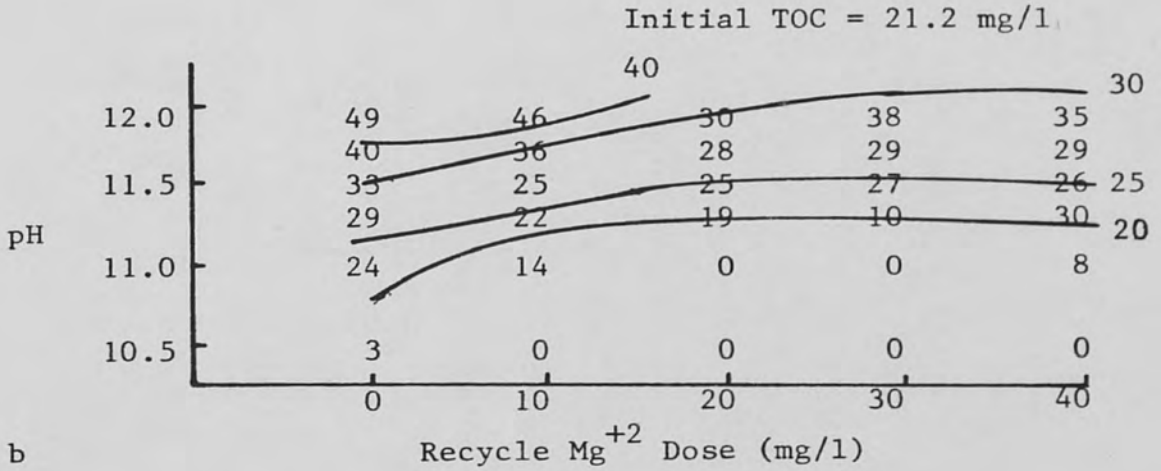
Using Lake Washington water, optimum coagulation dose and pH were determined for the low color water and the high color water using recycle magnesium supernatant from the carbonation basin as the coagulant. Three different types of lime were used for pH adjustment. These were pure reagent lime, commercial lime, and recalcined lime. Each series of jar tests were evaluated for reduction in THMFP, TOC and color. Isopleths were constructed

showing constant percentage lines of equivalent removal for these three parameters. More extensive testing was conducted on the low color, high magnesium lake water since the high color, low magnesium lake water was not available until late in the study period.

In Figures 10 through 12, the isopleths for the low color, high magnesium water are shown for treatment using recycle magnesium as the coagulant and the various types of lime for pH adjustment. Removal of THMFP during coagulation directly corresponds to color and TOC removal during coagulation. Regardless of the type of lime used, maximum removal of THMFP, TOC and color was obtained with a dose of 0 mg/l Mg^{+2} at pH 12. As the dose of recycle magnesium was increased, or as pH decreased, corresponding removal of THM precursors is decreased. In practice, at pH values below 11, inadequate magnesium hydroxide precipitation occurs. As seen in Figure 13, a solubility diagram for magnesium hydroxide only 0.39 mg/l Mg^{++} remain at pH 11, however, absolute equilibrium is not attained in practice and the Mg^{++} remaining is actually 10 mg/l or more at pH 11. Because of this lack of precipitation, levels of THMFP, TOC and color were actually higher in some cases than levels found in the raw lake water.

Maximum reductions in THMFP, TOC and color were 46%, 49% and 85% for the optimum dose and pH. This corresponds to levels of THMFP, TOC and color in the treated water of 830 µg/l, 10.8 mg/l and 8 cpu. The average magnesium concentration in the raw





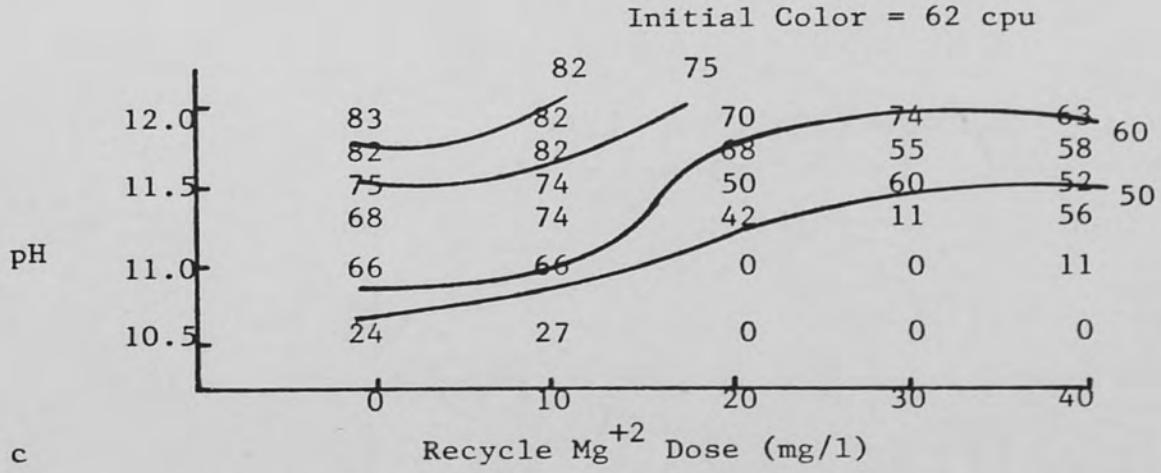


Fig. 10. Isopleths for removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium and pure reagent lime. Magnesium concentration in the raw water was 15 mg/1 as ion.

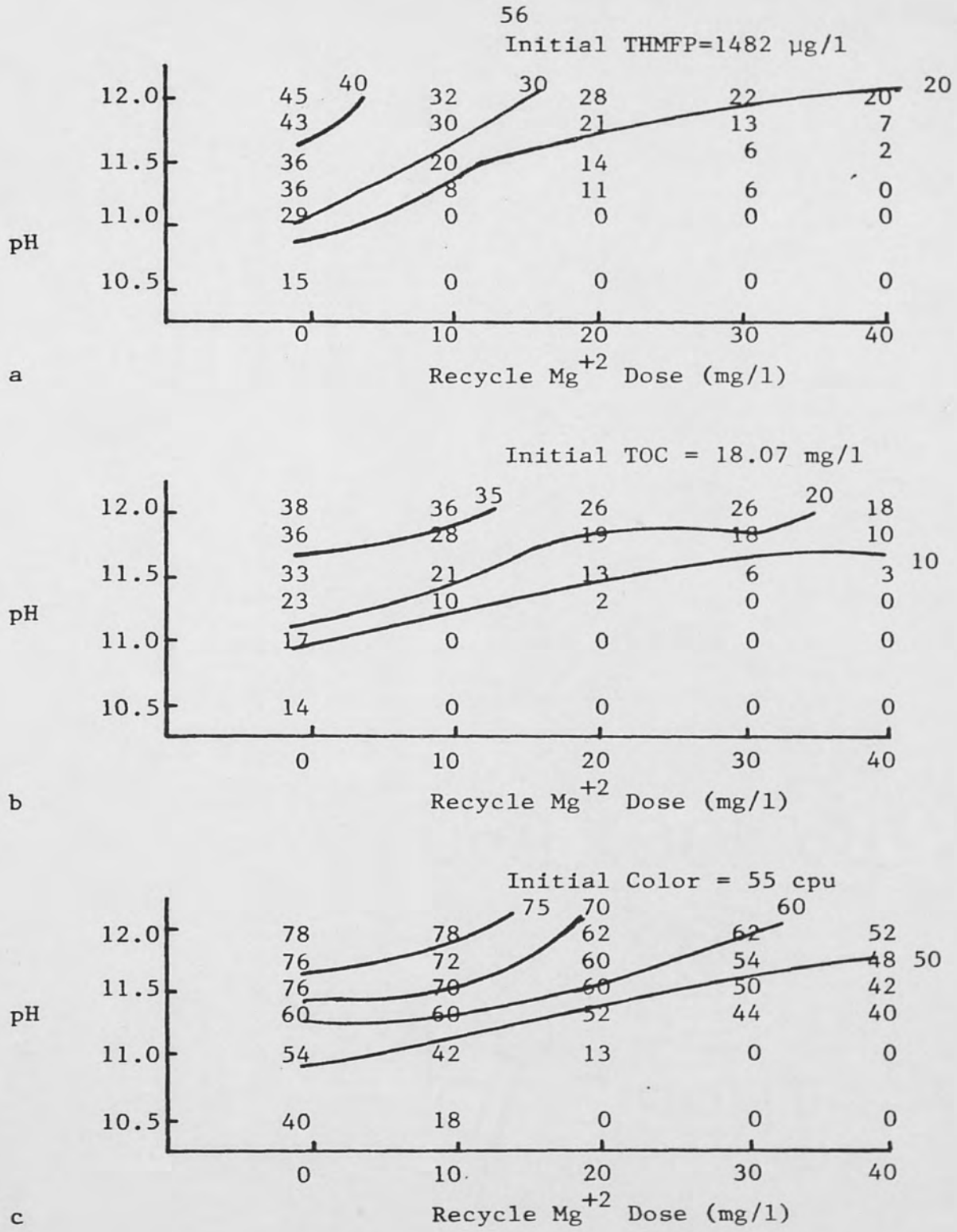
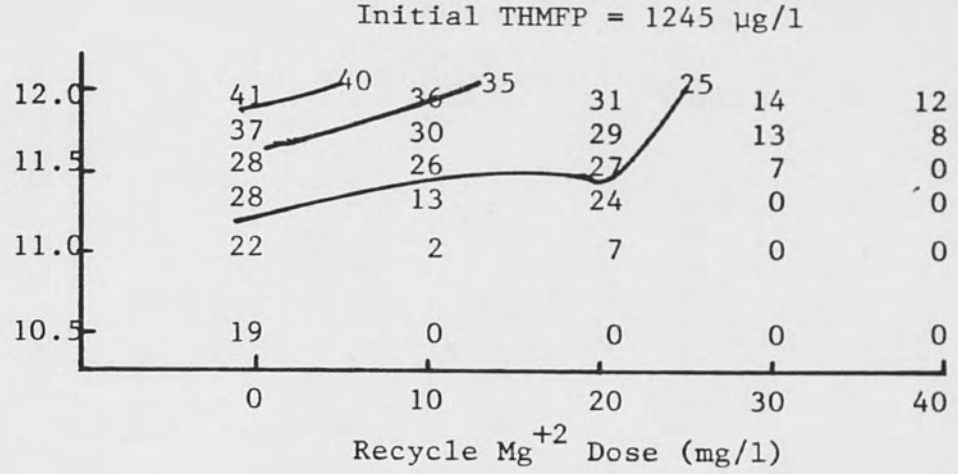
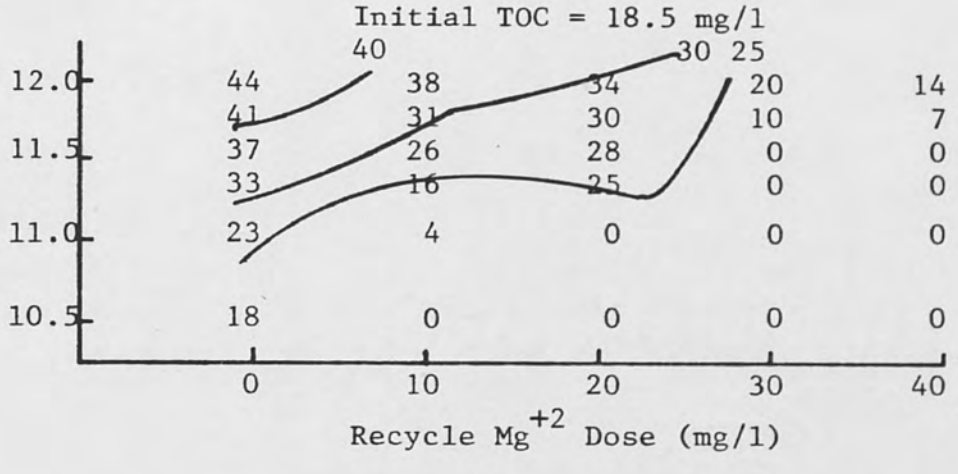


Fig. 11. Isopleths for removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium and commercial lime. Magnesium concentration in the raw water was 26 mg/1 as ion.



a



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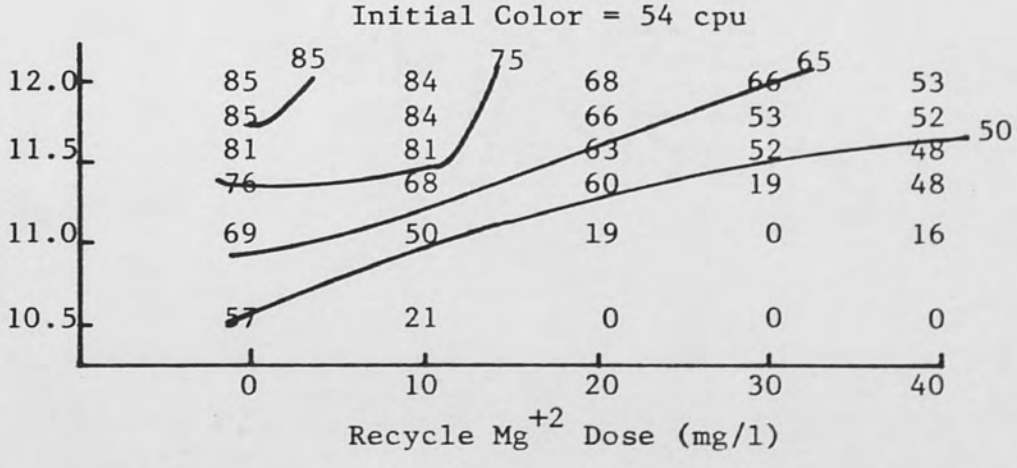


c

Fig. 12. Isopleths for removal of (a) THMPF, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium and recalcined lime. Magnesium concentration in the raw water was 20 mg/1 as ion.

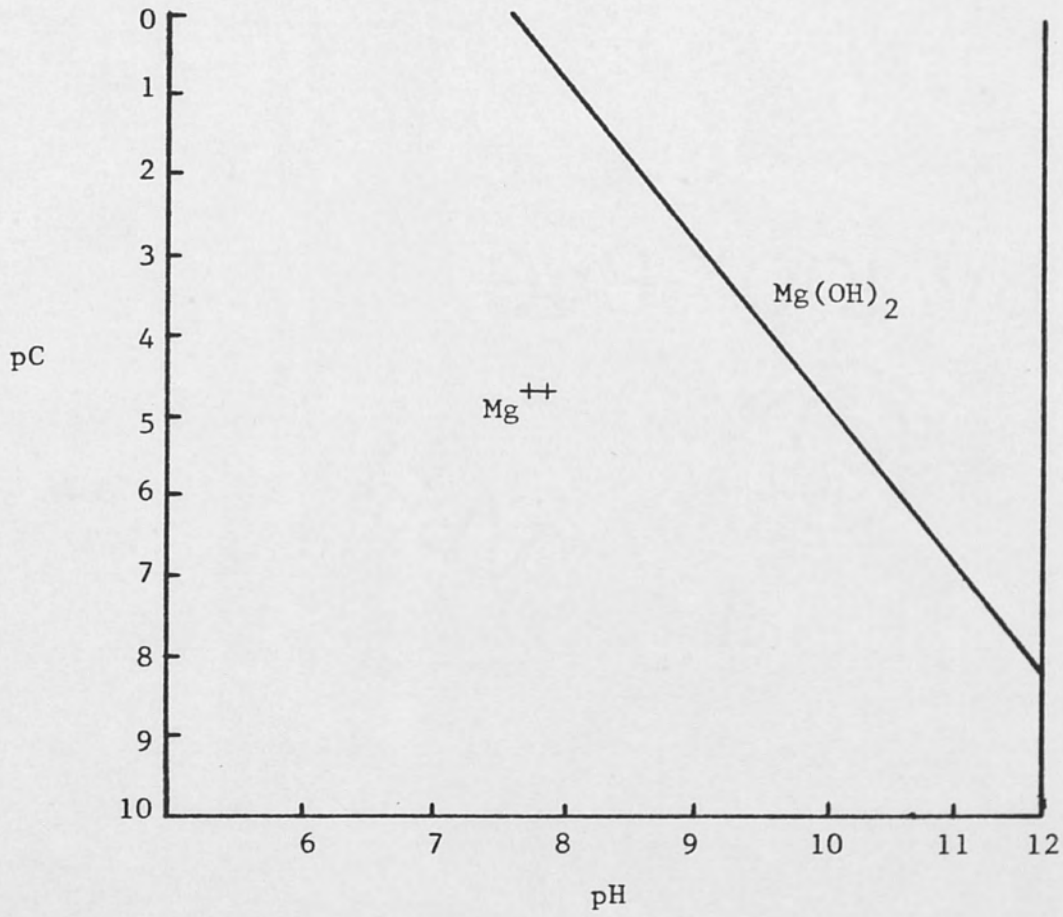


Fig. 13. pC-pH diagram for magnesium hydroxide solubility.

water was 20 mg/l Mg^{++}. At pH 12, virtually all this magnesium, or 0.84 mmole Mg^{++} is removed by coagulation. Therefore, the ratios of THMFP, TOC and color removed to Mg^{++} removed are 7.94 μmole THMFP/mmole Mg^{++}, 0.83 mmole TOC/mmole Mg^{++} and 56 cpu/mmole Mg^{++}. To determine the moles of THMFP, an average molecular weight of 128 was used corresponding to the percentage of each THM observed in the samples. These percentages were 80% $CHCl_3$, 17% $CHCl_2Br$ and 3% $CHClBr_2$.

Variations in different treatment efficiencies using the different types of lime were investigated because it was thought that the magnesium solids present in the recalcined lime would provide for better treatment. From metal analyses done on the recalcined lime, the magnesium portion of the recalcined lime represents approximately 5.7 percent by weight. Because not much variation was observed, it was concluded that the magnesium was not in a form which could aid treatment. Maximum THMFP reduction varied from 41% to 46% with the commercial lime achieving slightly better removal than recalcined lime, a difference of 75 μg/l, from 607 μg/l to 682 μg/l THMFP removed. The maximum TOC reduction varied from 38% to 49%, with less TOC removal occurring with the use of the commercial lime, a difference of 2.3 mg/l, from 8.1 mg/l to 10.4 mg/l TOC removed. The maximum color reduction varied from 78% to 85%, with commercial lime again achieving less reduction than either reagent or recalcined lime, a difference of 3 cpu from 46 cpu to 43 cpu color removed. This small variation is

attributed to variation in experimental results, since no clear trend exists.

The ineffectiveness of the recycle magnesium supernatant in removing organic matter during treatment is due to the high concentrations of organic matter in the recycle itself. Because carbonation of the sludge is practiced intermittently at the Melbourne plant, it is misleading to refer to average quality of the recycle; but measured Mg^{++}, THMFP, TOC and color were approximately 2500 mg/1 Mg^{++}, 48,000 µg/1, 500 mg/1, and 3200 cpu. During carbonation of the sludge, as the magnesium becomes soluble, the color also becomes soluble, probably due to the formation of organo-magnesium complexes during coagulation. This is substantiated by the fact that higher concentrations of magnesium were found in the recycle, 1000 to 3600 mg/1 Mg^{++}, than that which was predicted by equilibrium relationships 1050 mg/1 to 1670 mg/1 Mg^{++}. The addition of this recycle magnesium, as is, does not appear to have the capability to remove THM precursors for this low color, high magnesium lake water. The contribution of the magnesium ions to the coagulation process is outweighed by the organic loading on it. For every mg/1 of recycled magnesium used in the coagulation process, 19.2 µg/1 THMFP, 0.2 mg/1 TOC and 1.3 cpu color are recycled to the raw water being treated. For the typical Melbourne flow of 12 MGD and an optimum dose of 30 mg/1 Mg^{++}, this means an additional 570 µg/1 THMFP, 6 mg/1 TOC and 39 cpu color are being loaded in every liter of water treated. This accounts for the measured color, TOC and THMFP of

the treated water when recycled magnesium is used. The ineffectiveness of the recycle magnesium is also due to the high magnesium concentration in the raw water. Because of the high magnesium level, best treatment occurs without magnesium addition. In the treatment of the high color, low magnesium water this is not the case since the level of magnesium is considerably lower, approximately 5 mg/l Mg^{++}, and the levels of THMFP, TOC and color in the raw water are much higher, approximately 2700 µg/l, 42 mg/l and 365 cpu.

In Figure 14, isopleths are shown for the high color, low magnesium Lake Washington water treated by coagulation with recycle magnesium with recalcined lime used for pH adjustment. The recycle magnesium was very effective in reduction of THMFP, TOC and color. As opposed to the isopleths for the low color water, the constant percentage lines now migrate to the right upper corner instead of the left, which indicates the optimum treatment is attained at the maximum pH and recycle magnesium dose utilized. The maximum removal of THMFP was 52%, at a recycle magnesium dose of 40 mg/l Mg^{++} at pH 12. The TOC and color reductions were also optimum at this same dose and pH. Maximum TOC removal was 62%, and maximum color removal was 94%. These removals correspond to THMFP, TOC and color levels of 1440 µg/l, 16.5 mg/l, 20 cpu in the treated water.

The fact that addition of recycle magnesium increases THM precursor reduction for the high color lake water is possibly due to the method of carbonation treatment. The recycle used in this

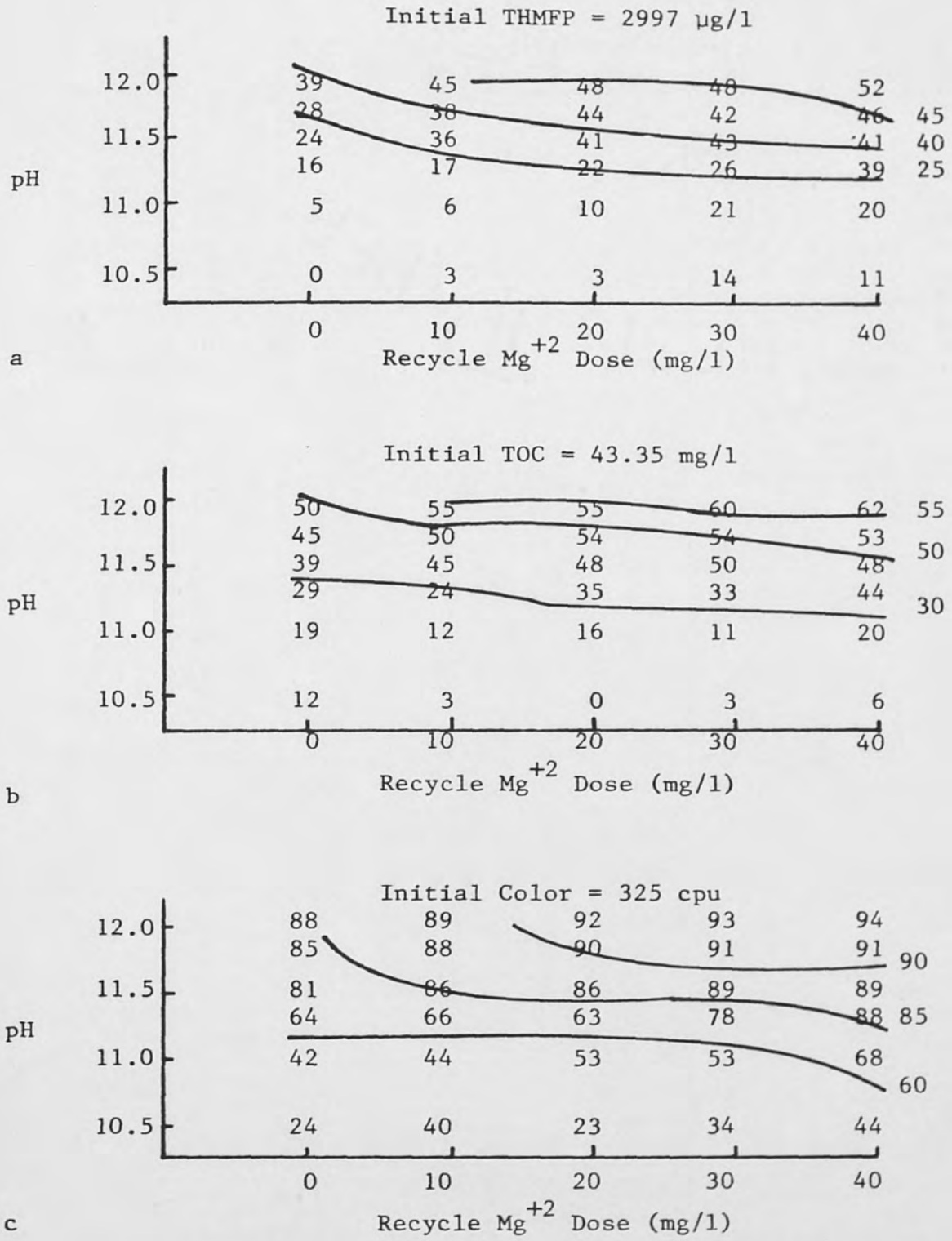


Fig. 14. Isopleths for removal of (a) THMPF, (b) TOC, and (c) color for a high color, low magnesium Lake Washington water treated by coagulation with recycle magnesium and recalcined lime. Magnesium concentration in the raw water was 5 mg/1 as ion.

part of the study was generated in the laboratory because the carbonation process was not in operation in Melbourne. This sludge was taken from the coagulation tank and never had been carbonated previous to this time. The magnesium concentration was 1500 mg/l Mg^{++}, and the TOC and color concentrations were 541 mg/l and 2500 cpu. The color is somewhat lower than usual, but TOC is approximately the same level indicating little variation between the UCF generated and Melbourne recycle magnesium.

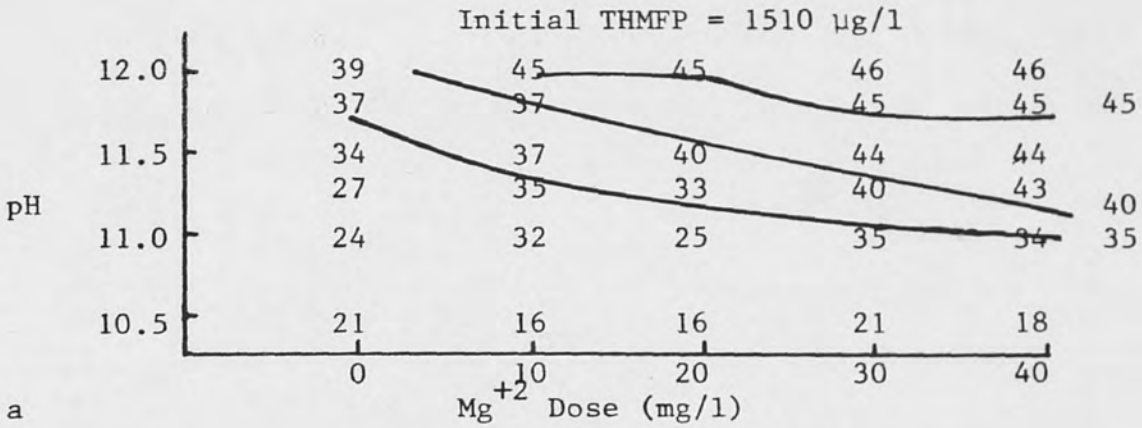
The most important factor in the effectiveness of the treatment with recycle magnesium for the high color water is the low concentration of magnesium present in the raw water, only 5 mg/l Mg^{++}. A ratio of 213 cpu/mmole Mg^{++} was found by Hatcher (1979) for optimum color removal with magnesium sulfate. The water he investigated also had a high color, 320 cpu. To achieve this ratio, an additional 36 mg/l Mg^{++} is required for the high color water used in this study. The optimum recycle Mg^{++} dose found was 40 mg/l Mg^{++} and corresponds well to Hatcher's work. The ratio found in the raw water for the low color condition was found to be 72 cpu/mmole Mg^{++} and, therefore, no magnesium addition was necessary.

At pH 12 and a dose of 40 mg/l Mg^{++}, virtually all of the magnesium or 1.88 mmole Mg^{++} is removed by coagulation. The ratios of THMFP, TOC and color removed to Mg^{++} removed was 6.5 µmole THMFP/mmole Mg^{++}, 1.2 mmole TOC/mmole Mg^{++}, and 163 cpu/mmole Mg^{++} for the high color water compared to 7.94 µmole THMFP/mmole Mg^{++}, 0.83 mmole TOC/mmole Mg^{++}, and 56 cpu/mmole Mg^{++} for the low color

water. The ratio for THMFP removal is lower and the ratios for TOC and color removal are higher than those determined for the low color water. This indicates for the high color water the THMFP does not increase as much as the color and TOC, which is verified by the data. For example, a 5.4-fold increase in color from 60 cpu to 325 cpu was accompanied by a 2.5-fold increase in THMFP, from 1200 µg/l to 3000 µg/l. For the case of the high color, low magnesium Lake Washington water, the addition of recycle magnesium is beneficial in reducing levels of THM precursors.

Coagulation with Magnesium Sulfate

Magnesium sulfate was evaluated for its capability in removing THM precursors for the low and high color Lake Washington water. In Figure 15, isopleths are shown depicting optimum coagulant dose and pH for low color, high magnesium water treated by coagulation with magnesium sulfate and recalcined lime. The addition of magnesium sulfate was effective in reduction of THM precursors. Maximum removals for THMFP, TOC and color were 46%, 50% and 85%. Optimum coagulant dose and pH were 20 mg/l Mg^{++} at pH 12. These removals are not much higher than that obtained with the 0 mg/l Mg^{++} dose because of the high concentration of magnesium in the raw water. As compared with Hatcher's optimum arithmetic ratio of 213 cpu/mmole Mg^{++} needed for color removal, the low color water with 0 mg/l dose has a ratio of only 72 cpu/mmole Mg^{++}. This indicates that adequate or excess magnesium is in Lake Washington water. If



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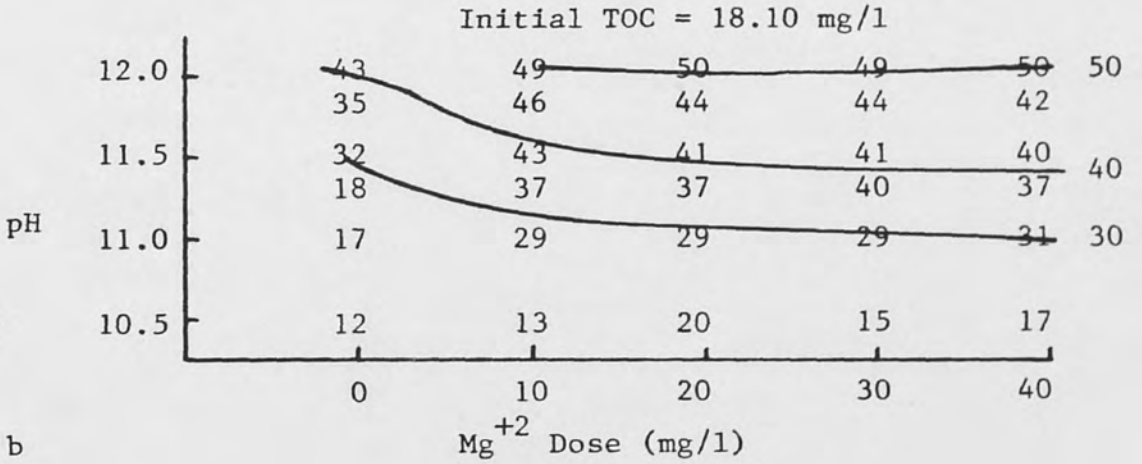

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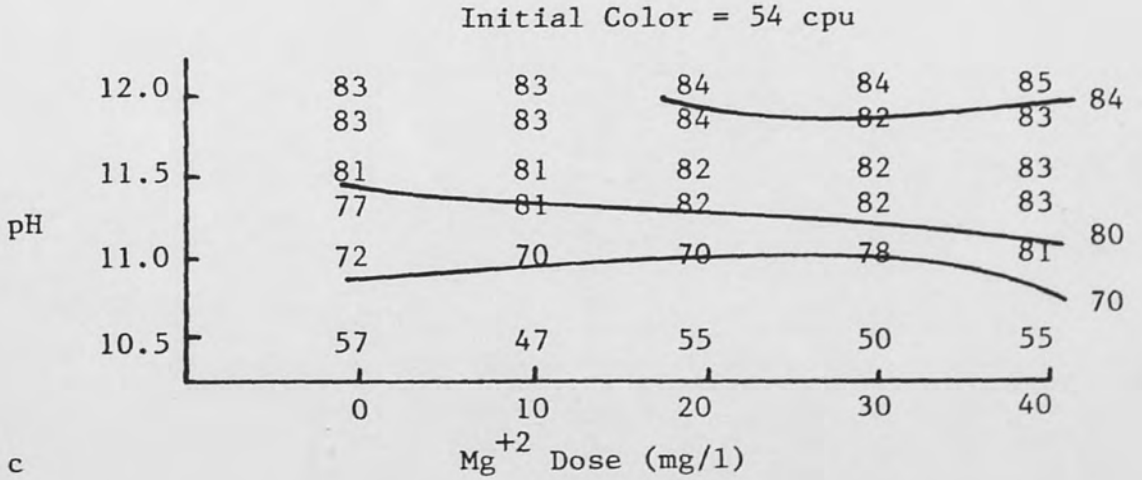


c

Fig. 15. Isopleths for removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with magnesium sulfate and recalcined lime. Magnesium concentration in the raw water was 18 mg/1 as ion.

Hatcher's ratio of 213 cpu/mmole Mg^{++} is used, only 5 mg/1 Mg^{++} is required to remove the 60 cpu in the raw water and 15 mg/1 Mg^{++} are in excess. It is possible that the optimum ratio which Hatcher determined for the high color water he treated may not correspond to the optimum ratio obtained in the case of low color water.

In Figure 16, isopleths are shown depicting optimum coagulation conditions for treating the high color, low magnesium lake water with magnesium sulfate and recalcined lime. Magnesium sulfate was also effective in reduction of THMFP, TOC and color in the highly organic lake water. Maximum removal occurred at a coagulant dose of 40 mg/1 Mg^{++} and pH 12, but significant removals occur at a dose of 20 mg/1. Best removals obtained for THMFP, TOC and color were 65%, 69% and 98%, an increase of 9% (230 µg/1), 4% (1.6 mg/1), and 3% (12 cpu) over the remvovals obtained by use of a 20 mg/1 Mg^{++} dose. The maximum removals obtained are not much greater than that observed by use of recycle magnesium to this water. Comparing magnesium sulfate to recycle magnesium, the magnesium sulfate removed 13% more THMFP (340 µg/1), 7% more (2.8 mg/1), and 4% more color (16 cpu) at optimum pH and dose (12 and 40 mg/1 Mg^{++}) than did recycled magnesium at the same conditions. For this highly colored water, some magnesium addition is necessary, whether in the form of magnesium sulfate, or recycle magnesium. The ratio of raw water color to magnesium dose applied was 220 cpu/mmole Mg^{++} in this case, comparing well to Hatcher's optimum ratio of 213 cpu/mmole Mg^{++} for high color water.

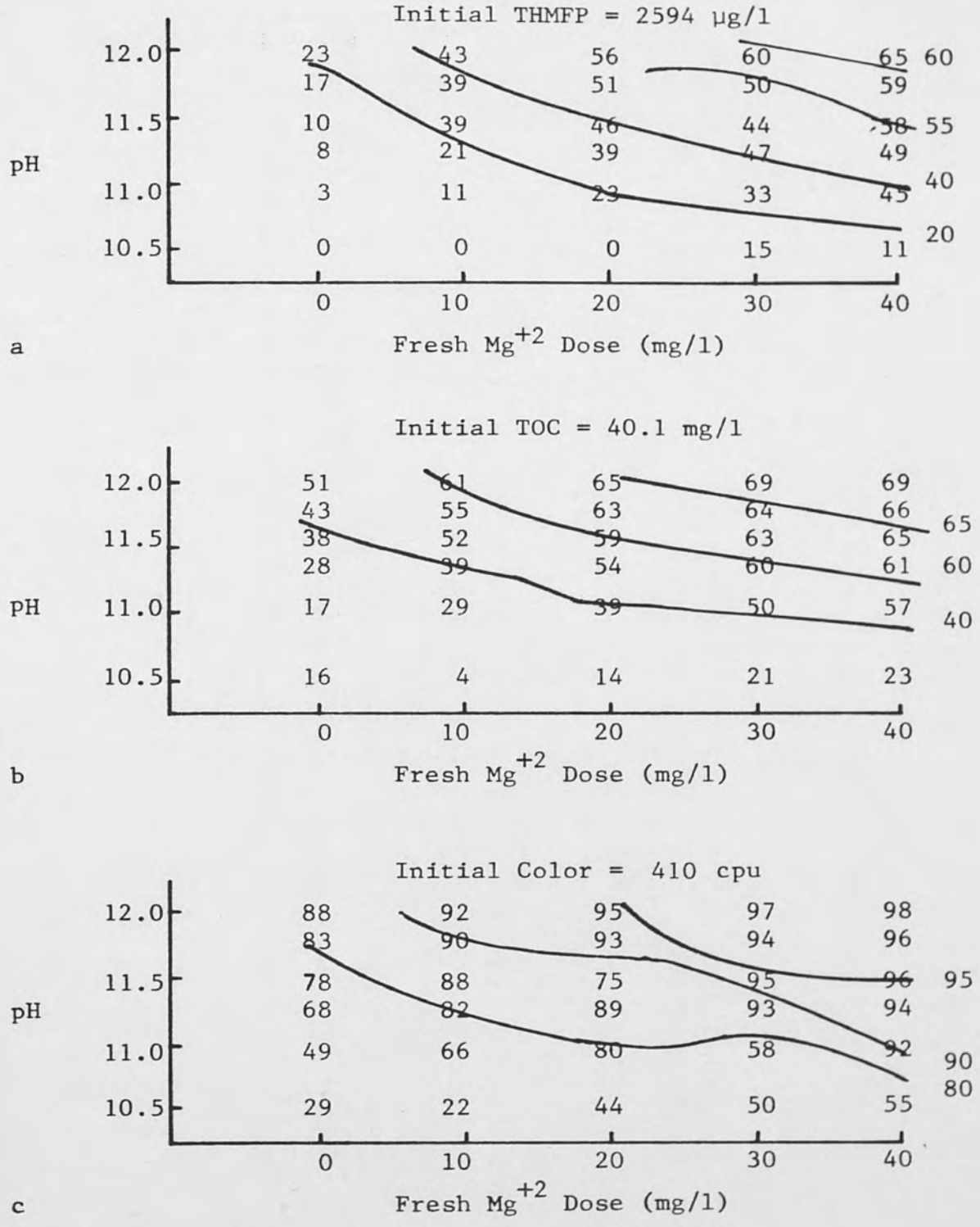


Fig. 16. Isopleths for removal of (a) THMFP, (b) TOC, and (c) color for a high color, low magnesium Lake Washington water treated by coagulation with fresh magnesium sulfate and recalcined lime. Magnesium concentration in the raw water was 5 mg/1 as ion.

The increased cost in using an operating pH of 12 in this process is seen in Figure 17 for low color, high magnesium Lake Washington water, using no magnesium addition. In raising the pH from 11.5 to 12, the cost is more than doubled, from $70 to $150 per million gallons (MG). This is based on a lime cost of $75/ton, with 85% purity. Furthermore, for every 10 mg/l Mg^{++} applied as coagulant, an additional lime cost of $19/MG is incurred. Because of this, the pH of coagulation is chosen to be 11.5, since the additional removal of THMFP, TOC and color is not that great, approximately 2% (30 µg/l), 10% (1.8 mg/l) and 2% (1 cpu) for the low color water and 7% (180 µg/l), 4% (1.6 mg/l) and 2% (8 cpu) for the high color water treated with magnesium sulfate coagulation at a 40 mg/l Mg^{++} dose.

It is important for the reader to note that for either low or high color water quality, the optimum treatment is achieved at maximum pH and magnesium dose. An interpretation of optimum conditions might be infinite pH and magnesium dose. Moreover, the selection of operating conditions for coagulation must be made with cost considerations and with regard to the water treatment system of which coagulation is a unit process. The final water quality must meet the 0.1 mg/l THMFP and 2 cpu's. However, at Melbourne, the coagulation process is currently the major process for removing THMFP and requires at least an operating pH of 11.5 and a coagulant dose of 20 mg/l Mg^{++} to be effective.

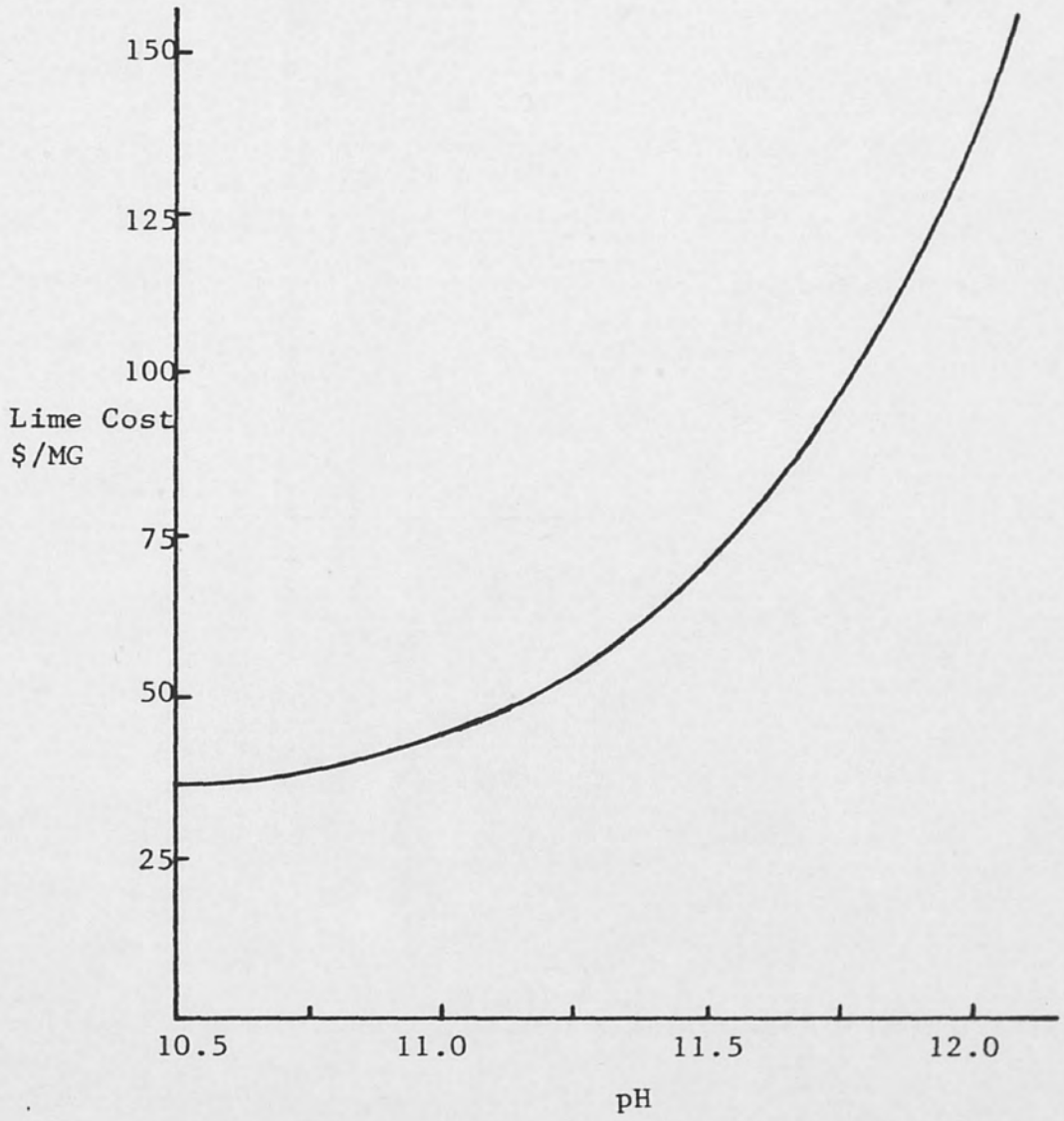


Fig. 17. Relationship between lime cost and pH of coagulation for low color, high magnesium Lake Washington water treated by magnesium coagulation, based on lime at $75/ton, 85% purity.

Correlation of THMFP, TOC and Color

A relationship was observed between THMFP, TOC and color removal in the isopleths which were presented. To further determine the correlation between THMFP, TOC and color levels for a given water, linear regression analyses were performed for Lake Washington water treated by coagulation with addition of either no magnesium, recycle magnesium, or magnesium sulfate at pH 11.5. In Figure 18, one can see that there is a correlation between THMFP and color levels ($r = .920$); TOC and color levels ($r = .834$); and TOC and THMFP levels ($r = .950$) for treated Lake Washington water. When color of the treated and filtered water is projected to zero via the regression equation in Figure 18 a and b, the THMFP is 803 µg/l and TOC is 11.7 mg/l. This indicates that there is organic matter present which does not produce color. The TOC and THMFP relationship in Figure 18c indicates that there is some TOC which does not produce THM's. This is significant because by analyzing a given water in this manner one may be capable of predicting THMFP in a general manner by measuring either color or TOC, saving time and expense, since measurement of THMFP is more difficult. Certainly this is valid for the Melbourne water.

Solubility of Magnesium

The fact that better removal of THM precursors occurred at pH 12 was significant, since most of the magnesium has precipitated from solution at pH 11.5. This is shown in Figure 19, where

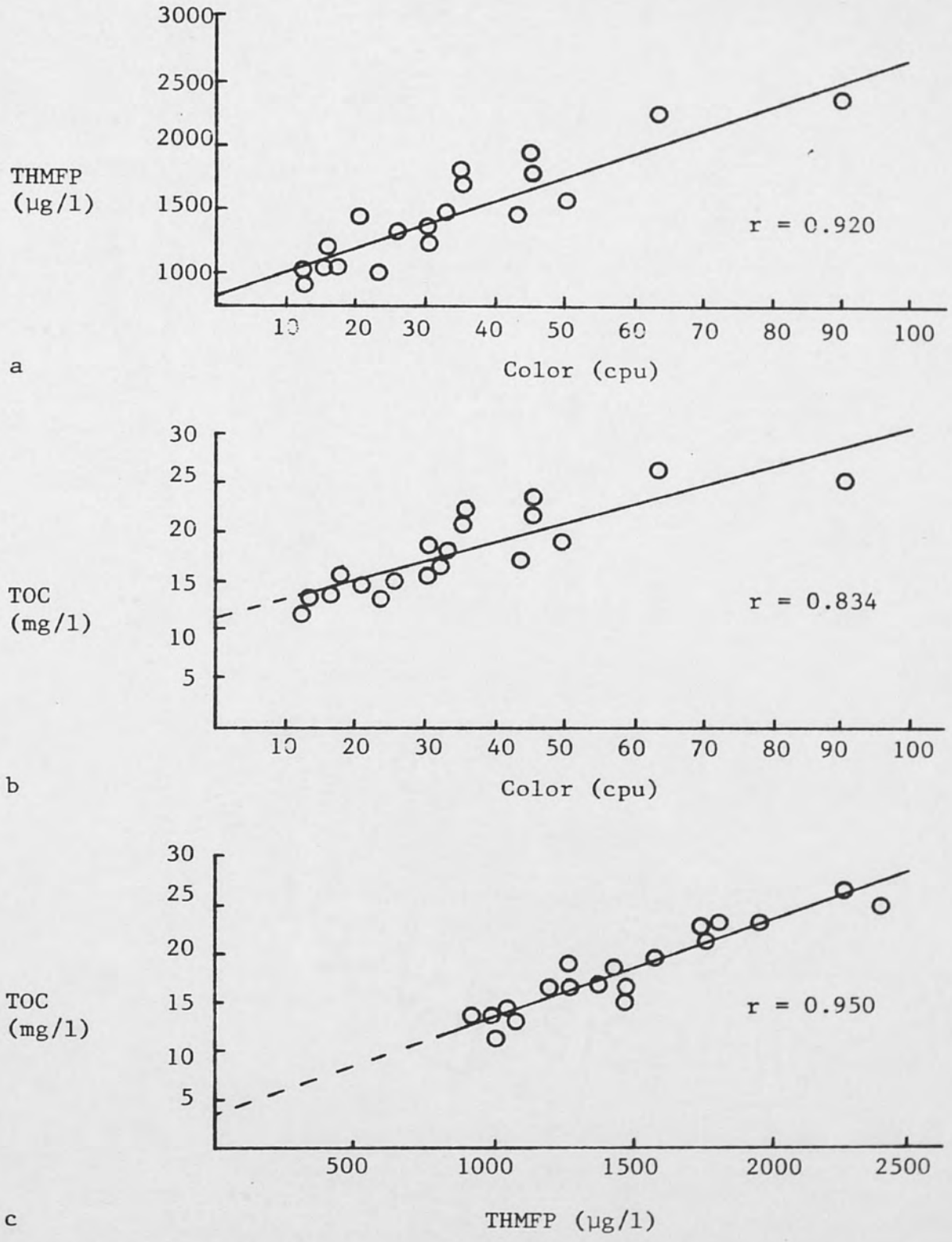
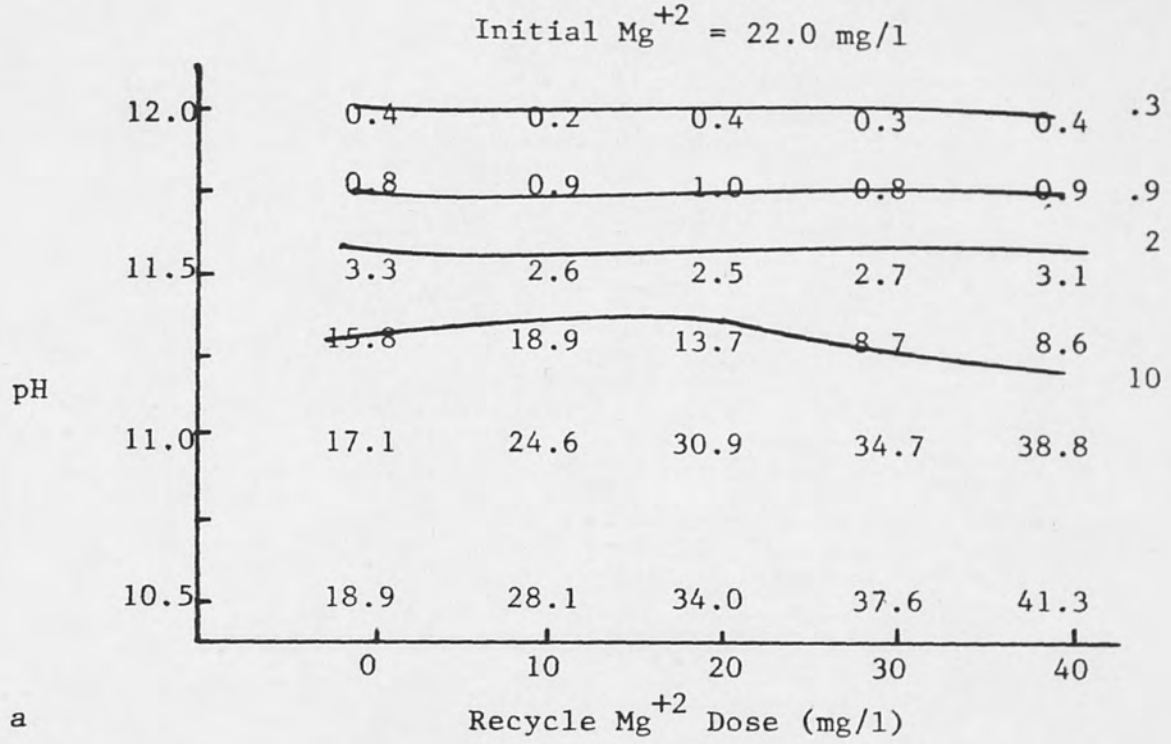


Fig. 18. Relationship between (a) THMFP and color, (b) TOC and color and (c) THMFP and TOC for Lake Washington water treated by magnesium coagulation, sedimentation and filtration at pH 11.5.



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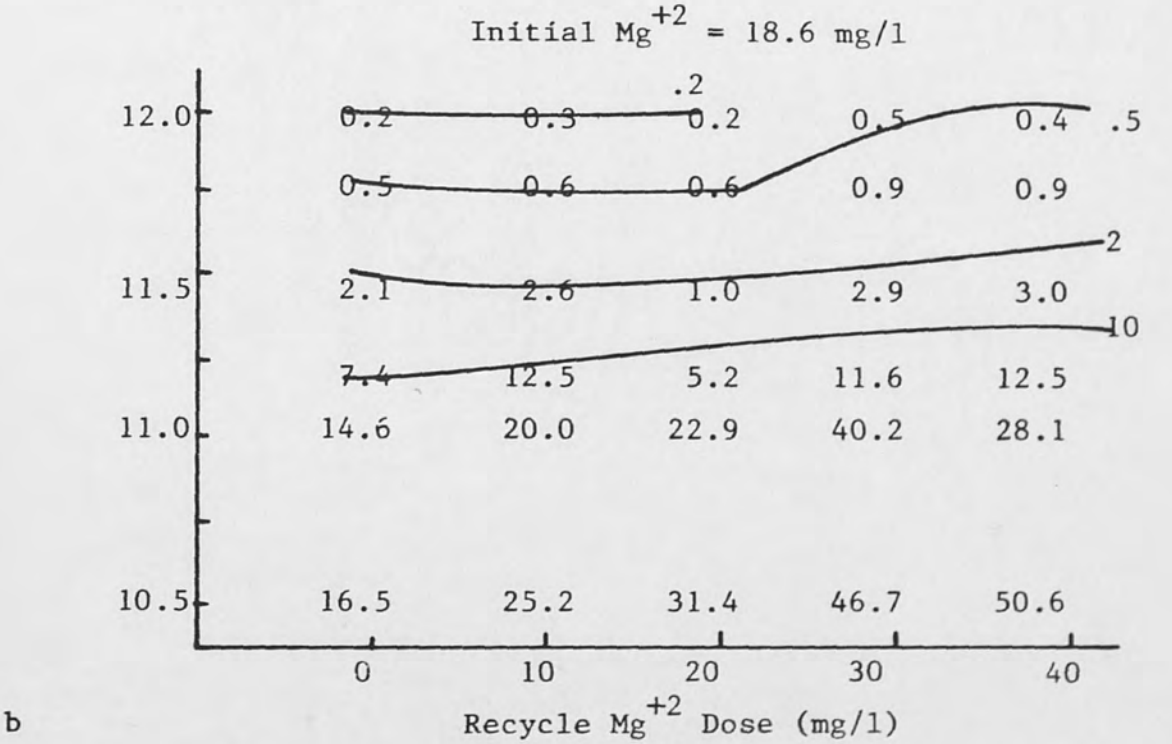
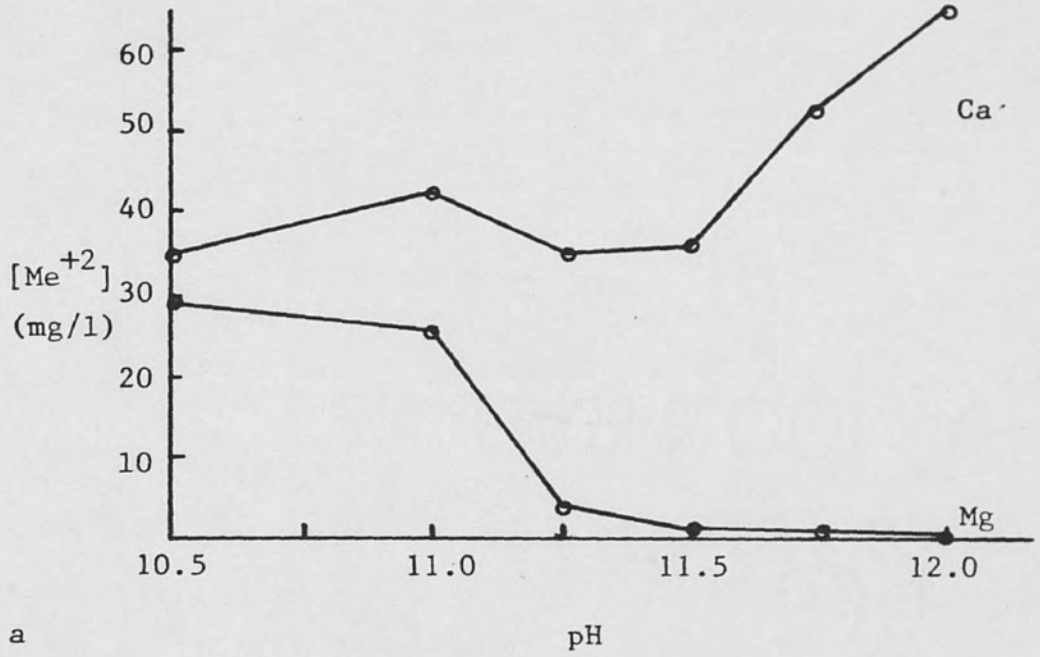


b

Fig. 19. Isopleths for mg/1 Mg^{+2} remaining for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium and (a) commercial lime and (b) recalcined lime.

only an average of 2.5 mg/l Mg^{++} is remaining in low color, high magnesium water treated with recycle magnesium and recalcined or commercial lime at pH 11.5. It is possible that the small amounts of magnesium, approximately 2 mg/l Mg^{++} (0.083 mmole) removed between pH 11.5 and 12 could be responsible for the average increases in THMFP, TOC and color removal observed (1.12 mole THMFP, .09 mmole TOC and 1 cpu) for treatment with recycled magnesium coagulation and commercial or recalcined lime. As magnesium dose is increased, the ratio of THMFP, TOC and color is removed to magnesium removed decreases. Best treatment at the 0 dose, pH 12 condition with recalcined lime corresponds to a removal ratio of 5.2 μmole THMFP/mmole Mg^{++}, .884 mmole TOC/mmole Mg^{++} and 60 cpu/mmole Mg^{++}. From these isopleths one can see that prior to pH 11, very little of the magnesium has precipitated. Because little THM precursor removal occurs below this pH, this supports the hypothesis that magnesium is responsible for organics removal in coagulation. The solubility for both types of lime follow similar trends, little variation observed in magnesium removal.

To further investigate the reason for increased reduction of THM precursors at pH 12, a series of jar tests were executed for the low color water in which sodium hydroxide instead of lime was used for pH adjustment and recycle Mg^{++} doses of 0 mg/l Mg^{++} and 9 mg/l Mg^{++} were utilized. The results shown in Figure 20 indicate that while almost all of the magnesium is precipitated, calcium levels are increased as pH of coagulation is increased. This



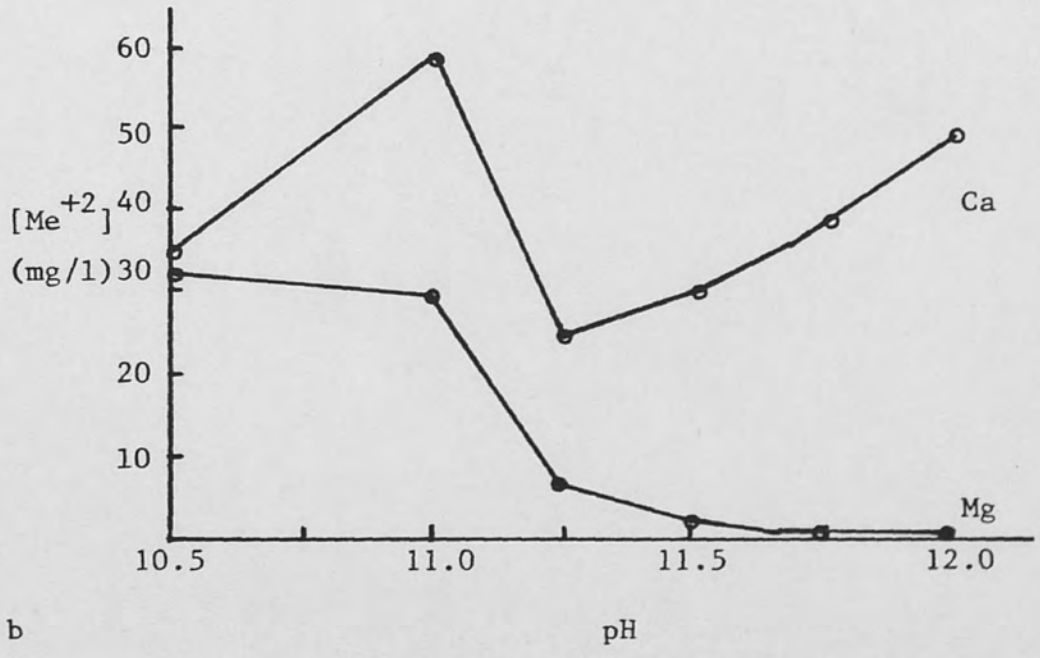


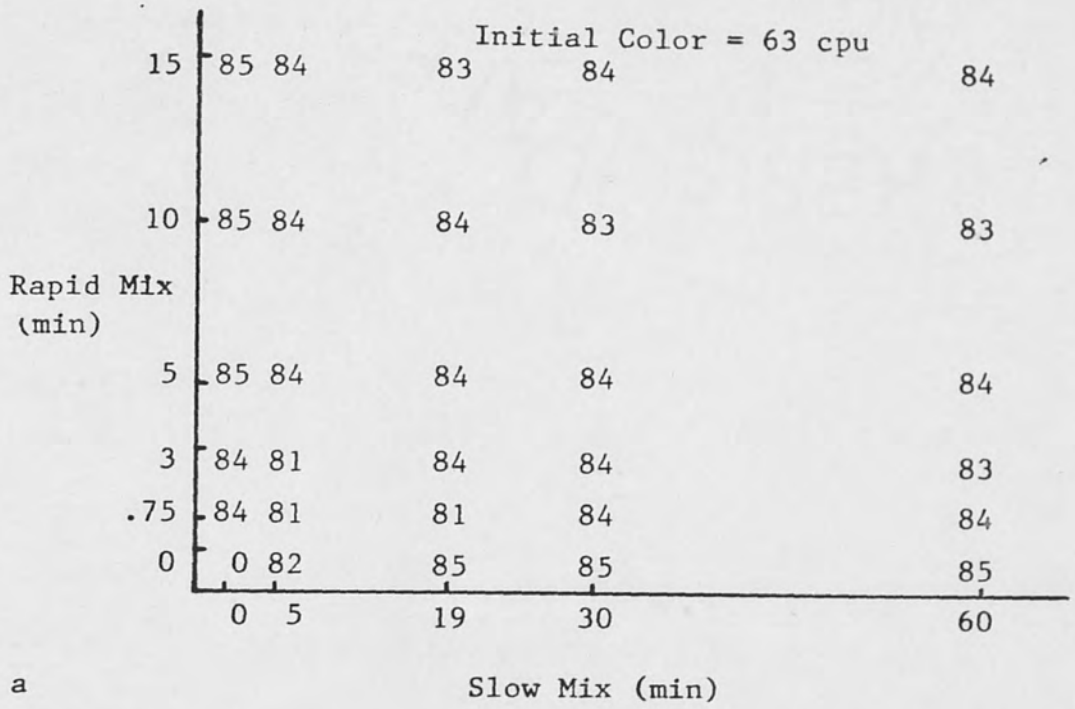
Fig. 20. Magnesium and calcium residuals for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium and sodium hydroxide. Recycle doses used were (a) 0 mg/1 Mg^{+2}, (b) 9 mg/1 Mg^{+2}. Magnesium and calcium concentrations in the raw water were 21.7 mg/1 Mg^{+2} and 69.2 mg/1 Ca^{+2}.

is unusual since lime was not used. This calcium solubility was attributed to ion-pair or complex formation at the higher pH values. For example, the $CaOH^+$ complex increases in concentration as pH increases. Some of $CaCO_3$ that had formed earlier at pH 9 to 10.5 was evidently not forming at pH values above 11.5. This may be due also to the extremely high organics in Lake Washington water.

It was suspected that incomplete magnesium precipitation was being realized when the data shown in Figure 10, 11 and 12 were analyzed. This data showed clearly for the low color, high magnesium water that increasing the dose of recycle magnesium to the jars increased the finished THMFP, TOC and color. The data shown in Figure 19 show clearly that complete magnesium precipitation was realized at the higher pH's represented in Figures 10, 11 and 12. Moreover, the reason for increasing recycle magnesium dose corresponding to increasing THMFP, TOC and color in the finished water is not due to incomplete magnesium precipitation but due to the high color (3200 cpu), TOC (500 mg/1), and THMFP (48,000 µg/1) in the recycle.

Variation in Mixing Conditions

Mixing during the rapid mix (coagulation) phase and the slow mix (flocculation) phase are important to the efficiency of any coagulation process. Using low color, high magnesium Lake Washington water, the effects of varying both slow and rapid mix times on THMFP, TOC and color are presented in Figures 21 through 23.



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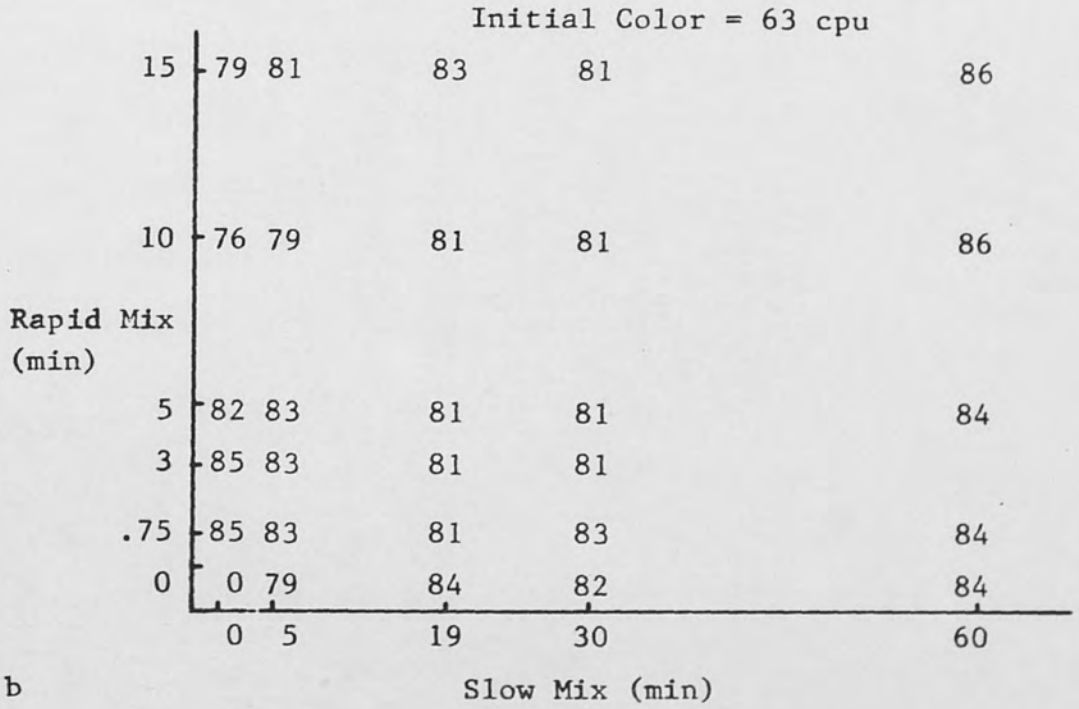

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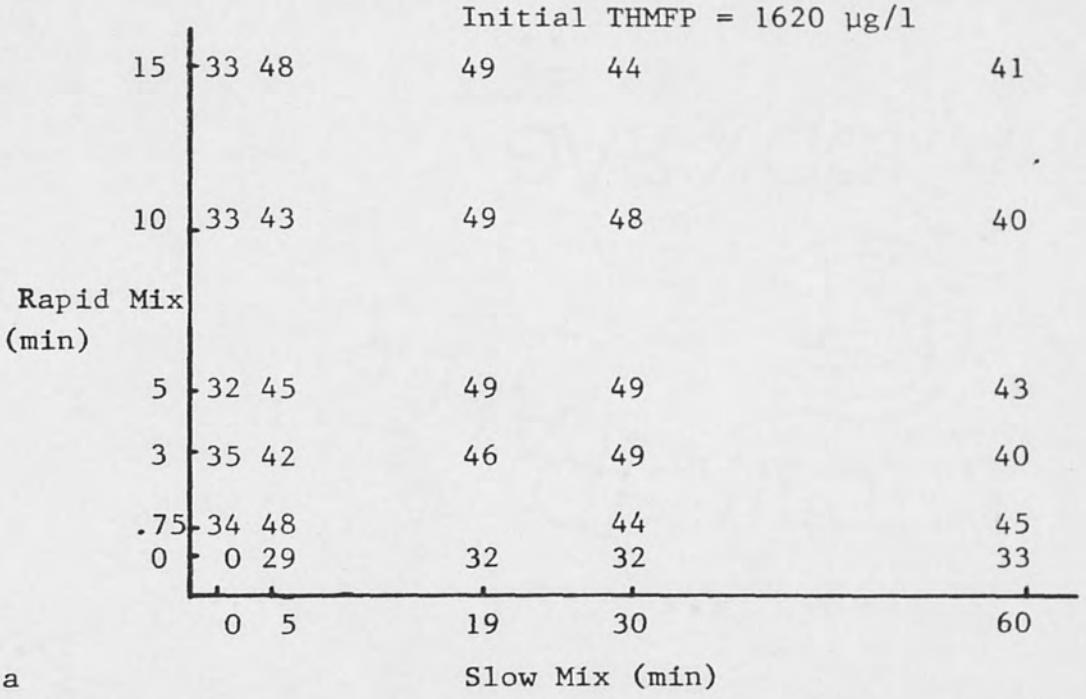
Fig. 23. Percent color removal as a function of variations in mixing times for low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium doses of (a) 0 mg/l Mg^{+2} and (b) 9 mg/l Mg^{+2} and recalcined lime at pH 11.5. The magnesium concentration in the raw water was 18.3 mg/l Mg^{+2}.



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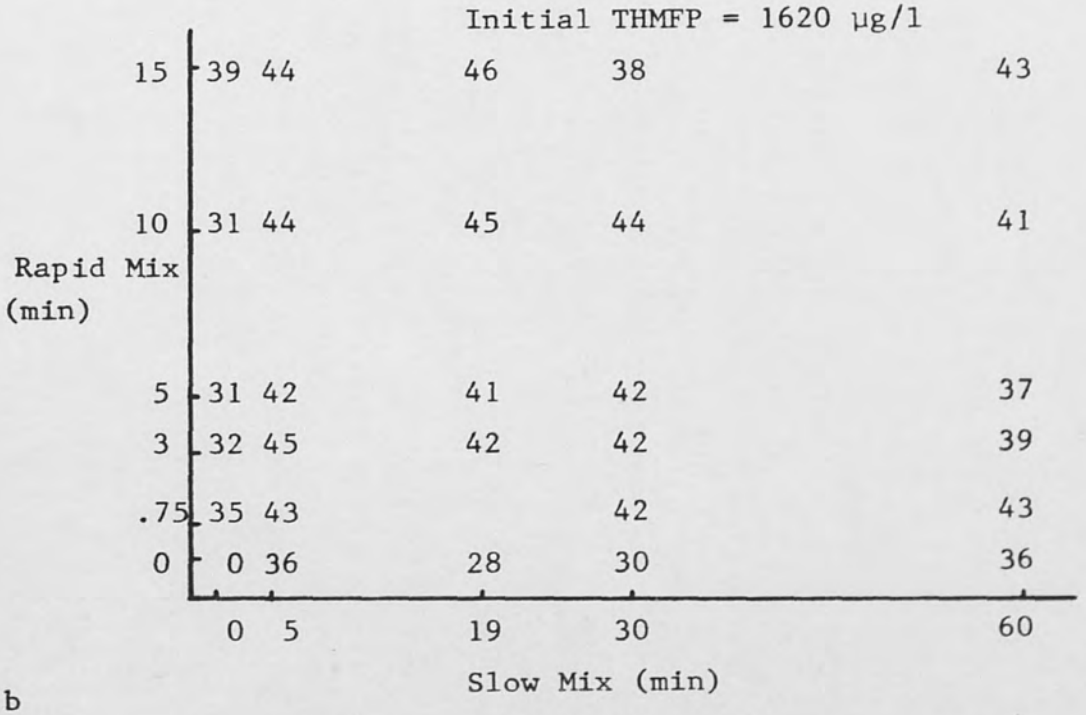

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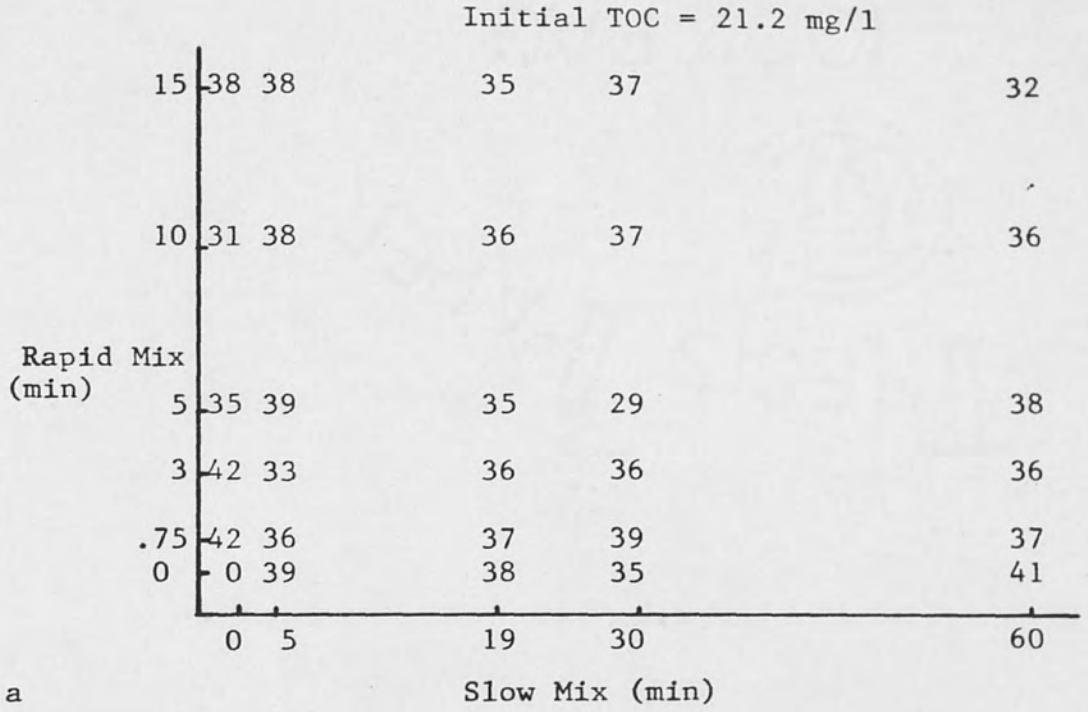
Fig. 21. Percent THMFP removal as a function of variations in mixing times for low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium doses of (a) 0 mg/l Mg^{+2} and (b) 9 mg/l Mg^{+2} and recalcined lime at pH 11.5. The magnesium concentration in the raw water was 18.3 mg/l Mg^{+2}.



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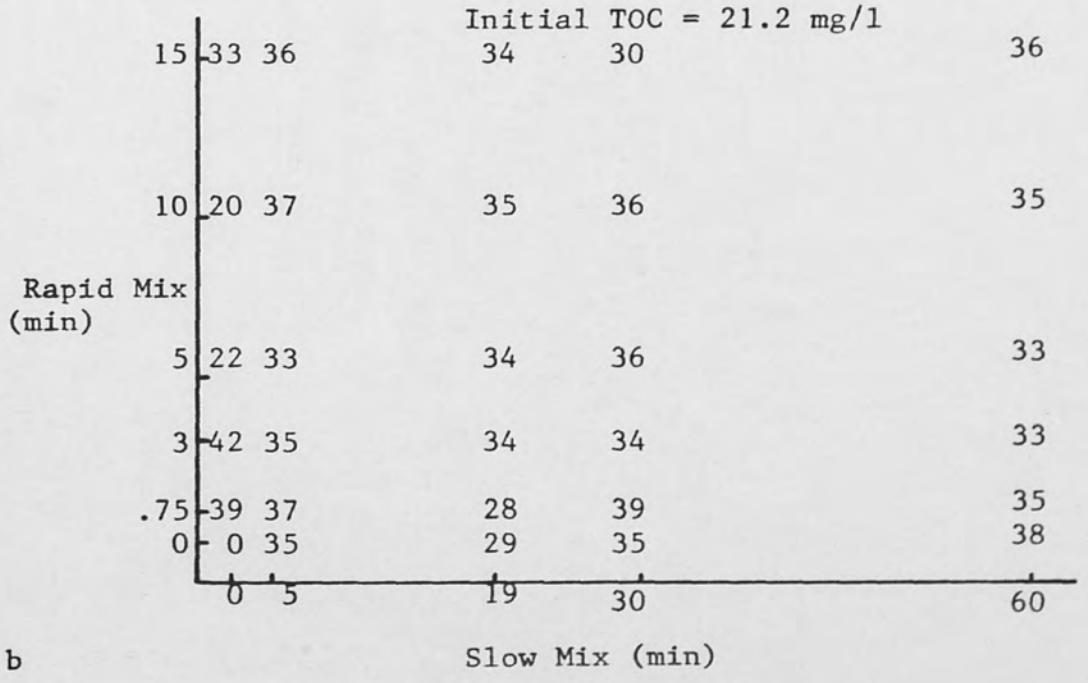

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Fig. 22. Percent TOC removal as function of variations in mixing times for low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium doses of (a) 0 mg/1 Mg^{+2} and (b) 9 mg/1 Mg^{+2} and recalcined lime at pH 11.5. The magnesium concentration in the raw water was 18.3 mg/1 Mg^{+2}.

Recycle magnesium doses of 0 and 9 mg/1 Mg^{++} were used with recalcined lime at pH 11.5. Rapid mixing times were varied from 0 to 15 minutes and slow mixing times were varied from 0 to 60 minutes. Constant removal lines were not drawn on these figures because of lack of variability of the data. Variations of mixing times did not significantly affect TOC or color removal but it appears that some combination of both rapid and slow mixing is necessary for optimum THMFP removal. The THMFP removal varied from 42 to 49% when both rapid and slow mix periods were used and varied from 29-35% when only one or the other mixing periods were utilized. Another significant finding is that small doses of Mg^{++} recycle do not significantly affect quality of the treated water compared to the 0 dose condition.

Turbidity removal was determined at 10 minutes settling time following flocculation for the various mixing conditions. An optimum recycle dose of 0 mg/1 Mg^{++} for the low color water was used, at pH 11.5, with recalcined lime for pH adjustment. As seen in Figure 24, mixing conditions do affect settling of the floc, represented by turbidity removal, which varied from 78% to 97%. Optimum settling of the floc occurs when the rapid mix is short, 45 seconds or less; and the slow mix time is at least 19 minutes. The use of optimum mixing conditions will result in longer filter runs due to an increased efficiency in sedimentation of the floc produced by coagulation.

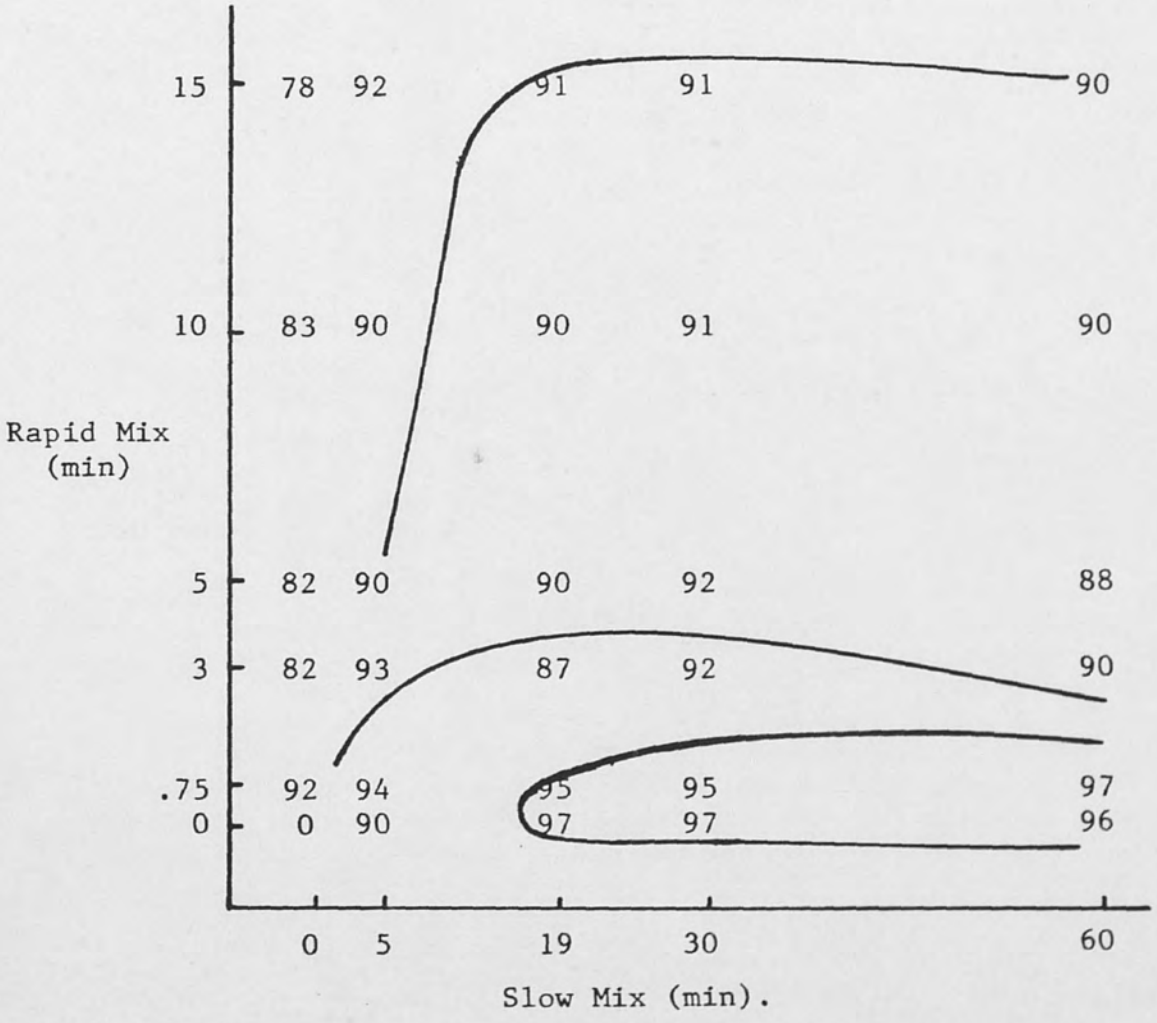

Fig. 24. Isopleth for turibidity removal as a function of variations in mixing times for a low color, high magnesium Lake Washington water treated by magnesium coagulation at a pH of 11.5 using recalcined lime. Settling time was 10 minutes, and magnesium concentration in the raw water was 18.3 mg/1 Mg^{+2}.

Alum Use as a Polymer

Alum was evaluated for its effectiveness in THM precursor reduction for the low color, high magnesium Lake Washington water. The optimum coagulation dose of 0 mg/l Mg^{++} recycle and a pH of 11.5 was utilized. Alum dose was varied from 0 to 5 mg/l Al^{+3}. In Figure 25, percent removal of THMFP, TOC and color are shown as a function of alum dose applied. The addition of alum was effective in increasing reductions of all three parameters. For THMFP, TOC and color, the increases in removal obtained with a minimum alum dose of 2 mg/l Al^{+3} were 10%, 20% and 15%; or, 50 µg/l THMFP, 4.2 mg/l TOC and 9 cpu. For the low color water, alum addition is much more effective than magnesium addition.

The removals obtained with alum addition appear to follow an adsorption isotherm of the Langmuir type. These removals are at first linear then level off to a limiting amount where no further removal is obtainable. To evaluate this relationship, a modified form of the Langmuir equation was used (Weber 1972):

$$P = \frac{k_1 [Al^{+3}]}{1 + k_2[Al^{+3}]} \qquad (22)$$

where:

P = percent removal

Al^{+3} = aluminum concentration, mg/l

k_1 = rate constant for adsorption

k_2 = rate constant for desorption

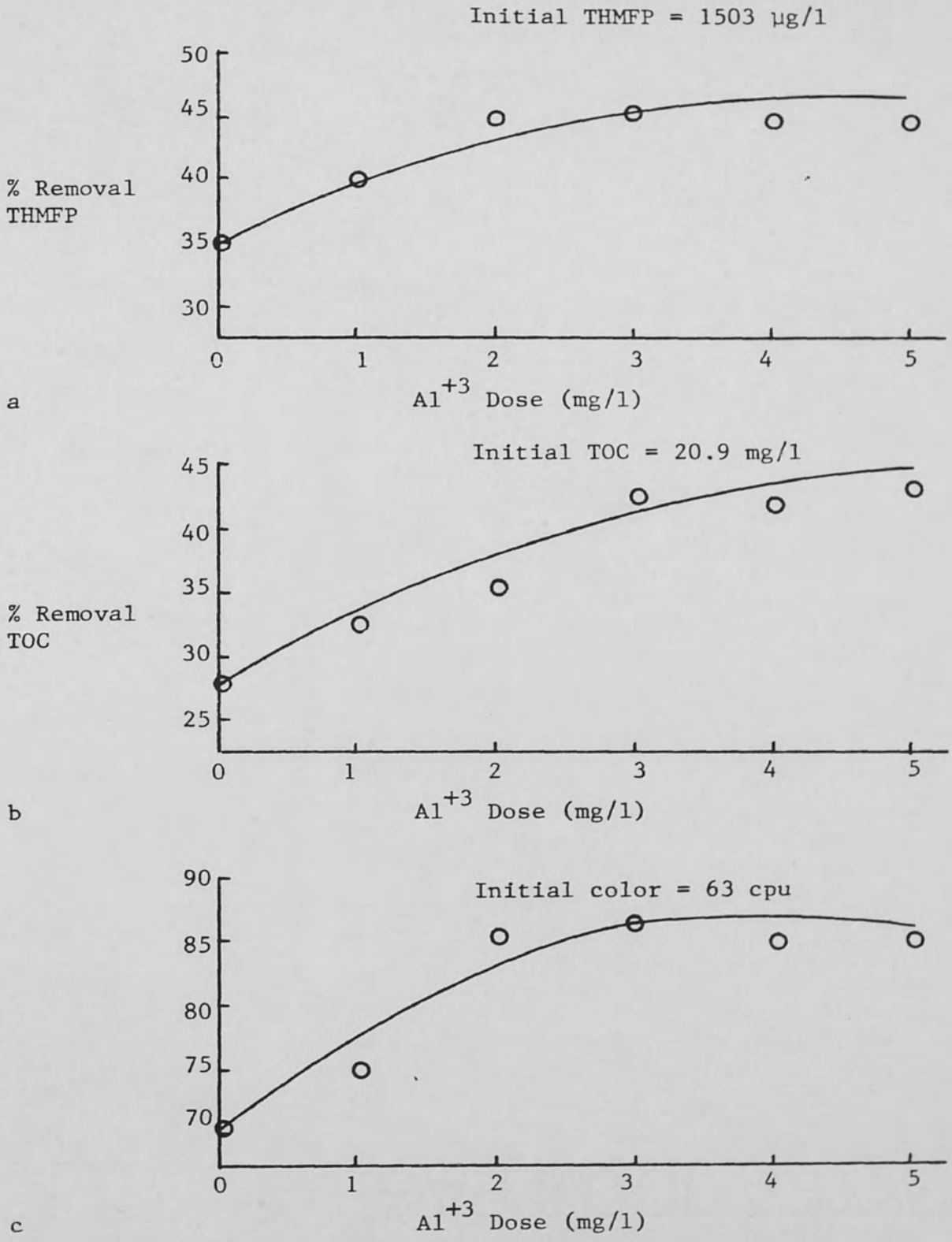

Fig. 25. Relationship between alum dose applied and % removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recalcined lime at pH 11.5. Magnesium concentration in the raw water was 21 mg/1 Mg^{+2}.

This model is based on the assumption that maximum adsorption occurs on the surface of the adsorbent. To linearize this equation, it was inverted, and then 1/P was plotted as a function of $1/[Al^{+3}]$ dose. (See Figure 26).

$$\frac{1}{P} = \frac{1}{k_1[Al^{+3}]} + \frac{k_1}{k_2} \qquad (23)$$

The fit for this relationship was good for all three parameters, THMFP ($r = .936$), TOC ($r = .934$) and color ($r = .916$); indicating that the alum was possibly adsorbing onto the floc formed in coagulation. It is evident that the alum was effective as a polymer to reduce THM precursors in the finished water.

The effect of alum addition on settling velocity of the floc formed during coagulation was also investigated. Turbidity was measured at various times during settling and by dividing the distance settled by the time settled, floc settling velocity was determined. Addition of alum increased the settling rate of the floc, as seen in Figure 27. Poorest sedimentation was observed when no alum was used, and optimum sedimentation was obtained with a dose of 2 mg/l Al^{+3}. At pH 11.5, aluminum is soluble. In the solubility diagram for aluminum hydroxide, $Al(OH)_3$, Figure 28, one can see that at pH 11.5, aluminum exists as an anionic species, $Al(OH_4)^-$. Because of this, aluminum would not appear to be effective as a polymer in precursor reduction at high pH values, out of the range of aluminum hydroxide precipitation, pH 5 to 8. It appears that the aluminum is adsorbed onto the surface of the

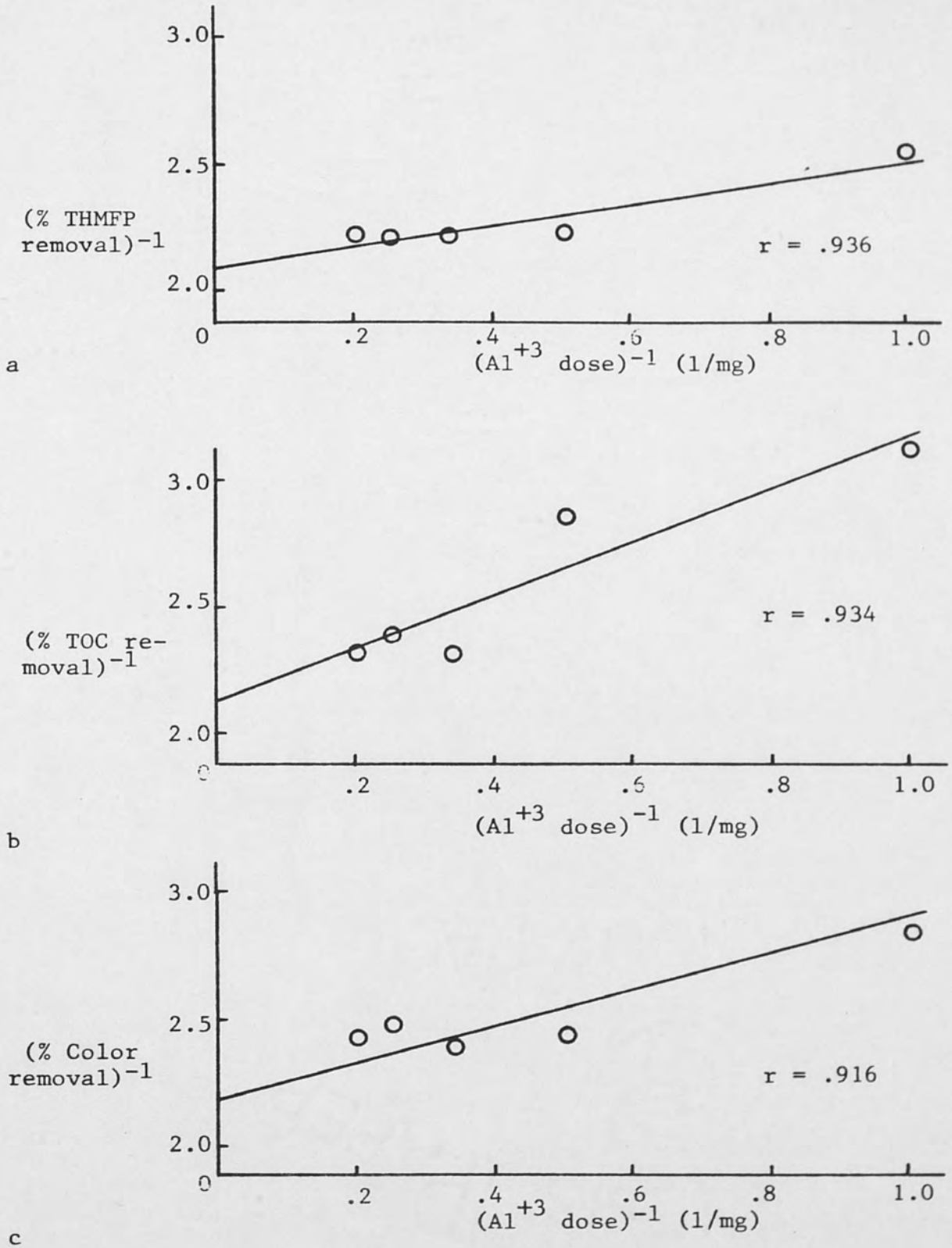

Fig. 26. Adsorption relationships for (a) THMFP, (b) TOC, and (c) color removal for alum addition to a low color, high magnesium Lake Washington water treated by magnesium coagulation at pH 11.5.

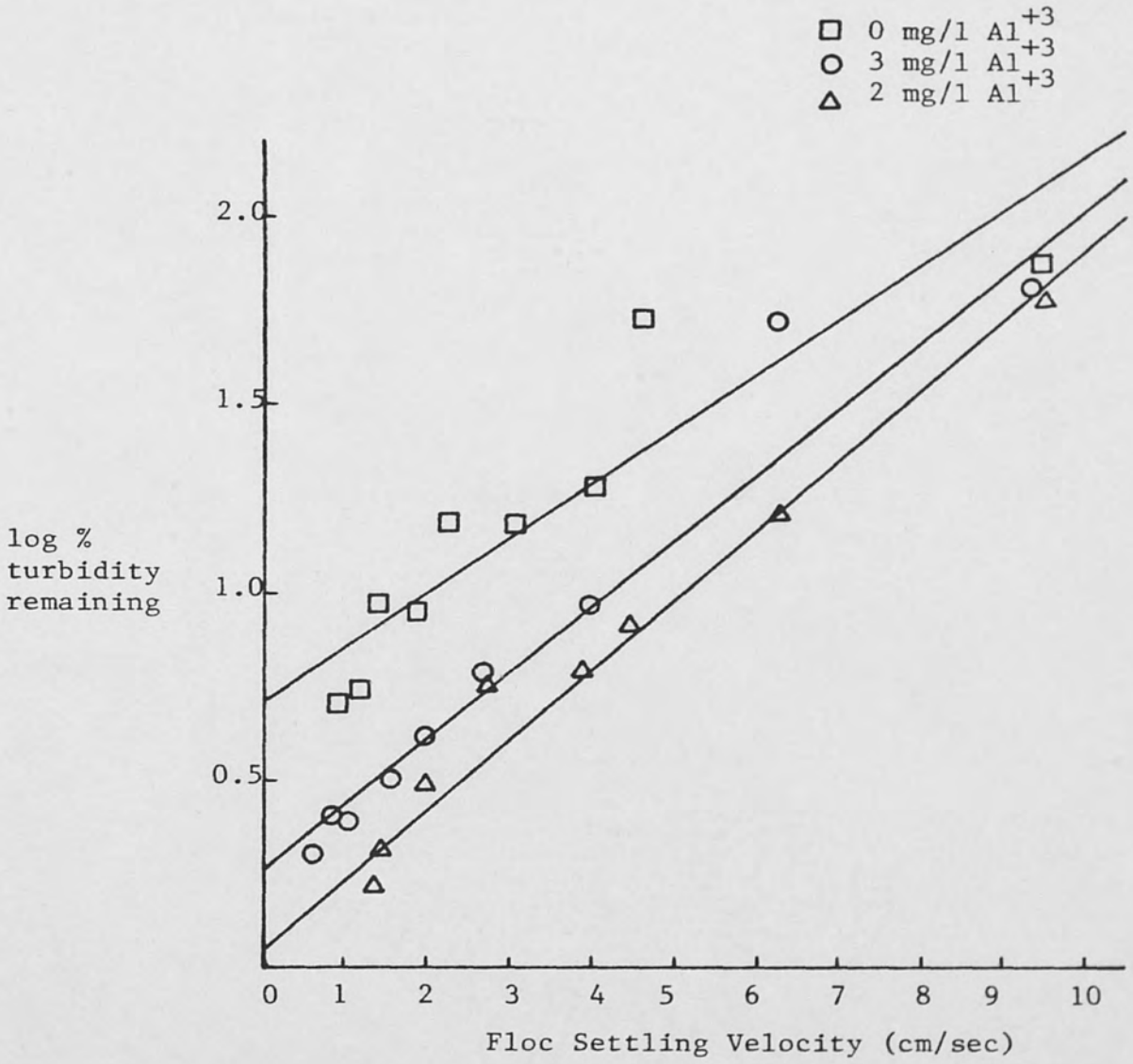

Fig. 27. Settling velocity distribution curves for a low color, high magnesium Lake Washington water treated by coagulation with recalcined lime at pH 11.5. Magnesium concentration in the raw water was 21 mg/l Mg^{+2}.

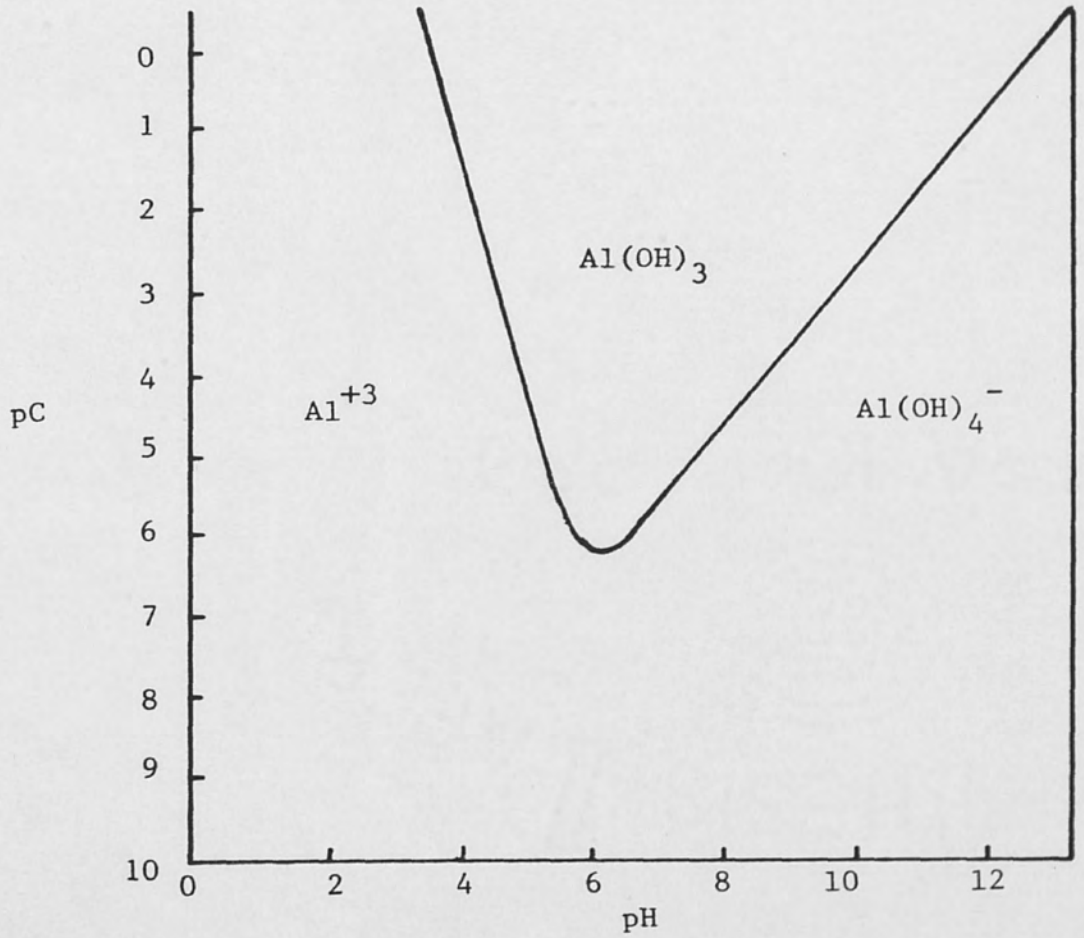

Fig. 28. pC-pH diagram for aluminum hydroxide solubility.

floc, thus causing the floc to become heavier. This could cause faster settling of the floc, and thus, more of a sweep-enmeshment type of sedimentation.

Because aluminum is in soluble form at pH 11.5, the concentrations in the treated water were measured, and are shown in Figure 29. It was observed that there is no significant increase in aluminum levels in the treated water at a dose of 2 mg/l Al^{+3}. Above this dose, there is a direct relationship between the aluminum dose applied and the residual level of aluminum in the treated water. The ratio of moles Al^{+3} dosed to moles Al^{+3} leaving in the water was found to be 3 to 1 above the 2 mg/l Al^{+3} dose. It is significant that alum at high pH values can promote organics removal and settling during treatment while not significantly increasing the aluminum residual in the finished water. This is especially so when the coagulation pH is 11.5 and the allowable $Al(OH_4)^4$ solubility at that pH is $10^{-1.2}$ mole/l, or approximately 6000 mg/l $Al(OH_4)^-$.

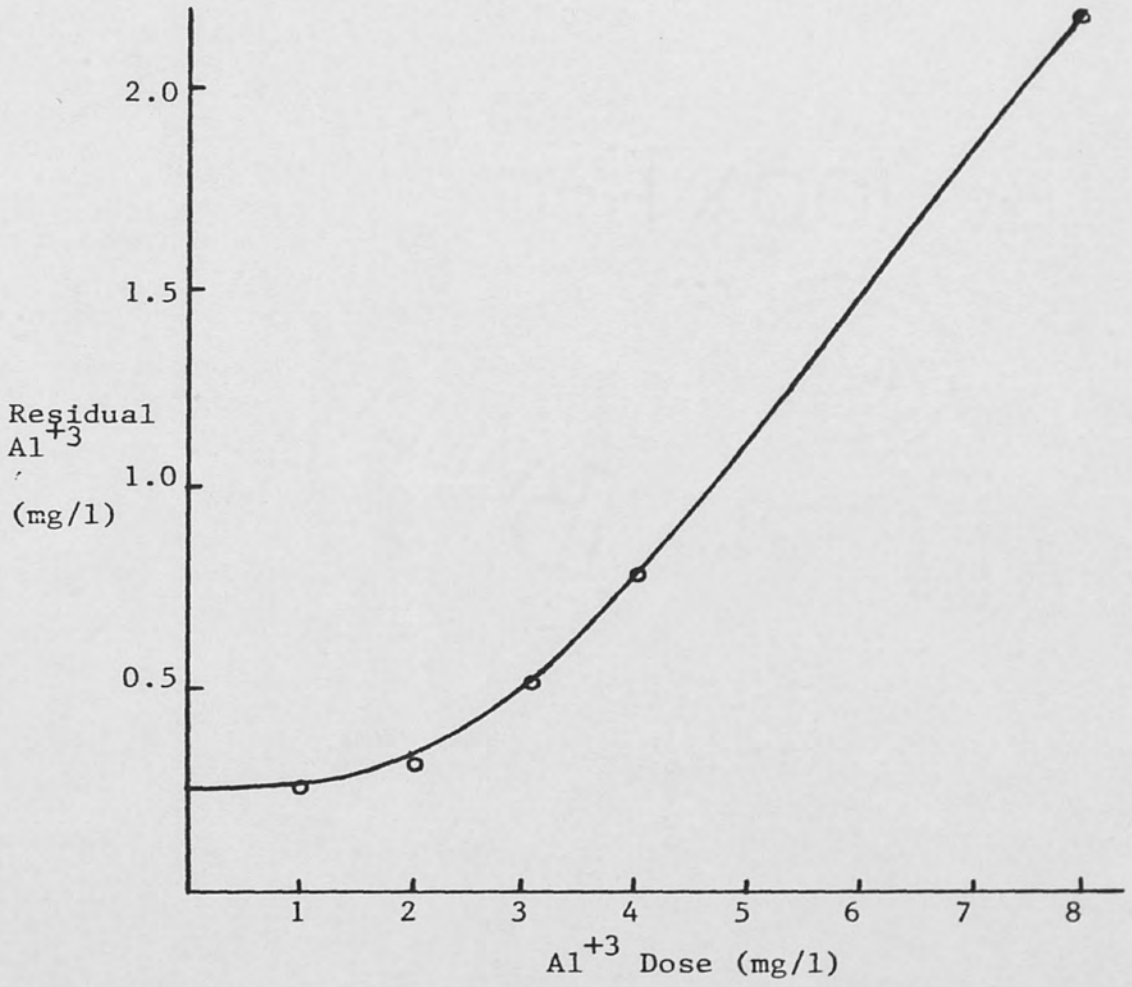

Fig. 29. Relationship between aluminum dose applied and aluminum remaining for a low color, high magnesium Lake Washington water treated by coagulation with recalcined lime at pH 11.5. Magnesium concentration in the raw water was 21 mg/l Mg^{+2}.

CHAPTER V

CONCLUSIONS

Lake Washington, the potable water source for the City of Melbourne, Florida experiences a seasonal change in water quality corresponding to rainfall occurrence. The dry period is characterized by a low color, high magnesium water due to groundwater influence, and the wet period is characterized by a high color, low magnesium water due to an increase in surface runoff and direct precipitation. Average color levels range from 50 cpu to over 200 cpu and average magnesium levels range from 20 to 5 mg/l Mg^{++} during the dry and wet periods, respectively. The poor quality of this water, with its high organic content, make it difficult to treat efficiently.

For the low color, high magnesium lake water, the recycle magnesium supernatant is ineffective as a coagulant to remove THM precursors. Because of the poor quality of the recycle, the organic loading on the coagulation process outweighs the benefits of increasing the magnesium ion concentration. Best treatment of the water occurred with no addition of recycle magnesium because of the high levels of magnesium, approximately 20 mg/l Mg^{++} present in the raw water. The optimum pH for coagulation is 12 but

11.5 is recommended because of the increase in cost for lime needed to operate at pH 12, $80/MG is not justified by the small increases in THMFP, TOC and color removal, approximately 30 µg/l THMFP, 1.8 mg/l TOC and 1 cpu color. There was very little variation in the color, TOC and THMFP removal by magnesium coagulation when either commercial, recalcined or reagent lime was used for pH control.

In the case of the high color, low magnesium water, recycle magnesium was effective in reduction of THMFP, TOC and color levels in the treated water. A recycle dose of 40 mg/l Mg^{++} at pH 12 was optimum for this water. Because the magnesium concentration in the raw water is low, approximately 5 mg/l Mg^{++}, the magnesium ions contributed by the recycle aid in coagulation. The effect of the organics also present in the recycle are less detrimental due to such a high level of organics present in this water. During the wet period, the recycling of the magnesium would be beneficial in reduction of THM precursors.

Magnesium sulfate is effective as a coagulant for reduction of THMFP, TOC and color in the low color and high color waters but it is expensive. For the low color, high magnesium water, a minimum dose of 20 mg/l Mg^{++} achieved maximum removals of THMFP, TOC and color levels of 46%, 50% and 85%. The best removal of THMFP, TOC and color was achieved with a coagulant dose of 40 mg/l Mg^{++} at pH 12 for the high color, low magnesium water achieving maximum removals of 65%, 69% and 98%. Because magnesium sulfate

is expensive, $.22/lb, a minimum dose of 20 mg/l Mg^{++} is sufficient for the low color case, but more is needed in the case for high color. For the high color water the magnesium sulfate is not much more effective than the recycle magnesium, indicating recycling the magnesium may be beneficial for this part of the year.

Linear relationships were found to exist between THMFP levels, TOC levels and color levels in water treated by recycle magnesium and magnesium sulfate at doses from 0 to 40 mg/l and pH 11.5. By performing an analysis such as this for a given water, it may be possible to estimate the THMFP by measuring color or TOC. Also, it was concluded that there is THMFP and TOC present in the water which does not produce color, and possibly some TOC which does not produce THM's.

The increase in THM precursor removal obtained with coagulation above pH 11.5 was determined to be due to an additional small amount of magnesium, approximately 2 mg/l which is also removed. There was no significant variation between the solubility of magnesium when different lime sources were used.

Variation in mixing conditions was determined to have no effect on reduction of THMFP, TOC or color levels, but it is an important factor in floc sedimentation. A maximum rapid mix (coagulation) of 45 seconds, and a minimum slow mix (flocculation) of 19 minutes was optimum for sedimentation.

Alum used as a polymer at pH 11.5 with magnesium coagulation increased the removal of color, TOC and THMFP. This removal can

accurately modeled by a Langmuir isotherm. A dose of 2 mg/l Al^{+3} achieved significant reductions of organics without significantly increasing the level of aluminum in the finished water. The use of alum at pH 11.5 also increased floc sedimentation rates in addition to increasing THMFP, TOC and color removal.

Even though significant reductions in the levels of THM precursors was observed in this study, using the magnesium-lime coagulation process, this treatment alone is not sufficient to produce a high quality potable water capable of meeting the THM standard of 0.1 mg/l. Further reduction in the levels of organic compounds is necessary to accomplish this objective. The use of activated carbon and alternate disinfectants, currently under investigation, may be effective in further reducing the levels of THM's in the finished water. By optimizing all aspects of the treatment process for THM precursor removal, the levels of THM's will be kept at a minimum.

CHAPTER VI

RECOMMENDATIONS

1. In coagulation of the low color, high magnesium Lake Washington water, THM precursor removal is optimized with the use of either fresh magnesium sulfate or alum at a pH of at least 11.5. Because magnesium sulfate is expensive, the use of alum should be considered. Because of the poor quality of the recycle magnesium supernatant, it should not be used in treatment of this type of water.

2. For the high color, low magnesium water, the use of the recycle magnesium in coagulation was beneficial in reducing levels of THM precursors in the finished water. The use of alum in coagulation for this water at high pH needs to be investigated also.

3. Minimum mixing conditions found to be most effective in sedimentation of the floc were 45 seconds rapid mix and 19 minutes slow mix periods.

4. By improving the quality of the recycle magnesium supernatant, it may be more effective as a coagulant for THM precursor removal, in both the low color and high color water.

5. By following these guidelines, maximum removals of THM precursors will be obtained for the magnesium process. These

reductions, although significant, are still not great enough to bring Melbourne's finished water into compliance with the standard of 0.1 mg/l THM's. Other methods of reducing levels of THM precursors are needed to accomplish this objective. An investigation of activated carbon adsorption and the use of alternate disinfectants is recommended to further reduce levels of THM precursors.

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