RESIDUAL ALUMINUM
IN POTABLE WATER

TECHNICAL COMPLETION REPORT

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THE UNIVERSITY OF NEW HAMPSHIRE

WATER RESOURCE RESEARCH CENTER

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RESIDUAL ALUMINUM IN POTABLE WATER

By:

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TECHNICAL COMPLETION REPORT

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ACKNOWLEDGEMENTS

ERRATA

Page 6   line 13...ppb(mg/e) and in seawater
                 should be ppb(ug/1)

Page 13   last line...(0.66 mg/1 or...)
                 should be 0.66 meq/1

Page 35   Table 6 Heading...$u_s(cm_s^{-1})$
                 should read $u_s(cms^{-1})$

Page 33   line following (7)...K = 0.9
                 should be $K_p = 0.9$

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

The behavior of aluminum in water treatment facilities using alum coagulation was studied with laboratory jar tests as well as actual plant monitoring. The important parameters looked at were pH, temperature and dosage. For surface waters with pH $>$ 6, the amount of dissolved aluminum is usually quite low, less than 40 ppb. Depending on hydraulic conditions, particulates can also be a substantial source of aluminum in the raw water.

The amount of dissolved aluminum in jar tests follow rules of hydrolysis equilibrium when the aluminum dosage is much greater than the amount of organics. The main species seem to be $Al(OH)_2^+$, $Al(OH)_3^0$ and $Al(OH)_4^-$. The minimum soluble aluminum is about 20 ppb at 25^0C and occurs at pH about 6.5, and 10 ppb at 5^0C at pH about 6.9. The presence of flouride at the mg/L level can increase the amount of soluble aluminum substantially when pH$<$ 7. These pH/solubility curves seem to give a reasonable estimate for the actual water treatment plant data, as long as the level of organics are low.

The amount of particulate aluminum must be a function of alum dosage and water treatment plant conditions. Literature research show that there is a stiochiometric relationship between alum dosage and the amount of humics/fulvics present. The optimum pH for coagulation appear to be on the acidic side, from around 5.2 at 25^0C to about 6 at 2^0C. The optimum pH for flocculation, settling and filtration would seem to be closer to neutral. It was determined that under our conditions, 10 to 20% of the particulate aluminum are within a size range of 20 μ and less, and that these particulates could be very difficult to remove without the use of coagulant or filtering aids.

This study points out the need for distinguishing between soluble and particulate phases and that any drinking water standards should take this as well as total dietary intake into account.

aluminum at the ppb level has a catalytic and limiting effect on the growth of diatoms. Driscoll et. al. (1980) reported the effect of aluminum speciation on fish and confirmed the importance of speciation. High amounts of aluminum could also influence the availability of phosphorus to plankton, as reported by Zarini (1983). The 1984 review issue of the Journal WPCF referenced nine reports on aluminum toxicity during the period of 1982 to 1983, mainly on fish. Aluminum can be toxic to plants as well.

WATER QUALITY

McKee and Wolf (1963) reported that aluminum concentrations between 100 to 500 ppb can be irritating to eyes. According to Kopp (1969), a five year survey of 1577 raw surface waters had a 31.2 percent frequency of detection for aluminum, with ranges from 1 to 2760, and a mean of 74 ppb. The same report on 380 finished waters had a 47.8 percent frequency of detection for aluminum, with ranges from 3 to 1600 and a mean of 179.1 ppb. More recently, Miller et. al. (1984) surveyed 186 utilities during 1980 and 1981 and reported a median concentration of 51 to 94 ppb for all finished waters, with maximum levels of 2.67 ppm (2670 ppb). For utilities using alum coagulation of surface waters, the median aluminum concentration was 112 ppb. Taylor and Symons (1984) reported that almost 30 percent of New England surface water sites have aluminum greater than 100 ppb. While there is currently no maximum contamination level (MCL) for aluminum in drinking waters, the 1983 proposed rules of the USEPA did mention the association of aluminum with senile dementia (a form of Alzheimer's disease) and dialysis encephalopathy. The American National Standards Institute limit for aluminum content of dialysates is 10 ppb. The NAS calculated a seven day

health advisory of 5 mg/l but did not calculate any values for chronic exposure. The WHO guideline for aluminum is 200 ppb based on aesthetic considerations. Typical dietary intake of total aluminum has been estimated by McKee and Wolf (1963) to be 10 to 100 mg/day.

WATER TREATMENT

The use of aluminum salts in water treatment utilities to remove color and turbidity is a common practice. It has been reported by Barnett et. al. (1969) that the use of alum can increase the total aluminum content in the finished water by almost an order of magnitude compared to the raw water. It would seem like a good idea to study the occurrence and control of aluminum in a water treatment facility.

OBJECTIVES

In order to understand more fully the major factors that affect the occurrence and control of aluminum, it is of utmost importance to distinguish between the particulate and dissolved phases. Since the levels of aluminum being measured are quite low (ppb level), one needed a reliable method of analysis. To gain more insight into the mechanisms involved, jar tests as well as actual plant monitoring were initiated. The specific objectives for this study were:

1. To evaluate the standard methods of atomic absorption spectrophotometry (AAS) versus visible spectroscopy using Eriochrome Cyanine R dye for aluminum determinations.

2. To evaluate the use of membrane filters to distinguish between dissolved and particulate phases. The pore sizes of 0.45, 0.22, 0.2 and 0.1 microns were investigated.

3. Laboratory experiments were conducted to evaluate the effects of pH (a master variable) and temperature (thermodynamic variable) on the partitioning of aluminum into soluble and insoluble phases when alum is added to colored water. In addition, the effect of flouride ion on this equilibrium was also studied.

4. The results obtained from the laboratory were to be compared with those obtained from actual monitoring of water treatment facilities.

5. Control strategies for the minimization of total residual aluminum in a water treatment facility were to be established.

METHODS

Determination of Aluminum

The two methods for aluminum determination recommended by Standard Methods (1980) are: (1) atomic absorption spectrophotometry (AAS) and (2) Eriochrome Cyanine R colorimetry. Recent techniques employed by researchers include inductively coupled plasma-atomic emission spectroscopy, fluorescence, laser stepwise photoionization, and variations of AAS (flameless) and visible colorimetry using other dyes.

In this study, it was determined early on that a sensitivity of better than 0.01 mg/1 (10 ppb) is necessary. This immediately ruled out AAS in the flame mode and laser stepwise photoionization. Fluorescence is technically very sensitive but subject to severe limitations such as background fluorescence and interferences. Atomic emission spectroscopy is supposed to be accurate and precise, but not generally available. Since one of the objectives of this study is to compare results obtained from the laboratory to results obtained from a water treatment plant, and the water treatment plant personnel used the Eriochrome cyanine R method, this was the primary method of choice. The use of flameless AAS with a graphite furnace was also explored. The terms ppb and $\mu g/l$ will be used interchangeably. The aluminum standard was a GFS standard for AAS.

A. Atomic Absorption Spectrophotometry:

The Instrumentation Center of the University of New Hampshire operates an Instrumentation Laboratory Model aa/ae 951 atomic absorption spectrophotometer equipped with an auto sampler (model 254) and a graphite furnace atomizer (model 655). The instruction manual was followed to the letter. The wavelength of measurement was 309.2 nm with Argon as the carrier gas (flow rate of 15 SCFH and a cell pressure of 20 psi). Figure 1 shows a typical calibration curve using this method. The linearity of the curve did not

extend beyond 100 μg/l. The reproducibility within a run was generally within 10 percent, but difficulties were encountered for samples with less than 30 μg/l Al. Loss of aluminum via adsorption to container walls and inconsistent nebulizer flow rate were the major suspected causes of error. The detection limit for this study was estimated to be 10 μg/l and the relative accuracy for samples containing less than 30 μg/l Al ± 30 %.

B. Eriochrome Cyanine R Method:

This is a visible spectrophotometric method and a Bausch and Lomb Spectronic 2000 was utilized in this study. There was a slight modification to the standard method. We were getting considerable absorbance for our blanks (non-zero-intercept at zero Al concentration). This was attributed to the presence of aluminum in our chemicals and/or nanopure water. EDTA was added to our blanks and the calibration curves were extrapolated to zero absorbance to get a determination of the background aluminum concentration; it typically varied from three to eight μg/l This was added to our standards, and excellent calibration curves were obtained, as shown in Figure 2. However, our dye was not very stable (faded in a week even with storage in a dark bottle), so new calibration curves were obtained for every run. Care should also be exercised in the acidification of samples. We discovered that the buffers were not sufficiently strong to maintain a final pH of 6, and the absorbance of the aluminum-dye complex is strongly pH dependent. Subsequently, we did not acidify our samples for the jar tests. Since a 5 cm cell path was utilized in our laboratory studies, we were able to measure 1 μg/l and the reproducibility at 10 μg/l was estimated to be better than ± 10 percent. The data from the water treatment plants was obtained with a standard cell path of 1.17 cm (1/2 inch outer diameter) and subject to fluoride interference, thus the detection limit of aluminum in the water treatment plant was estimated to be 10 μg/l and a relative accuracy of ± 50 percent at this level. For more details, see Shull and Gutham (1967).

11
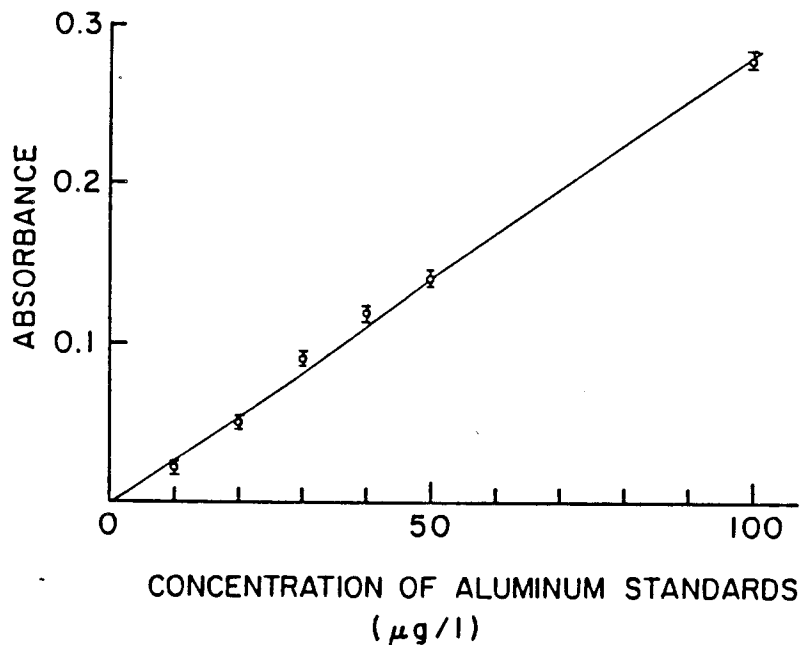
FIG.1 Calibration curve for aluminum using
       atomic absorption spectrophotometry
       in the non-flame mode with the
       graphite furnace. Bars denote
       standard deviation of 3 runs.
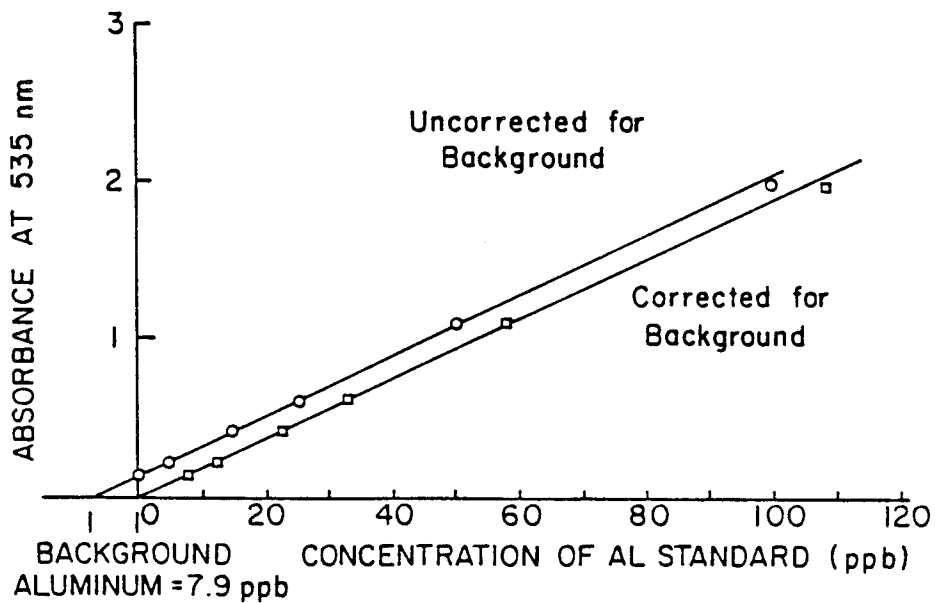
FIG.2 Calibration curve for aluminum using the
       Eriochrome Cyanine R method. Cell path
       was 5 cm. Background was nanopure water.
       Note: ppb = μg/L

Separation of Dissolved and Particulate Phases

The use of 0.45 μm membrane filtration to distinguish between solid and dissolved phases is a common and EPA approved method. Hem and Robertson (1967) and Kennedy et. al. (1974) presented evidence that particulate aluminum could be retained from a solution previously filtered through a 0.45 μm filter on a 0.1 μm filter. Danielsson (1982) stressed the importance of studying the effects of filter load.

In this study we evaluated the use of the following membrane filters: Millipore 0.45 μm (cellulose acetate), Nucleopore 0.22 μm (polycarbonate), Nalgene 0.2 μm (cellulose acetate) and Nalgene 0.1 μm (cellulose acetate). While there did seem to be a consistent trend of more retention as smaller pore sizes were used, the difference noticed was between 7 to 25 percent. Partly into this study, Nalgene discontinued the production of their pre-packaged 0.1 μm filter package. Consequently. we used the Nalgene 0.2 μm filter packages (Nalgene 150-4020), which had a volume of 115 ml and a diameter of 47 mm. Pre-wetting the filters did not alter the results to a significant degree, but we discarded the first 100 ml filtered and used the subsequent portions. This gave a filter load of 11.5 mlcm^{-2} in the units of Danielsson (1982), considered as low load.

Jar Tests

A. Model Water:

Jar tests were performed with solutions made up of nanopure water and analytical reagent grade chemicals unless otherwise noted. 5.6 mg/l of Aldrich humic acid (H1,675-2) was used to simulate color (80 color units on the platinum cobalt scale). Sodium bicarbonate at a concentration of 55.5 mg/l was used to simulate alkalinity (0.66 mg/l or 33 mg/l as $CaCO_3$).

13

B. Procedure:

Jar tests were performed with a Phipps and Bird Apparatus with paddle stirrers and one liter plastic jars (Nalgene 1201-1000). The jars were kept in a water bath thermostated to $\pm 1^{o}$C. Concentrated HNO_3 or NaOH was added to the stock model water for pH adjustments, followed by stock alum solution to give a final dosage of 40 mg/l alum (this would give a total aluminum addition of 3.24mg/l or 1.2×10^{-4}M). The pH range we studied was from 5.5 to 8.0, and the dosage conditions put us into the optimum sweep coagulation zone of Amirtharajah and Mills (1982). NaF was added to give 1 mg/l F^- (5.8×10^{-5}M) when the effect of fluoride was studied. The final ionic strength varied between 7×10^{-4}M to 2×10^{-3}M (assuming that most of the aluminum precipitated as aluminum hydroxide).

After all the chemical additions, the solutions were rapid mixed at 200 rpm for two minutes, flocculated at 15 rpm for 15 minutes followed by 15 minutes of settling. According to Cornwell and Bishop (1981), the rpms would have given a velocity gradient of about $350s^{-1}$ and $10s^{-1}$ for the rapid mix and flocculation respectively. The pH was measured with a Beckman model 71 pH meter and a combination glass electrode previously standardized with NBS buffer. The solutions were then filtered and the filtrate acidified if AAS was used for aluminum determination, otherwise the filtrate was analyzed by the Eriochrome Cyanine R method within a few hours.

Particle Sizing

Particle size distributions were determined on a model ZBI coulter counter. This operates on an electroresistivity technique. Known volumes of electrolyte solution (Isoton) are drawn through a a micro-orifice; as a particle passes through the orifice, it displaces a volume of electrolyte

solution equal to its own and varied the resistance across the orifice. The magnitude of the resistance change is proportional to the particle volume, and the number of pulses is equal to the number of particles passing through the orifice. The machine was calibrated with a known particle size distribution of polystyrene latex particles and a 30 μm orifice (aperture). According to the manuals, this would have given us us a useful particle size range of 1.2 to 12 um.

Settling Velocity

After a jar test, a portion of the solution was poured into a standard sedimentation pipette for settling tests. This is just a cylinder with a volume of about 550 ml. A two-way stockcock with a drawing tube and a 10 ml sampling section was inserted, and samples were drawn at specific time intervals. A magnetic stirring device was used to keep the solution in "homogeneous" suspension, a 20 cm settling height was used, and samples were analysed for total aluminum.

The assumptions, theory and background of the coulter counter and the sedimentation pipette could be found in Stockham and Fochtman (1977). The settling velocity data could be translated to a particle size distribution if Stokesian settling occurs and the Stokesian parameters known (in particular, the density of the floc).

Actual Plant Monitoring

The Arthur Rollins Water Treatment Plant located in Durham, New Hampshire is a 1.2 mgd facility that treats surface water from a storage resevoir impounded on the Oyster River. Treatment includes alum coagulation, flocculation, sedimentation, rapid sand filtration followed by chlorine disinfection and

and fluoridation. Weekly samples were taken in the beginning of September 1983 to mid-February 1984, and again from mid-May to July, 1984. Samples were taken from the raw water intake, after sand filtration and prior to distribution. The standard water quality parameters: temperature, pH, alkalinity, color, turbidity were determined along with fluoride and aluminum, all according to Standard Methods (1980).

For the sake of comparison, the January 1984 data of the Somersworth Water Treatment Plant were obtained. This is a 1 mgd facility treating the Salmon Falls River using a Neptune Micro-Floc system. The chemicals added include alum, caustic and a polymer. Apart from these differences, the sedimentation process goes through tube settlers, and there is no fluoridation. The water quality parameters of pH, temperature, color, alkalinity, total aluminum and average daily alum dosage were available.

RESULTS AND DISCUSSION

Water Treatment Plant Monitoring

The data from the Arthur Rollins Water Treatment Plant are included as Table A-1 in the appendix. The behavoir of total aluminum for the period September, 1983 to mid-February, 1984 is shown graphically in Figure 3. It should be noted that the amount of total aluminum leaving the plant was invariably greater than that in the incoming raw water. During this same period of time, the raw water had the following characteristics: temperature varied from 1 to $20^{o}C$, color varied from 33 to 110 color units, alkalinity varied from 7 to 40 mg/l as $CaCO_3$ and the raw water pH varied from 6.3 to 7.2. The pH of the water emerging from the sand filters had a pH range of 5.6 to 6.9, while the pH of the finished water ranged from 6.6 to 7.6. While there does seem to be some sort of U-shaped behavoir if one plotted total aluminum versus pH, there is a lot of scatter and there does not seem to be any simple relationships between raw water characteristics and the final amount of total aluminum.

It should also be mentioned that between the end of May and mid-July, 1984 the opposite picture occurred: the total aluminum in the raw water was higher than that of the finished water. The average alum dosage for the former period as calculated by the consumption of alum divided by the volume of water produced varied from 23 to 90 mg/l. While one would expect the final aluminum to be a function of alum dosage, such a relationship did not appear to be evident. The lack of direct relationship between alum dosage and aluminum content in finished water is further evidenced by the January, 1984 data of the Somersworth Water Treatment Plant (included as Table A-2). If one had plotted alum dosage versus aluminum content in the

finished water, one would get a substantial amount of scatter, even though the pH of the coagulation/flocculation process was kept between 6.00 to 6.65 and the finished water had a fairly constant pH of 7.00 to 7.46. However, the amount of aluminum in the finished water at Somersworth was usually less than that of the raw water, the Salmon Falls River. See Figure 4.

If one had looked carefully at the amount of aluminum in the raw water at Durham, one would notice generally low values (less than 40 ppb or so) except during the times when the reservoir overturned. This could be seen near the beginning of December, 1983 in Figure 3 and around April 12 to 19, 1984 in Table A-1. The temperature of the raw water then was around $5^{\circ}C$, near the temperature of maximum water density. Therefore, the water treatment plant received pulses of mainly particulate aluminum on those days, and the finished water of December 1, 1984 had a record high aluminum content of 550 ppb. The particulates collected on membrane filters on that day were subjected to SEM/EDAX analysis, and the raw water particulates were shown to be mainly composed of aluminum and silicon (clay) and the finished water particulates, mainly aluminum.

JAR TESTS

A. Soluble Aluminum, Influence of pH and Temperature

A total of six different jar tests were performed for this study, and the data reported in Table A-3 of the appendix. Figure 5 shows the relationship between dissolved aluminum and pH at $25^{\circ}C$ using our model water of humic acid and sodium bicarbonate, and Figure 6 shows the same for $5^{\circ}C$. The curves are least squares polynomial fits to the data. The U-shaped behavoir is in accord with a standard model of cation hydrolysis at equilibrium with a hydroxide
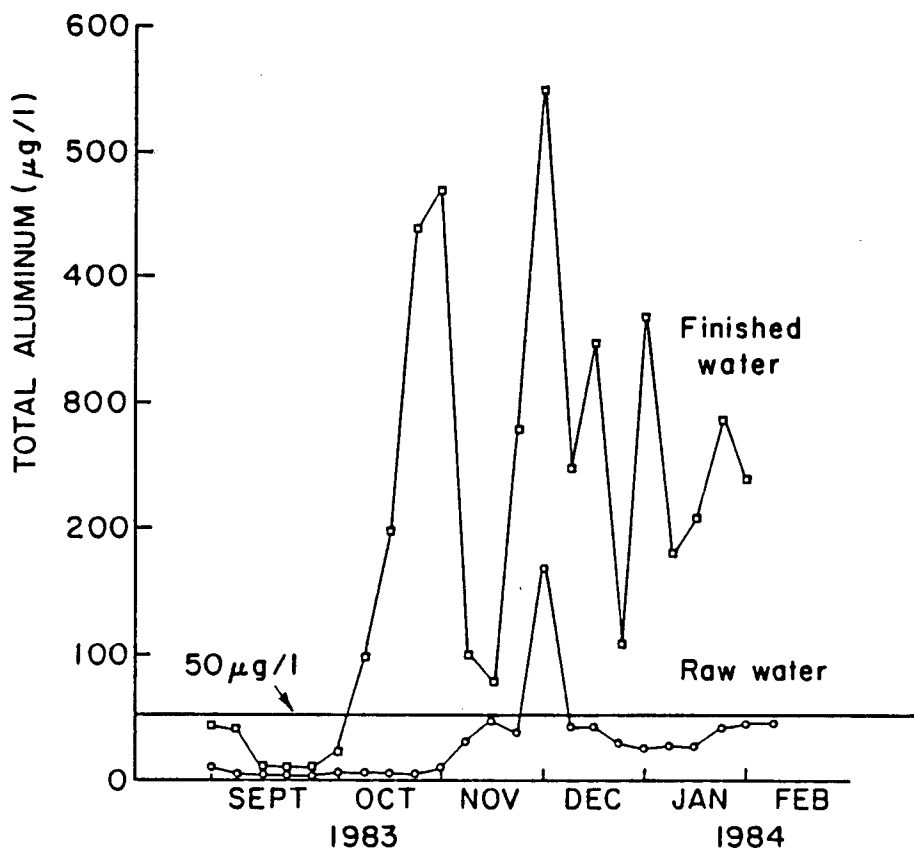
FIG.3   The behavior of aluminum at the Arthur
        Rollins water treatment plant, Durham,
        N.H. from Sept.1983 to early Feb.1984.
        The 50 µg/L line is for reference only.
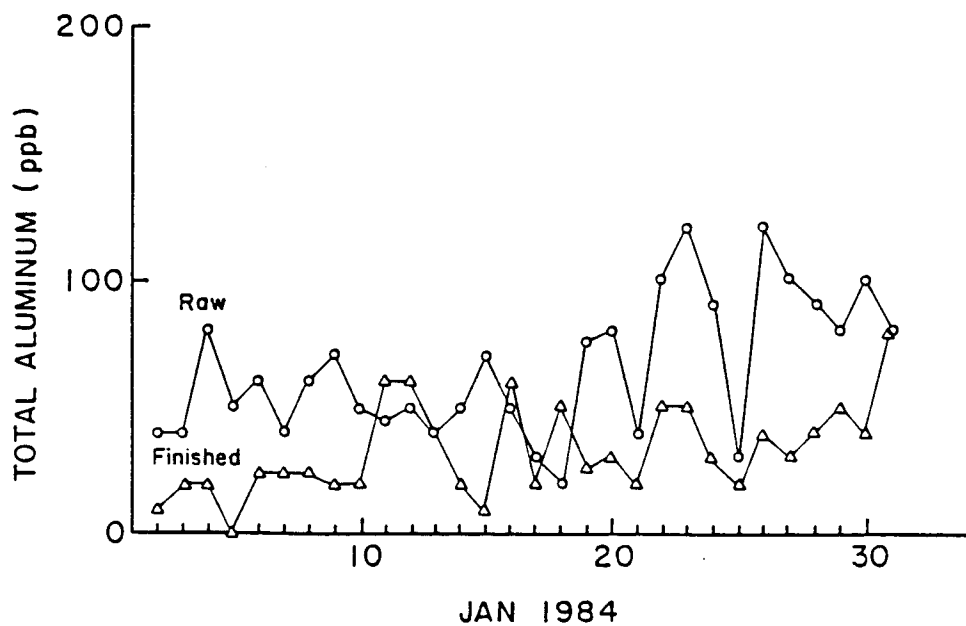
FIG.4   The behavior of aluminum at the Somersworth
        water treatment plant, Somersworth, N.H. during
        Jan.1984

19
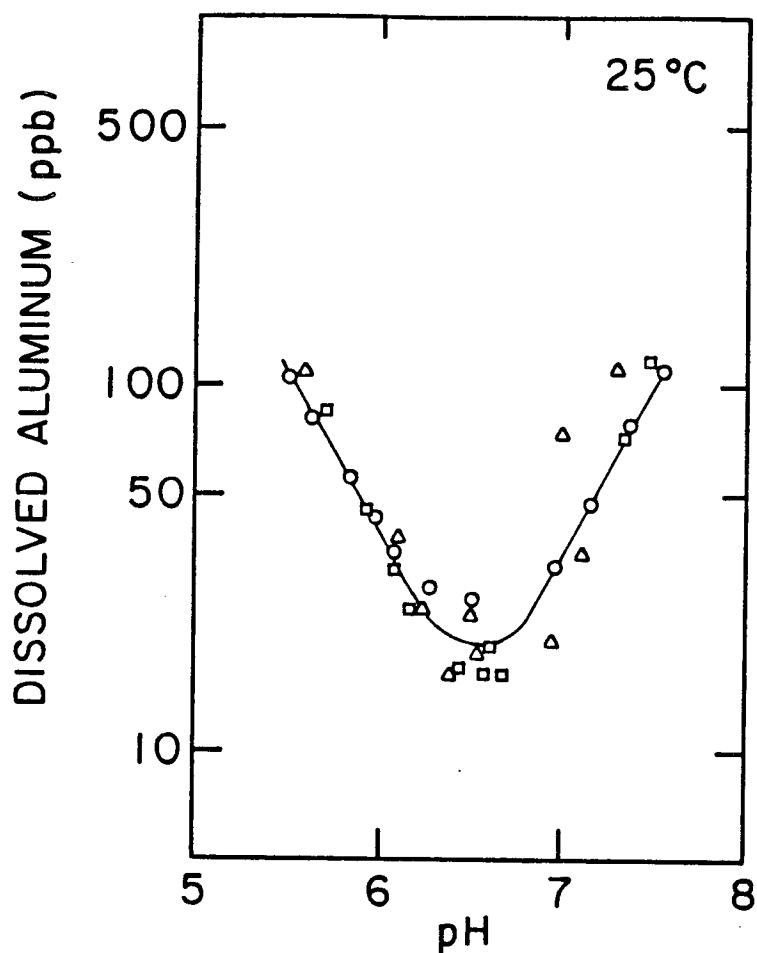
FIG.5 Amount of dissolved aluminum as a function
of pH at 25°C. Triangles are data obtained
using AAS and 0.1 μm membrane filtration; Circles
and squares are 2 different runs using Eriochrome
Cyanine R and 0.2 μm filters.
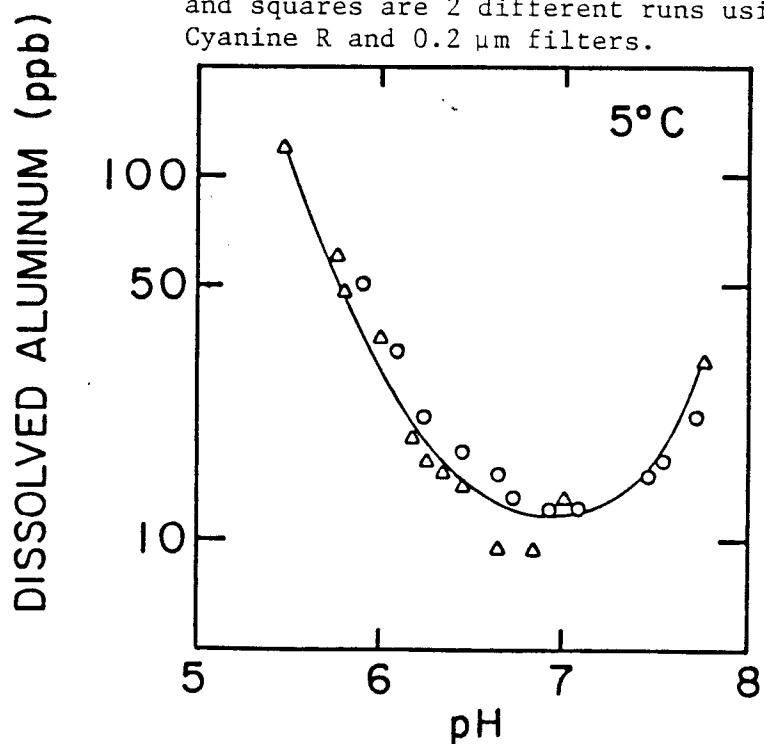
FIG.6 Amount of dissolved aluminum as a function
of pH at 5° C. Triangles and circles are
2 different runs. Aluminum determined by
Eriochrome Cyanine R method.

solid phase, as suggested by Baes and Mesmer (1981).

The hydrolysis of aluminum has been studied extensively by Black and Chen (1967), Stumm and O'Melia (1968), Hayden and Rubin (1974) and reviewed by Baes and Mesmer (1976). There were other studies, but those were either performed at vastly different ionic medium or did not report any equilibrium constants. Even with these four investigators, there is no agreement between the hydrolysis species nor the magnitude of the equilibrium constants. See Table 1. In this study, where total aluminum added (1.2×10^{-4}M or 3.2 mg/l) is much greater than the total dissolved aluminum ($10^{-5.5}$ to $10^{-6.4}$M, 10 to 100 μg/l) and the amount of organics (5.6 mg/l is 5.6×10^{-6}M, if we assume a molecular weight of 1000, see Edzwald et. al., 1979), the slopes of the aluminum/pH plots suggest the presence of $Al(OH)_2^+$, $Al(OH)_3^0$, and $Al(OH)_4^-$. Although the existence of polymeric aluminum species such as $Al_8(OH)_{20}^{4+}$ has been widely reported, it should be noted that such species are probably important only in the initial stages of color coagulation, and at low pH values (<5). What we are reporting here is a pseudo-equilibrium model; and it could be calculated that such polymeric species would be at very low concentrations when solid aluminum hydroxide is present. Of course, a case could be made that our filtration procedure removed the polymeric species.

If aluminum hydroxide solid exists, then we could write the following reaction:

$$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O \tag{1}$$
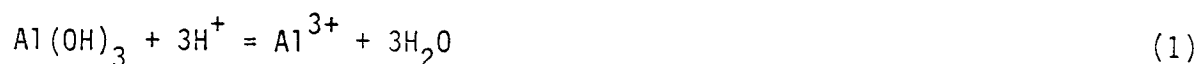
and define the solubility product $^*K_{s0} = \{Al^{3+}\}/\{H^+\}^3$. It follows from Table 1 then, that other hydrolysis species in equilibrium with $Al(OH)_3(s)$ would just be a simple function of $\{H^+\}$.

TABLE 1

A Summary of Recent Aluminum Hydrolysis Constants

SYMBOL	ACTIVITY EXPRESSION	log K at 25°C
$*K_1$	$\dfrac{\{Al(OH)^{2+}\}\{H^+\}}{\{Al^{3+}\}}$	-5.03(1); -5.0(2); -4.97(4); -5.55(3) Mixed constant[+], ionic strength 0.15M
$*\beta_2$	$\dfrac{\{Al(OH)_2^+\}\{H^+\}^2}{\{Al^{3+}\}}$	-9.3 (4)
$*\beta_3$	$\dfrac{\{Al(OH)_3(aq)\}\{H^+\}^3}{\{Al^{3+}\}}$	-15.0 (4)
$*\beta_4$	$\dfrac{\{Al(OH)_4^-\}\{H^+\}^4}{\{Al^{3+}\}}$	-21.84 (1); -23.0 (4); -22.75(3) amorphous
$*K_{s0}$	$\dfrac{\{Al^{3+}\}}{\{H^+\}^3}$	9.10 (1); 8.5 (4) for gibbsite 10.40 (3) amorphous; 10.05 (3) gibbsite, Mixed constants[+]
$*\beta_{2,2}$	$\dfrac{\{Al_2(OH)_2^{4+}\}\{H^+\}^2}{\{Al^{3+}\}^2}$	-6.27 (1); -7.7 (4)
$*\beta_{4,3}$	$\dfrac{\{Al_3(OH)_4^{5+}\}\{H^+\}^4}{\{Al^{3+}\}^3}$	-13.94 (4)
$*\beta_{15,6}$	$\dfrac{\{Al_6(OH)_{15}^{3+}\}\{H^+\}^{15}}{\{Al^{3+}\}^6}$	-47 (1)
$*\beta_{17,7}$	$\dfrac{\{Al_7(OH)_{17}^{4+}\}\{H^+\}^{17}}{\{Al^{3+}\}^7}$	-48.8 (1)
$*\beta_{20,8}$	$\dfrac{\{Al_8(OH)_{20}^{4+}\}\{H^+\}^{20}}{\{Al^{3+}\}^8}$	-68.7 (3) Mixed constant[+], ionic strength 0.15M
$*\beta_{32,13}$	$\dfrac{\{Al_{13}O_4(OH)_{24}^{7+}\}\{H^+\}^{32}}{\{Al^{3+}\}^{13}}$	-98.73 (4)
$*\beta_{34,13}$	$\dfrac{\{Al_{13}(OH)_{34}^{5+}\}\{H^+\}^{34}}{\{Al^{3+}\}^{13}}$	-97.6 (1); -97.4 (2)

Sources   (1) Black and Chen (1967)   (2) Stumm and O'melia (1968)
          (3) Hayden and Rubin (1974)   (4) Baes and Mesmer (1976)

[+] Mixed constants are that only the proton remains as activity, other species are written as concentrations.

For example:

$$\frac{\{AlOH^{2+}\}\{H^{+}\}}{\{Al^{3+}\}} = *K_1 \text{, therefore } \{AlOH^{2+}\} = \frac{*K_1 \{Al^{3+}\}}{H^{+\cdot}} \text{, since}$$

$$\{Al^{3+}\} = *K_{s0}\{H^{+}\}^3, \quad \{AlOH^{2+}\} = *K_{s0}*K_1\{H^{+}\}^2.$$

So if $AlOH^{2+}$ is the major dissolved aluminum species, a plot of log (dissolved aluminum concentration in M) versus pH would give a slope of -2; and if $Al(OH)_2^{+}$ is the major species, a slope of -1; and if $Al(OH)_3^{0}$ is the major species, a slope of 0 and if $Al(OH)_4^{-}$ is the major species, a slope of +1. Activities will be used interchangeably in this study with concentrations.

Our results are consistent with the assumption that the major dissolved species are $Al(OH)_2^{+}$, $Al(OH)_3^{0}$ and $Al(OH)_4^{-}$. The solubility equation is:

$$\text{Total soluble aluminum (M)} = *\beta_2*K_{s0}\{H^{+}\} + *\beta_3*K_{s0} + *\beta_4*K_{s0}\{H^{+}\}^{-1} \qquad (2)$$

The values of these composite constants were obtained by fitting our data graphically and numerically and listed in Table 2. These are composite, pseudo-constants as we are assuming activities to be equal to concentrations. The calculated soluble aluminum concentrations as a function of pH are listed in Table 3 and could be compared to the actual data of Table A-3, the agreement is generally within 30%, although in the worst case a departure of about a factor of two (2) was noticed. The presence of humic acid at this concentration apparently did little to solubilize aluminum. The use of AAS and Eriochrome Cyanine R gave comparable results within experimental error. The effect of temperature seemed to be most pronounced for $*\beta_4*K_{s0}$. This is in accord with theoretical predictions (see Baes and Mesmer, 1981).

TABLE 2

Composite Equilbrium Constants for This Study

	$T = 25^{\circ}C$	$T = 5^{\circ}C$
$^{*}\beta_2{}^{*}K_{so}$	1	1
$^{*}\beta_3{}^{*}K_{so}$	3×10^{-7}	2×10^{-7}
$^{*}\beta_4{}^{*}K_{so}$	9×10^{-14}	2×10^{-14}

TABLE 3

Calculated Soluble Aluminum as a Function of pH

Soluble Aluminum (ppb)

pH	$T = 25^{\circ}C$	$T = 5^{\circ}C$
5.4	116	113
5.5	94	91
5.6	77	73
5.7	63	59
5.8	52	48
5.9	44	40
6.0	38	33
6.1	33	28
6.2	29	23
6.3	26	20
6.4	25	17
6.5	24	16
6.6	25	14
6.7	26	13
6.8	28	13
6.9	31	13
7.0	35	13
7.1	41	14
7.2	48	16
7.3	58	18
7.4	70	20
7.5	86	23
7.6	105	28

B. Soluble Aluminum, Influence of Complexation

It is well known that complexation can increase the amount of soluble material in solution. The ligands that may form significant complexes with aluminum for this study are: hydroxide, fluoride, sulfate and organics. Table 3 lists all the equilibrium constants used in this study for 25^oC. The individual hydrolysis constants were calculated from the values of Table 2 and assuming $*\beta_4 = 10^{-23}$. It can readily be shown that sulfate complexes are not very important. The major source of sulfate to our model water came from the alum dosage itself. At a dosage of 40 mg/l alum, the resultant sulfate concentration is about $1.8 \times 10^{-4}M$. Therefore, the maximum amount of sulfate complexes are:

$$[AlSO_4^+] + [Al(SO_4)_2^-] = [Al^{3+}](KS_1[SO_4^{2-}] + KS_2[SO_4^{2-}]^2)$$
$$= [Al^{3+}](0.30) \tag{3}$$

For comparison sake, the amount of hydroxide complexes are strong functions of pH; see table A-5 in the appendix.

$$[Al^{3+}] + [AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-]$$
$$= [Al^{3+}](1 + *\beta_1\{H^+\}^{-1} + *\beta_2\{H^+\}^{-2} + *\beta_3\{H^+\}^{-3} + *\beta_4\{H^+\}^{-4}) \tag{4}$$

The value of the sum within the brackets is 17 at pH = 5.5 and increases to 170.4 at pH 6 and 1.46×10^5 at pH 7, much greater than 0.30. However, sulfate may be important in the determination of the surface change of the floc. The amount of fluorocomplexes could be similarly obtained as:

$$[AlF^{2+}] \quad [AlF_2^+] + [AlF_3^0] + [AlF_4^-] = [Al^{3+}] \sum_{i=1}^{4} KF_i\{F^-\}^i \tag{5}$$

Although the fluoride can also form the AlF_5^{-2} and AlF_6^{-3} complexes, they can easily be shown to be unimportant at our typical fluoride dosage of 1 mg/l = $5.3 \times 10^{-5}M$.

TABLE 4

Equilibrium Relationships Used in This Study (T = $25^{\circ}C$)

Equation	Equilibrium Constant	Source
(Hydroxide Ligands)		
$Al^{3+} + H_2O = AlOH^{2+} + H^+$	$*K_1 = 10^{-5}$	Stumm and O'Melia (1968)
$Al^3 + 2H_2O = Al(OH)_2^+ + 2H^+$	$*\beta_2 = 1.2 \times 10^{-10}$	This study
$Al^3 + 3H_2O = Al(OH)_3^0 + 3H^+$	$*\beta_3 = 3.4 \times 10^{-17}$	Ibid
$Al^3 + 4H_2O = Al(OH)_4^- + 4H^+$	$*\beta_4 = 10^{-23}$	Ibid
$Al(OH)_3(s) + 3H^+ = Al^{3+} + 3H_2O$	$*K_{so} = 8.7 \times 10^9$	Ibid
(Fluoride Ligands)		
$Al^{3+} + F^- = AlF^{2+}$	$KF_1 = 1.05 \times 10^7$	Johnson et. al. (1981)
$Al^{3+} + 2F^- = AlF_2^+$	$KF_2 = 5.77 \times 10^{12}$	Ibid
$Al^{3+} + 3F^- = AlF_3^0$	$KF_3 = 1.07 \times 10^{17}$	Ibid
$Al^{3+} + 4F^- = AlF_4^-$	$KF_4 = 5.37 \times 10^{19}$	Ibid
(Sulfate Ligands)		
$Al^{3+} + SO_4^{2-} = AlSO_4^+$	$KS_1 = 1.63 \times 10^3$	Ibid
$Al^{3+} + 2SO_4^{-2} = Al(SO_4)_2^-$	$KS_2 = 1.29 \times 10^5$	Ibid
(Fulvics)		
$Al^{3+} + L = AlL$	$KL = 2 \times 10^5$	Schnitzer & Hansen (1970)

The sum for the aluminum-fluoro complex assuming $\{F^-\} = 5.3 \times 10^{-5}M$ is 3.3 E4. By equating this sum to that of the sum of hydroxide, it could be shown that fluoro-complexes of aluminum are as important as hydrolysis complexes when pH is between 6.8 and 6.9. The hydroxide easily outcompetes fluoride at this concentration when pH>7.

A series of jar tests with the addition of a total of $5.3 \times 10^{-5}M$ F^- was performed under otherwise identical conditions. Total dissolved aluminum was determined by AAS (fluoride interferes with the Eriochrome Cyanine R method). The amount of fluoro complexes were calculated given the equilibrium constants and the mass constraint on the fluoride. The observed and computed "enhancements" ratio, defined as total dissolved aluminum in the presence of fluoride divided by the total dissolved aluminum in the absence of fluoride are listed in Table 4, the agreement is reasonable.

The influence of organics is not easy to ascertain; their molecular weight is usually unknown and the reported equilibrium constants are conditional constants, i.e., they only apply under the reported experimental conditions. However, if the conditional constant reported by Schnitzer and Hansen determined at pH = 2.35 can be applied to our system, the amount of aluminum-fulvic complex is only important if pH is less than 5, due to the low organic concentration (5.6 mg/l is about $5.6 \times 10^{-6}M$ if we assume a molecular weight of 1000). However, this small amount of humic acid was sufficient to give a color of 80. All the humic acid was observed to be removed after membrane-filtration, whether it was removed by adsorption or enmeshment or a combination of mechanisms cannot be answered by our experiments.

Figure 7 shows the comparison between our jar tests using humic acid with 1) the data from the Arthur Rollins Water Treatment Plant, 2) a series of jar tests using a natural Oyster River sample (initial color of 140) and

TABLE 5

The Effect of Fluoride on Soluble Aluminum

pH	Total dissolved Al (ppb) in the presence of 1 mg/l total F⁻	Observed Enhancement Ratio	Calculated free F⁻	Calculated Enhancement Ratio
6.3	313	11.6	3×10^{-5}	10.3
6.4	275	11.3	3.5×10^{-5}	8.4
6.5	183	7.6	4.0×10^{-5}	6.3
6.6	91	3.7	4.5×10^{-5}	4.4
6.8	80	3.0	5.0×10^{-5}	2.0
7.0	45	1.3	5.3×10^{-5}	1.2

3) a series of jar tests results obtained from Shull (1984), (experiment using Schuykill River water, total alum dosage 34 mg/l, pH adjusted by acetic acid and potassium hydroxide, dissolved aluminum determined by Erio-chrome Cyanine R method after 0.45 µm membrane filtration). For the water treatment plant, samples with pH>6.6 were generally those that had been fluoridated (1 mg/l F$^-$), samples with pH<6.6 were obtained after sand filtration. The agreement is fair. Some back-siphoning of fluoride seemed to have occurred for the sand-filtered samples, as measurements for fluoride showed levels close to 0.1 mg/l in these samples, so the increased aluminum levels in these samples are attributed to fluoride complexation. A comparison between the Oyster River samples with the Schuykill River samples is indicative that our 0.2 µm membrane filters removed more aluminum than the 0.45 µm filters. However, a comparison of our Oyster River data with that using humic acid showed substantial differences. The solubility curve seemed to have been shifted to the left.

The effect of natural water organics versus humic acid deserves further investigations. The choice of humic acid for our model water was a poor one with hind sight. First, according to Edzwald et. al. (1979), 80 percent of organic matter in water is fulvic in nature. Second, fulvic acid is much less efficient in producing color compared to humic acid, Narkis and Rebhun (1977) reported that at pH 8.0, a solution of 1 mg/l of humic acids has 26.5 cu while a solution of 1 mg/l of fulvic acids has only 2.8 cu. Thus, to obtain a color of 140 in natural waters, we would have needed only about 5 mg/l of humic acid but close to 50 mg/l of fulvic acid. This ten-fold increase in organic concentration was apparently sufficient to exert a
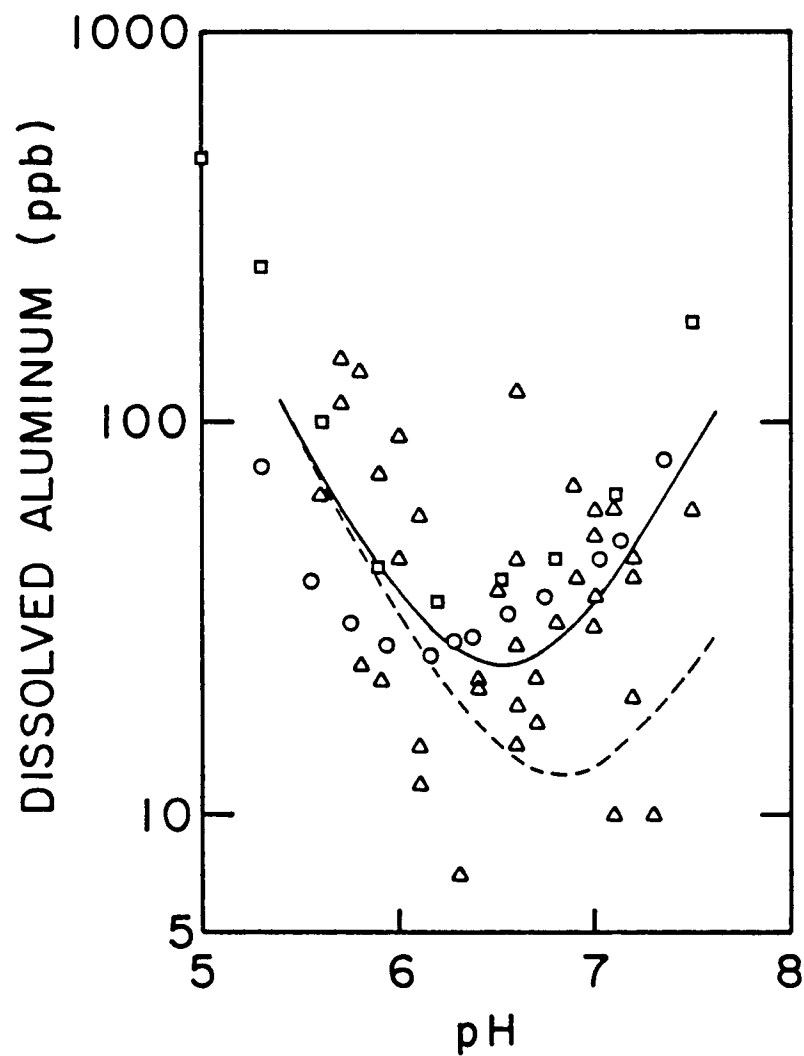
FIG.7 Comparison of Jar test data with actual plant
    monitoring. Triangles are data from the Arthur
    Rollins water treatment plant. Circles are jar
    test results using a natural water of 130 CU(Oyster
    River) and squares are jar test results for the
    Schuylkill River(Philadelphia, Pa.). The solid
    curve is our model curve for 25° C and the broken
    curve for 5°C.

significant effect on the aluminum speciation. Much has been reported about the presence of a precipitate of aluminum fulvate, but little is known about the characteristics of the precipitate. The important effect here is that the natural organic decreased the amount of dissolved aluminum when pH<6.3 and increased the dissolved aluminum when pH>6.3.

In summary, the amount of dissolved aluminum is a function of pH, temperature and the presence of complexation ligands. The minimum amount of dissolved aluminum occurs between pH 6 to 7 and is generally less than 50 ppb. This is in accord with Shull and Gutham (1967), although membrane filtration probably overestimates the efficiency of solids removal compared to sand filtration. Standard Methods' (1980) suggestion that a water treatment plant that is operated properly should contain less than 50 ppb aluminum actually left out the original contention by Shull and Gutham (1967) that the 50 ppb referred to "free" aluminum, or dissolved aluminum in our discussion.

C. Particulate Aluminum

Within our experiments, we have shown that the majority of the added aluminum (3.24 mg/l) was in a form that could be removed by membrane filtration. This would be called the particulate aluminum phase. The ultimate removal of such particulate phases is via gravitational settling or filtration in a conventional water treatment plant. The detailed processes that can occur include: nucleation, particulate growth via coagulation (herein defined as surface charge destabilization) and flocculation (defined as the agglomeration of destabilized particles), and gravitational settling. Filtration can be viewed also as coagulation and flocculation, whereby particulates in the water are removed via impact at the surfaces of a stationary media (the sand or other filtration media). For discussion of these mechanisms, see Amitharajah and Mills (1982), Stumm and O'Melia (1968).

Most theoretical discussions on particulate removal utilize the concept of particle size distributions. These could be obtained in various ways. The most common ones are by electro-resistivity (coulter counter), light scattering or settling. The settling velocities for three different particulates were obtained in this study. They are reported in Table A-4 and shown in Figure 8. In order to go from settling velocity to size, one needs to assume Stokesian settling and the knowledge of the particle density. Since we do not know the density, the results of Tambo and Watanabe (1979) will be assumed. Under similar experimental conditions, they obtained the following:

$$u_s = \frac{g}{34\mu} (\rho_f - \rho_w) d_f^2 \tag{6}$$

Where u_s is the settling velocity, g the acceleration due to gravity, μ the absolute viscosity of water, ρ_f the floc density, ρ_w the water density and d_f the floc diameter. In addition:

$$(\rho_f - \rho_w) = a (d_f/1)^{-K} p \tag{7}$$

Where a = 1.3 x 10^{-3} (g cm^{-3}), K = 0.9 (dimensionless), d_f the floc diameter in cm. The settling velocity as a function of floc diameter can thus be calculated as shown in Table 5.

A substantial amount of our particulates/floc (4 to 25%) remain at the top of our settling pippette even after one hour of quiescent settling. This translates to a settling velocity of 0.0055 cms^{-1} or less. From Table 5, these floc have sizes ranging between 20 to 30 μm. Measurements of particle size distributions by the coulter counter would give particle counts of about 20 to 40 x 10^6 per ml with peak diameter between 1.1 to 1.4 μm.
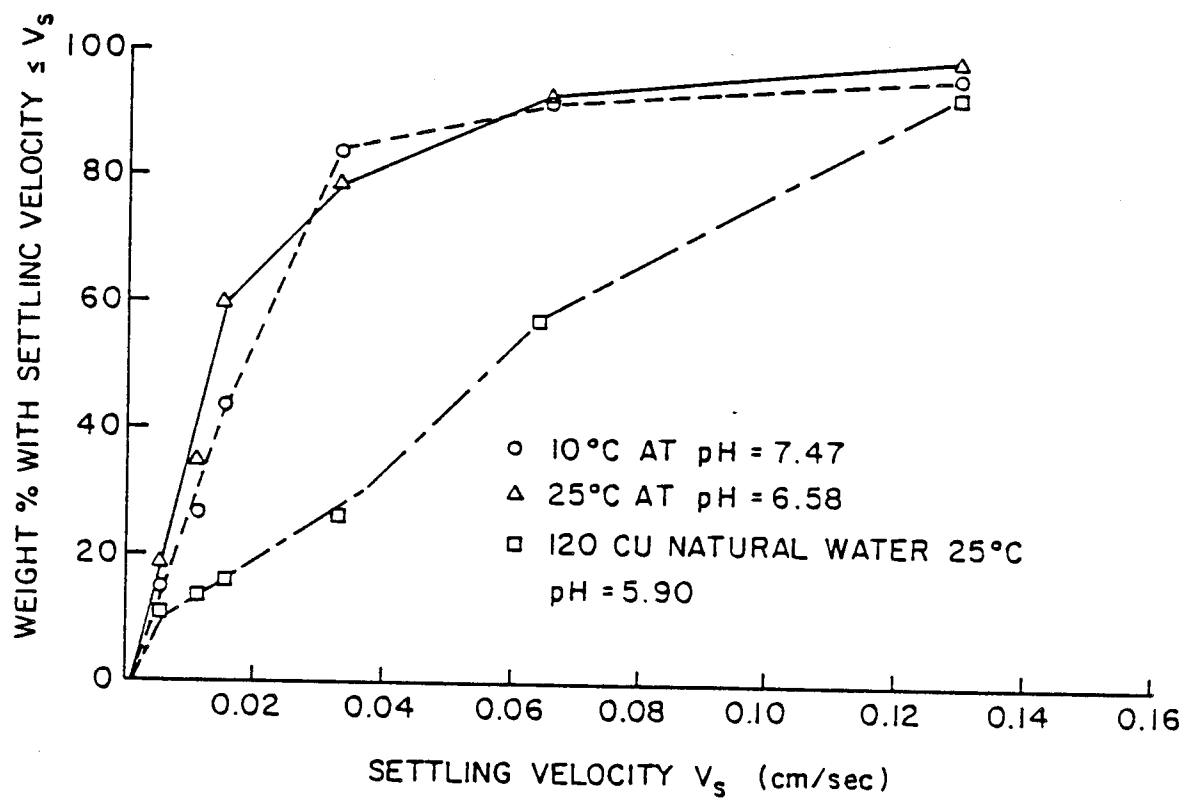
FIG.8 Settling velocity distributions of 3 different aluminum-
organic floc.

34

TABLE 6

Calculated Settling Velocity of Alum Floc
$T = 24^{o}C$

d_f (um)	$\rho_f - \rho_w$ (gcm^{-3})	u_s (cm$_s$$^{-1}$)
20	0.349	0.0044
30	0.242	0.0069
40	0.187	0.0094
50	0.153	0.012
60	0.129	0.015

TABLE 7

pH Range for Visible Floc Formation

T ^{o}C	Model Water	Natural Water
25	5,7 to 6.7	5.3 to 6.1
5	6.5 to 7,8	5.5 to 6.6

Therefore, floc breakage probably occurred as observed by Snodgrass et. al. (1984) as well. Snodgrass et. al. (1984) showed an increase of particle size between 1 and 2 um to 2 and 4 um from 15 minutes to 52 minutes under continuous stirring (pH 5.5). However, their total particle count tended to range from 2×10^5 to 2×10^6 per ml (probably due to cut-off of sub-micron sizes). Measurements of residual aluminum after settling in this study ranged from 0.14 mg/l to 0.82 mg/l. The surface overflow rate at the Arthur Rollins Water Treatment Plant was estimated to be 0.74 gpm/ft^2, which translates to 0.05 cms^{-1}. Under the assumptions of ideal sedimentation, only particles with settling velocities greater than this value will be removed completely. From our settling curves, 20 to 60% of our particulates have settling velocities greater than this value. The actual settling velocity distribution is, of course, a function of pH, temperature, dosage as well as mixing conditions prior to quiescent settling. The actual performance of the sedimentation tank is difficult to infer. A total aluminum content of 213 ppb (pH = 7, 10°C) was measured in the influent water prior to filtration on May 11, 1984. Assuming that the alum dosage was about 30 mg/l (2.43 mg/l aluminum), a raw water aluminum content of 40 ppb, the efficiency of aluminum removal prior to filtration is then almost 91%. The observed aluminum content after the sand filtration was 73 ppb (pH increased to 7.3), thus the efficiency of aluminum removal via filtration was only 66% for this day. In terms of particulate aluminum, the removal efficiency was 70%. The actual removal efficiency for filtration is also a function of pH, temperature, filter condition, the influent aluminum concentration and could be modified by filtering aids. A study by Hannah et. al. (1967) using alum coagulation of a natural water (Little Miami River) reported a residual

aluminum from 60 to 430 ppb after sand filtration (2 to 8 gpm/ft^2). The residual aluminum decreased from 110 ppb at an alum dosage of 20 mg/l to 60 ppb at an alum dosage of 70 mg/l and increased to 430 ppb at an alum dosage of 130 mg/l. They also measured the surface charge of the floc and reported that minimum residual aluminum coincided with zero charge. A particle count in the size range 0.59 to 4 μm in the filtrate gave values between 3.5 x 10^5 to 1.1 x 10^6 per ml. It was unfortunate that they did not report the pH of the tests.

APPLICATIONS

Our experiments showed that visible flocs form at specific pH ranges and that the range changes with temperature. Visible flocs imply good removal by sedimentation. The results are shown in Table 6. Shifts in the optimum pH for color and turbidity has also been reported by Mohtadi and Rao (1973) (5.2 at 20°C to 6.7 at 1°C for clay removal); Kowal and Mackiewicz (1975) 5.2 at 23°C to 6.3 at 1.5^{o}C for colloid removal). It would be remembered that the pH of minimum soluble aluminum shifted from 6.5 at 25°C to 6.9 at 5°C. Lower temperature increases the viscosity of water, thus decreasing sedimentation and filtration efficiencies if everything else remained constant. Morris and Knocke (1984) reported that smaller flocs are formed at lower temperatures (20°C versus 1°C). Perhaps this explains why the total aluminum in the finished water is so much higher than that of the raw water during the months of October to February for the Arthur Rollins Water Treatment Plant. The good removal efficiency of aluminum for the Somersworth plant is due to the polymer, which aided the filtration process.

It should be emphasized that the process of coagulation and flocculation contains many steps. The organic macromolecules responsible for color are

thought to be destabilized by the cationio aluminum species, and this is favored at acidic pH values, approximately 5.3 at $20^{0}C$. The destabilized organics are then brought together by fluid motion and agglomerate into larger flocs. If aluminum hydroxide floc is present, particle growth would probably be favored at a higher pH. 6.5 would seem like a good value for $20^{0}C$ at which to operate the folcculation/sedimentation and filtration processes. At low temperatures closer to $1^{0}C$, a pH of around 6 would seem to be better for the color destabilization step and the pH should be increased to 7 for the flocculation/sedimentation/filtration steps. Alternatively, flocculant and filtering aids could be utilized for these conditions to enhance particle growth.

In general, the most important parameter is deemed to be pH. The control of aluminum must be weighed together with the objectives of turbidity removal as well as fluoridation and corrosion control. The process of color and turbidity removal by the use of alum entails the addition of significant amounts of aluminum. The bulk of this aluminum ends up in a particulate phase, of which a substantial amount will not be easily removed by sedimentation (roughly estimated as 10 to 20% of total aluminum dosage). The combined sedimentation/filtration removal efficiency is not likely to exceed 99% for these particulates. These should be weighed before setting any standards for aluminum in drinking water.

CONCLUSIONS AND RECOMMENDATIONS

1. The Eriochrome Cyanine R method for aluminum determination is a reliable one for laboratory investigations. Atomic absorption spectrophotometry in the non-flame mode is more desirable for monitoring since the problem of interference is minimized. Both techniques are sensitive to ppb levels of aluminum under favorable conditions. For sub-ppb levels, one could use some sort of concentration step.

2. Under conditions of sweep coagulation (the addition of excess amount of aluminum compared to the organics present in this study: 40 mg/l of alum and a pH range of 5.5 to 7.5), the amounts of soluble aluminum are simple functions of pH. Laboratory jar tests give the following results:

    Soluble aluminum (moles/liter)

    $= 10^{-pH} + 3 \times 10^{-7} + 9 \times 10^{-14} \times 10^{pH}$ (25°C)

    with minimum soluble aluminum = 20 ppb occurring at pH 6.5

    $= 10^{-pH} + 2 \times 10^{-7} + 2 \times 10^{-14} \times 10^{pH}$ (5°C)

    with minumum soluble aluminum = 10 ppb occurring at pH 6.9

    The presence of fluoride, sulfate and organics can increase the amount of soluble aluminum in a water treatment facility. From the monitoring of actual water treatment facilities, it would seem unlikely for dissolved aluminum to exceed 100 ppb when pH is maintained between 5.5 and 7.5

4. Improvements in the control of aluminum in a water treatment facility could be achieved via pH control and/or the addition of coagulation-filtration aids. This helps with the surface charge destabilization step.

Improvements could also possibly be obtained by changing the transport step (mixing intensities and mixing times). The raw water can also be a major source of aluminum, especially if a resevoir is involved and overturn occurs.

Future research should be performed to:

1. Ascertain the actual mechanisms involved in the surface destabilization step. In particular, how important is the adsorption of organics on aluminum hydroxide floc in the whole picture of color removal? Does sulfate change the surface charge of the aluminum hydroxide floc to a great degree?

2. Ascertain the nature of the aluminum fulvate precipitate. Is it a different solid phase? How does the particle size distribution (settling velocity distribution) change as a function of dosage, pH, temperature, etc?

3. Investigate the actual behavoir of these aluminum fulvate precipitates in the filtration process.

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APPENDICES

DATA FROM THE ARTHUR ROLLINS WATER TREATMENT PLANT

DATE		RAW WATER				FILTERED WATER			FINISHED WATER		
	T (°C)	pH	Dis. Al	Tot. Al	pH	Dis. Al	Tot. Al		pH	Dis. Al	Tot. Al
1983											
1) 8/24	19.5	6.9	10	10	5.6	65	95		7.6	60	100
2) 9/1	18.5	7.0	10	12	5.9	22	22		7.2	20	45
3) 9/8	20.0	6.9	10	10	5.8	24	34		7.0	30	40
4) 9/15	18.5	7.2	"	"	6.3	7	23		7.1	10	10
5) 9/22	18.0	7.2	"	"	6.2	6	8		6.9	10	10
6) 9/29	14.0	7.1	"	"	6.1	12	20		7.1	10	10
7) 10/6	14.0	7.0	"	"	6.1	15	16		7.3	10	23
8) 10/13	13.0	7.0	"	"	6.0	45	93		7.2	45	100
9) 10/20	11.5	6.8	"	"	5.7	147	171		7.0	60	200
10) 10/27	8.0	6.9	"	"	6.0	93	205		6.6	120	440
11) 11/3	6.0	7.0	"	"	6.4	22	186		7.1	60	470
12) 11/10	7.5	6.6	27	33	5.9	74	107		6.9	70	100
13) 11/17	7.0	6.6	28	46	6.1	58	64		7.2	40	80
14) 11/22	6.0	6.7	17	39	5.8	135	185		6.9	40	280
15) 12/1	4.5	6.6	45	171	5.7	112	520		6.8	31	550
16) 12/8	2.0	6.5	40	41	6.4	23	184		6.9	40	250
17) 12/16	4.5	6.5	37	41	6.6	19	297		7.0	52	350
18) 12/21	2.0	6.7	22	31	6.6	15	18		7.0	35	110
1984											
19) 1/6*	1.5	6.6	-	27	6.4	-	36		7.3	-	370
20) 1/13	1.5	6.7	-	28	6.5	-	19		7.2	-	180
21) 1/20	1.5	6.7	-	28	6.5	-	195		6.9	-	210
22) 1/27	1.0	6.6	-	41	6.6	-	215		7.1	-	290
23) 2/3	1.5	6.8	-	43	6.9	-	200		6.9	-	240
24) 2/14	1.5	6.8	-	-	6.8	-	-		7.2	-	-

Continued

DATE	RAW WATER				FILTERED WATER				FINISHED WATER		
	T (°C)	pH	Dis. Al	Tot. Al	pH	Dis. Al	Tot. Al		pH	Dis. Al	Tot. Al
25) 4/12	5.0	6.8	-	161	-	-	-		-	-	-
26) 4/19	9.0	6.7	-	515	-	-	-		-	-	-
27) 5/11**	-	-	-	-	7.3	-	73		-	-	-
28) 5/23	13.0	6.8	-	-	6.2	-	20		6.9	-	9
29) 6/1	13.0	6.3	-	36	5.7	-	22		7.1	-	4
30) 6/7	16.5	6.6	-	35	5.7	-	22		7.4	-	4
31) 6/18	17.0	6.8	-	35	5.2	-	190		7.4	-	13
32) 6/22	17.5	6.7	-	40	5.6	-	N.D.		7.1	-	N.D.
333) 6/28	16.5	6.8	-	40	5.6	-	N.D.		7.1	-	N.D.
34) 7/5	18.0	6.7	-	26	5.4	-	N.D.		6.9	-	N.D.
35) 7/11	17.5	6.7	-	44	4.7	-	36		8.4	-	8
36) 7/17	19.0	6.5	-	35	5.1	-	22		7.2	-	4

NOTES: All Aluminum concentrations expressed as ppb (μ.g/l)

*The manufacturer stopped producing 0.1 μm filter holders.

**Analysed by Watertest Corp., New London, New Hampshire.

A new technician was doing the aluminum determinations after May, 1984.

- Not Determined

N.D. Not Detectable

TABLE A - 2

DATA FROM SOMERSWORTH WATER TREATMENT PLANT

		RAW WATER				Alum Dosage (mg/l)		FINISHED WATER		
DATE	T ^{o}C	Color	pH	Tot. Al(ppb)				pH	Tot Al(ppb)	
1984										
1/2	2	49	6.54	40		45		7.27	10	
1/3	1	42	6.52	40		44		7.11	20	
1/4	2	35	6.43	80		35		7.46	20	
1/5	2	61	6.33	50		21		7.30	1	
1/6	2	51	6.43	60		34		7.37	25	
1/7	2	25	6.13	40		20		7.06	25	
1/8	2	58	6.31	60		22		7.09	25	
1/9	2	50	6.54	70		23		7.43	20	
1/10	2	60	6.43	50		21		7.27	20	
1/11	2	17	6.51	45		20		7.26	60	
1/12	1	23	6.44	50		32		7.10	60	
1/13	2	65	6.60	40		21		7.25	40	
1/14	1	65	6.47	50		27		7.04	20	
1/15	2	20	6.68	70		22		7.17	10	
1/16	2	15	6.54	50		15		7.12	60	
1/17	2	18	6.56	30		27		7.15	20	
1/18	2	15	6.50	20		24		7.20	50	
1/19	2	18	6.47	76		26		7.22	25	
1/20	2	27	6.41	80		26		7.19	30	
1/21	2	17	6.34	40		13		7.24	20	
1/22	2	66	6.30	100		28		7.23	50	
1/23	1	70	6.58	120		19		7.30	50	
1/24	1	34	6.54	90		23		7.24	30	
1/25	2	22	6.49	30		14		7.02	20	
1/26	2	45	6.65	120		20		7.24	40	

DATA FROM SOMERSWORTH WATER TREATMENT PLANT

	RAW WATER				Alum Dosage (mg/l)		FINISHED WATER		
DATE	T ^{o}C	Color	pH	Tot. Al (ppb)			pH	Tot. Al (ppb)	
1984									
1/27	2	48	6.54	100	19		7.26	30	
1/28	2	60	6.31	90	17		7.00	40	
1/29	2	40	6.51	80	21		7.21	50	
1/30	1	45	6.42	100	19		7.1	40	
1/31	2	32	6.57	80	17		7.18	80	

TABLE A - 3

Dissolved Aluminum/pH Data

Conditions:

RUN #	T (^{o}C)	WATER	DATE	pH	Dissolved Al (ppb)
1	25	Model	12/29/83*	5.60	108
				6.10	38
				6.20	24
				6.40	16
				6.50	23
				6.60	19
				7.00	72
				7.33	108
2	25	Model	6/21/84	5.70	83
				5.91	45
				6.06	31
				6.18	24
				6.41	17
				6.53	18
				6.58	15
				6.67	16
				6.93	19
				7.10	35
				7.33	71
				7.46	114
3	25	Model	7/14/84	5.49	101
				5.61	79
				5.83	55
				5.95	43
				6.08	34
				6.27	28

TABLE A - 3 cont.

Conditions: Dissolved Aluminum/pH Data

RUN #	T (°C)	WATER	DATE	pH	Dissolved Al (ppb)
				6.49	26
				6.67	28
				6.94	32
				7.15	46
				7.38	75
				7.55	105
4	24	Natural	7/14/84	5.30	77
		Initial color		5.54	39
		140. pH 6.86		5.77	31
				5.92	27
				6.15	25
				6.27	27
				6.37	28
				6.56	33
				6.72	36
				7.01	45
				7.13	50
				7.35	78
5	5	Model	7/15/84	5.77	61
				5.90	52
				6.07	33
				6.24	23

TABLE A - 3 cont.

Dissolved Aluminum/pH Data

Conditions:

RUN #	T (°C)	WATER	DATE	pH	Dissolved Al (ppb)
				6.44	18
				6.65	16
				6.73	13
				6.91	12
				7.10	13
				7.50	15
				7.60	17
				7.75	23
6	5	Model	6/6/84	5.44	123
				5.80	50
				6.00	37
				6.16	20
				6.24	17
				6.33	15
				6.43	15
				6.65	10
				6.82	9
				7.02	13
				7.80	35

*Determined by AAS

Settling Velocity Tests After the Addition of
40 mg/l Alum and Jar Test Procedure

	Conditions			Data			
RUN #	T (^{o}C)	pH	WATER TYPE	TIME (MIN)[a]	u_s (cm/s)[b]	ABSORBANCE[c]	%
1	8 to 12	7.47	Model	0		1.446	100.0
				2.5	0.13	1.394	96.0
				5.0	0.066	1.341	92.7
				10.0	0.033	1.216	84.0
				22.0	0.015	0.644	44.0
				30.0	0.011	0.389	26.9
				60.0	0.0055	0.194	13.4
2	25°C	6.58	Model	0		0.546	100.0
				2.5	0.13	0.534	97.8
				5.0	0.066	0.561	91.7
				10.0	0.033	0.43	78.8
				20.0	0.017	0.326	59.7
				30.0	0.011	0.192	35.2
				60.0	0.0055	0.106	19.4
3	25°C	5.90	Natural[d]	0		0.516	100.0
				25.0	0.13	0.473	91.7
				5.0	0.066	0.293	56.8
				10.0	0.033	0.133	25.8
				20.0	0.017	0.089	17.2
				30.0	0.011	0.071	13.8
				60.0	0.0055	0.059	11.4

NOTES:

(a) Time at which samples were taken.

(b) Sampling depth = 20 cm. u_s =
settling velocity = 20 cm/time.

(c) The absorbance of the aluminum-dye
complex at 535 nm and a 5 cm cell path.
Values differ due to different sample
size.

(d) The natural water was raw water at the
Arthur Rollins Water Treatment Plant
collected on 6/12/84. Initial water
color 120, pH 6.7.

Calculation of Aluminum Hydrolysis

Given $\{Al^{3+}\} = *K_s O\{H^+\}^3 = 8.7 \times 10^9 \{H^+\}^3$, the total soluble aluminum is dominated by $Al(OH)_2^+$, $Al(OH)_3^0$ and $Al(OH)_4^-$ within our pH range, but the total can be calculated as:

$$\text{Total soluble aluminum} = (1 + \sum_{i=1}^{4} *\beta_i \{H^+\}^{-i})[Al^{3+}]$$

Given $*\beta_1 = *K_1 = 10^{-5}$, $*\beta_2 = 1.2 \times 10^{-10}$, $*\beta_3 = 3.4 \times 10^{-17}$ and $*\beta_4 = 10^{-23}$, we can calculate the expression within the brackets as a function of pH, T = 25°C.

pH	$1 + \sum_{i=1}^{4} *\beta_i \{H^+\}^{-1}$
5.5	16.9
5.6	25.6
5.7	39.9
5.8	63.3
5.9	102.7
6.0	170.4
6.1	289.6
6.2	505.8
6.3	910.5
6.4	1695.0
6.5	3270.4
6.6	6545.8
6.9	64388.0
7.0	146000.0
7.1	338179.0
7.2	796952.0
7.3	1904125.0
7.4	4599087.0
7.5	11203140.0