

THE MECHANISM OF ORGANIC  
REMOVAL DURING COAGULATION

by

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THE MECHANISM OF ORGANIC  
REMOVAL DURING COAGULATION

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## ABSTRACT

Coagulation is a common water treatment step primarily designed to aggregate and thereby help remove true particulate (turbidity causing) matter. Organic compounds of natural origin (i.e. humic and fulvic acids) have also been observed to be removed by Coagulation. This research was designed primarily to identify the limiting mechanisms responsible for the removal of natural organics by the coagulation process. This identification is thought to be crucial in the optimization of this important water treatment step as it may help to maximize the benefits obtained from coagulation, and it may also lead to the designing of new coagulants.

The examination of the literature related to this topic suggests two possible removal routes:

- (i) a reaction whereby the fulvic acids form an original compound with the coagulating ion  $Al^{3+}$  or one of its hydroxy complexes.
- (ii) the adsorption of the fulvic acid molecules or ions onto the surface of a solid precipitating independently of these compounds.

These two possibilities are examined in detail on theoretical grounds, and two following pieces of information are defined

as being discriminatory with respect to the two removal routes:

- (i) The shape of the isotherm, as defined in typical adsorption studies.
- (ii) The ligand number or OH/Al ratio of the precipitate, accessible by processing the dissolved Aluminum data with respect to pH.

These considerations lead to an experimental design allowing the convenient evaluation of these characteristics. An array of nine treatment dosages and four operating pH is applied on two raw waters, using four Aluminum based coagulants.

The results suggest that under these experimental conditions (dosage between .1 and 1 mM Al/L; pH between 5 and 8.5), the Fulvic acids are removed by Adsorption onto  $Al(OH)_3$ , regardless of the type of coagulant. Increasing pH and the presence of Sulfate in the coagulant were found detrimental to this adsorption. Increasing OH/Al ratio in the coagulant is detrimental at low pH, low dosage, and becomes beneficial at neutral to mildly alkaline pH conditions. A two stage treatment scheme was found efficient at neutral to mildly alkaline pH, using Alum.

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## CHAPTER 1

### INTRODUCTION

The natural water bodies constitute the water supply of all living communities. The human communities tap these resources for their needs, and most of the time, this natural water must be treated to fit to their use.

Among other undesirable substances, organic pollutants are the target of the water treatment. These compounds occur in most natural water sources. Natural organics originate in soils, where part of them is dissolved by rain. These soil compounds referred to as humic material, are responsible for the yellow to brown colour of the marsh waters, as well as some river waters. On the other hand, specific organic compounds found in natural waters result directly from man's activity.

The need for the removal of these substances comes from either aesthetic considerations (colour, taste, odour) or their potential impact on public health. In recent years, an increasing concern about drinking water quality promoted a research effort aimed at a better application of the physical chemical treatment operations through a better understanding of their underlying principles. These

procedures include Activated Carbon Adsorption, and several chemical oxidation processes.

Interestingly, the most widely used treatment process, i.e. coagulation - flocculation, received but little attention as a potentially powerful process for removing soluble organic contaminants. Although the interaction between coagulants and the humic material has been investigated to some extent, there is still a definite research need in this area, especially regarding naturally coloured waters, as outlined in a recent AWWA Committee Report (1979). On an engineering point of view, a better understanding of the phenomena involved in the organic removal by the coagulation process should lead to the formulation of a model. Thus, modelization constitutes an essential tool for the optimization of the process, and ultimately to the improvement of the performances of the process.

Such an improvement has consequences on all the physical chemical processes involved in a water treatment plant since the coagulation is the first step in this treatment, as shown in Figure 1-1. This statement has a special value when Activated Carbon Adsorption is used. Assuming that at equal cost, an improved coagulation process allows to increase the organic removal by this operation from 75% to 80%, a 5% improvement may look marginal. However, for the subsequent finishing steps (GAC filtration, ozonation

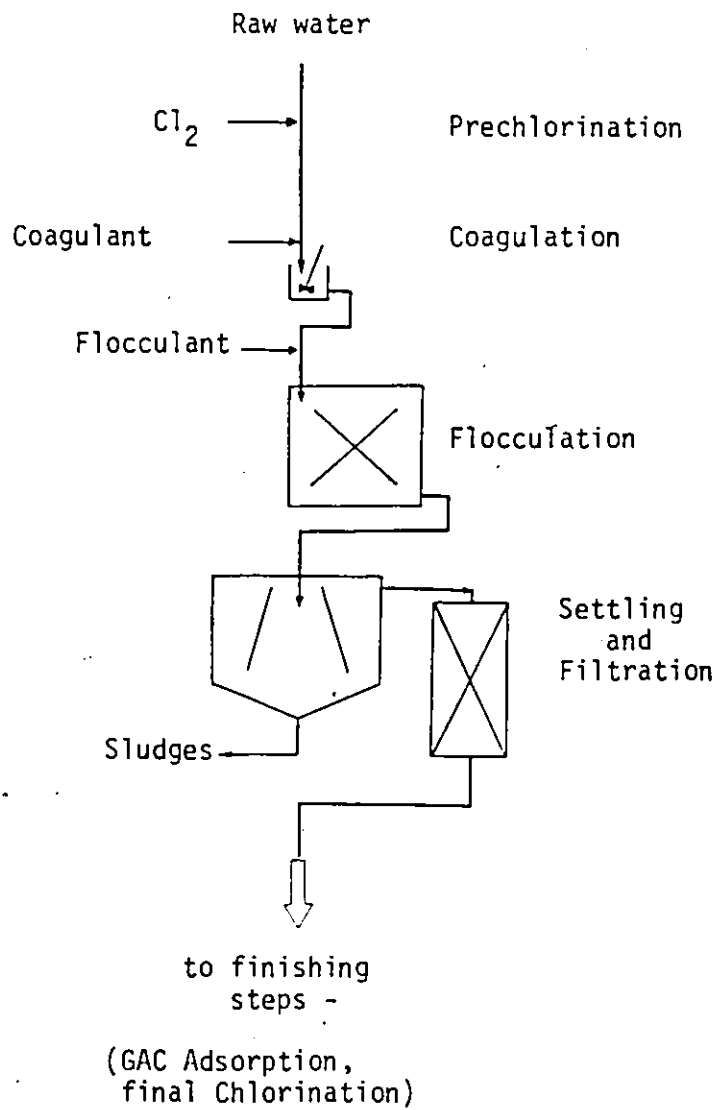


Figure 1.1 Place of the Coagulation Process in Water Treatment Plant.



final chlorination), the organic input is reduced by 20%, which means for instance, that the average life time of an Adsorption bed is increased by 20%. Such a fact has a beneficial effect on the cost efficiency of the plant, as a whole as well as a possible beneficial effect on the quality of the distributed water. Alternatively, a better understanding of the organic removal by the coagulation process may yield a better way to use the coagulant, and eventually may lead to a more cost efficient use of the coagulant, without cutting on the final quality of the water.

The purpose of this work is to identify the mechanism of the removal of natural organics by the coagulation step, and to provide the initial steps towards a quantification of this removal. The experiments are performed on a river water believed to be typical of coloured waters. Also, the engineering consequences of the nature of the phenomena involved are explored.

Since this work is geared towards applications more than towards pure knowledge, some assumptions are made, especially regarding aluminum chemistry, some of them being controversial. However, as it will be seen, they seem to be reasonably valid within the scope of this study.

## CHAPTER 2

### LITERATURE REVIEW

This chapter summarizes the knowledge available so far concerning some important aspects of this research. The nature and properties of colour causing materials are first reviewed. Particular emphasis is placed on their measurements as lump parameters, their complexation with metals, and the reaction products with chlorine. The second section concerns the nature of usual coagulants. The third section reviews the hydrolysis pattern of Al(III). The fourth section summarizes the different ways Al(III) hydrolysis products and colour causing organics interact according to the previous works reported so far.

#### 2.1 Colour Causing Organics

Coloured waters are ubiquitous. The substances responsible for this colour have been attributed to humic substances, and to ferric ions (Health and Welfare, 1978). The humic substances are the compounds of interest in this study. They originate in the soil and their occurrence in waters results from their dissolution and leaching by rain. Most of the information on these substances have been generated by the soil scientists. Some aspects of their aqueous

chemistry, especially regarding their oxidation by chlorine and hypochlorites have been investigated by water chemists.

### 2.1.1 Nature and Occurrence

The Dissolved Organic Carbon (DOC) present in natural waters is mostly due to the presence of humic substances, i.e. Humic and Fulvic Acids (HA and FA). The amount of material found in water ranges from 3 mg/L as DOC in temperate climates to 10 mg/L as DOC in subarctic zones (Christman, 1983).

The nature of HA and FA is essentially a mixture of polymeric material made of polycarboxyphenolic acids, and polysaccharides. The classical distinction between the different classes of humic materials refers to their solubility in water (Schnitzer, 1971; 1978):

- Humic Acids are essentially insoluble in water.
- Fulvic Acids are insoluble below pH 2.
- Humic Acids are soluble regardless of the pH.

The latest theories on the structure of these compounds consider that a limited number of relatively small carboxyphenolic molecules form polymers by H-OH bonds (Schnitzer, 1978). The extent of this polymerization may be a function of associated cations and pH. Wershaw and coworkers (1977) suggested a similar theory, considering humic materials as protein like polymers.

The fraction of humic substances found in natural

waters is considered as being mainly fulvates (Schnitzer, 1971; Davis et al, 1981; Prakash, 1983). Their physical-chemical properties of interest in this work are reviewed in the next section.

### 2.1.2 Physical-Chemical Properties

The physical-chemical properties of interest in this study concern the carbon content, the molecular weights, and the light absorption patterns, which are related to the measurement of the DOC. Also, the acid properties, and chelating abilities with respect to metallic cations are relevant to the coagulation process. Furthermore, the degradation products resulting from the oxidation with chlorine are of interest with respect to the disinfection process. This latter aspect will be presented in the next section.

#### (i) Carbon Content

The carbon content of the humic materials averages 50%. Variations in this content are associated with the type of humic compounds, and Schnitzer (1978) reported that in HA's the %C was higher than in FA's (56.2% and 47.7% respectively). These values are consistent with other reports (Schnitzer, 1971; Malcolm, 1976; Plechanov et al, 1983).

#### (ii) Molecular Weight

There is considerable disagreement on this topic, due to the polymeric nature of this material. As far as

aqueous FA are concerned, Schnitzer (1971) suggested a model of these compounds. The molecular weight of this average molecule is 670 g/M. In a later report, Schnitzer (1978), suggested that the disagreements found in the literature were due to the methods of investigation which give access to the different characteristics of a mixture of polymers i.e. the number average molecular weight  $\bar{M}_n$  or the weight average molecular weight  $\bar{M}_w$ . For instance, he reported that viscosity measurements suggest that FA are rod shaped (55 to 60  $\text{\AA}$  in length, 6.2  $\text{\AA}$  in diameter), and that the molecular weight ranges 1550 to 1750 g/mole. Osmometric measurements would be consistent with  $\bar{M}_n = 951$ , while gel fractionation techniques suggest a mean of molecular weight distribution function ca 1200. Light scattering experiments (Underdown et al, 1981) show a polydispersity ( $\bar{M}_w/\bar{M}_n$ ) of 5. This heterogeneity in molecular weights was also reported by Davis et al (1981), and Prakash et al (1983) for river water FA's. Plechanov and coworkers (1983) suggested that the apparent molecular weight varies also with pH (1600 at pH 2, 5000 at pH 7.9), based on gel chromatography experiments. They suggested that it was due to the expansion of the anion, analogous to a Fuoss effect.

The following table gives two consistent molecular weight distributions based on gel chromatography.

<u>Davis et al 1981</u>		<u>Prakash et al 1983</u>	
MW	% w/w	MW	% w/w
<500	42.5	<700	63
500 < 4000	39.5	700 < 1500	25.8
4000 <	18	1500 < 5000	11.2

This heterogeneity will be discussed with respect to water treatment processes in the Appendix A.2.

#### (iii) Light Absorption Pattern

This characteristic of aqueous FA is very homogeneous. Wilson (1959) reported that fulvates absorb the UV light according to a monotonous decreasing function of the wavelength. Schnitzer (1978) and Lawrence (1980) reported the same type of absorption spectrum while Plechanov and coworkers (1983), reported a maximum absorption at 205 nm, with shoulders at 230 and 270 nm. This method has been used as a convenient measurement of DOC (Peel, 1980; Randtke et al, 1981). Any wavelength can be selected in the UV range. Peel (1980) used 254 nm, which corresponds to one of the emission bands of a Mercury lamp. Randtke and coworkers (1981) used 350 nm.

#### (iv) Acidity

Schnitzer (1971) reported for his model of an aquatic fulvate a total acidity of 9.7 meq/g (6 eq/Mol) for the carboxylic acidity and 3.3 meq/g (1 eq/Mol) for the phenolic acidity. Furthermore, he suggested a value of  $10^{-4.5}$  for

the dissociation of the carboxyl acidity, which makes the carboxyl radicals totally dissociated as neutral pH. Malcolm (1976) reported 3 to 10 meq/g as cation exchange capacity. Gamble (1972) suggested that there was a continuum of dissociation constants for COOH groups. The suggested value of pk is 3.77. Plechanov and coworkers suggested a higher value for their aqueous HA, i.e. pk ca 2.6.

The phenolic acidity would dissociate at high pH. Gamble (1972) suggested a value of pk ca 9.2.

Schnitzer (1978) corrected the values he gave previously in 1971, and he reported, for FA:

Carboxyl acidity = 8.2 meq/g

Phenolic acidity = 3.0 meq/g

for an average of FA found all over the world. For subarctic climates, the values are slightly different:

Carboxyl acidity = 8.8 meq/g

Phenolic acidity = 2.2 meq/g

For HA (much higher molecular weights), the values are much lower, especially for the carboxyl acidity:

- Average =

Carboxyl acidity = 3.6 meq/g

Phenolic acidity = 3.9 meq/g

- Subarctic climates =

Carboxyl acidity = 3.2 meq/g

Phenolic acidity = 2.4 meq/g

(v) Complexation with Metallic Ions

Schnitzer (1971) reported that aqueous FA were able to complex Al and Fe, forming a bidentate chelate involving a phenolic radical and a carboxyl radical in ortho position. He further suggested a value of  $10^{-5.3} = (AlFA)/(Al)(FA)$  at pH 2. The complexation could involve more than one metallic ion per molecule of fulvate. He suggested a series of decreasingly soluble, increasing Me/FA ratio, with an insoluble  $(Me)_6FA$ , which corresponds to one metallic ion per COOH radical. This ratio was later suggested by Van Breemen et al (1979) and Randtke et al (1980).

Lind and coworkers (1975) investigated the effect of a set of carboxylic acids of increasing molecular weight and molecular complexity (from oxalic to salicylic acid) and the Quercetin on the solubility of Al and the equilibrium form of  $Al(OH)_3$ . Quercetin was chosen as a model molecule of fulvic acid, as it is a polyphenolic acid. They suggested that Quercetin and Al form two kinds of complexes of different Quercetin/Al ratio. They also suggested that the precipitation of Gibbsite was hindered, and that polycationic Al species (see Section 2.3.1) were stabilized by the presence of Quercetin. Perdue and coworkers (1976) attributed the correlation between TOC and the sum  $(Al + Fe)$  in the Satilla River; to the formation of soluble organic complexes. They also mentioned that  $Ca^{2+}$  was likely to compete with metals



for this complexation.

Gamble and coworkers (1980) reported that two types of sites in FA and HA are responsible for the complexation of Copper. Intermolecular complexes could contribute to for the aggregation of the humic material. Prakash et al (1983) suggested that the fulvate complexes with heavy metals, thereby reducing their toxicity. Interestingly, the removal of FA may have two opposite effects, according to the mode of action of the coagulants:

- It may also remove part of the total heavy metal content, by removing their complexes with FA.
- On the contrary, it may increase the free heavy metal content, as substitution may occur between the heavy metals and the coagulant ions.

(vi) Complexation with Other Organic Material

The possibility of complexes occurring between FA and pesticides was mentioned by Schnitzer (1978) and by Prakash et al (1983).

### 2.1.3 Reactions with Chlorine

The behaviour of natural organics with respect to the disinfection process applied in water treatment has been of considerable interest for the water treatment practitioners. The problem in this field was to identify the Trihalomethane (THM) precursors, i.e. the nature of the organics respon-

sible for the formation of THM's upon chlorination.

As already mentioned in Chapter 1, chlorination is often applied on the raw water in order to prevent algae blooming in the plant equipment. Chlorine is also used as a final disinfectant, and is applied at the inlet of the distribution network. Its effect on aqueous organics is to oxidize them. In addition to its oxidation potential chlorine forms additional compounds. Among them, Chloroform ( $\text{CHCl}_3$ ), and more generally speaking, Haloforms ( $\text{CHX}_3$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) are hazardous to health (Pierce, 1978).

The trihalomethane yield may vary with the origin/nature of the precursors, but also with the chlorination condition such as chlorine added, contact time, pH, as these conditions affect the kinetics of THM formation (Stevens et al, 1980). Christman et al (1983) reported 3 to 16  $\mu\text{g CHCl}_3/\text{mg}$  of DOC. This yield seems quite low, since much higher yields (ca 75  $\mu\text{g CHCl}_3/\text{mg DOC}$ ) were found on a river water from northern Ontario (Zenon, 1983).

Interestingly, the coagulation by Alum has been reported as removing selectively THM precursors (Babcock et al, 1979; Davis et al, 1981).

## 2.2 Coagulants

In water treatment, the most widely used coagulant is Alum  $\text{Al}_2(\text{SO}_4)_3 \cdot n \text{H}_2\text{O}$ . However, in the recent years,

alternative coagulants have been developed.

In Europe, Ferric salts have been used successfully for some years. Also, new Aluminum based coagulants have been developed and used. These latter coagulants all result from a partial hydrolysis of Aluminum, and may contain some Sulfate. They differ from each other by the extent of the hydrolysis, as well as their concentration. They also differ by the techniques used to manufacture them.

In Japan, Taki Fertilizer Company developed a product named PACS (Taki, 1969). This product is concentrated (1.9 M/L as Aluminum). The hydrolysis expressed as the OH/Al ratio, is ca 1.9 (Bersillon et al, 1980), and contains Sulfate. This product is extensively used in Japan (O'Melia et al, 1982). On the other hand, in Europe, a diluted version of prehydrolyzed  $AlCl_3$  has been developed (Fiessinger 1976, Fiessinger et al, 1977) and successfully used in industrial operations (Richard et al, 1979). The operating concentration is 0.15 M/L as Aluminum, the hydrolysis ratio is ca 2.5, and it does not contain any Sulfate. Since this latter product is manufactured on the site of its use, it may be optimized with respect to the quality of the raw water, by changing the hydrolysis ratio (Fiessinger, 1976).

Some research work has been done on the use of cationic organic polymers as coagulants, and their efficiency in removing of humic substances (Narkis et al, 1977). In many

parts of the world, however, the use of such polymers is disallowed in drinking water treatment practice.

### 2.3 Aluminum Hydrolysis

Aluminum based coagulants being by far the most frequently used, Al aqueous chemistry as well as its coagulating effects on aqueous colloids has been of considerable interest to the water treatment community. An important aspect of aluminum aqueous chemistry is the hydrolysis of Al(III), as it is the key to all the phenomena occurring during the coagulation - flocculation process.

#### 2.3.1 Hydrolysis of Soluble Species

The coagulation process proceeds by the addition of an Aluminum salt. The starting point is therefore the ion  $Al^{3+}$ . Actually, this ion is an aqueous complex where the  $Al^{3+}$  is coordinated to six molecules of water (Baes et al, 1976). For the sake of simplicity, these molecules of water will be omitted in the chemical equations below.

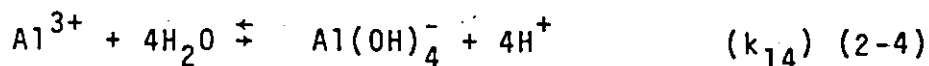
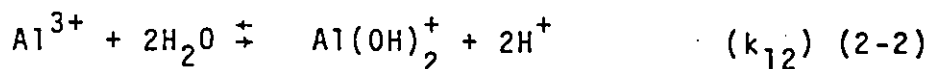
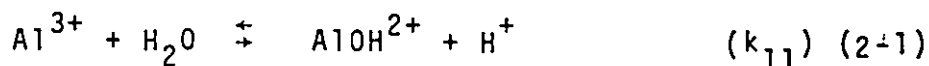
##### (i) Mononuclear Aluminum Hydroxide Species

A distinction should be done between two types of hydrolysis:

(a) "natural" hydrolysis, which refers to the formation of soluble Hydroxy Aluminum species in equilibrium with a solid Aluminum Hydroxide.

(b) "forced" hydrolysis, whereby an undersaturated aluminum salt solution is forced to hydrolyze by any physical chemical procedure. This latter hydrolysis is generally performed on concentrated solutions, and the resulting soluble or suspended Hydroxy Aluminum may not reach the equilibrium forms. This may constitute the origin of the disagreement between different authors regarding the nature and structure of these complexes.

$Al^{3+}$  reacts with water, forming a set of mononuclear ions:



The first and last equations are widely accepted, and mass action law constants for these equations are well established. The formation of  $Al(OH)_4^-$  is also said to occur with a change in the coordination number, which goes from 6 to 4 (Baes et al, 1976). Some authors question the existence of  $Al(OH)_2^+$  and the molecular species  $Al(OH)_3|_{aq}$  (O'Melia et al, 1982). However, in a recent investigation on the solubility of Gibbsite, May et al (1979) gave a set of mass action law constants for the hydrolysis of  $Al^{3+}$ , where the

specie  $\text{Al}(\text{OH})_2^+$  is included in the mononuclear ions. Their experimental technique as well as their data processing technique (nonlinear parameter estimation) suggest that their calculated values are reliable. This investigation does not take into account the possible existence of molecular  $\text{Al}(\text{OH})_3|_{\text{aq}}$ . The mass action law expressions allow the calculation of a speciation diagram giving the percentage of each of the species with respect to the total amount of material:

$$k_{11} = [\text{AlOH}^{2+}][\text{H}^+]/[\text{Al}^{3+}] \quad (2-5)$$

$$k_{12} = [\text{Al}(\text{OH})_2^+][\text{H}^+]^2/[\text{Al}^{3+}] \quad (2-6)$$

$$k_{14} = [\text{Al}(\text{OH})_4^-][\text{H}^+]^4/[\text{Al}^{3+}] \quad (2-7)$$

Since, at 0 ionic strength, the total mononuclear ion content is

$$\text{Al}_m = [\text{Al}^{3+}] + [\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}(\text{OH})_4^-] \quad (2-8)$$

the substitution of equations (2-5) to (2-7) into equation (2-8) gives =

$$\text{Al}_m = [\text{Al}^{3+}] \left( 1 + \frac{k_{11}}{[\text{H}^+]} + \frac{k_{12}}{[\text{H}^+]^2} + \frac{k_{14}}{[\text{H}^+]^4} \right) \quad (2-9)$$

Setting  $\text{Al}_m$  to 1, the fractional contribution of each mononuclear ion is given by the following expressions:

$$\text{Al}^{3+} = 1 / \left( 1 + \frac{k_{11}}{[\text{H}^+]} + \frac{k_{12}}{[\text{H}^+]^2} + \frac{k_{14}}{[\text{H}^+]^4} \right) \quad (2-10)$$

$$\text{AlOH}^{2+} = \text{Al}^{3+} \frac{k_{11}}{[\text{H}^+]} \quad (2-11)$$

$$\text{Al(OH)}_2^+ = \text{Al}^{3+} \frac{k_{12}}{[\text{H}^+]^2} \quad (2-12)$$

$$\text{Al(OH)}_4^- = \text{Al}^{3+} \frac{k_{14}}{[\text{H}^+]^4} \quad (2-13)$$

The figures 2.1 and 2.2 represent the speciation diagrams of mononuclear aluminum hydroxide ions using the mass action law constants given by May (1979) and Parks (1972). The comparison of these two diagrams shows that the predicted contribution of  $\text{Al(OH)}_2^+$  to  $\text{Al}_m$  is much smaller in May's case than in Park's case. This comparatively small contribution, plus the possible existence of polycations in the same pH range as  $\text{Al(OH)}_2^+$  may be the reason for some authors' lack of confidence in the existence or thermodynamic validity of this species.

#### (ii) Polycations

The possible existence of polycationic soluble species was first suggested by Brosset and coworkers (1954) as the mononuclear species were not sufficient for explaining their titration curves. Until recently, only indirect evidences for their existence were found. Hem et al (1967) used the kinetics of complexation of a dye with aluminum as suggesting the occurrence of these polycationic species in very diluted solutions. The same method was used later (Bersillon et al, 1978) in concentrated solutions, and similar suggestions were inferred. The most often proposed structure of

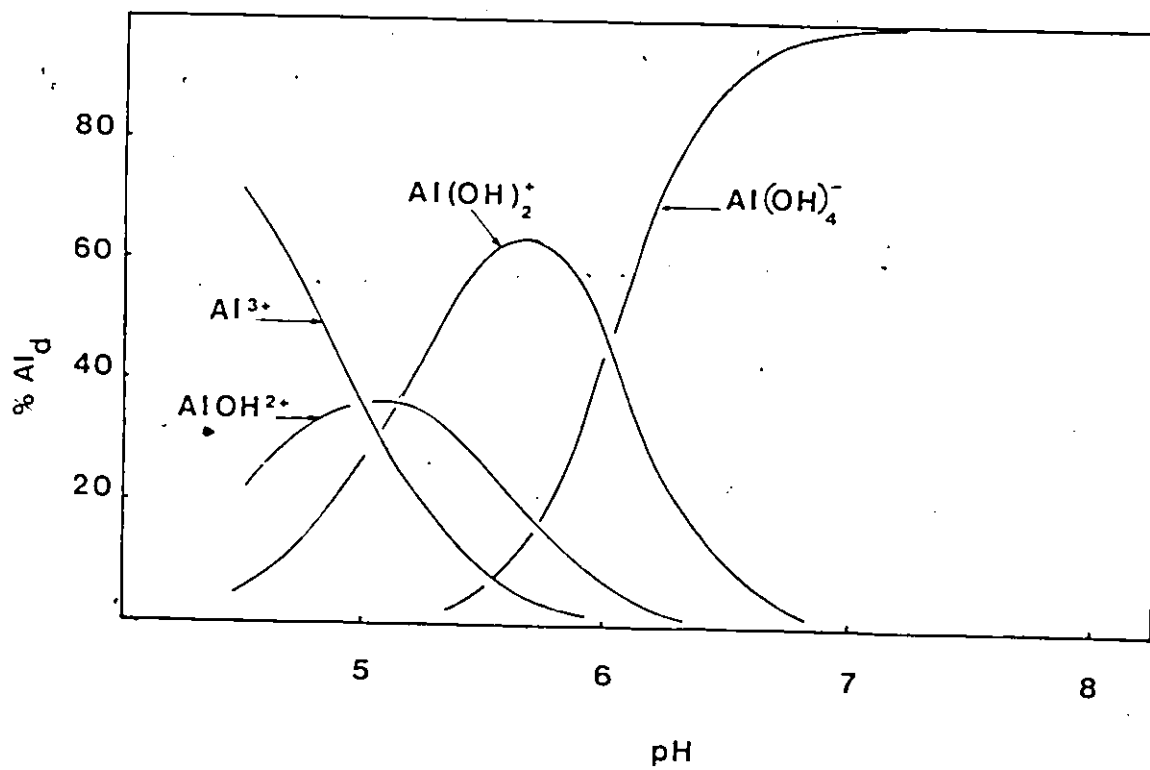


Figure 2.1 Aluminum Speciation Diagram after May et al (1979).



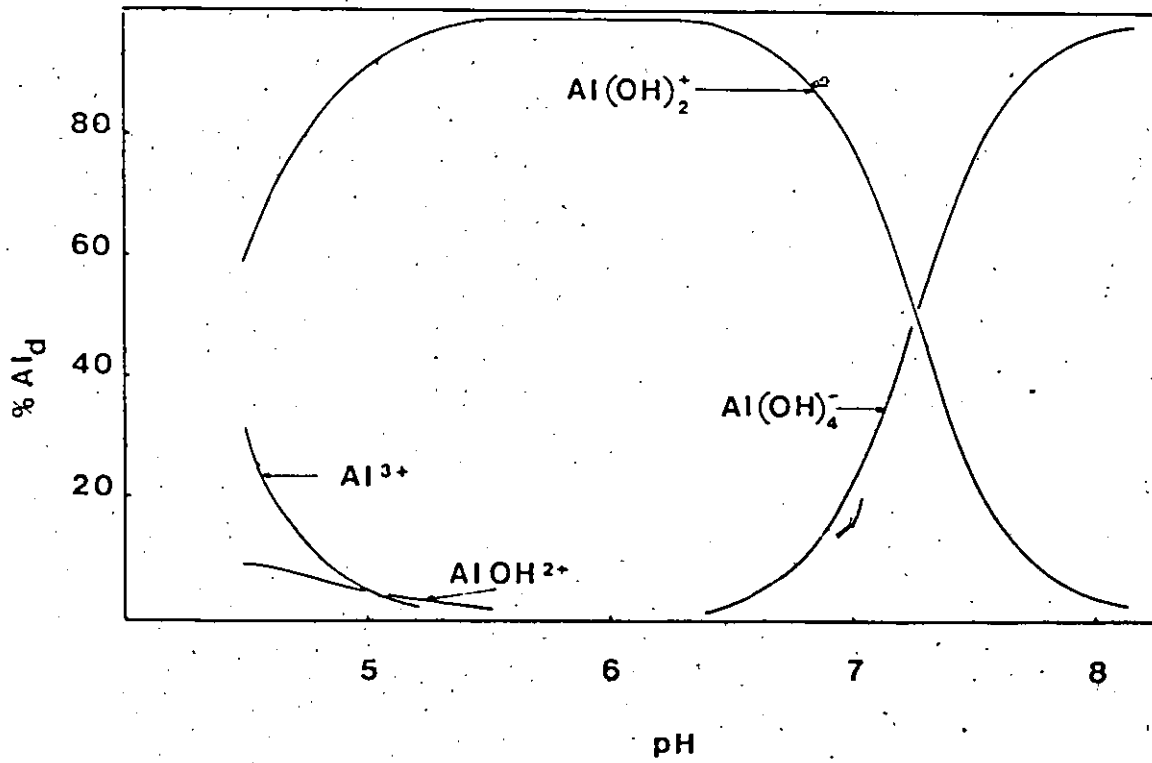


Figure 2:2 Aluminum Speciation Diagram after Parks (1972).

these polycations was derived from the sheet-like structure of the crystalline aluminum trihydroxides (Brosset et al, 1954, Hsu et al, 1964).

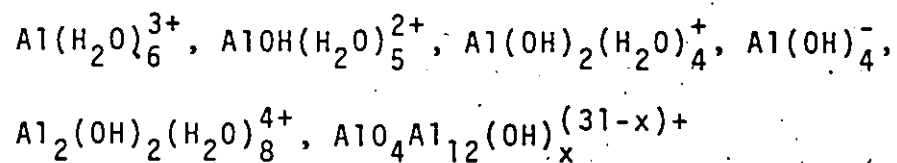
In an attempt to understand the chemistry involved in partially neutralized aluminum chloride solutions, and to explain the differences in coagulating ability of these products, Bottero and coworkers (1980) undertook an investigation using  $^{27}\text{Al}$  NMR and potentiometric titration techniques on 0.1 M  $\text{AlCl}_3$  solutions. They found that the results of both the NMR and the potentiometric titration could be adequately represented by an equilibrium between the mononuclear species  $\text{Al}(\text{OH})_i^{(3-i)+}$ ,  $i$  being equal to 1, 2 and 4, the dimer  $\text{Al}_2(\text{OH})_2^{4+}$  and a tridecamer  $\text{Al}^{\text{IV}}_4(\text{Al}^{\text{VI}})_{12}(\text{OH})_{28}^{3+}$ . The tridecamer was actually found earlier by Akitt et al (1972) by  $^{27}\text{Al}$  NMR measurements.

Further indirect evidences were provided by Bersillon et al (1980) for the occurrence of this polycation by treating partially neutralized  $\text{AlCl}_3$  solutions with  $\text{Na}_2\text{SO}_4$ , as these experiments yielded Basaluminite  $(\text{Al}_{13}\text{O}_4(\text{OH})_{25})_2(\text{SO}_4)_6$ . This aluminum hydroxysulfate was investigated by Johansson (1960, 1963), who found the tridecamer in the crystal lattice of this mineral, and suggested that the hydroxy aluminum structure unit may also occur in solution.

Baes et al (1976) added to the dimer and the tridecamer a 3rd polycation  $\text{Al}_3(\text{OH})_4^{5+}$ , based on potentiometric

measurements at low OH/Al ratio.

Thus, qualitatively, there seems to be a consensus among the authors met on the soluble hydrolysis products of Al(III):



The charge of the tridecamer is probably not accessible directly, and therefore in potentiometric modelling, it is correlated to the values of the other parameters. For instance, Bottero et al (1982a) suggest that this charge as well as the value of  $K_{13,x}$  decrease with decreasing total Aluminum concentration. He infers from this finding that at low concentrations (<1 mM/L as Al), the polycationic species do not form, and/or do not survive a dilution step.

On the other hand, Baes et al (1976), using fixed values of the charge of their polymeric species, show two speciation diagrams calculated for  $\text{Al}_T = 0.1 \text{ M/L}$  and  $\text{Al}_T = 1 \cdot 10^{-5} \text{ M/L}$ . These diagrams suggest that at high concentration, the tridecamer prevails over a wide pH range (5 to 8), whereas its contribution does not exceed 20% at low concentration.

(iii) Transient "Precipitates"

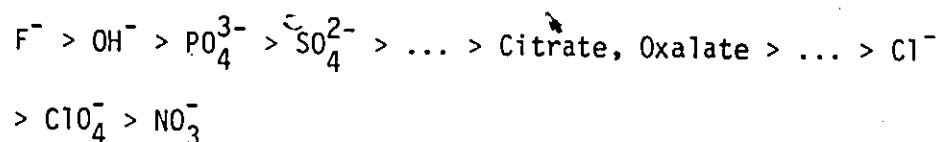
These species occur in forced hydrolyzed, high concentration, high OH/Al ratio Aluminum solutions. They evolve

rapidly with time, as suggested by Bottero et al (1982b). This author investigated .1 M/L  $AlCl_3$  solutions hydrolyzed to OH/Al ratio equal to 2.5 by small angle X Ray scattering. He showed that shortly after the end of the hydrolysis process, the particles of gel were rod shaped, with a diameter of  $15 \text{ \AA}$ , and a length of  $310 \text{ \AA}$ . These particles constituted 72% of the total Aluminum content, the rest of it being tridecameric. After one day, these particles undergo a rearrangement and dissolution : they only constituted 60% of the total Aluminum, and their shape was found to be platlet like,  $60 \text{ \AA}$  thick and  $500 \text{ \AA}$  in diameter.

These findings suggest non-equilibrium species, and their insertion in a model assuming equilibrium is questionable. However, such models are quite useful for engineering purposes, as they may lead to an improved control of coagulant quality.

### 2.3.2 Complexation with Anions

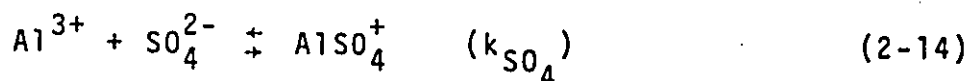
The hydroxyl ion is not the only ligand forming soluble complexes with Al(III). In 1946, Marion et al studied the pH of maximum precipitation of  $Al(OH)_3$ . They suggested a sequence of anions of decreasing affinity for Al(III):



The quantification of soluble complexes equilibrium constants was given by Hem (1968), for Hydroxide, Fluoride and Sulfate. These results were later incorporated into a computer model for the water chemistry WATEQ (Truesdell et al, 1974). Also, organo-complexes formation constants were given by Lind et al (1975).

Other anions such as Silicate (Hem et al, 1973), and even Bicarbonate (Letterman et al, 1979) were reported as altering the precipitation of Al(III). However, their mode of interaction remains unclear, as it will be seen in Section 2.3.3.

$SO_4^{2-}$  is of special interest in water treatment since fairly large quantities of it are added when using Alum as a coagulant. A soluble complex is formed according to the reaction



Also, field observations reported by Perdue et al (1976) suggest that the aqueous organics form soluble complexes with Al(III) and Fe(III), enhancing the solubility of these two elements.

### 2.3.3 Precipitates

The precipitates of interest for the present work are Aluminum Hydroxides.

The equilibrium form of Aluminum trihydroxide at standard condition is the Gibbsite. Bayerite and Nordstrandite are two other crystalline species of  $Al(OH)_3$ . They differ from Gibbsite by the way the sheet-like units are stacked along the c axis (Lippens, 1961).

Gibbsite has been reported as precipitating from partially neutralized Aluminum Chloride and Chlorate solutions upon aging (Hsu et al, 1964). Bayerite was found by Hem and coworkers (1967), in diluted Aluminum chloride solutions, depending on the ionic environment.

In his solubility study of Gibbsite, May et al (1979) attributed the shift of solubility of their mineral at neutral and alkaline pH to a rearrangement of the solid phase yielding Boehmite  $AlOOH$ . They suggested that Gibbsite was not stable in these pH conditions.

The solubility products of these crystalline compounds as well as Microcrystalline Gibbsite and amorphous trihydroxide are listed in the Table 2-1. The higher solubility of Microcrystalline Gibbsite is attributed to surface effects, whereas the higher solubility of amorphous  $Al(OH)_3$  is attributed to a lower order in the structure. The two values referring to the present work will be discussed later in Section 5.1.

Other precipitates involving OH and another anion are reported in the literature. Basaluminite has been

TABLE 2-1: SOLUBILITY PRODUCTS  $[H^+]^3/[Al^{3+}]$   
FOR THE FORMATION OF  $Al(OH)_3$

Mineral	$\log [H^+]^3/[Al^{3+}]$	Source
Gibbsite	- 7.90	Parks (1972)
	- 8.50	Baes et al (1976)
	- 8.11	May et al (1979)
Microcrystalline Gibbsite	-10.09	Hem et al (1967)
Amorphous $Al(OH)_3$	-10.39	Latimer (1952)
	- 9.31	DeHek et al (1978)
	- 9.84	This work.
	-10.19	This work.
Bayerite	- 8.41	Parks (1972)
	- 9.0	Baes et al (1976)
Nordstrandite	- 8.85	Hem et al (1973)

3  
 already mentioned. In a recent investigation on Aluminum natural concentration in streams, Nordstrom, (1982) observed Sulfate bearing deposits. He analyzed his data with respect to  $Al(OH)_3$ , and a continuous set of aluminum hydroxy sulfates. He concluded that for  $[SO_4^{2-}] \leq 1.10^{-4}$  M/L, and  $pH \leq 4.5$ , Basaluminite is likely to precipitate.

On the other hand, Ross et al (1971) reported the formation of poorly organized  $Al(OH)_{2.5}X_{.5}$  precipitates, X being Chloride or Nitrate. This investigation was conducted at high aluminum concentration (0.2 M/L), and using a fast forced hydrolysis process (fast titration). These gels were reported to yield Gibbsite upon aging. The weak bond between  $Cl^-$ ,  $NO_3^-$ , and  $Al(III)$  is consistent with Marion's sequence.

DeHek and coworkers (1978) reported that even Sulfate could be washed out of the precipitate obtained by titration of Aluminum. The titration was consistent with the formation of an amorphous Aluminum trihydroxide, and the X Ray analysis of the washed precipitates showed what they referred to as "microbayerite" at low to neutral pH, and "pseudo boehmite" at moderately high pH. They concluded that the Sulfate acts as a catalyst for the formation of  $Al(OH)_3$ . The role of this ion will be further discussed in the Chapter 5.

Little is known about the nature and formation of



the precipitate occurring when an Aluminum salt is rapidly diluted at pH near neutral. This type of mixing conditions may cause irreversible phenomena to take place. The quantification of such phenomena is very difficult as the rapidity of the reaction make them very difficult to study.

In Chapters 6 and 7, a model is developed to quantify the precipitation of Aluminum.

The assumptions necessary for the development of this model are based on the above background. The next chapter summarizes these assumptions. They will be discussed and used in Section 5.1.

#### 2.3.4 Soluble Aluminum Speciation

In this work, the speciation of aluminum at high concentration (0.1 M/L) is that suggested by Bottero's work (1980). When diluted and precipitated through the coagulation process, aluminum salts undergo hydrolysis leading to the formation of mononuclear hydroxide ions. Polynuclear species do not form or do not survive this type of treatment.

The species responsible for the residual soluble aluminum are in equilibrium with the precipitate, and with each other.

#### 2.4 Organic - Aluminum Interplay

Referring to the coagulation process, and the way

it is carried out, i.e. by addition of a relatively concentrated Aluminum solution to a natural water, the observed organic removal occurs, due to one, or a combination of the following phenomena:

- (i) A reaction, whereby an insoluble salt combining Aluminum and the organic materials in an original product, later referred to as Aluminum Fulvate precipitates.
- (ii) An adsorption of the organic material on the surface of an insoluble compound resulting from the independent hydrolysis of Aluminum. The nature of the bond between the absorbate and the absorbant can be physical (electrostatic, Vander Walls force) and/or chemical.
- (iii) A coagulation of the organic material by the Aluminum ions, whereby surfacic charges of the colloids are neutralized by ionic species of opposite charge, reducing and eventually allowing the aggregation of the colloids into separable flocs.

The above elementary phenomena do not exclude one another and may occur simultaneously.

#### 2.4.1 Reaction

In the Section 2.1.2, the chelating properties of

the fulvic and humic acids have been presented, and the formation of an insoluble compound has been suggested. In the water treatment community, there is a school of thought suggesting that a direct reaction occurs between Al and colour causing material.

The formation of an "Aluminum Fulvate/Humate" as the result of a direct reaction between Al and the organics was suggested by Stumm et al (1962), based on the ability of humic materials to complex Al and Fe. Hall et al (1965) investigated the removal of acid fractionated organics by Alum coagulation. They concluded that the organics react with a polynuclear species represented by the stoichiometric expression " $Al_2(OH)_5^+$ ", based on the comparison of the optimum pH for the removal of organics and Kaolinite, and the Alum requirement for halving the initial colour content. In the more recent works on this topic, researchers tend to think that the precipitate involving humic material and Aluminum is characterized by a stoichiometric relationship between carboxyl radicals and Al (Van Breemen et al, 1979; Randtke et al, 1981). Randtke (1981) reported that the removal pattern was a function of the origin of the humic material, whereas Van Breemen (1979) suggested that the stoichiometry of the precipitate varies with the original organic content.

Semmens et al (1980) reported an interesting set

of experiments carried out on the Mississippi River water. Some aspects of the results suggest that adsorption occurs, as an organic uptake is observed when the sludges generated by Alum treatment are added to the raw water without addition of coagulant. An analogous feature was reported by Wilson (1960), as colour removal keeps on occurring while Alum addition is stopped temporarily, on a treatment plant. On the other hand, some other aspects of their results suggest that the removal of colour is due to a reaction, as the splitting of the coagulant dose into two successive treatments does not improve the organic removal. This latter aspect will be discussed in Section 5.3.

O'Melia et al (1982) compared the coagulating abilities of Alum with those of Taki's PACS. They suggest that in the case of the PACS, the removal of organics occur through a reaction, whereas Alum gives less clear results.

#### 2.4.2 Adsorption

The adsorption of humic material on solids has been thoroughly studied by soil scientists. The solids used are generally metallic oxides (Al(III) and Fe(III)). The technique used is to add to a water containing humic material, well defined oxide particles. This technique is quite different from the addition of hydrolyzing salts, and

the surfacic phenomena may be different as well. However, relevant concepts regarding surface physical chemistry are outlined. Furthermore, adsorption has been suggested as responsible for the removal of micropollutants (Thebault et al, 1981) and surface active organics (Bottero, 1981b) by Aluminum coagulation. Also, Colthurst et al (1982) suggested that organics adsorb on the solid precipitate  $MnO_x$  resulting from water treatment by  $KMnO_4$  addition. Furthermore, Davis et al (1978b) determined the specific surface area of freshly precipitated  $Fe(OH)_3$  to  $600 \text{ m}^2/\text{g}$ , while Bottero (1981a) derived values ranging from 880 to  $1260 \text{ m}^2/\text{g}$  for  $Al(OH)_3$  gels resulting from polyaluminum chlorides precipitation, depending on the original OH/Al ratio, and the treatment pH. With such high values of the specific surface area, one can reasonably expect that adsorption participates to the removal of solutes.

The theories underlying the mechanism of adsorption do not make any distinction between organic and inorganic adsorbates.

Adsorption may occur as the result of physical or chemical interaction between the adsorbant and the adsorbate. The adsorption theories developed with respect to oxide and hydroxide surfaces tend to favour chemical rather than physical interaction. However, Healy (1971) suggested that

electrostatic forces are responsible for the adsorption. He developed a surface ionization theory whereby the partition of positively and negatively charged surface sites is pH dependent. The ions of opposite charge adsorb accordingly.

Rubio et al (1979) reported that the EDTA adsorbs according to a Langmuir isotherm. This was also found by Tipping (1981) for the adsorption of humic substances on  $\text{Fe}_2\text{O}_3$ . Both reported that the maximum adsorptive capacity is decreasing with pH. While Tipping only reported this variation, Rubio explained it by a ligand exchange mechanism. This mechanism was further developed and used in similar experiments (Chang et al, 1983) involving chelating agents. An analogous model was proposed by Kummert et al (1980) for the adsorption of organic acids on  $\text{Al}_2\text{O}_3$ . They also suggested that the extent of the adsorption was proportional to the tendency of the organic acids to form soluble complexes with Al. Also, ligand exchange was put forward by Goldshmid et al (1978) as the mechanism responsible for Phosphorus removal by Aluminum salt treatment, at high pH and low P/Al ratio.

Davis and coworkers (1978a, 1978b, 1980) developed a general model combining the double layer theory describing the electrostatic potential at a given distance from a

charged surface with the formation of a chemical bond between the adsorbate and the adsorbant. This model will be discussed in detail in the Section 3.3. Davis (1982) suggested that this model may apply to natural dissolved organics adsorbing an oxide. This model is interesting as it can be used to describe pH and surface ionization effects as well as possible competition between several adsorbates.

In the discussion of his data on Sulfate bearing Aluminum hydroxides, Nordstrom (1982) suggested that there is no clear cut difference between chemical adsorption and chemical reaction. Actually, the chemical adsorption equilibrium can be described by equations similar to the mass action law formulation. This is true for the ligand exchange model, as well as, to some extent, for Davis' model.

#### 2.4.3 Coagulation

Coagulation is the aggregation of colloids wherein surfacic charges are neutralized by counter ions on a purely electrostatic basis. Ong et al (1968) suggested that this mechanism is responsible for the precipitation of soil extracts at pH near neutral, as the concentration of cations necessary to observe an aggregation is independent of the concentration of the organics, and that this Critical Coagulation Concentration obeys the Schulze-Hardy rule.

## CHAPTER 3

### THEORETICAL EXPECTATIONS

#### 3.1 Possible Removal Pathways

Figure 3.1 summarizes all the possible ways the aqueous organics can be removed by an aluminum salt. In this diagram, the Aluminum-hydroxy polymers are included, as possible starting points, or as compulsory hydrolysis steps in the formation of an Aluminum-Hydroxy Fulvate.

Two different removal mechanisms are suggested in this diagram, i.e. Reactions and Adsorption. These mechanisms are not necessarily exclusive, however, it is probable that one of them dominates the removal pattern of Fulvates by the coagulation process. This dominant phenomenon may be a function of treatment conditions (pH, Coagulant dosage).

This chapter discusses theoretical models that connect the different removal routes pointed out above to the treatment parameters accessible to the practitioner. This analysis provides the background for the design of the experimental part of the present study.

#### 3.2 The Reaction Hypothesis

##### 3.2.1 General Considerations

In this section, the formation of a specific solid



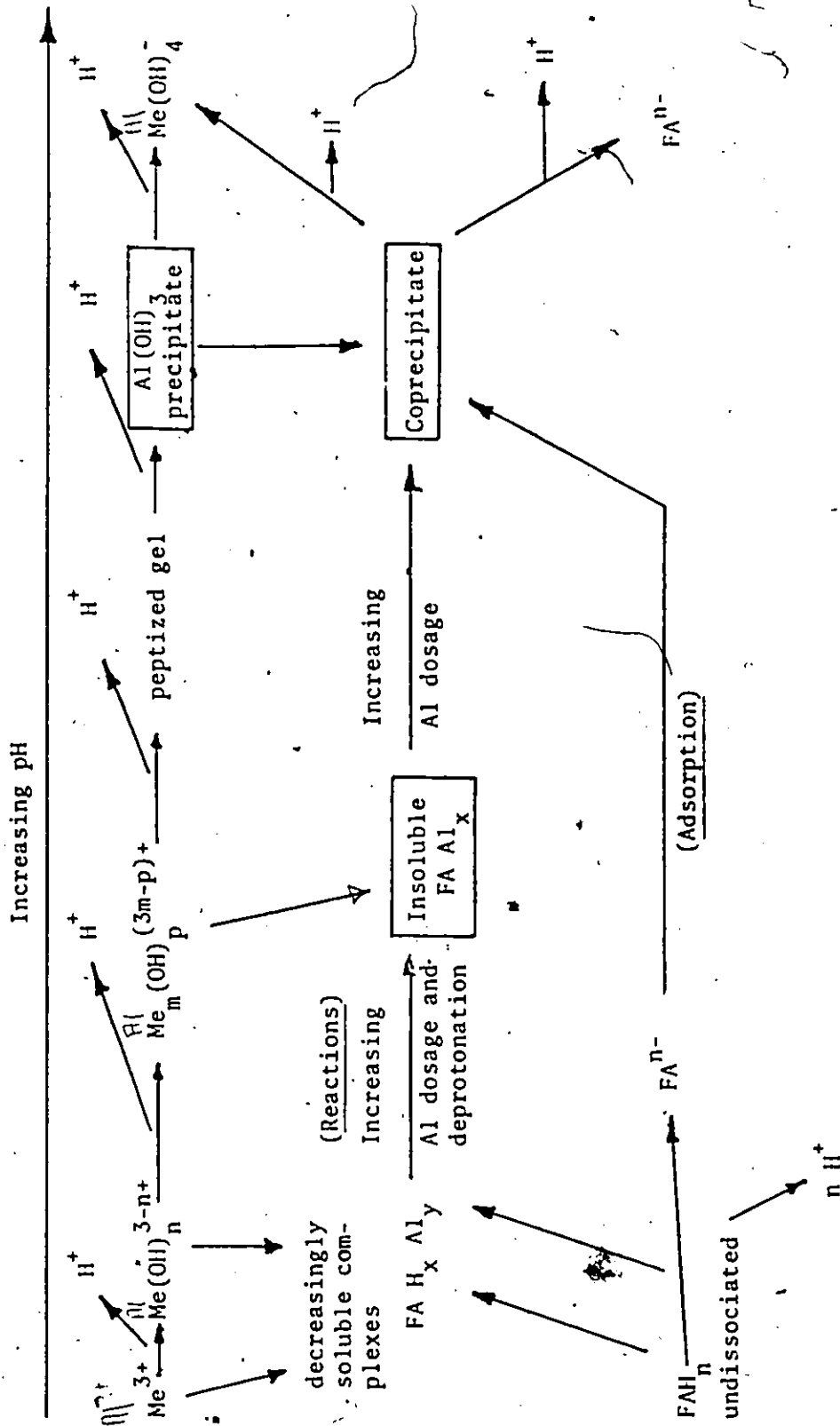
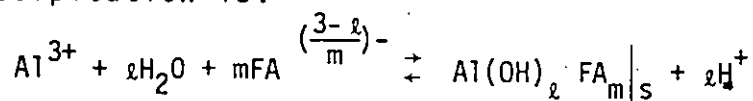


Figure 3.1 Different Removal Routes.

involving Al and Fulvates is assumed either as the only solid precipitating (straight reaction), or precipitating with  $\text{Al}(\text{OH})_3$ . Additionally, the consequences of this hypothesis are examined at equilibrium conditions.

In the following, the Fulvates are assumed homogeneous in physicochemical properties (molecular weight, and acidity). The complications brought by the heterogeneity of this material (see Chapter 2) are discussed later.

The general chemical equation corresponding to this precipitation is:



$$\text{and } k = \frac{[\text{H}^+]^\ell}{[\text{Al}^{3+}][\text{FA}^{\left(\frac{3-\ell}{m}\right)-}]^m} \quad (3.1)$$

Since this equation is formulated with respect to  $\text{Al}^{3+}$  (its coefficient is set to unity), its application extends to the equation related to the formation of  $\text{Al}(\text{OH})_3$ . In this case,  $\ell$  and  $m$  are equal to 3 and 0 respectively, and the equation 3.1 takes the standard form of  $k_s$ :

$$k_s = \frac{[\text{H}^+]^3}{[\text{Al}^{3+}]} \quad (3.2)$$

The values of the stoichiometric coefficients  $\ell$  and  $m$ , if accessible, permit the identification of the mechanism responsible for the removal of Fulvates.

(i) Ligand Number  $\lambda$ 

The stoichiometric coefficient  $\lambda$  corresponds to the OH/Al ratio of the precipitate and is referred to as the ligand number of the precipitate. According to equations 3.1 or 3.2, its value is accessible by the evaluation of the slope of  $\log[Al^{3+}]$  as a function of pH. This requires the knowledge of the pH, and the activity of  $Al^{3+}$ . This latter variable can be calculated from the value of the residual Aluminum  $Al_d$ , according to equation 2.9, and under the assumptions summarized in Subsection 2.3.4:

$$[Al^{3+}] = Al_d / \left( 1 + \frac{k_{11}}{[H^+]} + \frac{k_{12}}{[H^+]^2} + \frac{k_{14}}{[H^+]^4} \right) \quad (3.3)$$

This equation is written for 0 ionic strength conditions, and must be corrected accordingly. This point is further developed in Section 5.1.

(ii) Precipitate Loading

The precipitate loading is defined as the amount of organics fixed per unit of solid precipitated. Its value is accessible experimentally by a mass balance:

$$q = \frac{FA_o - FA_e}{Dose - Al_d} \quad (3.4)$$

where

$q$  is the loading expressed as mg DOC/mM Al  
 $FA_o$  is the raw water Fulvate content (mg DOC/L)  
 $FA_e$  is the equilibrium (final) Fulvate content  
 (mg DOC/L)

Dose is the Aluminum dosage (mM Al/L)

$Al_d$  is the equilibrium (final) dissolved Aluminum  
(mM Al/L)

The meaning and significance of this variable will be specified later.

### 3.2.2 Straight Reaction

In this case, the equation (3.1) is fully applicable. The format of the mass action law constant suggest that providing that the Fulvates are fully known and homogeneous (molecular weight and number of carboxyl radicals per molecule), the ligand number  $\ell$  and the stoichiometric coefficient  $m$  are accessible simultaneously as the coefficients of the logarithmic expression:

$$\frac{1}{m} \log[Al^{3+}] + \frac{\ell}{m} pH + \log k = -\log[FA]_e \quad (3.5)$$

$\frac{1}{m}$  and  $\frac{\ell}{m}$  can be calculated by multivariable regression analysis.

This situation however, is idealistic, due to the inherent heterogeneity of the natural Fulvates. Therefore, one must rely on successive approximations more than on a direct, straight-forward determination.

#### (i) Ligand Number $\ell$

Rearranging equation (3.5), one gets:

$$\log[Al^{3+}] = -\ell \cdot pH - m(\log[FA]_e + \log k) \quad (3.6)$$

According to previous works reported in the literature (see Section 2.4.1), the expected ligand number of the precipitate would be 2 or 2.5. No specific information is available on an expected value of  $m$ , except that derived from Schnitzer's (1971) model of the typical Fulvic Acid molecule. In this case, the solid would have the formula  $(Al(OH)_2)_6FA$ , thereby suggesting a value of  $m$  equal to 0.167. In any case, the polyacidic character of Fulvates suggest that  $m$  is smaller than 1.

Assuming a maximum Fulvate removal of 90% and a polydispersity of 5 (a measure of the spread of the molecular weight distribution function, see Section 2.1), the DOC can be formulated as

$$DOC(mg/L) = \% C \sum_{i=1}^n MW_i (FA_i) \quad (3.7)$$

where  $\%C$  = FA carbon content, assumed homogeneous, as suggested in Chapter 2.

$MW_i$  = Molecular weight of the species  $FA_i$  (mg/mM)

$(FA_i)$  = concentration of the species  $FA_i$  (mM/L)

The expected variation of  $(FA)_e$  when expressed as DOC is a function of the polydispersity, and variation in the residual, for instance their product (here  $5 \times 10 = 50$ ), which introduces a dispersive term of 1.70 in the right-hand side of equation (3.6). This also assumes homogeneity in the values of  $\log k$ , which is reasonable since  $k$  refers

here to the mass action law constant reduced with respect to Al (see equation 3.1).

Since Fulvate removal is expected to be a function of the Aluminum dosage, an experimental design involving wide enough pH and Aluminum dosage ranges should yield resulting  $[Al^{3+}]$  values defining a strip across the  $p[Al^{3+}]$ -pH plane ( $pAl = -\log[Al^{3+}]$ ) with an average slope equal to  $\lambda$ , and a maximum vertical width corresponding to  $m \log$  (polydispersity times variations in  $\log k$ ). Figure 3.2 represents such a strip, with  $\lambda = 2$ , and a vertical width of 2.

Therefore, a linear regression analysis of  $pAl$  as a function of pH will yield an average value of the slope which must be representative of the value of  $\lambda$ , and according to equation 3.1, this value is necessarily below 3.

#### (ii) Precipitate Loading

In the ideal case presented at the beginning of this Subsection, the Fulvates were assumed homogeneous. In this case the DOC is directly proportional to the molar concentration of Fulvates. Therefore, the precipitate loading, as defined by equation (3.4) is directly proportional to the stoichiometric coefficient  $m$ , and the loading is therefore expected to be independent of the coagulant dosage and the residual DOC.

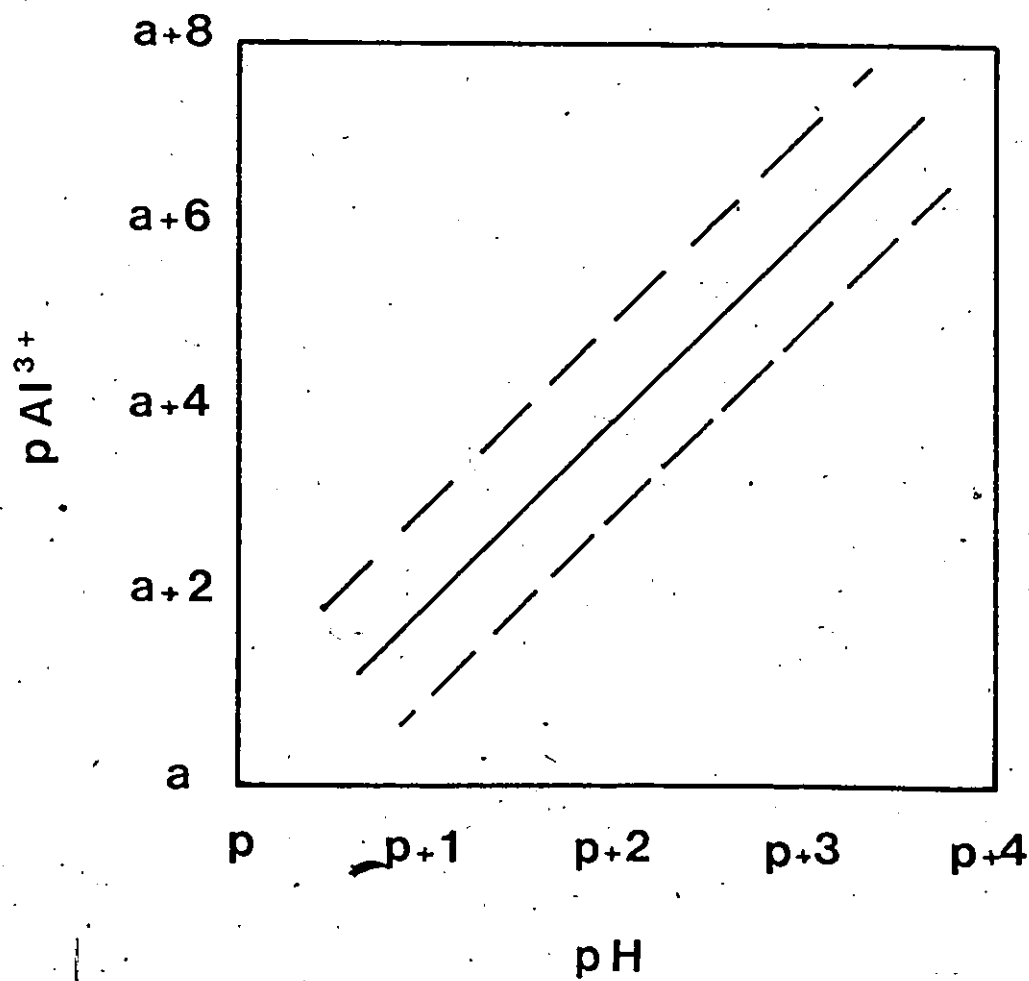


Figure 3.2 Graphical Representation of the Dispersion Brought by Fulvate Heterogeneity (a and p are arbitrary values).

In the most probable case of a mixture of compounds however, the precipitate loading has no real significance in the context of the reaction hypothesis, and its standard graphical representation as a function of the residual DOC can display any shape.

### 3.2.3 Coprecipitation

The coprecipitation refers to the coexistence of two distinct solid equilibrium phases, i.e. in the present case an Aluminum Hydroxy Fulvate, and an Aluminum Trihydroxide. The presence at equilibrium of these two solids implies that both equations (3.1) and (3.2) are satisfied. Such constraints make the coprecipitation, or more specifically the coexistence of these two solids at equilibrium an occasional event. On the other hand, in many engineering situations, equilibrium is not reached within the reactor and, therefore, coprecipitation may occur on a wider basis than suggested by the above constraints.

### 3.2.4 Formation of an Irreversible Precipitate

The formation of an irreversible precipitate can only be stopped by the exhaustion of one of the reagents. In the present case, either the Aluminum is exhausted or FA is exhausted. If the Aluminum is exhausted, the residual



Aluminum is expected to be very low, and no pattern with respect to the pH should be found. On the other hand, if FA is exhausted, extra addition of Aluminum should not affect the value of the residual FA, which should be very low. The former case is expected to happen at low Al/FA ratio (low coagulant dosage) whereas the latter corresponds to high coagulant dosage.

### 3.3 The Adsorption Hypothesis

The removal of Fulvates by Adsorption assumes that the precipitate is no longer an Aluminum Hydroxy Fulvate, but a solid precipitating independently of the presence of Fulvates. In the present case,  $Al(OH)_3$  is the most likely to precipitate.

#### 3.3.1 The Ligand Number

In the case of the precipitation of  $Al(OH)_3$ , the equation 3.2 holds, and the slope of the best fitting line for the experimental values of  $\log[Al^{3+}]$  as a function of pH is expected to be close to 3.

As mentioned in Section 2.3.3, the presence of Sulfate brought by its addition as Alum may favour the precipitation of an Aluminum Hydroxy Sulfate. If this is the case, the ligand number is no longer 3. Thus the experimental design should include the use of coagulants

other than Alum, and should also include blank runs whereby the ligand number of the precipitate can be assessed in the absence of Fulvates. The comparison of these results with those yielded by a set of experiments performed on a Fulvate containing water will show the effect of Fulvate and Sulfate on the value of  $\lambda$ , and will permit a better discrimination between Adsorption and Reaction.

### 3.3.2 The Precipitate Loading

The concept of the precipitate loading is the most significant in the context of the Adsorption hypothesis. The adsorption is characterized by a relationship between the dispersed phase equilibrium concentration, here  $FA_e$  and the surface concentration  $q_e$ , expressed as unit of adsorbate per unit of adsorbent:

$$q_e = f(C_e).$$

All the equations are monotonously increasing functions of the liquid phase concentration of the adsorbate ( $C_e$ ). These equations are referred to as isotherms. Their formulation is either empirical, or based on theoretical considerations regarding the interactions between the adsorbent surface and the adsorbate molecules. An extensive discussion of these equations and their theoretical derivation is presented by Adamson (1976).

### 3.3.2.1 Most Usual Isotherm Equations

Two Isotherms are very often used in Adsorption studies.

(i) The Freundlich isotherm assumes a uniform distribution of the energy of interaction adsorbate-adsorbent -

$$q_e = k C_e^{1/n} \quad (3.8)$$

where  $k$  and  $n$  are constants. The determination of their value is easily done by a log-log graphical method.

(ii) The Langmuir isotherm assumes that the energy of interaction adsorbent-adsorbate is independent of the coverage of the surface, and that all the adsorption sites are equivalent. Its mathematical formulation is as follows:

$$q_e = q_{\max} \frac{kC_e}{1 + kC_e} \quad (3.9)$$

where  $q_{\max}$  is the loading of the adsorbent at saturation, and  $k$  is a constant representing the ratio of the adsorption to desorption rate constants.

These 2 equations often fit adsorption data, at least for limited ranges of liquid phase concentrations, and they are widely used. In certain cases of chemical adsorption, other equations may be encountered, such as a compromise between the 2 forms =

$$q_e = q_{\max} \frac{kC_e^n}{1 + kC_e^n} \quad (3.10)$$

### 3.3.2.2 Special Cases

In the former chapter, the adsorption of Fulvate as well as inorganic anions, specially Sulfate, has been suggested as possibly occurring. Since Alum (Aluminum Sulfate) is the most widely used coagulant, a competition for adsorption sites must be considered in the range of the phenomena likely to be encountered. Liapis et al (1971) use a generalized form of the equation (3.10) to describe the multicomponent adsorption of organics on Activated Carbon =

$$q_e^i = q_{\max}^i \frac{k_i (C_e^i)^{n_i}}{1 + K_1 (C_e^1)^{n_1} + \dots + k_i (C_e^i)^{n_i} + k_p (C_e^p)^{n_p}} \quad (3.11)$$

where  $q_e^i$  is the equilibrium loading for the component  $i$ .

$q_{\max}^i$  is the maximum loading for the component  $i$ .

$C_e^i$  is the liquid phase concentration of the component  $i$ .

$k_i, n_i$  are the coefficients corresponding to the component  $i$ . This expression is not linearizable, and needs special parameter evaluation techniques to be properly evaluated.

More recently, Davis et al (1978a) developed an adsorption model integrating the double layer theory and the formation of surface complexes to account for ion behaviour in the presence of oxide surface. He later suggested that this model may apply to natural aqueous

organics as well (Davis, 1982). Figure 3.3 shows a schematic representation of the surface neighbourhood according to this model. The equations describing the adsorption are as follows:

(i) Surface Ionization

For a Hydroxide surface, neutral sites S-OH hydrolyze according to the following equations:



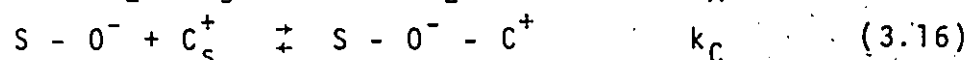
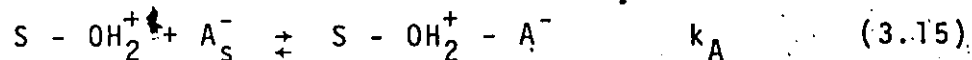
where  $\text{H}_s^+$  represents the protons in the immediate neighbourhood of the surface. Its concentration is related to the bulk  $\text{H}^+$  concentration by an equation of the kind:

$$\text{H}_s^+ = \text{H}_{\text{bulk}}^+ \exp(-e \psi_0 / kT) \quad (3.14)$$

where  $\psi_0$  represents the electrical potential at the inner boundary of the inner layer,  $k$  the Boltzmann constant. Electrical attraction causes a concentration gradient which is responsible for a possible "physical" adsorption of counterions. This summarizes the surface ionization model.

(ii) Chemical Bonding

Davis' model further assumes chemical bonding between surface sites and adsorbed species  $\text{C}^+$  and  $\text{A}^-$ :



Here again,  $\text{C}_s^+$  and  $\text{A}_s^-$  are concentrations near the

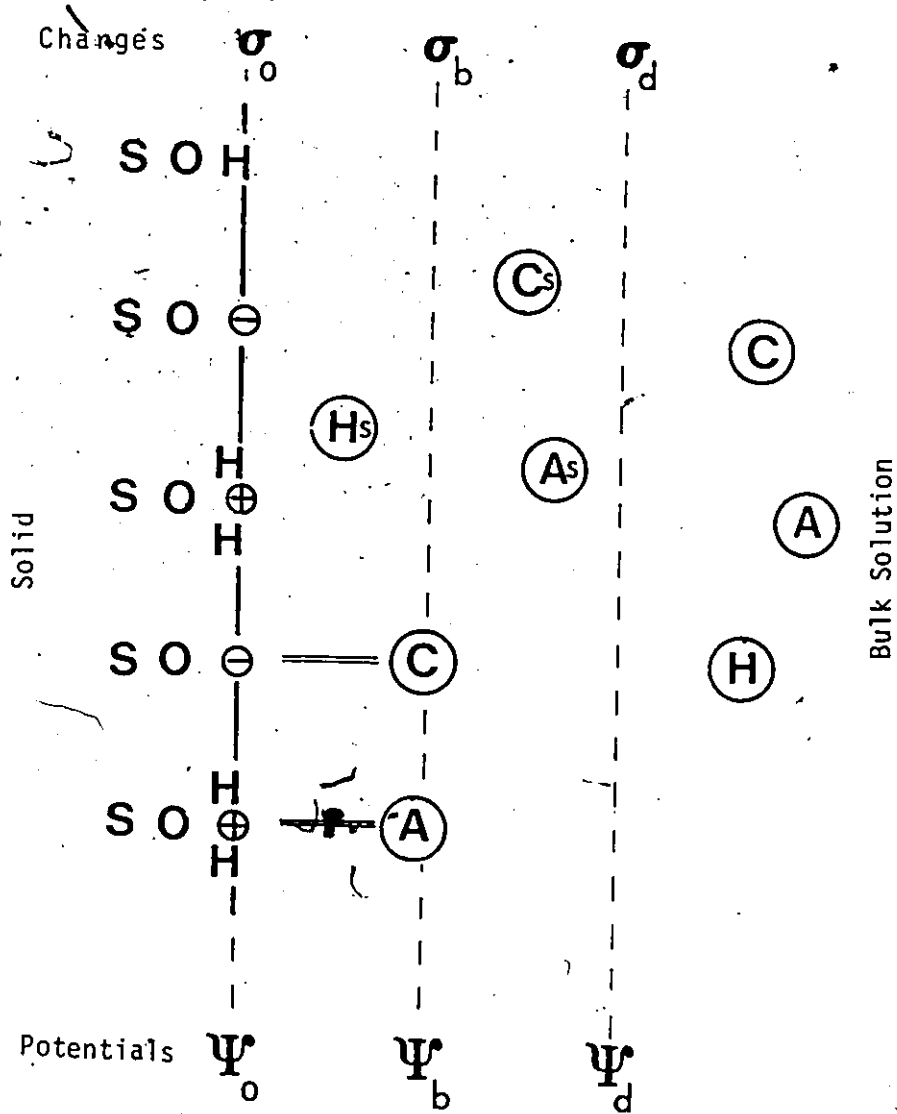


Figure 3.3 Ionic Distribution Near the Surface (after Davis, 1980), H =  $\text{H}^+$  ion; C = Cation; A = Anion

surface of the solid, but not in the inner layer, where they cannot go. These concentrations are related to the bulk concentrations by an equation similar to equation (3.14):

$$C_s^+ = C_{bulk}^+ \exp(-e\psi_b/kT) \quad (3.17)$$

$$A_s^- = A_{bulk}^- \exp(e\psi_b/kT) \quad (3.18)$$

This determines 3 surfaces of potential  $\psi_o$ ,  $\psi_b$ , and  $\psi_d$  as shown in Figure 3.2. The values of these potentials are functions of surface charges =

$$\sigma_o = F/A(\text{SOH}_2^+ + \text{SOH}_2^+ - A^- - \text{SO}^- - \text{SO}^- - C^+) \quad (3.19)$$

$$\sigma_b = F/A(\text{SO}^- - C^+ - \text{SOH}_2^+ - A^-) \quad (3.20)$$

$$\sigma_d = -11.74 \sqrt{C} \sinh(ze \psi_d/2kT) \quad (3.21)$$

where  $F$  = Faraday constant  
 $A$  = specific surface area  
 $C$  = bulk electrolyte concentration  
 $z$  = electrolyte charge

Electroneutrality of the system requires that

$$\sigma_o + \sigma_b + \sigma_d = 0 \quad (3.22)$$

and the potentials are related by the equations

$$\psi_o - \psi_b = \sigma_o/C_1 \quad (3.23) \quad \psi_b - \psi_d = -\sigma_d/C_2 \quad (3.24)$$

where  $C_1$  and  $C_2$  are dielectric constants of the inner and outer bonded layers respectively. This model allows to account for variations in the adsorptive behaviour due to

pH and to the presence of competing adsorbate.

This model can be transposed in terms of loading as a function of the bulk concentration, by converting the number of sites occupied by a given adsorbate into a solid concentration. This conversion is performed by dividing this number of sites, for instance  $\text{SOH}_2 - A_1$  by the total number of adsorption sites present

$$(\text{SOH} + \text{SOH}_2^+ + \text{SO}^- + \sum_i \text{SOH}_2 - A_i + \sum_j \text{SO} - C_j).$$

This solid concentration is proportional to the loading.

The final expression is:

$$q_{A_1} = q_{\max} \frac{k_H k_{A_1} (H^+) (A_1^-) \exp\left(\frac{e}{kT}(\psi_b - \psi_0)\right)}{1 + k_H (H^+) \exp\left(-\psi_0 \frac{e}{kT}\right) \left\{1 + \sum_i k_{A_i} (A_i^-) \exp\left(\psi_b \frac{e}{kT}\right)\right\} + k_{OH} / (H^+) \exp\left(\psi_0 \frac{e}{kT}\right) \left\{1 + \sum_j k_{C_j} (C_j^+) \exp\left(-\psi_b \frac{e}{kT}\right)\right\}}$$

This expression, written for monovalent Anions  $A_i^-$  and Cations  $C_j^+$ , must be combined with the relations (3.19) to (3.24) in order to account for  $\psi_0$  and  $\psi_b$ . It can be simplified by neglecting the effect of the electrostatic forces, thereby yielding a first approximation of the form:

$$q_{a_1} = q_{\max} \frac{k_H k_{FA} (H^+) (A_1^-)}{1 + k_H (H^+) \left(1 + \sum_i k_{A_i} (A_i^-)\right) + k_{OH} / (H^+) \left(1 + \sum_j k_{C_j} (C_j^+)\right)} \quad (3.25)$$

This expression is linearizable.



### 3.3.2.3 Heterogeneity of the Fulvates

The natural heterogeneity of the Fulvates suggest that theoretically derived Isotherms such as the Langmuir or the Davis Isotherms will probably not fit adequately the data. The Freundlich Isotherm, or one of its derived forms such as equation (3.11) will be more suitable.

### 3.4 Significant Dependent Variables

From the above analysis, it appears that the discrimination between reaction and adsorption relies entirely on the value of the ligand number. This can be evaluated using equation (3.3) for the calculation of the activity of  $Al^{3+}$ , and the resulting values processed as suggested by the equation (3.5).

If the resulting value is 3, the Adsorption hypothesis is most likely, and one can proceed to the analysis of the residual organics in terms of Adsorption Isotherms.

On the other hand, if the presence of Fulvate in the raw waters alters the ligand number to a value smaller than 3, the reaction hypothesis becomes the most likely, and tentative modeling can be attempted using equation (3.5) as a first approximation. Therefore, it is essential to measure both the residual organics and the residual Aluminum to be able to identify the mechanism of Fulvate removal. Once this identification is made, the parameter values for the different removal models can be evaluated.

CHAPTER 4  
EXPERIMENTAL METHODS

4.1 Raw Waters Origin and Storage

4.1.1 Fauquier Raw Water

Four hundred litres of water from the Groundhog River at Fauquier (Ontario) was provided by Zenon Environmental Inc. (Burlington, Ontario). This water was sampled in October 1981, and stored in a continuously stirred stainless steel tank. This 400 litres aliquot was stored in the laboratory in two 45 Imperial gallons closed polyethylene drums, previously acid washed and rinsed several times with distilled water and with the raw water itself. The water was stirred gently with bubbling air during 30 minutes before withdrawing the required aliquots for the coagulation experiments. Neither bacterial deposits nor important degradation of the quality of the raw water occurred. This water is further referred to as FRW.

4.1.2 Distilled Water

The water used for the preparation of the reagent, the rinsing of the glassware, and the dilution of FRW was distilled, resin treated, and activated carbon filtered.

The activated carbon filter Empty Bed Contact Time was at least 10 hours. The ion exchange resin and the activated carbon were changed as soon as the deterioration of the quality of the distilled water was detected, by an increase in the conductivity or the UV Absorbance ( $A_{254}^{10\text{ cm}}$ ). This water is further referred to as DW.

#### 4.1.3 Fauquier Diluted Water

Approximately 60 litres of FRW were diluted up to 200 litres with DW, and spiked with the proper amount of reagent grade  $\text{NaHCO}_3$  to adjust the alkalinity to ca 1 meq/L (50 mg/L as  $\text{CaCO}_3$ ). After this dilution, this water was aerated continuously during one day, and then stored and used as FRW. This water is further referred to as FDW.

#### 4.1.4 Blanks

A set of Jar test was performed, using as raw water one litre aliquots of DW spiked with proper amounts of 0.2 N  $\text{NaHCO}_3$  solution to match FRW alkalinity.

### 4.2 Reagents and Coagulants

#### 4.2.1 Stock Solutions

Aluminum chloride ( $\text{AlCl}_3$ ) was prepared by dissolving 66.7 g of reagent grade anhydrous  $\text{AlCl}_3$  into one litre of

DW. The resulting solution was filtered on Sartorius .45  $\mu\text{m}$  pore diameter membrane and stored in a polyethylene bottle. The aspect and aluminum content was assessed periodically during its use.

Aluminum sulfate (Alum) was prepared and stored like  $\text{AlCl}_3$ , by dissolution of 166.5 g of reagent grade  $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ . These two stock solutions were found to be stable with time, and contained .417 Mol/L and .446 Mol./L as Al respectively. Standard 1.00 N Sodium Hydroxide and Hydrochloric Acid were used as standard stock solutions for all the neutralizations and pH adjustments.

#### 4.2.2 Coagulant Operating Solutions

- (i) Alum was prepared by diluting 22.5 mL of the corresponding stock solution to 100.0 mL with DW.
- (ii)  $\text{AlCl}_3$  was prepared by diluting 24.5 mL of the corresponding stock solution to 100.0 mL with DW.
- (iii) Partially neutralized Aluminum Chloride solutions were prepared as follows:  
A proper aliquot of 1.00 N NaOH stock solution was diluted to 75 mL with DW, and added dropwise to a 24.5 mL aliquot of  $\text{AlCl}_3$  stock solution under vigorous stirring

(ca 1000 rpm with a magnetic stirrer).

This neutralization was carried out in 250 mL Erlenmeyer flasks. The stirring caused a vortex exposing the rotating magnet. The tip of the buret was located below the top of the flask, and centered in such a way that the diluted NaOH dropped onto the magnet. The neutralization required 30 mn.

Two partially neutralized Aluminum Chloride solutions were used, differing by the NaOH/AlCl<sub>3</sub> ratios:

<u>R = NaOH/AlCl<sub>3</sub></u>	<u>Reference Name</u>
1.8	<u>Alpol</u>
2.5	<u>Algel</u>

All these operating solutions were used no sooner than one hour and no later than four hours after their preparation.

The choice of these coagulants was made by reference to Bottero's (1980) speciation diagram:

<u>Coagulant</u>	<u>% monomers</u>	<u>% Al<sub>13</sub><sup>*</sup></u>	<u>% Al(OH)<sub>3-x</sub><sup>x+</sup></u>
AlCl <sub>3</sub>	100	—	—
Alpol	0	100	0
Algel	0	30	70

\* Al<sub>13</sub> refers to Al<sub>13</sub>O<sub>4</sub>(OH)<sub>31-n</sub><sup>n+</sup>

- (iv) A set of experiments was performed, using Alum or  $\text{AlCl}_3$  neutralized to NaOH/Al ratio equal to 3. These suspensions were prepared by rapid addition of 30 ml of NaOH 1 N to the proper aliquots of Alum or  $\text{AlCl}_3$  stock solution, followed by a dilution with DW up to 100 ml, and storage under moderate stirring for approximately one hour prior to use.

All the coagulants were prepared at 0.1 Mol/L.

#### 4.3 The Jar Test Method

##### 4.3.1 Equipment

All the coagulation tests were performed on a Phipps and Bird Flocculator\* equipped with 6 blade stirrers, and 6 10 cm x 10 cm glass jars calibrated to one litre. This flocculator is also equipped with a speed controller, and the stirrers can be removed independently.

The blades and shafts were rinsed with DW after each use. The glass jars were systematically washed, rinsed with DW, and air dried after each use.

The flocculated waters were vacuum filtered (pressure 70 Torrs) using 0.45 $\mu$  pore diameter Sartorius\*\* membranes. These membranes were kept in DW, and washed with at least 150 ml of DW prior to the filtration of the samples.

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\* Phipps and Bird, Richmond, VA, USA.

\*\* Sartorius, Gottingen, W. Germany.

#### 4.3.2 Operating Conditions

##### (i) pH Values

Four values of pH were selected as target values for the flocculated waters:

5, 6, 7.4, 8.5

These values were chosen with respect to Parks' speciation diagram for monomers, as being the values for a maximum of  $Al(OH)_2^+$  (5 and 6), expected maximum precipitation of  $Al(OH)_3(s)$  (7.4) and maximum of  $Al(OH)_4^-$  in the flocculated waters.

##### (ii) Coagulant Dosages

The basic scheme for the coagulant dosages was chosen such that the expected "optimum" coagulant dosage was included in the investigated range. This led to set the six dosages to .1, .2, .4, .6, .8, 1.0 mM Al/L, 1 mM Al/L corresponds to 300 mg/L as Alum  $14 H_2O$ . Since the molecular weight of the coagulants are not equal, the treatment dosage, as well as all the results are expressed in terms of molar values of Aluminum. Additional treatment dosages (.12, .15, .18 mM Al/L) were applied as needed.

##### (iii) Time Frame and Mixing Conditions

The time frame applied to most of the experi-

ments is shown in the Figure 4.1. The pH adjustment was performed systematically after the addition of the coagulant dose. The time frame and G values used were consistent with usual experimental conditions.

The pH was measured on the flocculated waters, as the filtration of the sample caused an important release of the dissolved gases, especially at the lower end of the pH range. This was attributed to CO<sub>2</sub> release, thereby likely to modify the pH.

#### 4.4 Specific Methods of Investigation

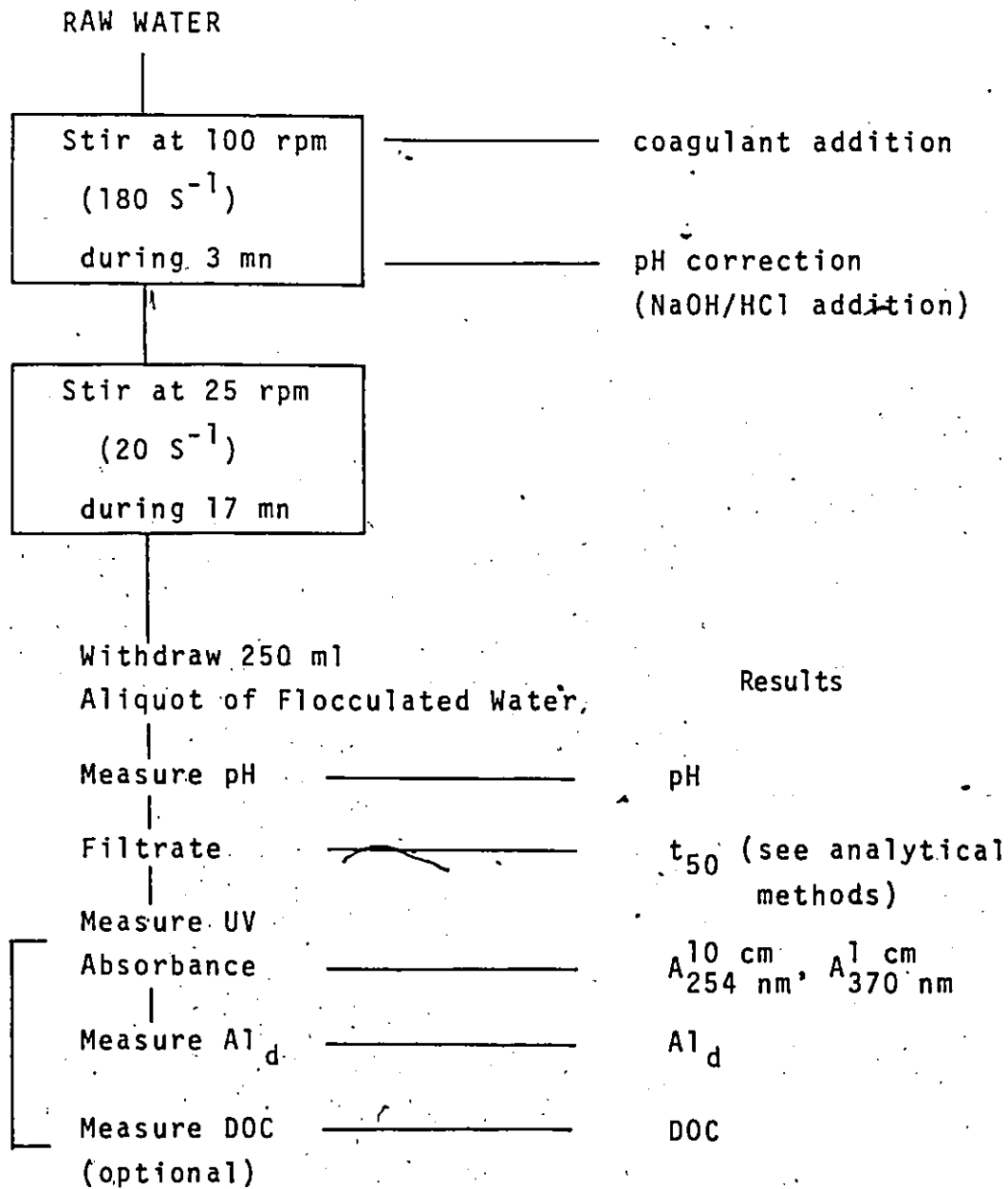
##### 4.4.1 Reversibility

The reversibility of the organic removal was assessed by treating a 200 ml aliquot of FRW and a 200 ml of Blank with 0.3 mM/L of Alum at pH ca 6.5 in 250 mL closed polyethylene bottles designed for centrifugation. The stirring was done using a magnetic stirrer, following the time schedule of the Jar Test. After the slow stirring period, the magnets were removed, and the samples were centrifuged during 5 min. at 5000 g.

The supernatant from the FRW was removed from its bottle and tested for UV absorbance and pH, and the result-



Figure 4.1 Jar Test Time Frame.



ing floc was dispersed in the supernatant from the Blank. Another 200 mL aliquot of FRW was contacted with the floc issued from the Blank, and adjusted for pH. The stirring and centrifuging schedule was applied on the two containers, and the resulting supernatants were tested for UV Absorbance and pH.

#### 4.4.2 Kinetics

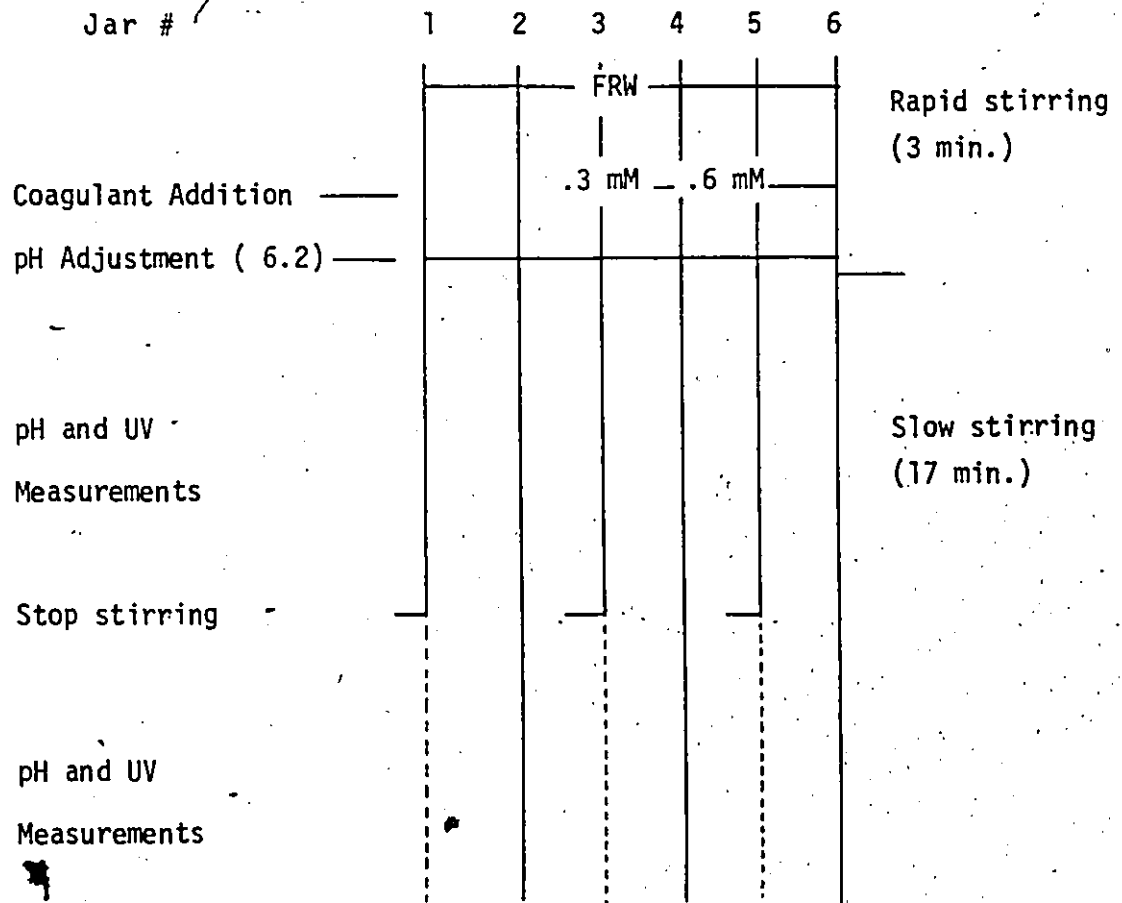
The kinetics of the interaction between FA and Alum was assessed on FRW, using a modified Jar Test schedule as shown in Figure 4.2. The pH and the UV Absorbance were measured on 40 ml aliquots of flocculated or settled water. Three jars out of six were kept under slow stirring in order to assess separately the influence of atmospheric CO<sub>2</sub> transfer on the quality of the treated water, as stirring favours this transfer by surface renewal.

The pH and UV Absorbance could not be measured before 3mn, due to the time required for sample preparation.

#### 4.4.3 Double Treatment

These experiments were performed in two steps. The first step was a standard Jar Test, to which a one hour settling period was added. The second step was performed on 500 mL aliquot of settled water resulting from the first step. The flocculation period was shortened to 5 min in

Figure 4.2 Modified Jar Test Schedule  
for the Kinetic Experiment.



order to simulate filtration contact time.

#### 4.5 Analytical Methods

##### 4.5.1 Equipment

- (i) The light absorption measurements were performed on a Bausch and Lomb Spectronic 21\* equipped with a special measurement compartment for holding 10 cm pathlength cells. Absorbance was measured with respect to a matched empty cell, using either 1 cm square quartz cells or 10 cm cylindrical quartz cells.
- (ii) The pH was measured with an Orion Research Model 601 pH meter\*\* equipped with a combined Electrode Orion Model 91-05. The standardization was made daily with colourkey buffers pH standards at 7.00, 4.00 or 10.00 according to the expected pH range.
- (iii) The DOC measurements were performed on a Dohrmann DC-54 Ultralow level TOC Analyzer\*\*\*. The standardization was systematically made using 2.00 mg/L TOC solutions of Potassium Phtalate, prepared by dilution of 200.0 mg/L Stock Potassium Phtalate solution with DW.

---

\* Bausch and Lomb Co., Baton, N.Y.

\*\* Orion, Cambridge, Mass.

\*\*\* Dohrmann Co., Santa Clara, Cal.

#### 4.5.2 Measurements

- (i) The Alkalinity was measured as the acid requirement to reach pH 4.3. This was estimated by titration of 100 mL aliquots of sample with 0.01 N HCl. This measurement is expressed as meq/L (1 meq/L corresponds to 50 mg/L expressed as  $\text{CaCO}_3$ ).
- (ii) The DOC Content was estimated by a correlation curve between  $A_{254 \text{ nm}}^{10 \text{ cm}}$  or  $A_{254 \text{ nm}}^1$  and corresponding samples tested by direct measurement of the DOC content, picked in such a way that the observed absorbance was covered. Once established, the correlation was checked by random sampling.
- (iii) The Filtration Time ( $t_{50}$ ) was measured as the time required to filter 50.0 ml of flocculated water through a clean 0.45  $\mu\text{m}$  pore diameter membrane under controlled pressure gradient ( $\Delta P = 690$  Torr). This filtration time was then reduced by subtracting the time required to filter 50.0 mL of DW under the same conditions, and expressing the result as sec.  $\text{Mol}^{-1}$  L of precipitated Aluminum. This method is analogous to LaMer's filtration technique. (LaMer, 1956).

(iv) The dissolved Aluminum ( $Al_d$ ) was measured by the Ferron Method (Rainwater et al, 1960). Correction for the sample colour was made by measuring  $A_{370\text{ nm}}^{1\text{ cm}}$  on the sample and DW and subtracting these values corrected for dilution to the mixture (diluted sample and reagent). The calibration curve was checked each time an Aluminum determination was performed, with at least two standards plus a Blank (DW). The detailed analysis procedure is given in Appendix A-1.

CHAPTER 5  
RESULTS AND DISCUSSION

For the sake of clarity, this chapter is focussed on the determination of the ligand number and the precipitate loading, based on the experimental results presented in detail in Appendices A.2 and A.3.

Appendix A.2 reports the results concerning the organics contained in FRW and identifies them as Fulvates, based on their response to acidic treatment, their optical properties, and their titration. Additionally, the correlations found between DOC and  $A_{254\text{nm}}$  suggest that the coagulation process preferentially removes the molecules responsible for this light absorption, thereby confirming the heterogeneity of the natural Fulvates, and the selectivity of the coagulation process suggested by some previous investigations (see Subsection 2.1.3).

Appendix A.3 reports and discusses the basic results of the Jar tests performed on FRW, FDW and Blanks, in terms of residual organics and Aluminum as a function of the coagulant dosage and the operating pH. Also, the visual assessment of the flocculation and the filterability are reported and discussed as general trends with respect to

the operating conditions (coagulant dosage, pH, and type of raw water). These later results are interpreted at the end of the present chapter, with respect to the conclusions on the nature of the mechanism responsible for the organic removal.

## 5.1 Ligand Number and Solubility

### 5.1.1 Calculation of $Al^{3+}$ Activity

$Al^{3+}$  Activity can be calculated on the basis of equation (2.9). As already stated in Section 2.3, the application of this equation to  $Al_d$  needs the assumption that neither polynuclear Al-OH species nor organic complexes exist in measurable amounts at equilibrium. For the Alum runs, the cation  $AlSO_4^+$  was added to the mononuclear Al-OH species.

Since equation 2.9 is written for activities, corrections must be done to account for the ionic strength, which necessitate to calculate this parameter. This ionic strength being a function of the concentration of all ionic species, further information is needed on the ionic content of the raw water, as all the additions (coagulants and titrants) are known.

An analysis of Fauquier water sampled at the same time as the water used in this study showed negligible



amounts of the major expected elements, and potentially interfering ions, i.e.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe(II)}$  and  $\text{Fe(III)}$ ,  $\text{Al(III)}$  and  $\text{F}^-$  (Zenon, 1983).

The Alkalinity was assumed to be due to carbonic species only, and the compensating cation was assumed to be  $\text{Na}^+$ , the analysis of which is not reported in the above investigation. This led to include in the calculation the speciation of carbonic species as a function of pH. Therefore, the necessary inputs are:

- (i) initial Alkalinity (mM/L)
- (ii) Coagulant Nature (Alum,  $\text{AlCl}_3$ , Alpol, Algel)
- (iii) Coagulant Dosage (mM/L)
- (iv) Titrant nature and dosage (HCl, NaOH, in mM/L)
- (v) pH
- (vi)  $\text{Al}_d$  (mM/L)

At equilibrium, the species taken into consideration are:

$\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$ ,  $\text{Al(OH)}_2^+$ ,  $\text{Al(OH)}_3$ ,  $\text{AlSO}_4^+$ . The sum of their concentrations represents  $\text{Al}_d$ .

$\text{H}^+$  and  $\text{OH}^-$ , calculated from the pH  
 $\text{SO}_4^{2-}$ , introduced as Alum. This anion is actually distributed between  $\text{SO}_4^{2-}$  and  $\text{AlSO}_4^+$ .  $\text{SO}_4^{2-}$  was assumed completely dissociated within the operating pH range.

$\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{=}$ , whose the sum of the concentration corresponds to the Alkalinity. The  $\text{CO}_2$  release was assumed negligible for the period of investigation.

$\text{Na}^+$ ,  $\text{Cl}^-$ , introduced by the coagulant and the titrants.

All these ionic species, except  $\text{Na}^+$  and  $\text{Cl}^-$  must be calculated as concentrations and activities, in order to evaluate the ionic strength. This is necessary since no conductivity measurements are available. The ionic strength is evaluated as

$$\mu = \frac{1}{2} \sum_i C_i z_i^2$$

where  $C_i$  = concentration of the ion  $i$ .

$z_i$  = charge of the ion  $i$ .

Activities and concentrations are related to each other by the equation:

$$A_i = f_i C_i$$

where  $A_i$  = activity of the ion  $i$  (noted with square brackets)

$f_i$  = activity coefficient

$C_i$  = (concentration of the ion  $i$  (noted with parenthesis).

$f_i$ 's are evaluated by the Debye-Hückel relationship:

$$\log f_i = - \frac{0.5 z_i^2 \sqrt{\mu}}{1 + 0.3 r_i \sqrt{\mu}}$$

where  $\mu$  and  $z_i$  are already defined.

Table 5.1: Characteristics of the Ions  
Used in the Calculation of  
the Activity of  $\text{Al}^{3+}$ , (after  
Truesdell et al, 1974)

Species	Charge $z_i$	Hydrated radius $r_i^0$ (Å)
$\text{Al}^{3+}$	3	9
$\text{AlOH}^{2+}$	2	5.4
$\text{Al(OH)}^+$	1	5.4
$\text{Al(OH)}_4^{2-}$	-1	4.5
$\text{AlSO}_4^+$	1	5.4
$\text{SO}_4^{=}$	-2	5
$\text{H}^+$	1	9
$\text{OH}^-$	-1	3.5
$\text{HCO}_3^-$	-1	5.4
$\text{CO}_3^{=}$	-2	5.4

$r_i$  is the "hydrated radius" of the ion  $i$ .

This relationship is suggested by many authors (Adamson, 1973; Truesdell et al, 1974; Lindsay, 1979). In this investigation, Truesdell's values for  $r_i$ 's were taken as consistent with most of the published data. They are given in Table 5.1.

The equations used in the computation of the activity of all the ions are as follows:

(i) Water Dissociation:

$$[H^+] = 10^{-pH} \quad (5.1)$$

$$[OH^-] = 10^{-14}/[H^+] \quad (5.2)$$

(ii) Carbonic Equilibrium:

$$[H_2CO_3] = Al_k / \left( 1 + \frac{k_{HCO_3}}{[H^+] f_{HCO_3}} + \frac{k_{CO_3}}{[H^+]^2 f_{CO_3}} \right) \quad (5.3)$$

$$[HCO_3^-] = [H_2CO_3] k_{HCO_3} / [H^+] \quad (5.4)$$

$$[CO_3^{2-}] = [H_2CO_3] k_{CO_3} / [H^+]^2 \quad (5.5)$$

(iii) Aluminum Containing Species:

$$[Al^{3+}] = Al_d / \left( \frac{1}{f_{Al^{3+}}} + \sum_{i=1,2,4} \frac{k_{1,i}}{[H^+]^i f_{Al(OH)_i}} + \frac{k_{AlSO_4} [SO_4^{2-}]}{f_{AlSO_4}} \right) \quad (5.6)$$

for  $i = 1, 2$  and  $4$ :

$$[Al(OH)_i^{(3-i)+}] = [Al^{3+}] k_{1,i} / [H^+]^i \quad (5.7, 5.8, 5.9)$$

$$[\text{AlSO}_4^+] = k_{\text{AlSO}_4} [\text{SO}_4^{2-}] [\text{Al}^{3+}] \quad (5.10)$$

(iv) Sulfate Distribution:

$$[\text{SO}_4^{2-}] = f_{\text{SO}_4^{2-}} ((\text{SO}_4)_T - [\text{AlSO}_4^+] / f_{\text{AlSO}_4}) \quad (5.11)$$

where  $(\text{SO}_4)_T$  = Total Sulfate introduced  
as Alum.

These 11 relationships constitute a complete set of equations that fully specify the chemical system. Since the ionic strength is calculated, and since the Sulfate may be involved, a computer program is necessary to solve these equations. This program proceeds by successive approximations of the ionic strength, and if necessary, of  $\text{SO}_4^{2-}$ . The values of the mass action law coefficients used in this calculation are given in Table 5.2.

An extra equation was introduced in the computation scheme, representing the ionic balance of the solution:

$$\text{IB} = \sum_i z_i C_i \quad (5.12)$$

where IB = ionic balance (algebraic value as meq/L).

$z_i, C_i$  as already defined.

The value of IB should be as close to 0 as possible, and is used as an index of the validity of the assumptions.

The listing of this program is given in the Appendix A.7.

## 5.1.2 Results

The program outputs are presented in Appendix A.4.

Table 5.2 Reactions Accounted for, in the Calculation of the Activity of  $Al^{3+}$ , and Corresponding Mass Action Law Constants

Reaction	k	Source
$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$	$1.02 \cdot 10^{-5}$	May et al (1979)
$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+$	$7.41 \cdot 10^{-11}$	$d^0$
$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + 4H^+$	$6.92 \cdot 10^{-23}$	$d^0$
$Al^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4^+$	$1.62 \cdot 10^9$	Truesdell et al (1974)
$H_2CO_3 \rightleftharpoons HCO_3^- + H^+$	$4.31 \cdot 10^{-7}$	Adamson (1973)
$H_2CO_3 \rightleftharpoons CO_3^{2-} + 2H^+$	$2.41 \cdot 10^{-17}$	$d^0$

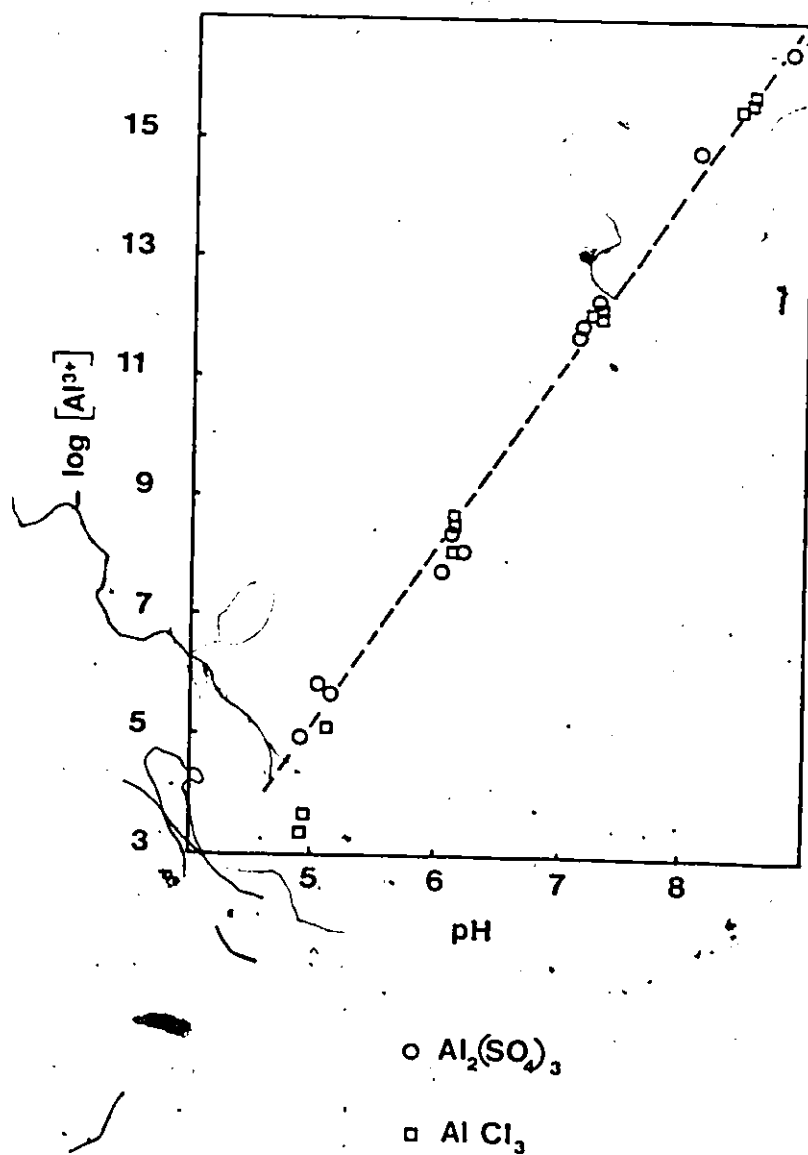


Figure 5.1 =  $-\log[\text{Al}^{3+}]$  as a Function of pH :  
Blank Runs.

A.5 and A.6 for FRW, FDW, and Blank tests respectively. In this section, they are represented graphically in the Figures 5.1 to 5.5 as  $-\log[Al^{3+}]$  as a function of pH. In all cases the resulting slope is very close to 3, thereby suggesting the precipitation of  $Al(OH)_3$ .

(i) Blanks

These experiments represent the baseline of this part of the present investigation. Since organics are not involved, Aluminum fulvate is not expected to precipitate, and the expected value of the OH/Al ratio in the precipitate is 3, unless polymers form or survive in the dilution process, or an Aluminum Hydroxy Sulfate precipitates.

Figure 5.1 shows that for Alum, all the points define a line, the slope of which is 3. This straight line is drawn, and corresponds to a  $k_s$  value ca  $10^{-10}$ . In the subsequent figures, the same line is represented for comparison purpose. In the case of  $AlCl_3$ , this is true for all the experimental points except the 2 highest dosages (0.5 and 1 mM/L) at pH 5.

This suggests that in the absence of organics, Aluminum precipitates as  $Al(OH)_3$  between pH 5 and 8.5. The presence of Sulfate introduced as Alum does not influence the nature of the precipitate (apparently Aluminum Hydroxy Sulfates does not precipitate in these experimental conditions). When Sulfate is not involved, a fraction of



the Aluminum is not removed by filtration at concentrations above 0.1 mM/L, and at pH near 5. This may be interpreted as either the formation of polynuclear Al-OH soluble complexes, or the formation of  $\text{Al}(\text{OH})_3$  in particles which are not removed by membrane filtration (diameter smaller than 0.45  $\mu\text{m}$ ). Both explanations are consistent with the fact that the calculated ionic balance is strongly positive for these experimental points, suggesting an overestimation of the cationic part of the ion population. Interestingly, in the case of Alum, an opposite tendency is observed as, at pH near 5, a mild but definite excess in negative charge is found. This is interpreted as an indirect evidence of the adsorption of  $\text{SO}_4^{2-}$  on the precipitate, helping its aggregation, as suggested by the flocculation pattern which is discussed in Section 5.3.

The case of the two other coagulants is represented in Figure 5.2. In this figure, a dashed line is drawn to represent the line defined by the Alum and  $\text{AlCl}_3$  runs. The calculated points are on that line for pH above 7. If the pH is below this value, there is an important apparent supersaturation with respect to the above defined  $\text{Al}(\text{OH})_3$ . At pH near 5, a high positive excess is found as in the case of  $\text{AlCl}_3$ . On the other hand, at pH 6, the ionic balance displays a mild negative excess. This phenomenon

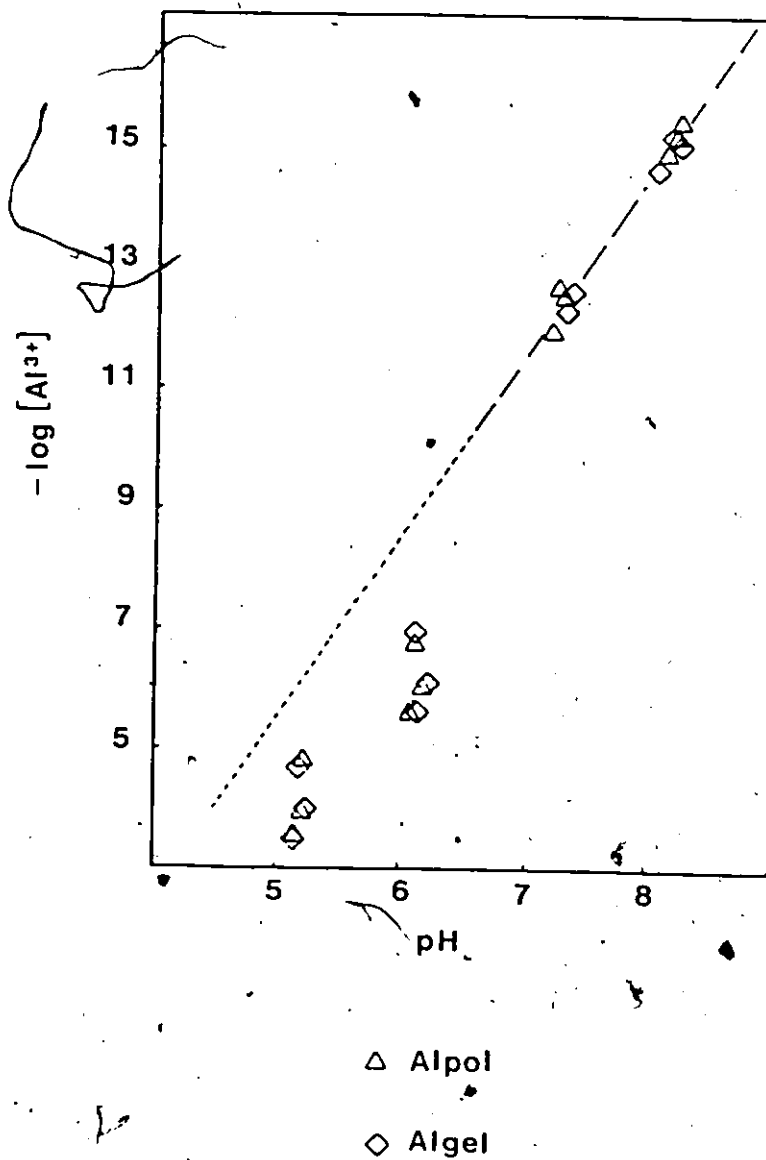


Figure 5.2  $-\log [Al^{3+}]$  as a Function of pH =  
Blank Runs.

remains unexplained.

(ii) FRW and FDW

The results corresponding to the experiments performed as these waters are represented in Figures 5.3 to 5.5. As in the case of the Blank run, the bulk of the calculated values of  $[Al^{3+}]$  define a straight line, the slope of which is near 3.

The same tendencies noted in the Blank runs are found in this set of experiments. However, the excess charges and apparent supersaturations are less important than in the Blanks. The results corresponding to the experiments performed with Alpol and Algel are more scattered, than the rest of the results, and the excess of positive charge at low pH is more frequent than in the results of the other experiments. However, the systematic supersaturation at low pH noted in the Blank runs is less pronounced here. This suggests that the hypothesis made on the influence of Sulfate on the precipitation of the solid phase in the interpretation of the Blank runs may apply also to the influence of Fulvate. This will be discussed further in Section 5.3.1.

The tests on FDW were performed last, while the bulk of the present findings were already established. Therefore, the Al determinations were performed as a verification of these findings, on a limited number of samples.

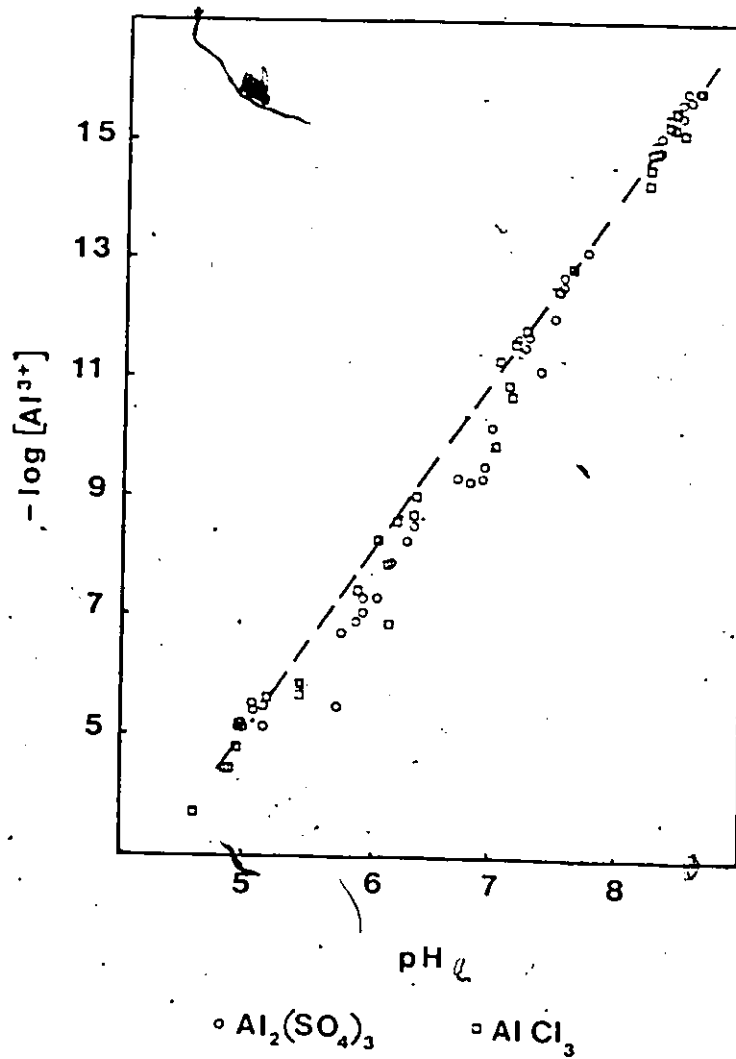


Figure 5.3.  $-\log [Al^{3+}]$  as a Function of pH = FRW Runs.

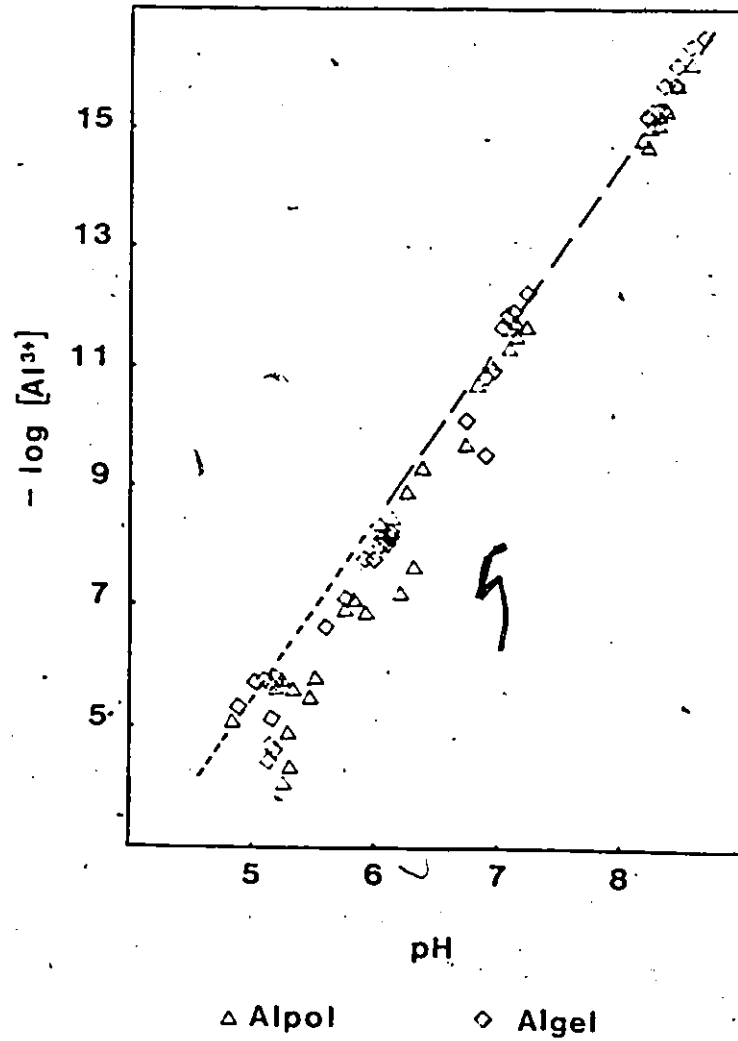


Figure 5.4  $-\log[Al^{3+}]$  as a Function of pH = FRW Runs.

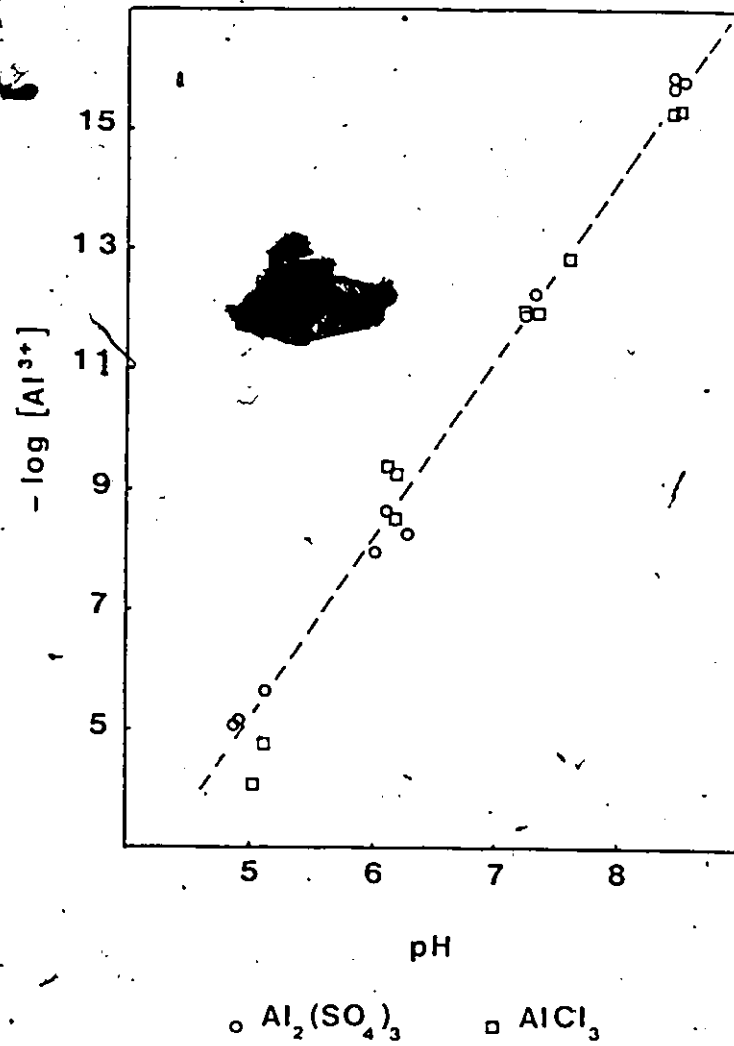


Figure 5.5  $-\log[Al^{3+}]$  as a Function of pH =  
FDW Runs.

As shown in Figure 5.5, these results are in agreement with the rest of the data.

### 5.1.3 Discussion

#### (i) Ligand Number

As suggested in Section 3.2 the ligand number of the precipitate can be estimated by the slope of  $\log[Al^{3+}]$  as a function of pH. This is a consequence of equations (3.3) or (3.5). The linear regression analysis of the data presented in the two former subsections is summarized in the Table 5.3. It shows that  $-\log[Al^{3+}]$  and pH are strongly correlated ( $r > .95$ ) and that in all cases, the value of the slope is very close to 3, thus suggesting that the solid is  $Al(OH)_3$ .

#### (ii) Aluminum Solubility

The solubility of  $Al(OH)_3$  is estimated by the equation (3.5) or more conveniently by its logarithmic expression

$$\log k_s = -\log[Al^{3+}] - 3 \text{ pH.}$$

The averages of these values are presented in Table 5.4. A statistical analysis of these data (ANOVA) shows that they can be grouped into two sets:

- (i) a first set corresponding to all the samples except Alum and  $AlCl_3$  applied on FRW. For

Table 5.3 Slopes and Correlation Coefficients Determined  
by Linear Regression Analysis of  $\log[Al^{3+}]$  vs pH.

		Coagulant			
		Alum	$AlCl_3$	Alpol	Algel
Water					
Blank	Slope	-3.01	-3.10	-3.03	-3.04
	c.c.	.993	.996	.966	.995
FRW	Slope	-3.05	-2.99	-3.21	-3.15
	c.c.	.980	.989	.990	.994
FDW	Slope	-2.99	-3.08	N/A	N/A
	c.c.	.994	.981	N/A	N/A



Table 5.4 Averages of the Ionic Product  $-\log[Al^{3+}] - 3 \text{ pH}$   
as a Function of the Coagulant and the Raw Water

Coagulant		Raw Water		
		Blank	FRW	FDW
Alum	Ave	-9.89	-10.26	-9.870
	S.D.	.337	.524	.293
	n	12	39	12
AlCl <sub>3</sub>	Ave	-9.90	-10.12	-9.978
	S.D.	.212	.406	.558
	n	9	37	12
Alpo1	Ave	-9.49	-9.89	—
	S.D.	.293	.369	—
	n	6	27	—
Alge1	Ave	-9.62	-9.80	—
	S.D.	.103	.422	—
	n	6	32	—

these data, the value of the solubility  $[H^+]^3/[Al^{3+}] = k_{13}$  is  $10^{-(9.838 \pm .07)}$ .

- (ii) The second set corresponding to Alum and  $AlCl_3$  applied on FRW. For these data, the value of  $k_{13}$  is  $10^{-(10.192 \pm .108)}$ .

These values are in very good agreement with the literature. Interestingly, they are located between de Hek's value (De Hek et al, 1978) for amorphous  $Al(OH)_3$ , and Bottero's value (Bottero et al, 1980) for the peptized gel occurring in high OH/Al ratio PAC solutions ( $10^{-9.31}$  and  $10^{-10.3}$  respectively). Since De Hek's gels were washed, this is interpreted as differences in the specific surface area of the elementary  $Al(OH)_3$  particles: the higher the specific surface area, the higher the solubility. The difference of solubility between the two sets defined above is tentatively attributed to a poisoning of the growth of the elementary  $Al(OH)_3$  particles by adsorbed Fulvate molecules, as the higher solubility corresponds to experiments performed on the water containing the most organics. Interestingly, the precipitate issued from the hydrolysis of Alpol and Algel seems to be immune to this effect. This, however, remains unexplained.

## 5.2 Organic Removal

The precipitate being identified as  $Al(OH)_3$  in the

entire domain of experimental conditions, the adsorption hypothesis is most likely to be representative of the organic removal, as pointed out in Chapter 3. Therefore, the organic removal can be investigated in terms of adsorption isotherms, as defined in Section 3.3.2.

### 5.2.1 Isotherms

#### (i) Results on FRW

The results are reported in Figures 5.6 to 5.9, and the isotherms are grouped according to the nature of the coagulant. The general shape of these isotherms is that of a monotonously increasing function, as expected in the Adsorption hypothesis.

The results yielded by Alpol and Algel experiments are definitely typical of Adsorption, as at all pH's, the loading increases smoothly with increasing equilibrium concentration. In the case of Alum and  $AlCl_3$ , this typical behaviour is clear only at pH 8. Interestingly, partial results may suggest a straight reaction at pH near neutral, and for relatively low coagulant dosages, as the isotherms display a very clear horizontal plateau (around  $q = 35$  mg/mM) under these conditions.

On the other hand, high coagulant dosages at pH's below 7 yield very steep isotherms, whose position is pH dependent. Therefore, the most likely mechanism is Adsorp-

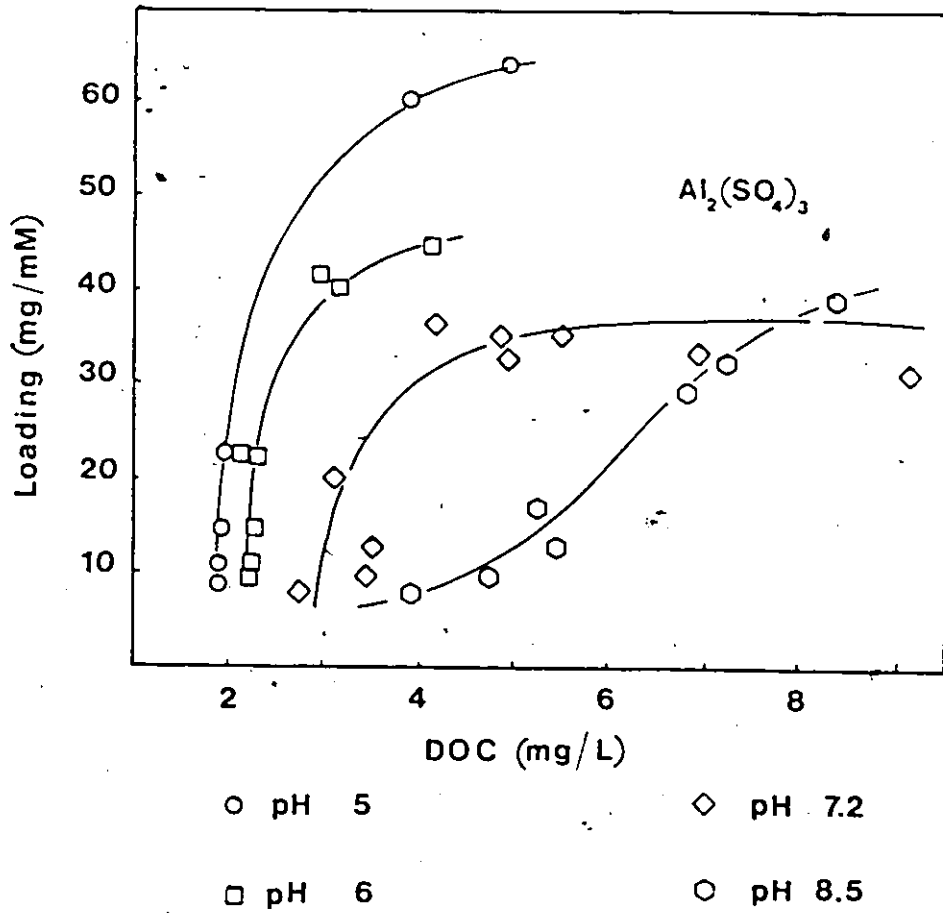


Figure 5.6 Adsorption Isotherms as a Function of pH. FRW-Alum Runs.

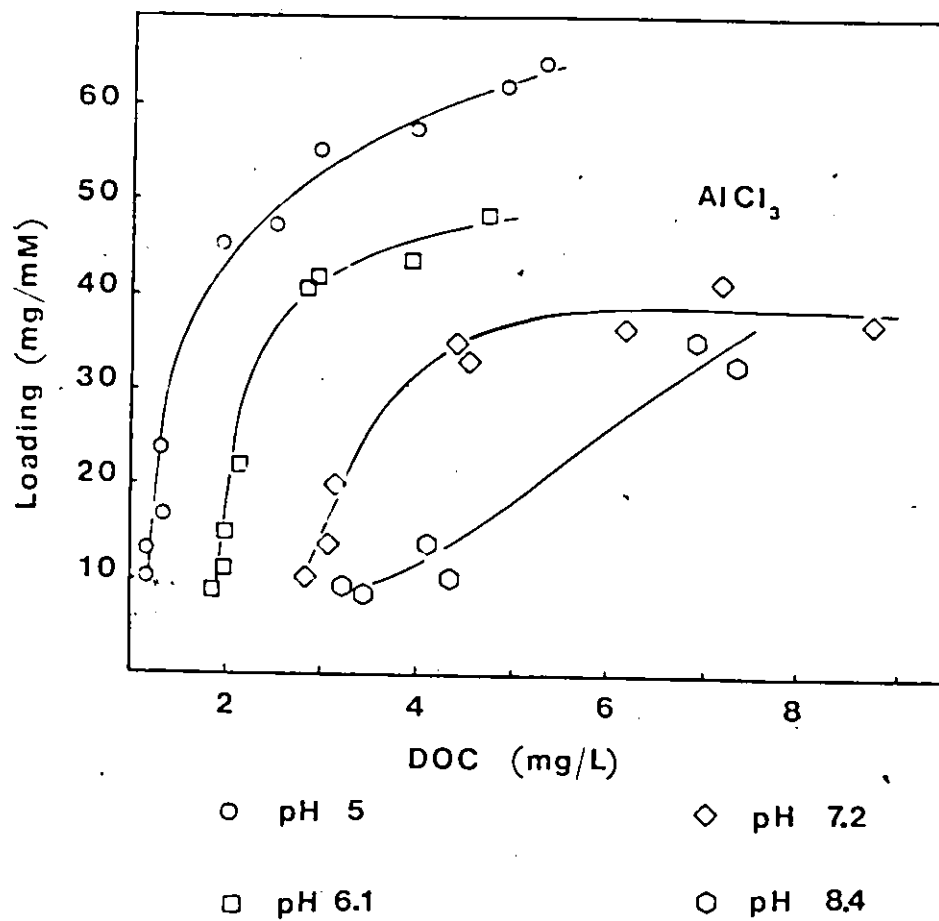


Figure 5.7 Adsorption Isotherms as a Function of pH. FRW- $AlCl_3$  Runs.

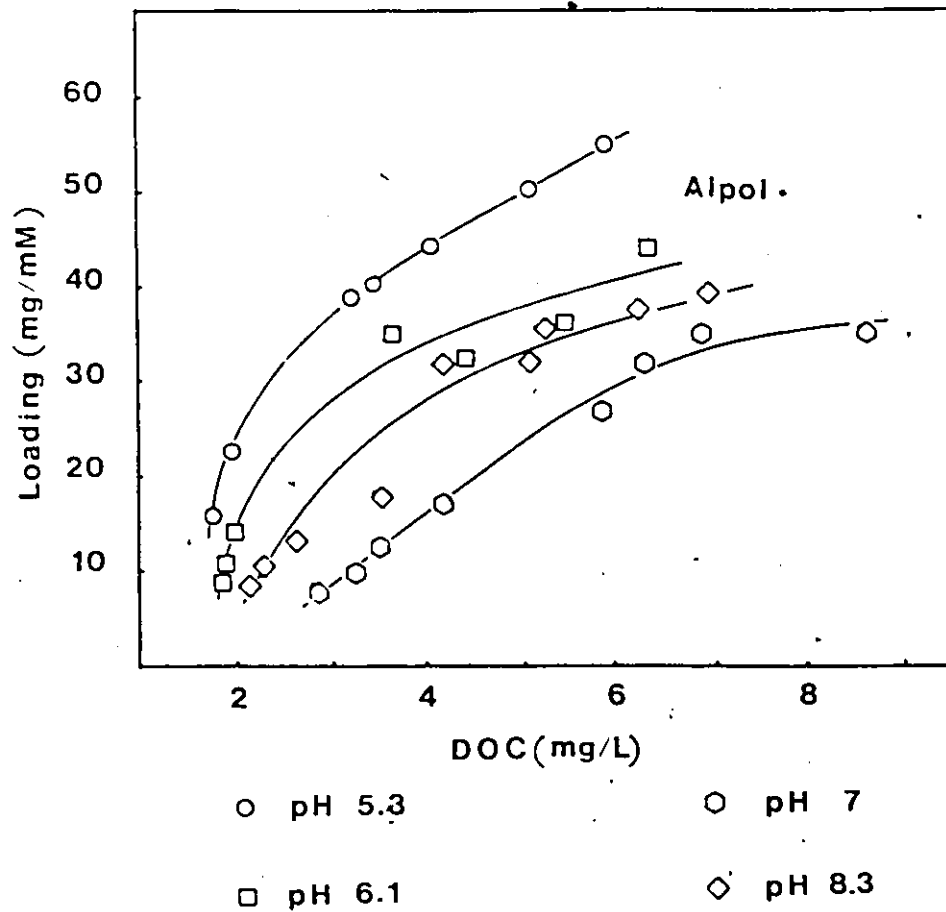


Figure 5.8 Adsorption Isotherms as a Function of pH. FRW-Alpol Runs.

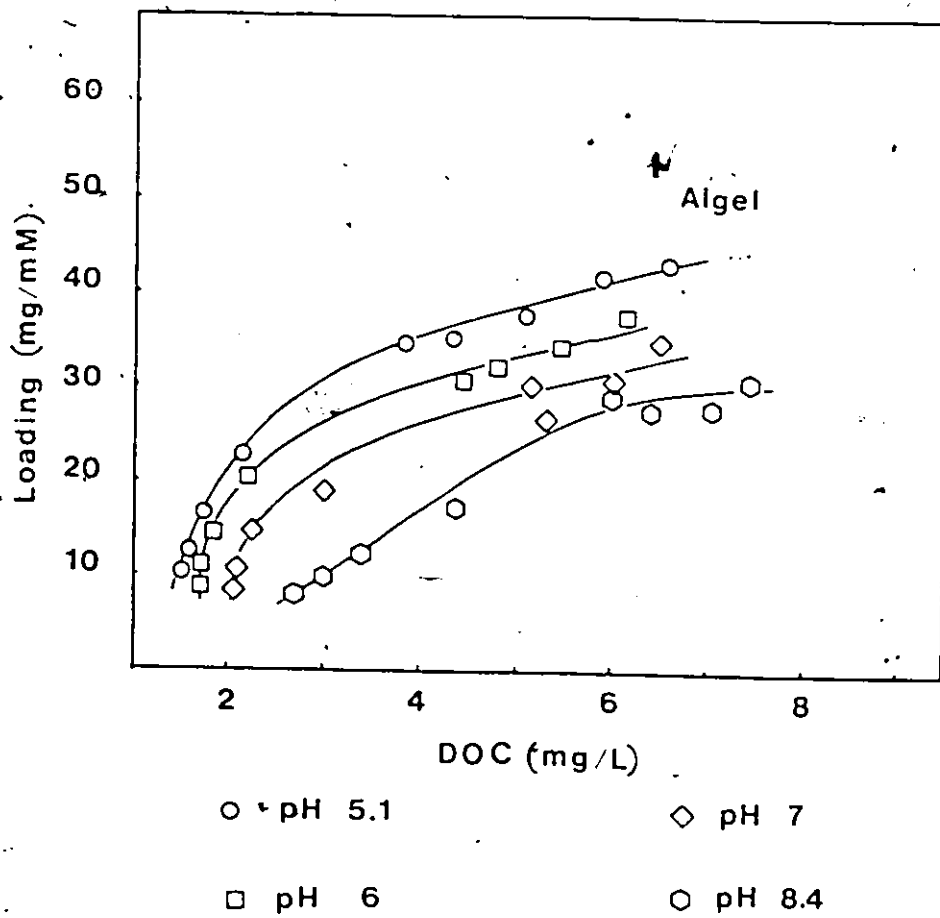


Figure 5.9 Adsorption Isotherms as a Function of pH. FRW-Algel Runs.

tion. However, a set of reactions corresponding to the heterogeneous nature of the Fulvates may also account for the observed behaviour, as suggested by Randtke et al (1981). The latter hypothesis, however, can be discounted in view of the ligand number results.

(ii) Results on FDW

Since the isotherms obtained on FRW with  $AlCl_3$ , Alpol and Algel show essentially similar features, the two latter coagulants were not tested on FDW. On the other hand, the influence of Sulfate was thought to be crucial, based on the wide use of Alum as coagulant. The loadings were estimated by calculating the amount of dissolved Aluminum according to equation (2.9), with the corresponding  $k_s$  values, as previously shown in Table (5.4). This calculation was performed by the use of the program ADSPREC, described in Appendix A-7.

The resulting isotherms are represented in Figures 5.10 and 5.11 where it can be seen that they are almost linear and nearly vertical.

The comparison of the isotherms corresponding to FRW and FDW shows also, that they are not the extension of each other. When comparing the apparent intercept of the isotherm plots with the DOC axis, a fairly good agreement exists between the two sets of experiments in terms of percentage of the initial DOC content. This is shown in



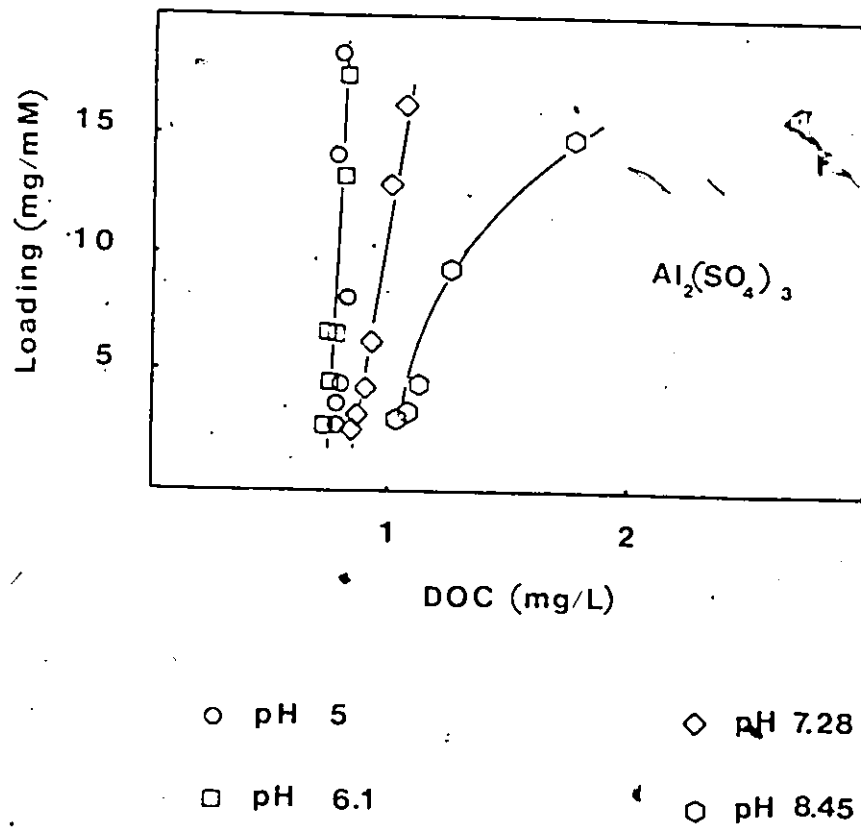
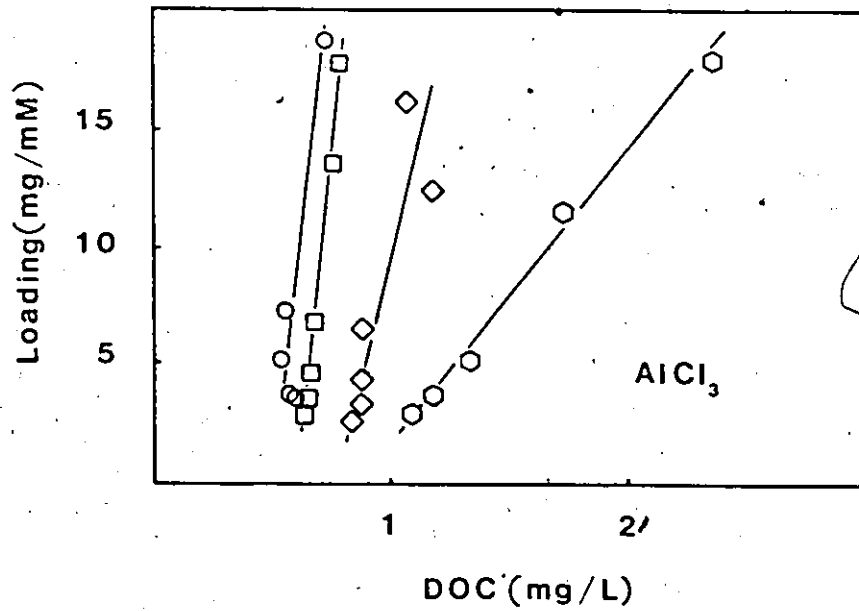


Figure 5.10 Adsorption Isotherms as a Function of pH, FDW-Alum Runs.



○ pH 5.19

◇ pH 7.48

□ pH 6.14

○ pH 8.53

Figure 5.11 Adsorption Isotherms as a Function of pH. FDW- $AlCl_3$  Runs.

Table 5.5 Non-removable Fraction (% DOC<sub>0</sub>) in FRW and FDW, as a Function of the pH and the Coagulant Nature

pH	FRW		FDW	
	AlCl <sub>3</sub>	Alum	AlCl <sub>3</sub>	Alum
5	9.8	17.9	14.6	21.1
6	17.3	21.1	17.6	21.1
7.4	25.6	27	23.4	23.4
8.5	—	—	25	29.3

Table 5.5, and suggests that a part of the initial Fulvate content is insensitive to treatment by coagulation. This is consistent with Babcock et al (1979), who found that the complete removal of Fulvate was not possible. It also confirms the heterogeneity of the natural organics, already suspected from light adsorption data, and from the DOC- $A_{254\text{nm}}$  correlation. Additionally, the presence of Sulfate apparently increases the non-removable fraction of the DOC. This latter point is explained later.

### 5.2.2 Influencing Factors

The adsorption of Fulvates on  $\text{Al}(\text{OH})_3$  is influenced by three factors affecting the shape and position of the isotherms, as discussed below.

#### 5.2.2.1 The Influence of pH

The increase in the pH causes the isotherms to be less and less favorable, as the maximum loading drops, and the bottom part of the isotherms shifts towards higher final concentrations. This behaviour is found for all the coagulants. At pH's below 7, the isotherms are characterized by a fairly steep initial slope, and tend to level off for higher concentrations. This tendency extends to pH ca 7, for Alpol and Algel, whereas a well defined plateau is

displayed by Alum and  $AlCl_3$ .

At a pH of approximately 8.4, all the coagulants show very similar isotherms, both in shape (quasi linear) and in position.

#### 5.2.2.2 The Influence of Sulfate

This ion influences the bottom part of the isotherms. Its influence is less and less marked with increasing pH and increasing final DOC concentration. Since higher final concentrations are reached with lower coagulant dosages, the effect of Sulfate seems quantitative, the more Sulfate introduced as Alum, the wider the deviation from  $AlCl_3$  results. Therefore, there must be a competitive effect due to Sulfate, as the organic loading gets lower with increasing  $SO_4^{2-}$ . In order to verify more specifically this important point, a special experiment was performed, using an equal amount of coagulant (0.5 mM/L) and the same pH (6.05), but varying the amount of introduced Sulfate from 0 (pure  $AlCl_3$ ) to 1.5 meq/L (pure Alum), by the use of mixtures of  $AlCl_3$  and  $Al_2(SO_4)_3$ . The results of this experiment are reported in Figure 5.12, as the remaining DOC as a function of the  $SO_4/Al$  ratio. This experiment shows clearly a quantitative effect as opposed to a threshold effect, thereby confirming the idea formulated earlier, of a competition between  $SO_4^{2-}$  and FA for adsorption

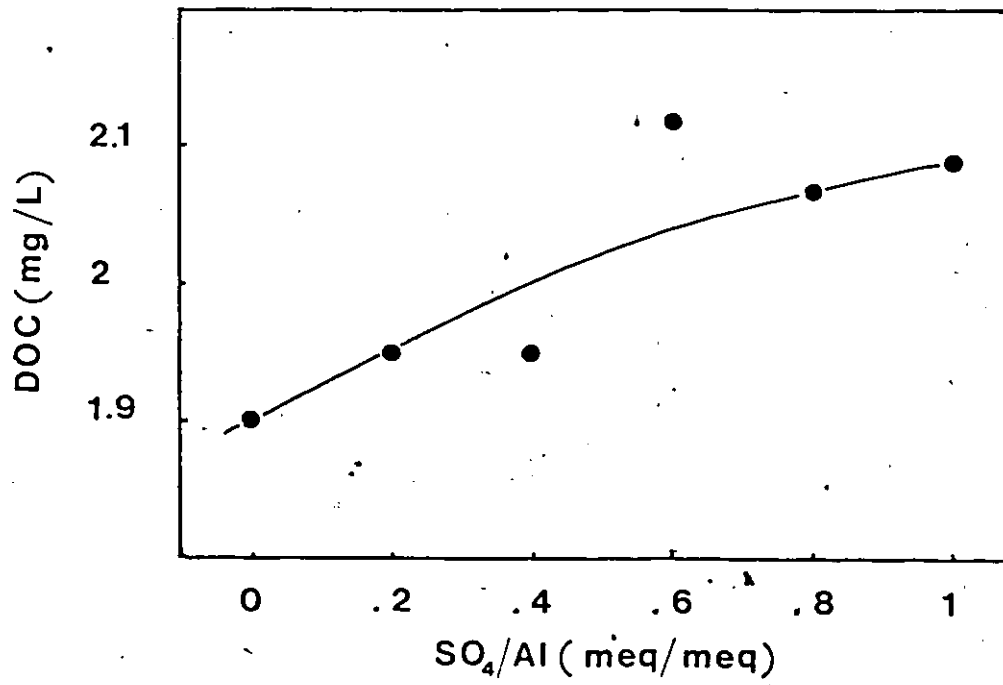


Figure 5.12 Influence of  $\text{SO}_4^{2-}$  on the Residual Organics. Al dosage = 0.5 mM/L.

sites. This should be calculatable by a quantitative adsorption model.

#### 5.2.2.3 The Influence of the OH/Al Ratio

An increase in the OH/Al ratio tends to lower the loadings at low pH's. At pH near neutral, the isotherms become more linear, as the high loadings become lower and low loadings become higher with increasing OH/Al ratio. At pH near 8, the OH/Al ratio has no effect on the isotherms.

#### 5.2.3 Discussion

The findings presented so far in this chapter strongly suggest that the mechanism of removal of Fulvates by the coagulation process is Adsorption, as the precipitate has the solubility of  $Al(OH)_3$ , and the Fulvate solid concentration is a monotonously increasing function of the liquid Fulvate concentration. In order to quantify this adsorption, the reversibility of the removal and its kinetics must be assessed in order to confirm the equilibrium hypothesis required for the validity of the equilibrium equations.

##### 5.2.3.1 Reversibility

An experiment was run according to the method described in Section 4.4. The results are reported in Table

5.6. The loading of the floc obtained by treating FRW and subsequently exposed to DW was calculated by assuming that DW does not contain organics, and by assuming that the  $A_{284\text{nm}}^{1\text{cm}}$  - DOC correlation is valid.

The loadings reported in Table 5.6 are calculated by mass balance:

$$q = q_0 + \frac{\text{DOC}_o - \text{DOC}_e}{Al_p} \quad (5.13)$$

where  $q$ ,  $\text{DOC}_o$  and  $\text{DOC}_e$  are as defined previously.

$q_0$  is the initial loading of the floc when exposed to distilled water.

$Al_p$  is the Aluminum involved in the precipitate.

When FRW is treated with Alum,  $q_0$  is set to 0, and the resulting loading is calculated according to equation (3.4). When the floc is exposed to either DW or FRW,  $Al_p$  is set to the amount of floc added per volume of water, and equation (5.13) is applied algebraically.

In the experiment referred to as "DW + loaded floc",  $q_0$  is set to 25.4, and  $Al_p$  to .3, as the floc used in this case comes from FRW + .3 mM/L, whereas in the experiment entitled "FRW + unloaded floc",  $\text{DOC}_o$  is set to 9.91,  $Al_p$  to .3, and  $q_0$  to 0.

Accounting for these assumptions and the non-removable fraction of the organics which remains in treated FRW, the release of organics by the floc into the distilled water



Table 5.6 Results of the Reversibility Experiment, Using Alum as Coagulant.

	FRW	FRW +.3 mM/L	DW + Loaded Floc	FRW + Unloaded Floc
DOC(mg/L)	9.91	2.29	1.55	6.58
pH	8.01	6.53	7.0	6.46
Loading (mg/mM)	—	25.4	20.2	11.1

is quite substantial. Actually, the theoretical loading corresponding to the final pH and organic concentrations is around 25 mg/mM; and the pH change may account for ca 1 mg/L of organics released in the water, due to the increase in the non-removable fraction with increasing pH. This suggests that the removal is reversible. This experiment also indicates that the unloaded precipitate can adsorb part of the organics. However, the extent of this adsorption is much smaller than what is observed when the precipitate is formed in situ. This difference could be due to specific surface area differences.

#### 5.2.3.2 Kinetics

The results of the kinetic experiment described in Subsection 4.2.2 are reported in Figures 5.13 to 5.15. The organic removal is completed within 3 mn after the addition of the coagulant. After that time, the remaining organic concentration is stable up to 200 mn in settled waters, whereas a tendency to an increase in residual organics is detected if the stirring is not stopped. This increase corresponds to an increase in pH, detected in all stirred samples, including acidified FRW. The increase in residual organics is therefore attributed to the increase in pH. This latter trend is in turn, attributed to a better exchange with atmospheric CO<sub>2</sub> due to the surface renewal

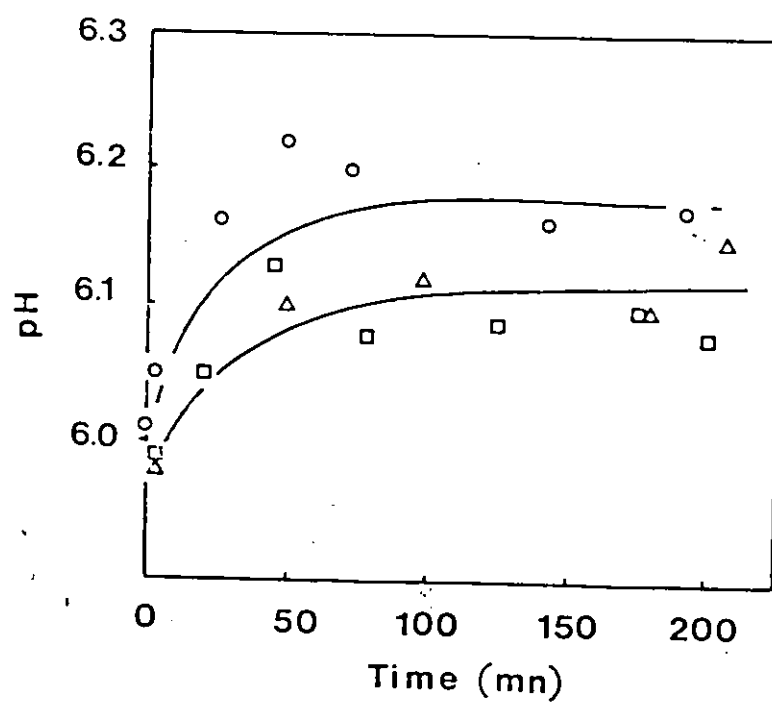


Figure 5.13 pH as a Function of Time.  
Mixing Time = 20 mn. Open circles = FRW;  
Open Squares = FRW + .3 mM/L Alum.  
Open Triangles = FRW + .6 mM/L Alum.

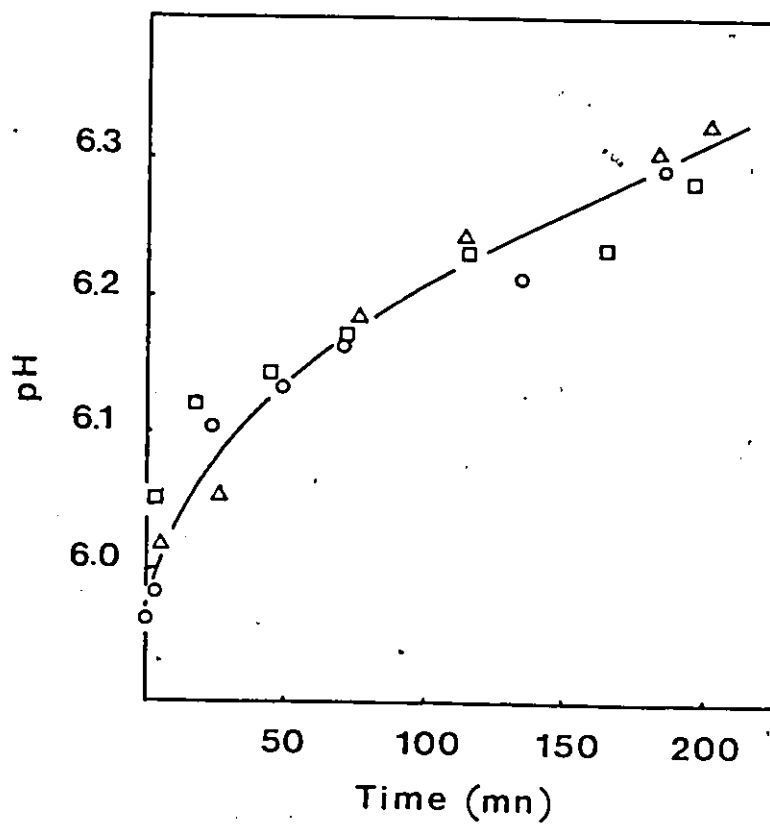


Figure 5.14 pH as a Function of Time.  
Mixing Time = 200 mn.  
Open Circles = FRW:  
Open Squares = FRW + .3 mM/L Alum.  
Open Triangles = FRW + .6 mM/L Alum.

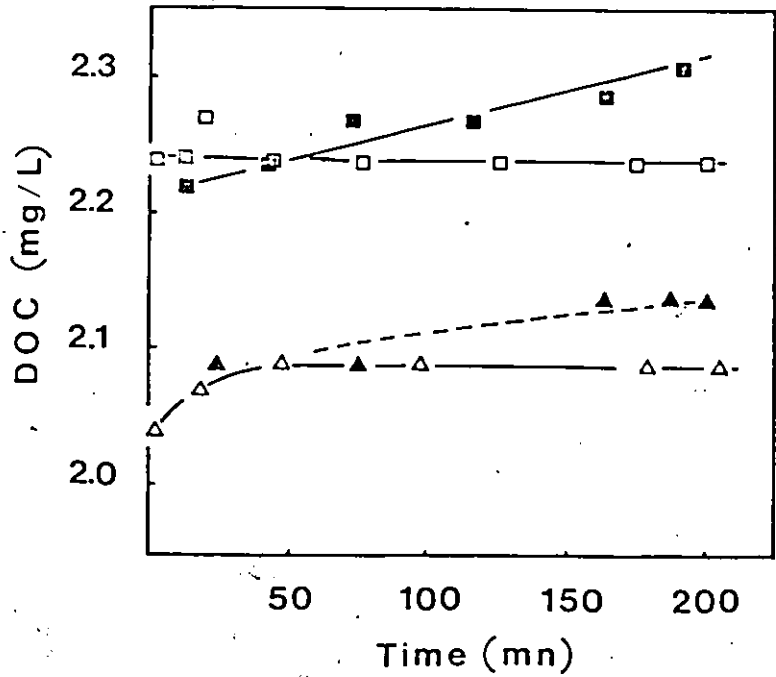


Figure 5.15 DOC as a Function of Time.  
 Squares = FRW + .3 mM/L Alum.  
 Triangles = FRW + .6 mM/L Alum.  
 Open symbols = 20 mn Mixing Time.  
 Solid symbols = 200 mn Mixing Time.

caused by the stirring. This drift in the pH values was already detected by Sommens et al (1980) who also attributed this pH drift to the transfer of atmospheric  $\text{CO}_2$  into their samples. This experiment was repeated at pH 5.3, 7.0 and 8.1, and in all these cases, the organic removal was completed within 3 mn.

The two specific points discussed above (Reversibility and Kinetics) show that Fulvate adsorption is a reversible equilibrium, and that the overall rates of removal (precipitation of  $\text{Al}(\text{OH})_3$  and adsorption combined) is very high.

These conclusions allow one to proceed to mathematical modelling on the basis of the experimental data available that can be assumed to represent equilibrium.

#### 5.2.4 Tentative Modelling

Ideally, the Adsorption model should account for the influences of the pH and the Sulfate content. Among the different models available, those which rely on surface ionization (Healy, 1971; Davis et al, 1978a) are quite appealing, as they account for the influence of pH. Davis' model, which was developed for oxide surface assumes also the formation of chemical surface complexes. The equations describing this model have been presented in Section 3.3.2.

For the present case, this model is attractive since

it accounts for the influence of pH, the influence of  $\text{SO}_4^{=}$ , and their interplay. However, it is quite complicated for application purposes. Also, the determination of the different constants ideally requires a multiresponse type of experimental design, which was not planned in this research.

A simplified version (equation 3.25), neglecting the potential terms  $\psi_i$ , was tried, using single response, linearizing the resulting equation for the loading, and applying multi-parameter linear regression techniques. It was assumed that the non-adsorbable fraction was pH independent, but possibly different from one coagulant to the other, thereby accounting for differences in the surface structure. The resulting coefficients yielded a very poor fit, and this model was discarded as not "fittable" within the present experimental design. Its potential value is nonetheless acknowledged, and should be evaluated in a later research. It is believed that the non-adsorbable fraction, and its possible pH dependency should also be researched further, as a potential cause of the failure in the application of Davis' model. Furthermore, the heterogeneity of Fulvates probably complicates the formulation of the isotherm equation, thereby contributing to the lack of fit mentioned earlier.

Equation (3.11) is next most likely model, using two components. The format of this equation does not account for the influence of pH. Therefore, the parameter estimation

must be performed at constant pH. The evolution of the values of the parameters with respect to pH is discussed below.

Since this expression is not linearizable, a non-linear parameter estimation routine had to be used. Also, since this expression does not account for the influence of pH, the estimation of the parameters was performed for each pH range (5, 6, 7.4, 8.5). The values corresponding to the influence of Sulfate were estimated with the assumption that the parameter values for the adsorption of Fulvates were those found for  $AlCl_3$  in similar pH conditions. This technique is very approximative, as ideally, these parameters should be estimated together with the Fulvate adsorption data and a response corresponding to an independent assessment of the Sulfate adsorption. Therefore, the same problem, already mentioned for Davis' model, is once again encountered.

The parameter estimates are reported in Table 5.7. For all coagulants, the value of  $q_{max}$  decreases with increasing pH, when this latter variable is below 8. This parameter is proportional to the specific surface area, and therefore, the trend suggested by Bottero (1981) and mentioned in Section 2.4.2, is confirmed. However, when the pH reaches 8, the value of  $q_{max}$  is much higher. Actually, this corresponds to quasi linear isotherms (see Figures 5.6 to 5.9), which suggest a drastic change in adsorptive pattern. This would be consis-



Table 5.7 Parameter Estimates for the Fulvate Adsorption Data

Coagulant	pH	$q_{\max}$	$k_{FA}$	$n_{FA}$	$k_{SO_4}$	$n_{SO_4}$	$C_{nads}$
AlCl <sub>3</sub>	5	71.4	1.55	1.15	—	—	1.01
	6.1	48.3	3.37	2.34	—	—	1.59
	7.2	42.8	1.24	1.61	—	—	2.42
	8.4	68.1	.083	1.56	—	—	2.09
Alpol	5.3	99.7	.423	.663	—	—	1.44
	6.1	39.3	3.35	1.04	—	—	1.79
	7.0	50.5	.115	1.93	—	—	.84
	8.3	108.	.051	1.33	—	—	1.49
Algel	5.1	87.	.416	.516	—	—	1.41
	6.0	72.8	.442	.583	—	—	1.48
	7.0	68.0	.332	.657	—	—	1.71
	8.4	158.	.124	.433	—	—	2.84
Alum	5.0	71.4	1.55	1.15	5.12	1.35	1.01
	6.0	48.3	3.37	2.34	1.77	2.98	1.59

tent with a change in the nature of either the adsorbent or the adsorbate. Interestingly, May et al (1979) suggest that for pH values above 7, Gibbsite is no longer stable, and undergoes reorganization yielding Boehmite. The amorphous gel formed by rapid precipitation, as it is the case in the present study may be influenced in a similar way, having therefore quite different surface properties if the pH is high enough. The behaviour of the other coefficients and their physical meaning remain unclear.

### 5.3 Practical Implications

#### 5.3.1 Double Treatment

The fact that the removal of Fulvates is caused by an Adsorption rather than by a reaction has an interesting consequence in terms of Treatment Strategy.

The dosage requirement to reach a predetermined target concentration can be calculated from the isotherm equation. Neglecting the effect of the pH and the solubility of the solid phase, the isotherm equation is:

$$(C_0 - C_e)/Dose = f(C_e) \quad (5.14)$$

where  $C_0$  = initial concentration

$C_e$  = target or equilibrium concentration

Dose = coagulant dosage

$f(C_e)$  = analytical expression of the Isotherm such as Equation 3.11 in the present case. Its form will not be

detailed here for the sake of simplicity. Therefore, the dose requirement is:

$$\text{Dose} = (C_0 - C_e)/f(C_e) \quad (5.15)$$

$f(C_e)$  is a monotonously increasing function of  $C_e$ , which is unfavorable since the dose requirement increases faster than in the case of a stoichiometric requirement. On the other hand, this same property allows to get a better quality of treated water, or alternatively to lower the coagulant dosage, by splitting the coagulant on two successive separation operations, for instance settling and filtration.

Given a target concentration  $C_e$ , the requirement is given by the equation (5.15). If an intermediate stage is set up, and a lower dosage is applied, yielding a more concentrated effluent, say at the concentration  $C_1$ , located between  $C_0$  and  $C_e$ , the corresponding dosage is:

$$\text{Dose}_1 = (C_0 - C_1)/f(C_1) \quad (5.16)$$

In the second treatment step, a dose requirement  $\text{Dose}_2$  must be applied such that

$$\text{Dose}_2 = (C_1 - C_e)/f(C_e) \quad (5.17)$$

Summing equations (5.16) and (5.17).

$$\text{Dose}_1 + \text{Dose}_2 = (C_0 - C_1)/f(C_1) + (C_1 - C_e)/f(C_e) = \text{Dose}_3$$

and  $\text{Dose}_3$  is necessarily smaller than the nominal dose  $(C_0 - C_e)/f(C_e)$  since  $f(C_1)$  is greater than  $f(C_e)$ , and therefore,  $(C_0 - C_1)/f(C_1)$  is smaller than  $(C_0 - C_1)/f(C_e)$ .

It can be shown that the shape of the Isotherm as well as the splitting ratio influence the efficiency of the double treatment process. Interestingly, the recycling of the used adsorbent is beneficial only if the adsorption is irreversible. This explains why Semmens et al (1980) did not find any beneficial effect of the sludge recycling, since, according to the present work the adsorption is reversible.

The double treatment constitutes also an experimental test for the Adsorption Hypothesis as Adsorption is the only mechanism allowing a beneficial effect of this strategy. In the case of a reaction, or a set of reactions, a double treatment is bound to fail, i.e., no beneficial effect is expected.

Five experiments were performed, according to the procedure presented in the Section 4.4. In these experiments, the coagulant nature and nominal dosage, as well as the operating pH were varied. The results are reported in Table 5.8.

All the treatments performed at pH 6 show marginal improvements in the quality of the treated waters when a double treatment procedure is followed. These results are consistent with Semmens' results (Semmens et al, 1980) who also tried a double treatment procedure, at pH ca 5. This

Table 5.8 Double Treatment Experiments

Run #	Coagulant Nature	Dosage mM/L	pH	DOC** mg/L	Remarks*
1	Alum	.3	5.96	2.31	Reference 1
		.2	6.30	3.03	Interim 1
		.1	6.03	2.22	Result 1
2	Alum	.6	6.30	2.22	Reference 2
		.4	5.74	2.36	Interim 2
		.2	6.16	2.14	Result 2
3	Alum	.6	7.35	3.43	Reference 3
		.4	7.17	3.84	Interim 3
		.2	7.26	3.01	Result 3
4	Alum	.6	8.33	4.72	Reference 4
		.4	8.24	5.00	Interim 4
		.2	8.26	3.97	Result 4
5	AlCl <sub>3</sub>	.3	6.14	2.24	Reference 5
		.2	6.48	3.13	Interim 5
		.1	6.06	2.22	Result 5

\* Reference run = Standard treatment dosage (1 step)  
 Interim run = Result of the 1st step in the 2nd step treatment  
 Result run = Result of the completed double treatment

\*\* As measured by UV Adsorbance.

author actually concluded that no improvement at all was brought by the double treatment.

On the other hand, the run performed at pH near 7 and 8 (run 3 and 4) show a definite improvement of the quality of the treated water, brought by the double treatment (12% and 16% respectively). This is explained by the differences in the slopes of the isotherms. At pH 5 and 6, the isotherms are quasi vertical, whereas at pH 7 or 8, the isotherms have a much gentler slope. In other words, at pH 5 or 6, an increase in the treatment dosage does not improve the quality of the treated water as much as at pH 7 or 8. This is probably the reason for Semmens' negative conclusions of double treatment.

In practice, lowering the pH may not be desirable, as corrosion problems are likely to occur in the reactors and the piping. Since a standard treatment plant includes generally a coagulation - flocculation process followed by settling and filtration, a double treatment is easily feasible. Furthermore, the recycling of the backwash waters would provide additional suspended material, thereby possibly helping the settling step. It is also possible that the floc from this second step adsorbs some of the organics of the raw water, since its own loading is likely to be quite low.

The testing of this possibility requires a pilot

study, not feasible within the scope of this investigation, but certainly worth trying.

If such a process is feasible and efficient, it may be an interesting alternative to more sophisticated, more expensive methods of the Fulvate removal such as the ozonation and/or Activated Carbon Filtration.

### 5.3.2 Precipitate Separability

The flocculation patterns presented in Appendix A-3 suggest that Fulvates and Sulfate widen the flocculation domain towards low pH's. The effect of Fulvate is quantitative, as the flocculation domain is larger with increasing initial Fulvate content. This phenomenon can be interpreted as a cross linking effect of the Fulvate whereby this compound act as a flocculant for the elementary particles of  $Al(OH)_3$  precipitate. This is consistent with the Adsorption hypothesis, and also explains why the presence of Fulvate reduces the apparent Aluminum supersaturation observed at the low end of the pH range, noted in Section 5.1. This effect causes the elementary particles to aggregate, thereby yielding flocs large enough to be removed from the liquid phase by filtration.

The presence of Sulfate has a similar effect, probably even stronger, as the filterability of the floc is much better in its presence. This is in agreement with

Marion's sequence presented in Chapter 2.

Thus, one can summarize the mechanism of removal of Fulvate as follows:

- (i) Hydrolysis of Aluminum species contained in the coagulant, yielding  $\text{Al}(\text{OH})_3$ .
- (ii) Adsorption of Fulvate and/or Sulfate on the surface of the  $\text{Al}(\text{OH})_3$  precipitate.
- (iii) The adsorbed fulvates or sulfate help to flocculate the precipitated particles of  $\text{Al}(\text{OH})_3$  and, thereby, permitting the easier removal of these flocs by either settling or filtration.



CHAPTER 6  
CONCLUSIONS

The conclusions of this research are as follows:

- (i) The examination and processing of the remaining Aluminum suggest that the equilibrium solid is amorphous  $Al(OH)_3$ .
- (ii) The solubility of the amorphous  $Al(OH)_3$  is  $10^{(-10.192 \pm .108)}$  for  $AlCl_3$  and Alum when applied on a high organic content water. At lower organic content, and for prehydrolyzed  $AlCl_3$  coagulants at all organic contents, the solubility of the  $Al(OH)_3$  is  $10^{(-9.838 \pm .07)}$ . Both values are in agreement with previous investigations on this topic.
- (iii) The analysis of the precipitate loading suggests that the Fulvates are removed by Adsorption, regardless of the coagulant nature, or the operating pH.
- (iv) The removal of Fulvate is limited at high coagulant dosage by a non adsorbable fraction of the Fulvate. This fraction increases with increasing pH. The mechanism of this phenomenon remains unclear.
- (v) The maximum adsorptive capacity of the precipitate decreases with increasing pH. This is in agreement with previous investigations which state that increas-

ing pH is detrimental to Fulvate removal.

- (vi) The presence of Sulfate hinders the removal of Fulvate. This is interpreted as a competitive adsorption of this anion on  $Al(OH)_3$  particles. This detrimental effect tends to decrease with increasing pH, in a similar way to Fulvate adsorption, which is in agreement with a competitive effect.
- (vii) The maximum adsorptive capacity of the floc decreases with increasing OH/Al ratio in the coagulant. This is interpreted as a decrease in the specific surface area of the solid phase.
- (viii) The cross examination of the adsorptive behaviour of the solid and the solubility data, suggests that the adsorbed Fulvate hinders the growth of the elementary particles of  $Al(OH)_3$ . This would account for the difference in solubility observed when the initial organic content is changed. However, the present experimental design does not allow to quantify this effect.
- (ix) The absorption of Fulvate is reversible.
- (x) The kinetics of the Fulvate, removal is very fast, as the organic removal is completed within 3 minutes.
- (xi) The split dose coagulant (or double) treatment procedure did not improve treatment results at low pH. This is attributed to the very steep slope of the isotherms

in these conditions. On the other hand, the same procedure was found successful in the neutral to mildly alkaline pH region, where it brings an improvement of the quality of the treated waters.

- (xii) The presence of Fulvate and Sulfate widens the flocculation domain towards low pH's, but has no influence on the high pH end of this domain.
- (xiii) The overall Adsorption pattern is in qualitative agreement with Davis' model for adsorption of anions on oxide and hydroxide surfaces. However, the data generated in this research do not permit a secure parameter estimation, due to the complexity of the model, and the inadequacy of the experimental design with respect to this model.

CHAPTER 7  
SUGGESTIONS FOR FURTHER RESEARCH

These suggestions concern two points believed to be important:

- (i) The quantification of the adsorption of natural Fulvate on  $Al(OH)_3$ , when the gel is formed in situ.
- (ii) The application to the drinking water industry of the present finding, i.e., the testing, at least at the pilot plant scale, of the double treatment process.

7.1 Quantification of the Adsorption Model

This is quite important, specially with respect to the competition between Sulfate and Fulvate. This should be investigated in a multiresponse type of experimental design, for instance by measuring systematically the residual Fulvate and Sulfate in Alum jar test experiments. This should be done at several pH values so as to evaluate the variations of the different coefficients, in the Isotherm equation with respect to this parameter.

A most important question to be solved is the nature of the non-removable fraction of the natural Fulvates, and its evolution with pH.

## 7.2 Double Treatment Process

The technical and economical feasibility of this process should be investigated at the pilot plant scale, as representing a possible alternative to Activated Carbon treatment and/or preoxydation treatment (Chlorine or Ozone). In the case of particularly difficult waters (high organic, low suspended solids content), the recycling of the back washwaters from the filters, in a double treatment scheme should be investigated as a possible way of improving the organic removal (double treatment) and the settling in the first step (increase in the suspended solids).

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APPENDIX A1  
ALUMINUM DETERMINATION BY  
THE FERRON METHOD

This method of determination of aluminum in very diluted solution is derived from rainwater at Al (1960)

A1.1 Reagents

- (i) Hydroxylamine - HCl (10 g/L)
- (ii) Ferron Orthophenanthroline (1 g-1 g/L)
- (iii) Sodium Acetate Solution (350. g/L)

A1.2 Operating Methods

(i) In acid washed glass, Erlenmeyer flask, mix the proper amounts of Ferron-Orthophenanthroline solution and Sodium Acetate in a 5 to 2 ratio, and such that 10 mL of the mixture is available for each standard and sample.

(ii) In 125 ml Erlenmeyer Flasks, place 2.0 mL of Hydroxylamine - HCl solution.

(iii) Prepare a set of standards containing from 0 to 100  $\mu\text{g}$  of Al metal in 50 mL of sample and pour into the 125 mL flasks and mix with the Hydroxylamine - HCl.

(iv) Withdraw proper aliquots of samples containing no more than 100  $\mu\text{g}$  of Al metal, and dilute to 50 mL total volume if necessary with distilled Al free water (blank).

Pour into the 125 mL flasks and mix with the Hydroxylamine - HCl.

(v) After minimum 20 mn, pour 10 mL of the Ferron-Orthophenanthroline - Sodium Acetate solution and mix.

(vi) Allow another 20 min waiting time before reading the absorbance of the mixture at 370 nm, against a match empty cell. This allows to perform a correction of the reading according to the Absorbance of the sample or its dilution at this wavelength. The corrected Absorbance obeys the Beer-Lambert Law. This method allows to detect concentrations of Aluminum of  $1 \mu\text{g}$  of Al/50 mL (.02 ppm or  $1 \mu\text{M/L}$ ), and the standard error is  $0.7 \mu\text{g}$  of Al/50 mL.

(vii) The color correction is done as follows:

$$\text{- for standards} = A_1^{370} \Big|_{\text{read}} - A_1^{370} \Big|_{\text{distilled water}}$$

$$\text{- for samples} = A_1^{370} \Big|_{\text{read}} - \left\{ A_1^{370} \Big|_{\text{sample}} * \text{volume} \Big|_{\text{aliquot}} + A_1^{370} \Big|_{\text{DW}} * \text{vol} \right\} \text{DW} / \text{vol} \Big|_{\text{T}}$$

## APPENDIX A-2

### CHARACTERIZATION OF COLOUR CAUSING ORGANICS

The characterization of the colour causing organics includes their identification, (Fulvates/Humates) as well as the possible homogeneity/heterogeneity of the material.

#### A.2.1 Identification of the Material

##### (i) Acid treatment

In order to assess the presence of Humic acids (acid insoluble) in FRW, an aliquot of this raw water was acidified to pH 2.2 with concentrated HCl, and left under stirring overnight. Two 100 mL of the resulting samples were withdrawn. One of them (1) was neutralized to pH ca 7 with concentrated NaOH and membrane filtered. The other (2) was first filtered, then neutralized. An aliquot of FRW untreated was also membrane filtered (3).

The samples 1 and 3 did not leave much suspended material on the membranes whereas the sample 2 left a visible brown deposit. Furthermore,  $A_{254 \text{ nm}}^{1 \text{ cm}}$  was measured on the 3 samples. A slight difference was found between the samples (2) and (3) (.622 and .630 respectively), whereas the sample (1) showed an 8% drop in  $A_{254 \text{ nm}}^{1 \text{ cm}}$  (.580).



The slight drop between samples (2) and (3) is attributed to either slow re-dissolution of the Humates or to coagulation due to the increase in the ionic strength. On the other hand, the difference between the sample (1) and the others, and the brown mark left on the membrane suggest that a small part of the original organic content of the water qualify as Humic acid, as it precipitates at low pH.

(ii) Light Adsorption Spectrophotometry

Aliquots of filtered FRW and Alum treated (.3 mM/L), filtered FRW referred to as FTW were tested for their light adsorption spectra with respect to DW. The results are shown in Figure A2.1, where the Adsorbance is reduced with respect to the DOC values of the corresponding samples. Both adsorption spectra are monotonously decreasing functions of the wavelength. They differ in shape as the Adsorbance of FTW is much higher than the Adsorbance of FRW up to 220 nm. The drop of FTW's Adsorbance with increasing wavelength is also much sharper than FRW's up to approximately 250 nm. Above this wavelength, the two spectra are approximately parallel.

Both Adsorption spectra qualify as those of fulvates (see Section 2.1.2). However, the difference in shape suggest that these "fulvates" are not similar.

(iii) Fulvate Titration

This titration was performed according to the method recommended by Kramer (1983), and the values of the concentration and acid dissociation constant were calculated from the basic titration data. FRW contained 110  $\mu\text{eq/L}$  as Fulvates, with an average  $\text{pk}$  of 5.06.

When reduced to the DOC content, the Fulvate acidity is 10 meq/g of C, which is in agreement with Schnitzer (1971). The  $\text{pk}$  value is also quite close to the average  $\text{pk}$  value give by this author ( $\text{pk} \approx 4.5$ ). This value corresponds to Type II COOH ( $\text{pk} = 4.49$  to 5.72) defined by Gamble (1970), which are carboxyl radicals not in ortho position with respect to the phenolic hydroxyl. This makes these compounds less likely to form chelates with metallic ions, since stronger chelates are formed between metallic cations and the couple phenol-ortho carboxyl site of Fulvates (Schnitzer, 1978), or Quercetin (Lind et al, 1975).

A.2.2  $A_{254}^{1 \text{ cm}} / A_{254}^{10 \text{ cm}}$  - DOC Correlation

This information, primarily for the calibration of the photometric method of the DOC determination brings also another clue to the heterogeneity of the fulvates contained

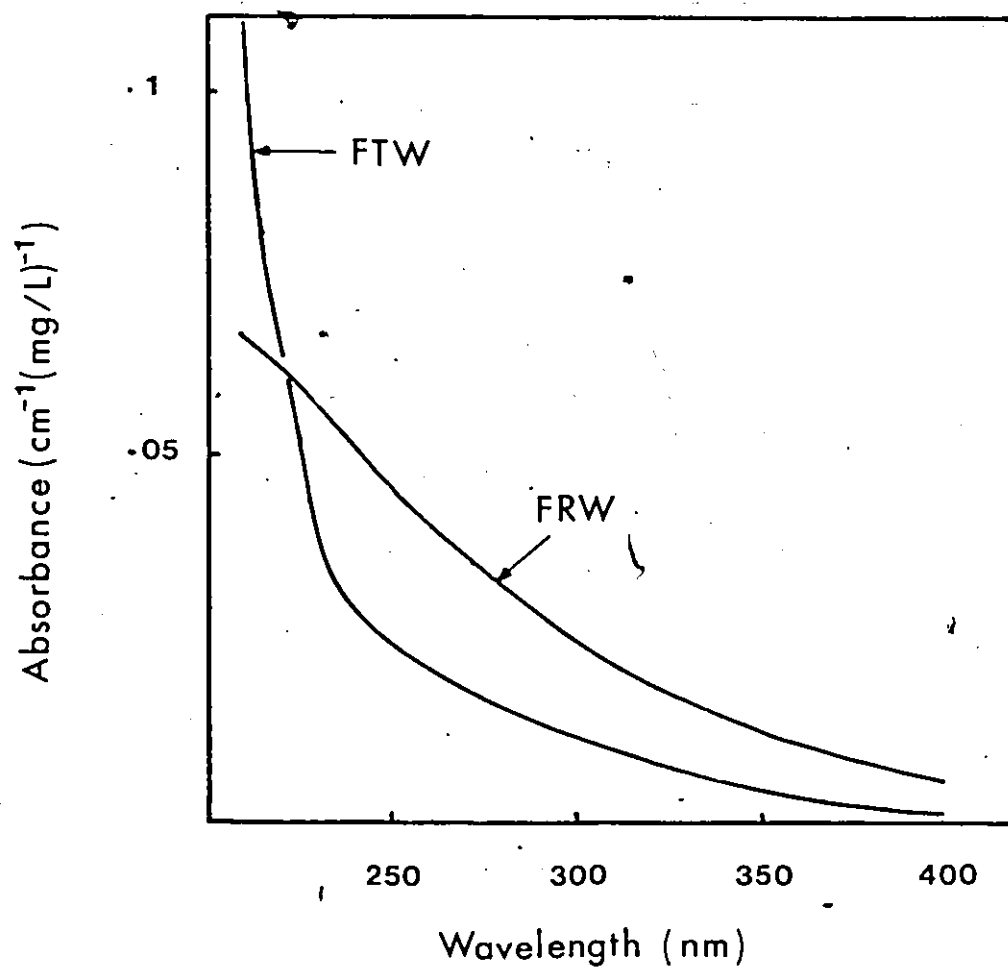


Figure A2.1 Organics Light Absorption Spectra.  
FRW = Filtered FRW.  
FTW = Filtered Treated FRW (.3 mM/L).  
Absorbance is reduced with respect to  
the DOC content.

in FRW and FDW as well. The Figures A2.2 to A2.4 show the Absorbance at 254 nm of dilutions of FRW with DW and the Absorbance - DOC experimental correlations for FRW and FDW respectively. Although dilutions of FRW suggest that the original Fulvate content obeys the Beer Lambert law, the correlations found with treated waters are clearly parabolic in shape. This is interpreted as a preferential removal of comparatively stronger light absorbant "Fulvates" by the coagulation treatment.

#### A.2.3 Amounts of DOC in the Raw Waters

The FRW UV Absorbance slowly but steadily decreased with time, from .630 to .540, over a 10 month period. The reason for this decrease is unclear, as the UV Absorbances of treated waters were found to be quite reproducible. DOC measurements on FRW fell from 12.08 mg/L to 10.06 during the same period. These amounts correspond to what could be expected as DOC content with respect to the origin of the water supply.

#### A.2.4 Discussion

The preferential removal of certain Fulvate compounds

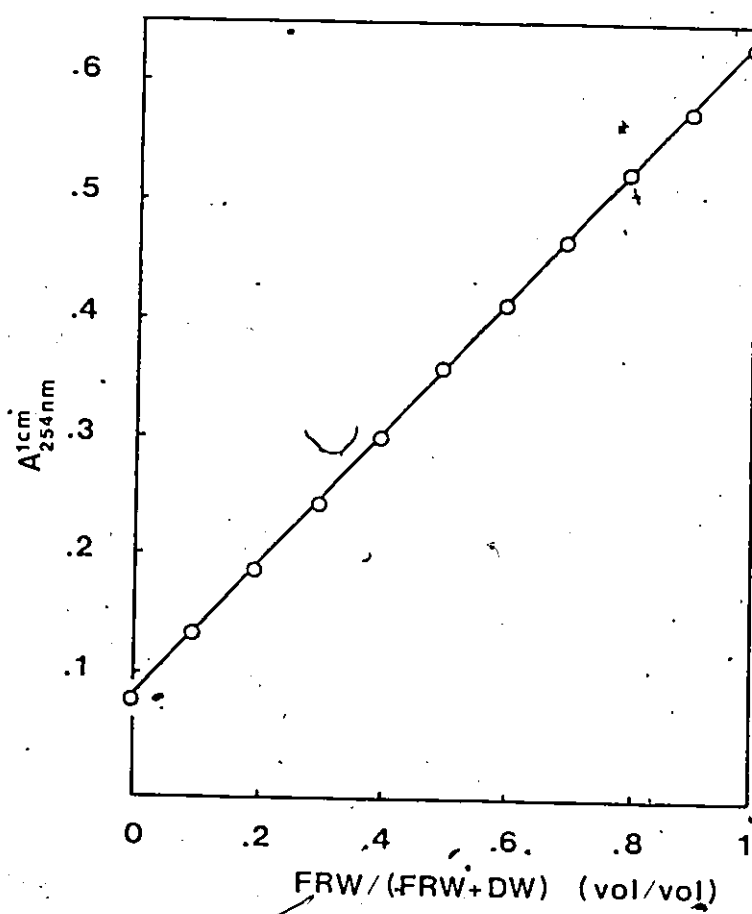


Figure A2.2 UV Absorbance as a Function of FRW Dilution.

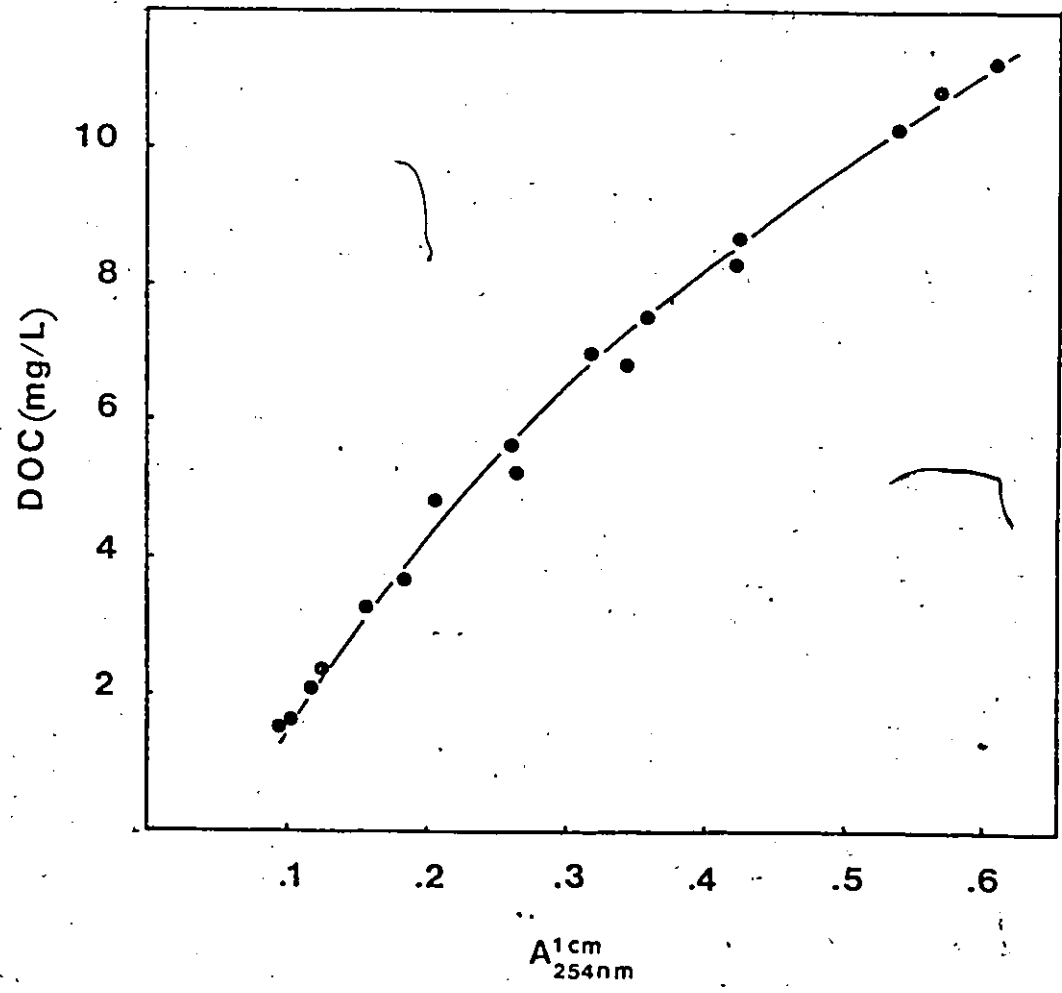


Figure A2.3 UV Absorbance - DOC Correlation for FRW Experiments.

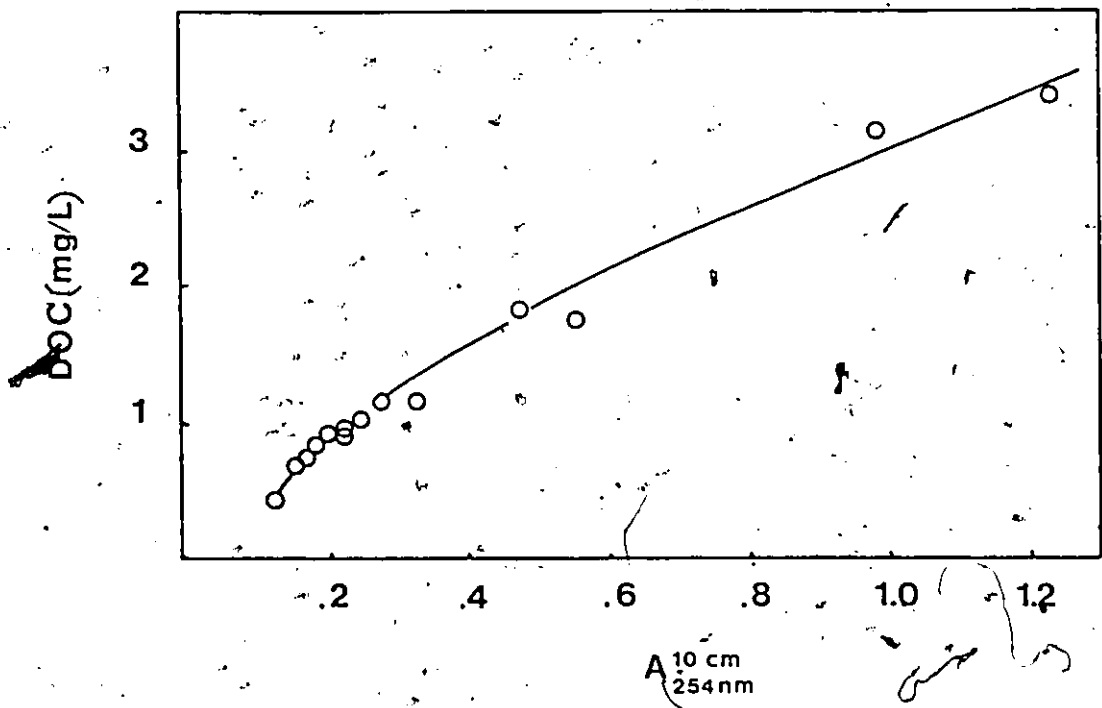


Figure A2.4 UV Absorbance - DOC Correlation for FDW Experiments.

suggested by the above results contributes to the recent tendency to consider aquatic Fulvates as a mixture of different molecular weights, and different properties, as already discussed in the section 2.1.

The selective character of the removal on colour causing material was found by Babcock et al (1979), who related these compounds to Trihalomethane precursors. In a recent investigation on a similar water to FRW, lower THM/DOC yields were found on waters treated by coagulation than on the raw water (Zenon, 1983).

The selectivity of the removal by coagulation was also found on other characteristics of aqueous organics. Randtke et al (1981) reported that the adsorbitivity of the DOC on Activated Carbon was affected by Alum pretreatment.

Also, Davis et al (1981) reported that the high molecular weight fraction of a lake water is adsorbed preferentially to the other fractions on Aluminum oxide surface.



A.2.5 REFERENCES

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APPENDIX A-3  
GENERAL OBSERVATIONS

This Appendix summarizes the basic results of the experiments performed in this work, in terms of general trends with respect to the three independent parameters investigated:

- (i) nature of the coagulant
- (ii) treatment dosage
- (iii) Operating pH

The complete set of results are tabulated in Appendices A-4 and A-5, for the experiments performed on FRW and FDW. Blank runs are tabulated in Appendix A-6.

A.3.1 Residual Organics

The residual organics are presented in Figures A3.1 to A3.6, as a function of pH and coagulant dosage for each coagulant.

In all cases (coagulants and raw waters), the overall residual organic patterns are similar in shape: the residual organics is decreasing with increasing coagulant dosage and decreasing pH. The influence of the coagulant dosage is relatively more pronounced on FRW than on FDW, whereas the pH influence is more pronounced on FDW than on FRW. This is

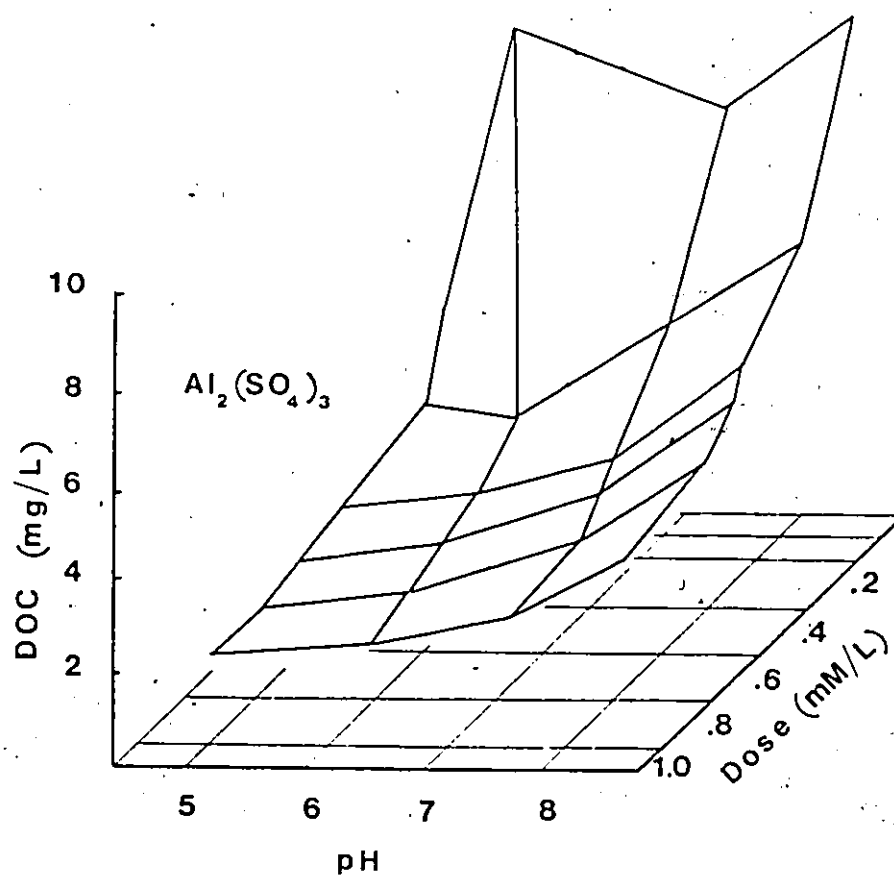


Figure A3.1 Remaining DOC as a Function of Alum Dosage and pH. Case of FRW.

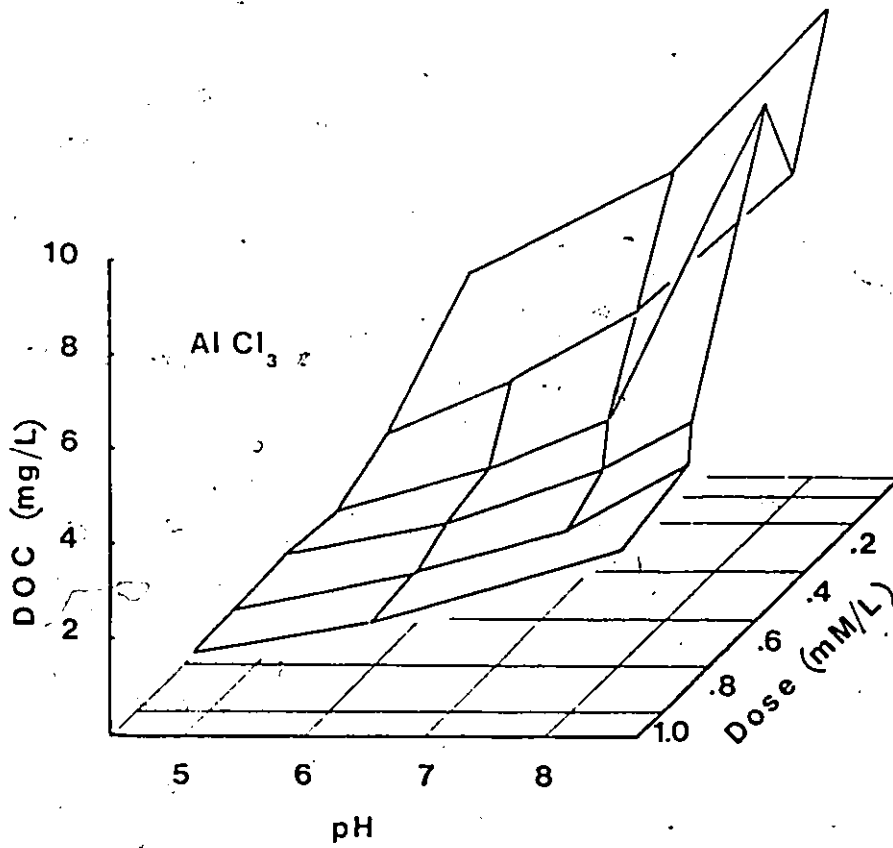


Figure A3.2 Remaining DOC as a Function of AlCl<sub>3</sub> Dosage and pH. Case of FRW.

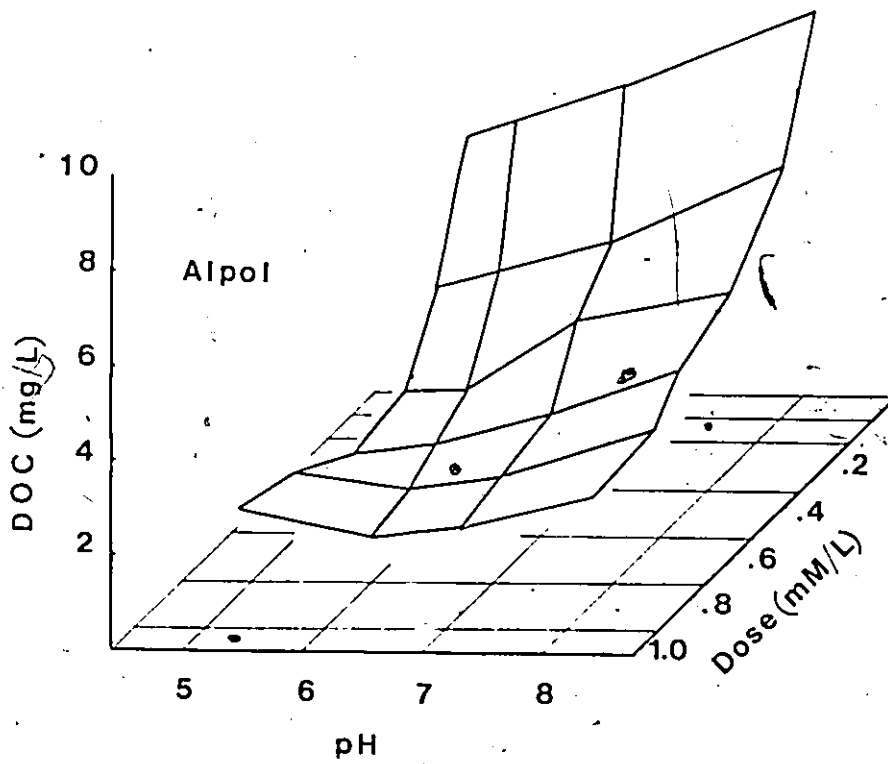


Figure A3.3 Remaining DOC as a Function of Alpol Dosage and pH. Case of FRW.

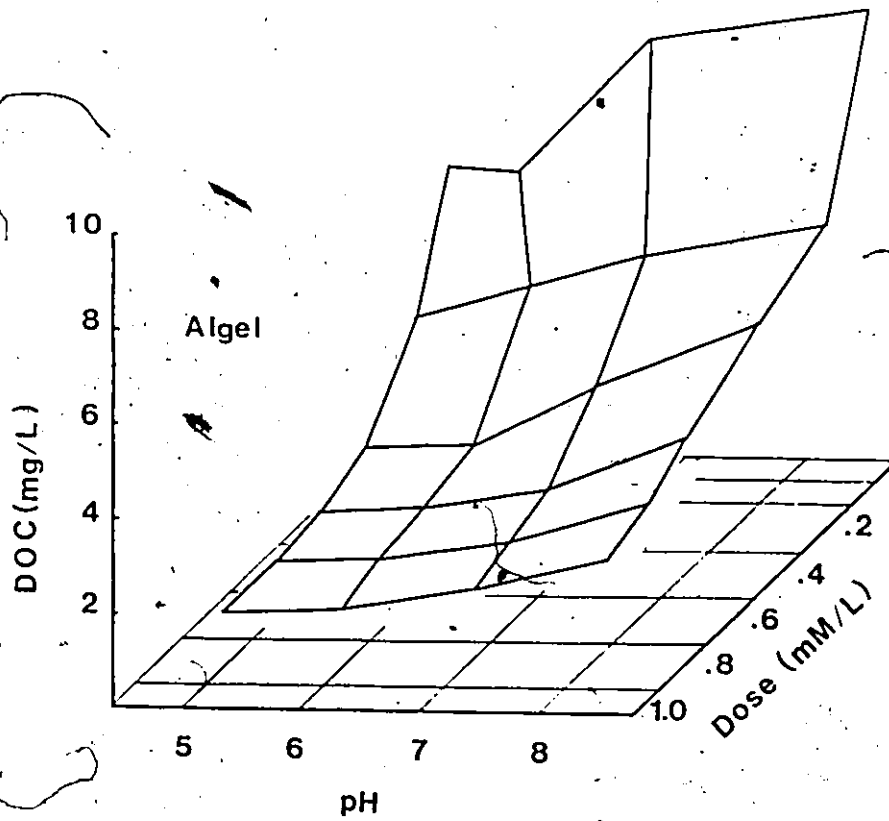


Figure A3.4 Remaining DOC as a Function of Algal Dosage and pH. Case of FRW.

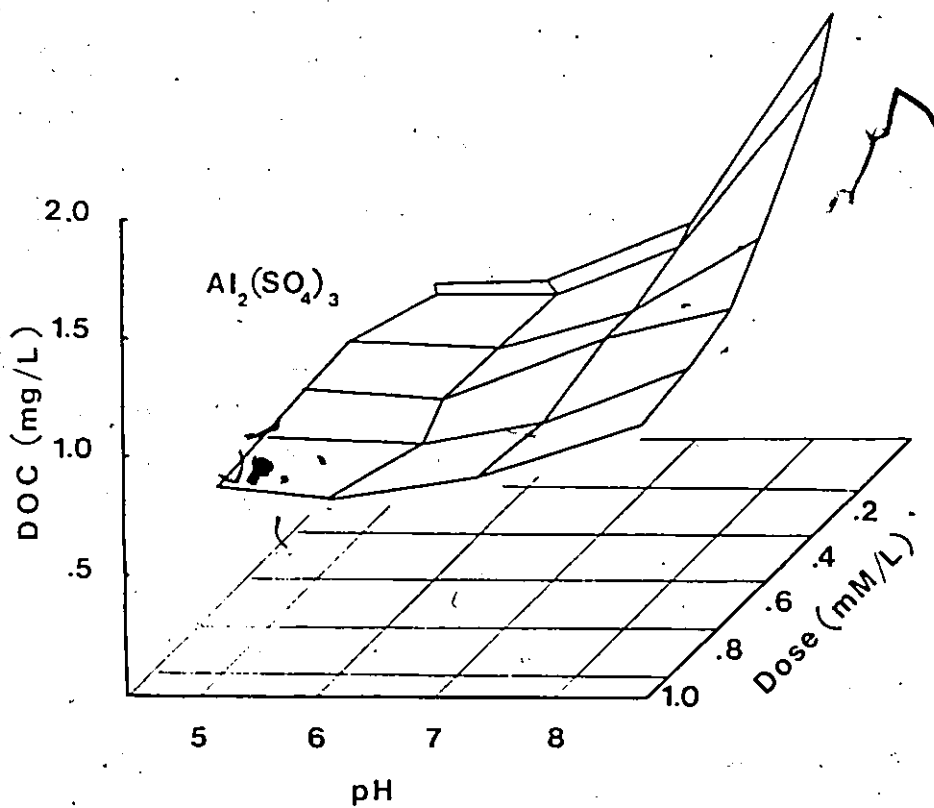


Figure A3.5 Remaining DOC as a Function of Alum Dosage and pH. Case of FDW.

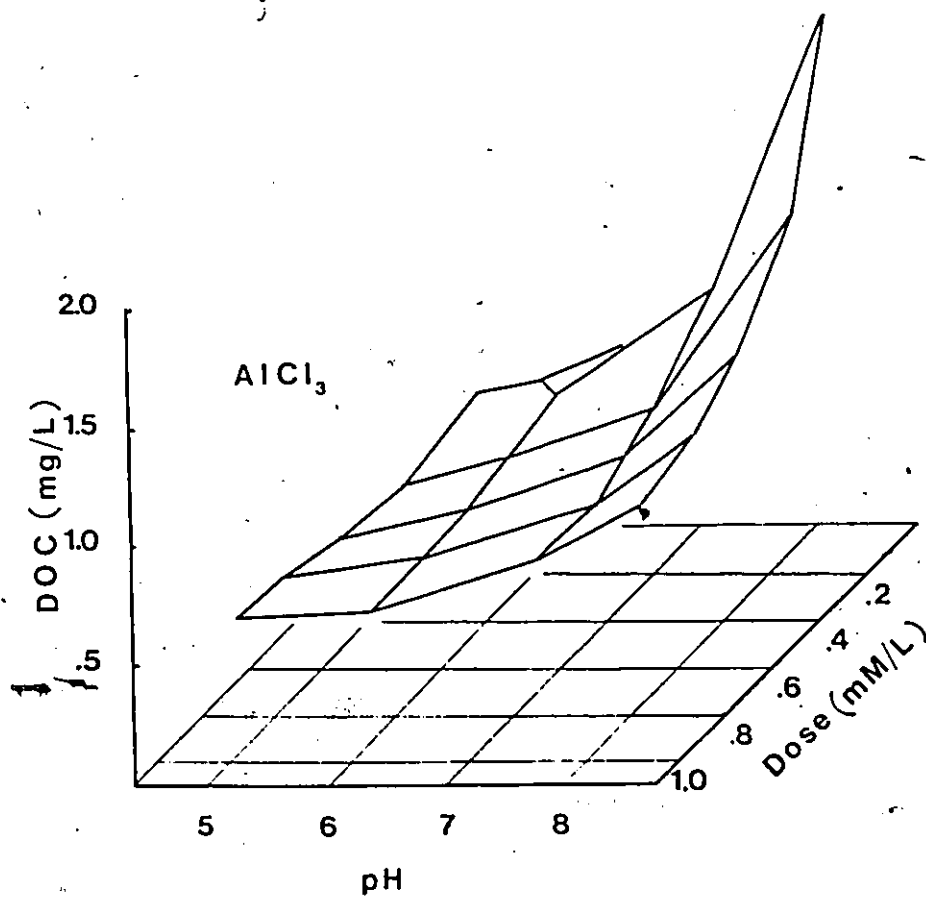


Figure A3.6 Remaining DOC as a Function of AlCl<sub>3</sub> Dosage and pH. Case of FDW.



a consequence of the organic adsorption isotherms (see Chapter 5) which are very steep in the low equilibrium concentration range.

In the case of Alpol and Algel, the influence is less pronounced. In the former case (Alpol), local minima of the residual organics are located in the axis high dosage, medium pH range to medium dosage, low pH. This is attributed to a sharp increase of the dissolved Aluminum at low pH, high dosage of this coagulant (see Section A.3.2).

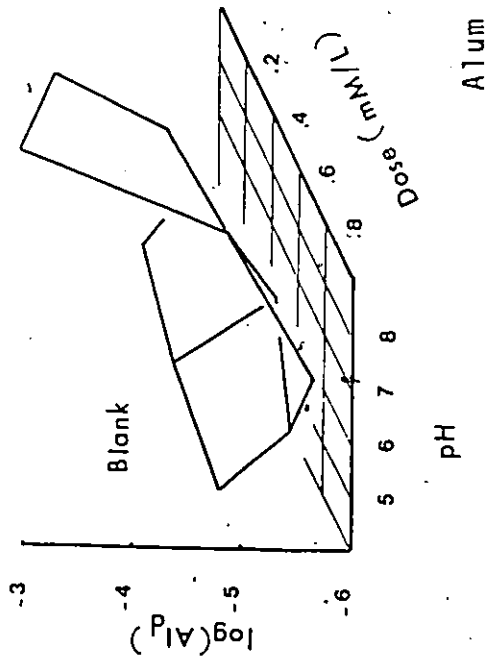
The comparison between  $AlCl_3$  and Alum shows that at low pH, high dosages of Alum result in a comparatively higher residual organics. This is discussed in detail in Chapter 5, and is attributed to a competitive adsorption of Sulfate. This competitive effect is stronger with decreasing pH.

### A.3.2 Residual Aluminum

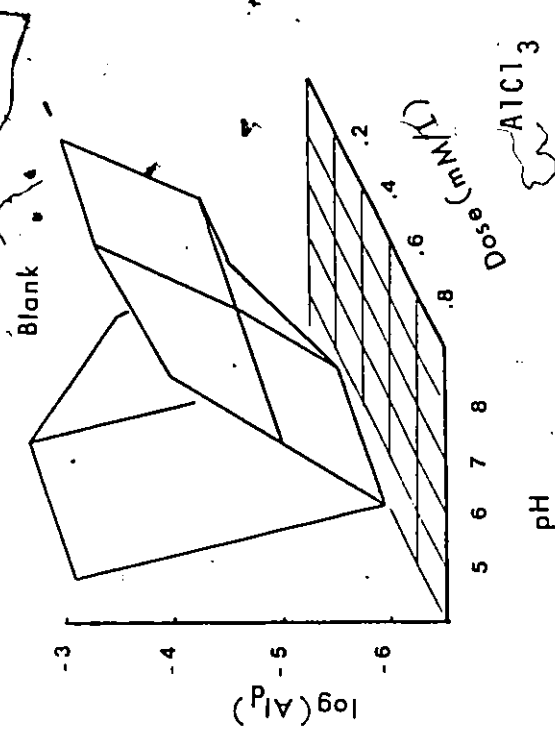
These results are reported in Figures A3.7 to A3.10.

All the surfaces defined by the plot  $\log(Al_d)$  as a function of pH and dosage are V-shaped, with a minimum in the 6 to 7 pH range. The sharpness varies from one coagulant to another, and depends also on the organic content of the water specially in the case of Algel.

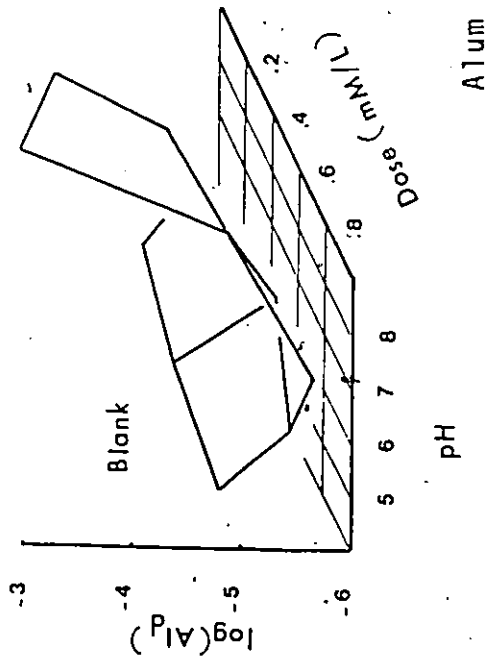
The comparison between Alum and  $AlCl_3$  shows some discrepancies due to the presence of Sulfate. In the low end of



AlCl<sub>3</sub>



AlCl<sub>3</sub>



Alum

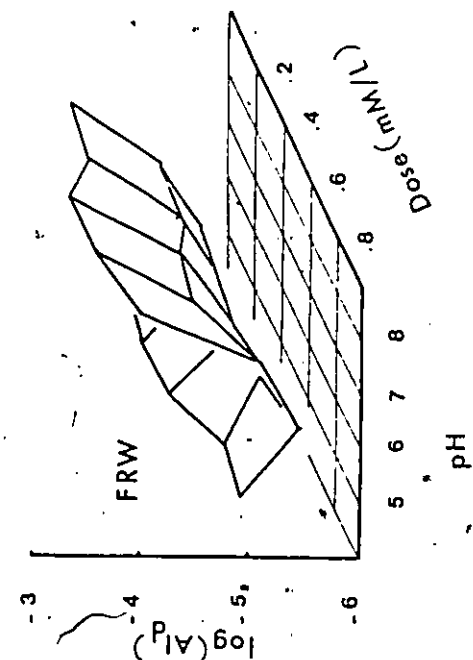


Figure A3.7  
Residual Aluminum (Al<sub>D</sub>) as a Function of pH and Coagulant Dosage.

Figure A3.8

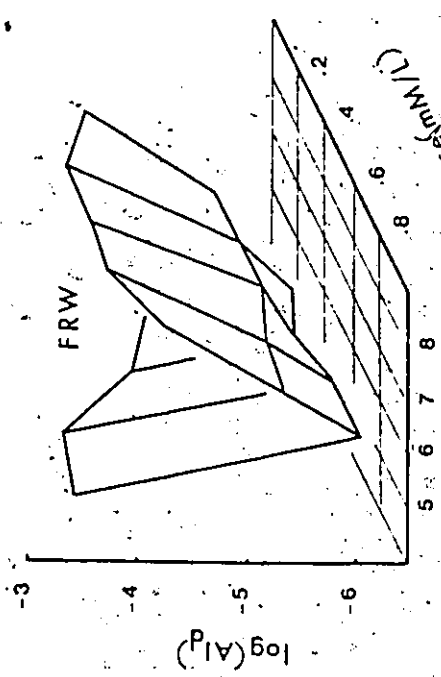
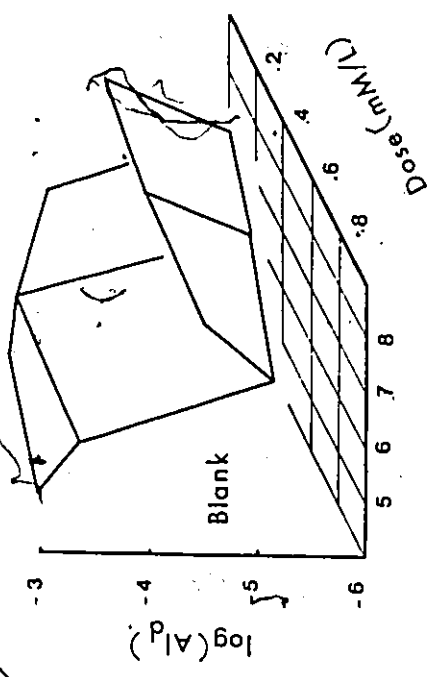
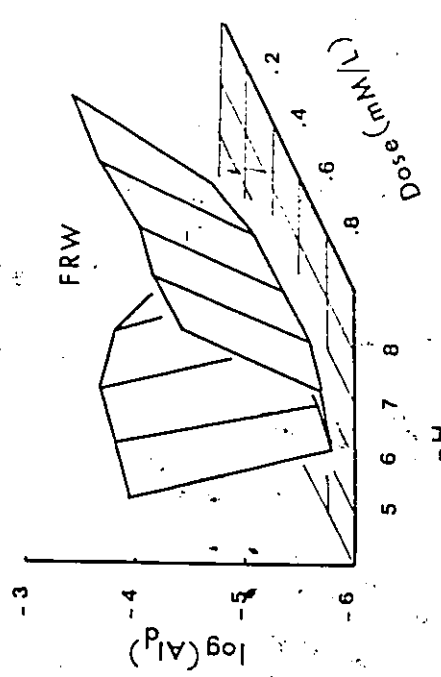
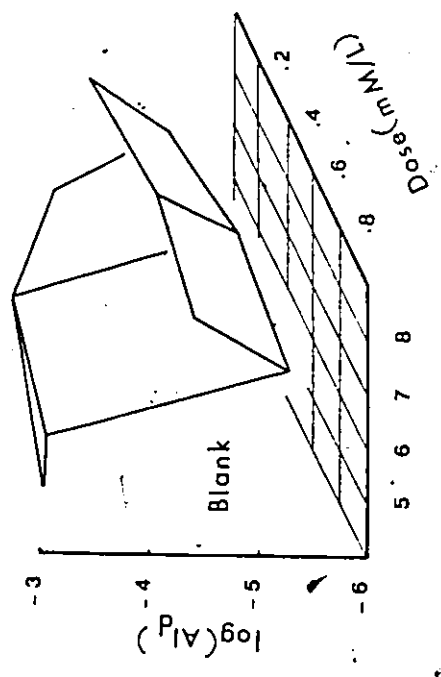


Figure A3.9

Figure A3.10

Residual Aluminum ( $Al_D$ ) as a Function of pH and Coagulant Dosage.

the pH range, most of the Aluminum introduced as  $AlCl_3$  is filterable whereas if Alum is used, a substantial amount of the Aluminum introduced is removed by filtration. When used on FRW, the discrepancies between these two coagulants are less important, which shows that for  $AlCl_3$ , the presence of organics in the precipitation environment helps the formation of filterable particles.

The solubility patterns obtained with Alpol and Algel are characterized by a relatively high solubility at pH 6 in the absence of organics. However, when applied on FRW, these coagulants yield a solubility pattern analogous to  $AlCl_3$  and Alum. This is interpreted in a similar way to the case of  $AlCl_3$ , i.e., the presence of Fulvates helps to the formation of aggregates removable by filtration. At high dosage and low pH, (1 mM/L and 5 respectively), the Aluminum hydroxy polymers may survive the dilution step, as they have been shown to exist in such conditions (Bottero et al, 1981). This is consistent with the residual organics found in these conditions of treatment with Alpol, as pointed out in the former section.

The solubility of the precipitate is discussed in detail in Section 5.1.

### A.3.3 Physical Characteristics of the Precipitates

The physical characteristics of the precipitates were

assessed by visual observation and by the time required to filter 50 mL of flocculated water through a .45  $\mu\text{m}$  pore diameter membrane, under a controlled pressure gradient.

The visual observation, graded on 3 levels, allows to assess the extend of precipitation and flocculation: treatment conditions (coagulant dosage and pH) graded 0 do not yield a visible precipitate. Grade 1 is given to treatment conditions yielding a precipitate visible to the naked eye as a homogeneous cloudiness in the jar, but with no individual floc particles. Generally, no settling occurs for such conditions. Grade 2 is given when definite flocculation occurs.

When reduced to the mass of precipitates, the filtration time, noted  $t_{50}$  is a semiquantitative assessment of the porosity of the floc. This measurement is recommended by LaMer et al (1956). A lower filtration time indicates that the floc particles are bigger, thereby increasing the porosity of the filtration cake. Alternatively, a high filtration time indicates that the floc particles are very small, and tend to clog the filtration cake.

(i) Flocculation patterns

The visual assessment of the flocculation is reported in Figures A3-11 to A3-15. The examination of these figures suggest that the maximum flocculation zone is affected by the

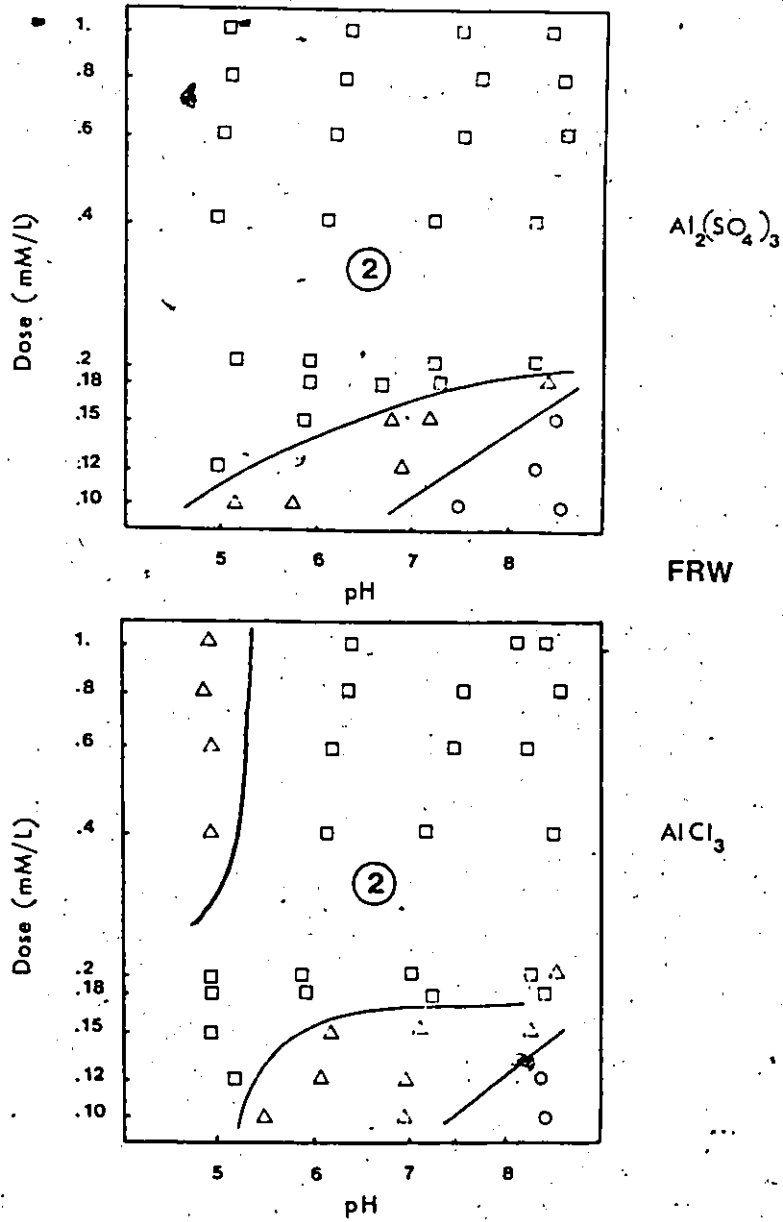


Figure A3.11 Flocculation Patterns in FRW Experiments.  
 Open circles = no visible precipitation.  
 Open triangles = precipitation, no flocculation.  
 Open squares = maximum flocculation.

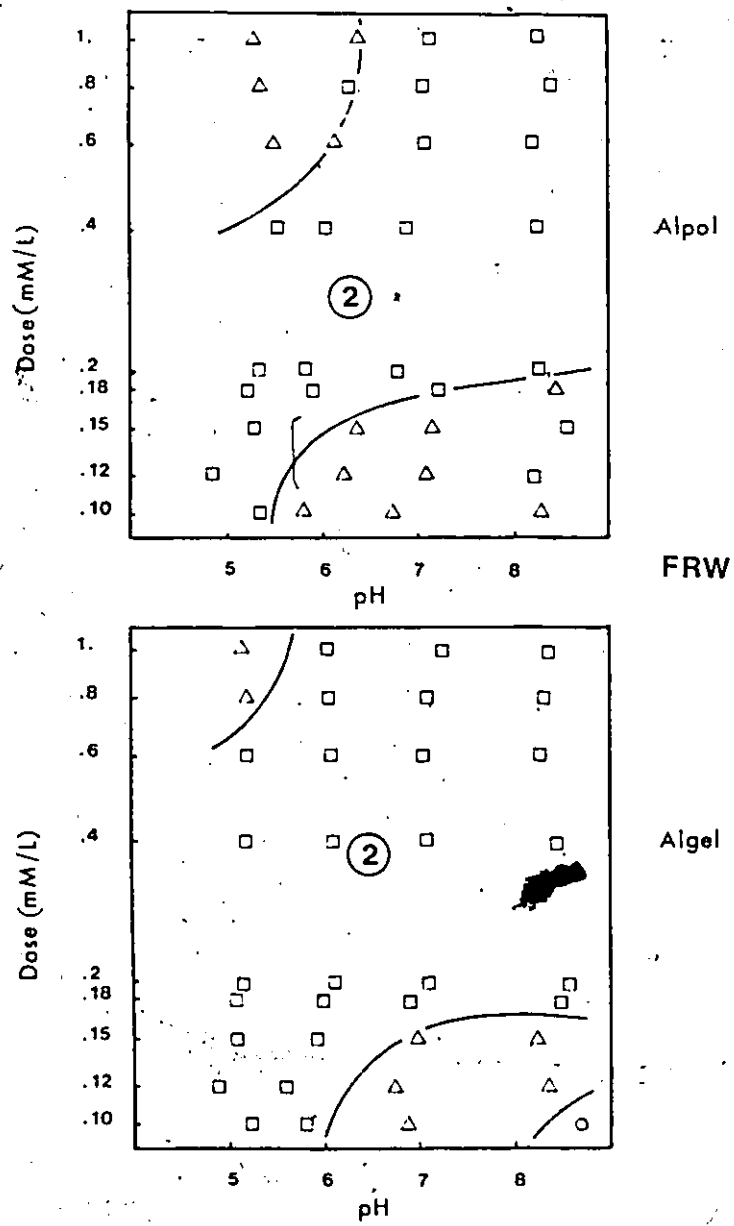


Figure A3.12 Flocculation Patterns in FRW Experiments.  
Open circles = no visible precipitation,  
Open triangles = precipitation, no flocculation,  
Open squares = maximum flocculation.

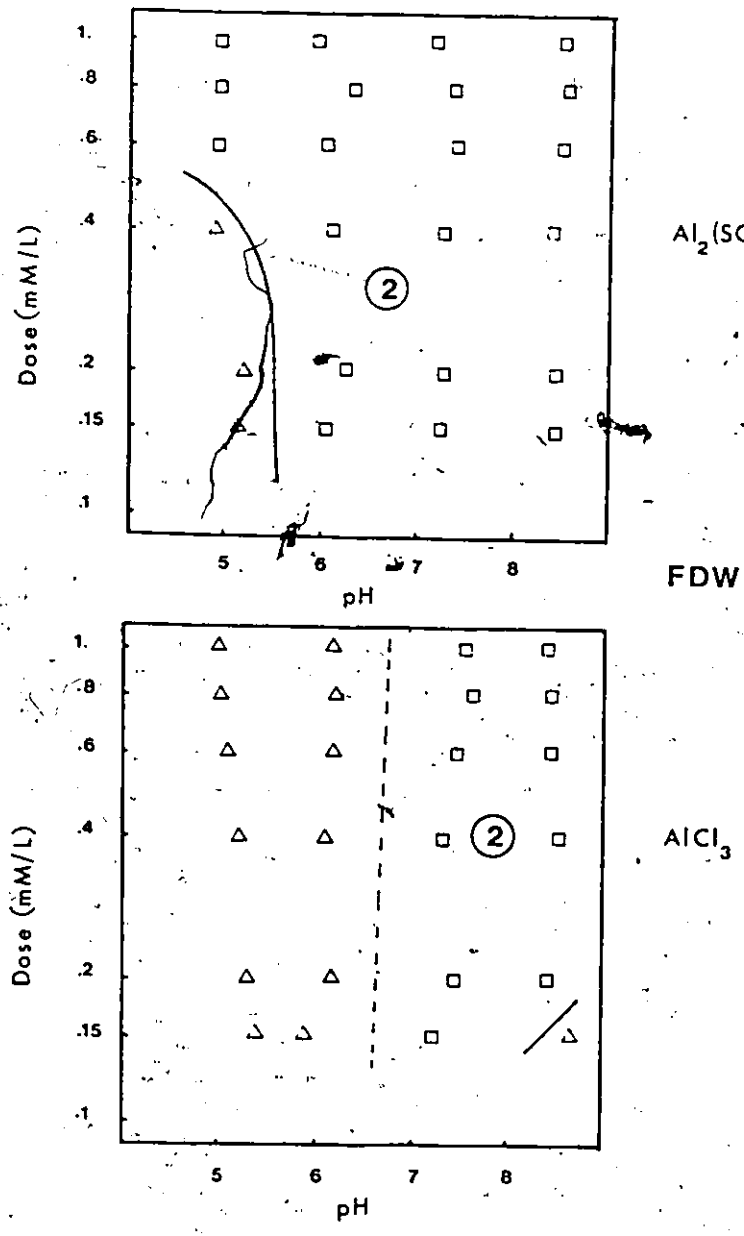


Figure A3.13 Flocculation Patterns in FDW Experiments  
Open circles = no visible precipitation,  
Open triangles = precipitation, no flocculation,  
Open squares = maximum flocculation.



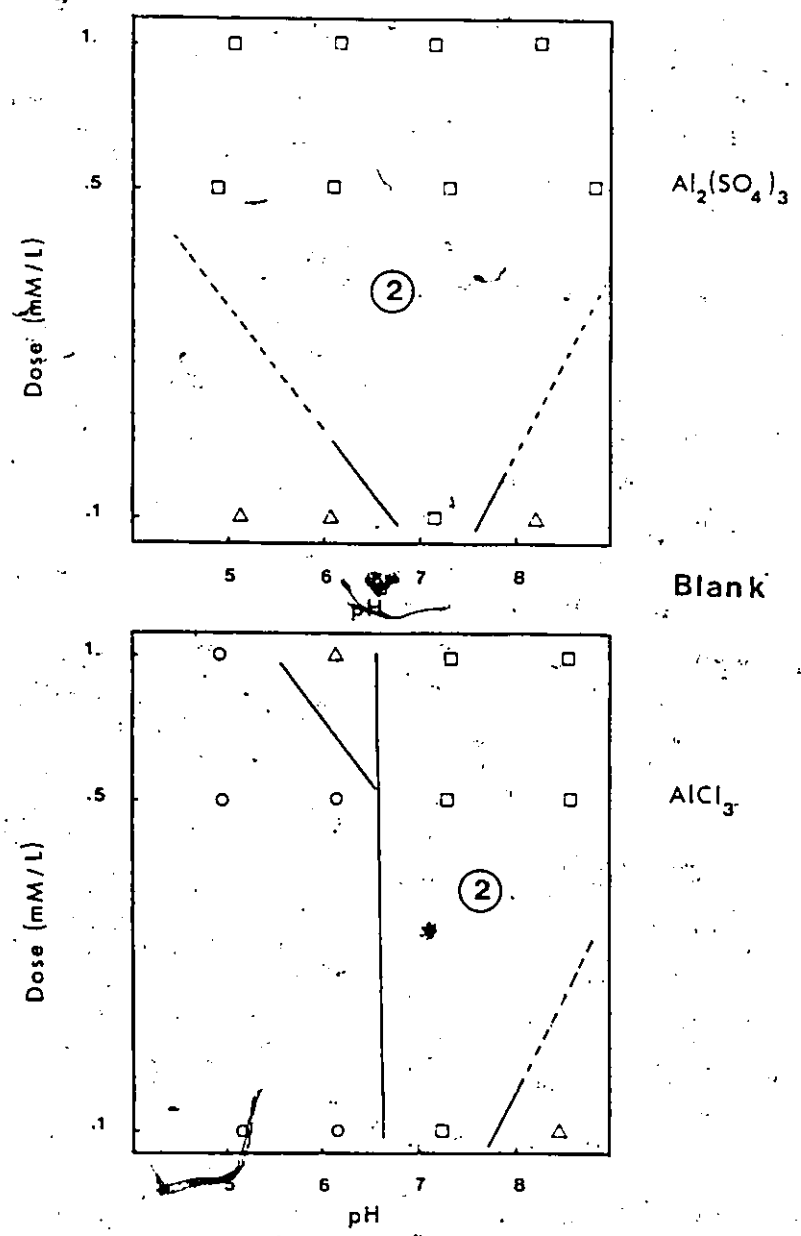


Figure A3.14 Flocculation Patterns in Blank Experiments.  
 Open circles = no visible precipitation,  
 Open triangles = precipitation, no flocculation,  
 Open squares = maximum flocculation.

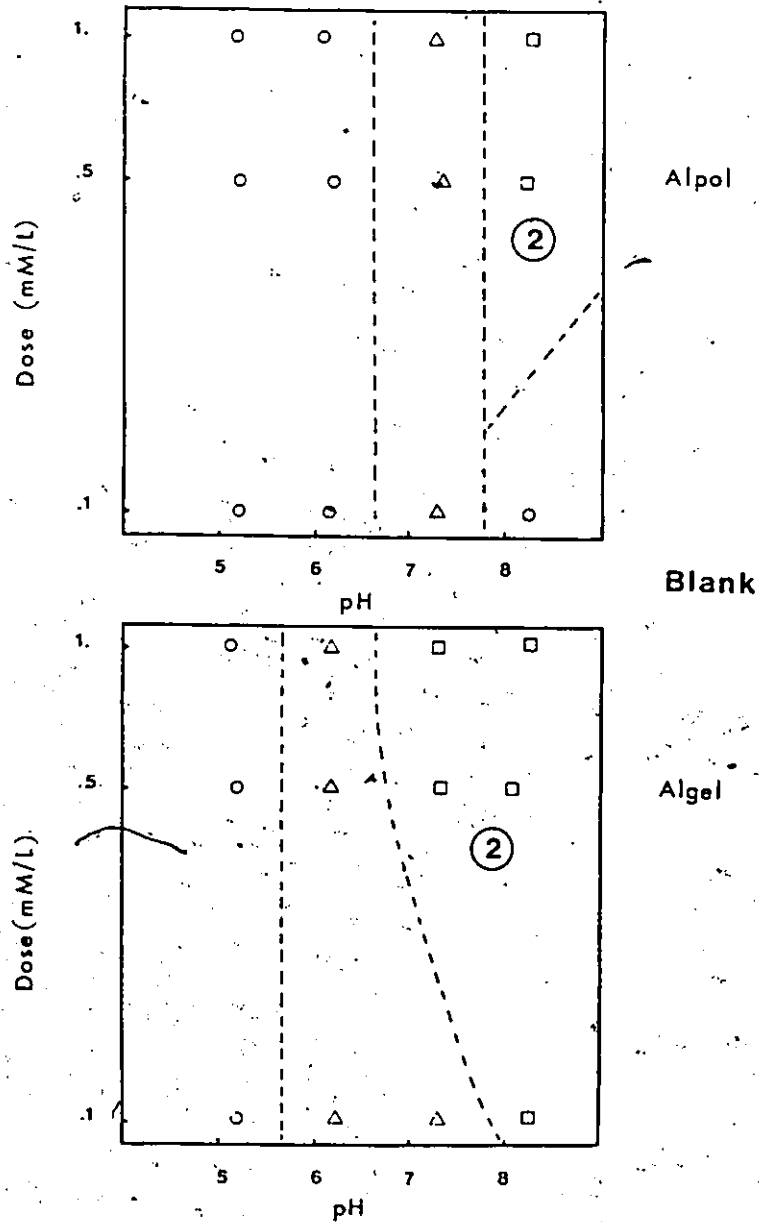


Figure A3.15. Flocculation Patterns in Blank Experiments.  
 Open circles = no visible precipitation,  
 Open triangles = precipitation, no flocculation,  
 Open squares = maximum flocculation.

presence of Sulfate and Fulvate. This zone is identified in these figures as zone 2. The comparison of the patterns yielded by  $AlCl_3$  and Alum, shown in Figures A3.11 to A3.13, suggest that the presence of Sulfate widens the flocculation range towards lower pH.

The presence of Fulvate tends to shift the maximum flocculation pH range towards low pH's, specially at low coagulant dosage. These treatment conditions correspond to a maximum in the precipitate loading, as shown in Section 5.1. This suggest that adsorbed Fulvates enhance the flocculation specially at low pH, whereas they hinder it at high pH.

These trends are in agreement with the adsorption hypothesis, as discussed in Chapter 5.

The patterns yielded by Alpol and Algel are presented in Figures A3.14 and A3.15, and they show in strong similarity with the  $AlCl_3$  pattern.

#### (ii) Filterability

Figure A3.16 shows the overall filterability patterns in the case of FRW, as a function of the treatment dosage and pH, for each coagulant. It shows that Alum yields a floc more easily filterable than the other coagulants. Except for  $AlCl_3$ , which displays an erratic pattern, there seems to be a pH dosage range of maximum filterability (minimum Filtration

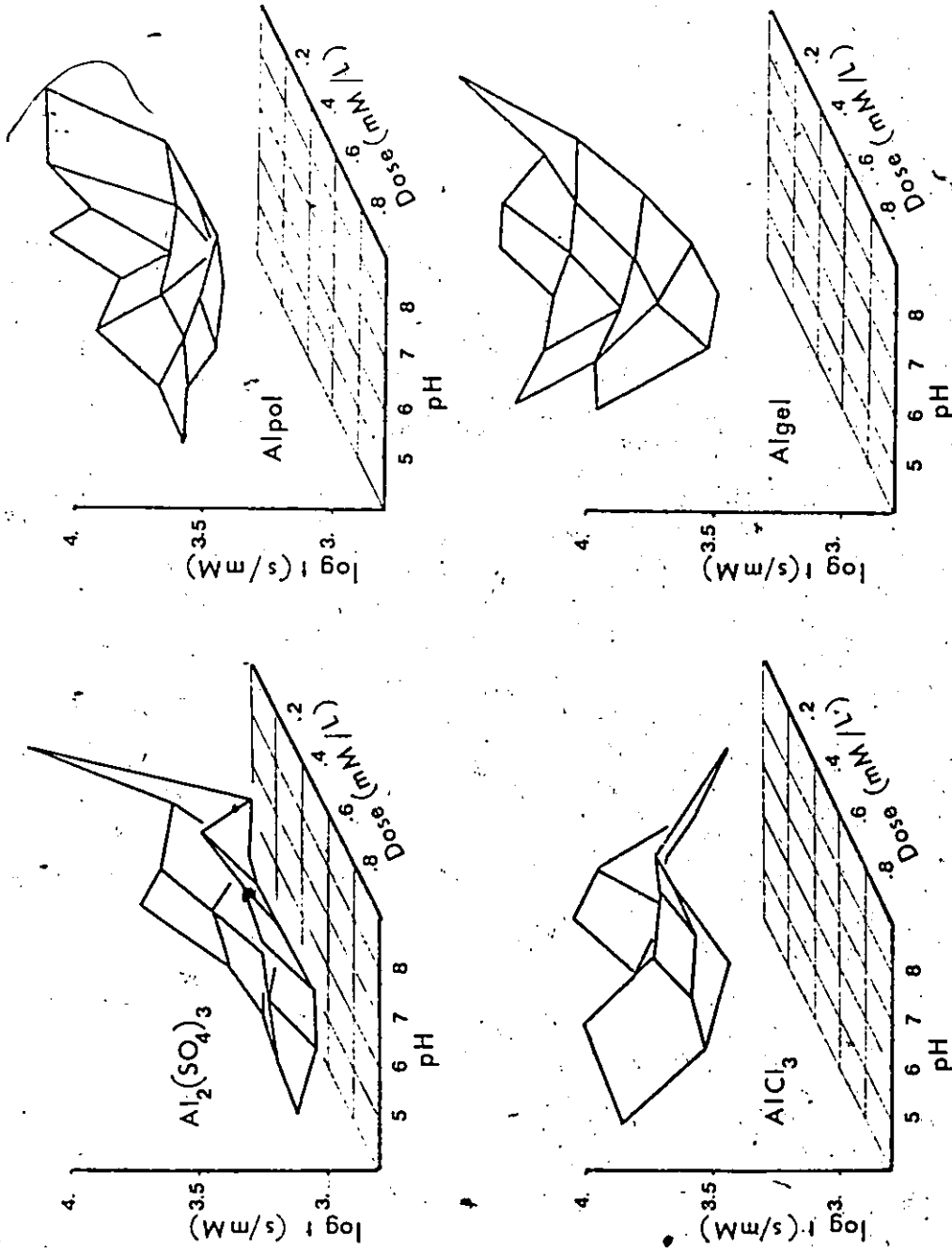


Figure A3.16 Filterability of FRW Flocculated Waters as a Function of the Operating Conditions.

time). The position and extent of this range vary with the coagulant nature: for Alum, this range is quite wide, and located in the medium pH, medium dosage area. For the other two coagulants, the maximum filterability range shifts towards higher dosage - higher pH values, and becomes narrower. In the case of Algel, the maximum filterability is not within the limits of the field of investigation. However, a "valley" of local lower filtration times appears along the low pH, low dosage - high pH, high dosage diagonal of the pH - dosage plane.

This shows that for this type of raw water, Alum yields a precipitate easier to remove from the water than the other coagulants. On the other hand,  $AlCl_3$  seems more efficient, regarding the organic removal.

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APPENDIX A4

JAR TEST RESULTS FOR FRW

FRW  
ALUM JAR TEST RESULTS

Dose mM/L	Titrants		pH	A <sub>1</sub> <sup>25 nm</sup> 1 cm	DOC mg/L	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
	HCl	NaOH						
0	0	0	7.92	.573	10.57	—	—	6.7
.1	.92	0	5.16	.240	4.88	.0107	1	7.7
.12	.95	0	5.00	.194	3.87	.0114	1	26.
.20	.62	0	5.16	.165	3.20	.0164	2	14.
.40	.15	0	4.94	.113	1.95	.0201	2	15.3
.60	0	.30	4.97	.113	1.95	.0197	2	19.1
.80	0	.90	5.07	.111	1.90	.0113	2	26.1
1.0	0	1.40	5.05	.111	1.90	.0135	2	32.3
0	0	0	7.55	.610	11.02	—	—	6.0
.1	.67	0	5.75	.468	9.08	.100	1	8.5
.15	.45	0	5.90	.205	4.11	.0073	2	19.
.18	.30	0	5.96	.162	3.13	.0022	2	17.
.20	.26	0	5.92	.155	2.96	.0063	2	13.
.40	0	.25	6.08	.126	2.27	.0041	2	17.
.60	0	.92	6.18	.126	2.27	.0044	2	19.5
.80	0	1.65	6.30	.125	2.24	.0048	2	29.
1.0	0	2.25	6.36	.124	2.22	.0041	2	29.
0	0	0	7.70	.608	11.00	—	—	5.5
.1	0	.15	7.48	.470	9.11	.0398	0	6.
.12	0	0	6.92	.529	9.98	.0748	0	6.
.15	0	.25	7.20	.268	5.46	.0111	1	41.
.18	0	.35	7.28	.240	4.87	.0118	1	13.
.20	0	.35	7.23	.247	5.02	.0081	2	12.1
.40	0	.90	7.19	.161	3.10	.0063	2	14.3
.60	0	1.75	7.54	.179	3.52	.0163	2	20.
.80	0	2.40	7.73	.175	3.43	.0230	2	25.
1.0	0	2.90	7.53	.146	2.75	.0093	2	29.
0	0	0	7.80	.605	10.96	—	—	6.3
.1	0	.45	8.54	.606	10.97	.1000	0	6.2
.12	0	.50	8.31	.565	10.46	.1022	0	5.2
.15	0	.60	8.50	.421	8.32	.0956	0	40.
.18	0	1.20	8.44	.356	7.18	.0796	1	30.
.20	0	.70	8.31	.334	6.77	.0574	2	24.
.40	0	1.30	8.28	.256	5.21	.0630	2	13.
.60	0	2.20	8.62	.266	5.42	.1796	2	22.6
.80	0	2.80	8.58	.232	4.70	.1537	2	28.6
1.0	0	3.35	8.48	.196	3.91	.1185	2	38.3

COMPUTER OUTPUT OF THE PROGRAMME PRECIP  
FOR ALUM JAR TESTS

#	COAG DOSAGE MMOL/L	PH	HCO3 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MU MEQ/L
1	0.10	5.15	0.077	0.000	0.02	-5.51	1.47
2	0.12	5.00	0.055	0.000	-0.04	-5.36	1.54
3	0.20	5.16	0.079	0.000	0.04	-5.36	1.63
4	0.40	4.94	0.049	0.000	-0.04	-5.15	1.98
5	0.60	4.97	0.053	0.000	-0.19	-5.22	2.65
6	0.80	5.07	0.066	0.000	-0.23	-5.54	3.54
7	1.00	5.05	0.063	0.000	-0.32	-5.48	4.39
8	0.10	5.75	0.260	0.000	0.18	-5.45	1.53
9	0.15	5.90	0.339	0.000	0.06	-6.93	1.50
10	0.18	5.96	0.375	0.000	0.08	-7.60	1.53
11	0.20	5.92	0.351	0.000	0.08	-7.02	1.56
12	0.40	6.08	0.455	0.000	-0.11	-7.65	2.20
13	0.40	5.76	0.266	0.000	-0.17	-6.75	1.98
14	0.60	6.18	0.528	0.000	-0.12	-7.91	3.17
15	0.80	6.30	0.618	0.000	-0.08	-8.26	4.18
16	1.00	6.36	0.664	0.000	-0.13	-8.52	5.11
17	0.10	7.37	1.177	0.002	-0.28	-11.37	1.58
18	0.10	7.48	1.199	0.002	-0.12	-12.02	1.65
19	0.12	6.92	1.017	0.001	-0.19	-9.51	1.57
20	0.12	6.90	1.008	0.001	-0.20	-9.35	1.58
21	0.15	6.80	0.954	0.000	-0.18	-9.26	1.60
22	0.15	7.20	1.131	0.001	-0.06	-11.45	1.80
23	0.18	6.70	0.894	0.000	-0.15	-9.65	1.64
24	0.18	7.28	1.154	0.001	-0.08	-11.73	1.95
25	0.20	6.97	1.042	0.001	-0.39	-10.19	1.79
26	0.20	7.23	1.140	0.001	-0.12	-11.53	2.00
27	0.40	7.19	1.129	0.001	-0.15	-11.62	2.87
28	0.60	7.54	1.211	0.003	-0.01	-12.58	3.95
29	0.80	7.73	1.236	0.005	0.00	-13.17	4.89
30	1.00	7.53	1.210	0.003	-0.04	-12.75	5.71
31	0.10	8.54	1.254	0.028	-0.02	-15.85	1.93
32	0.12	8.31	1.260	0.017	-0.05	-14.84	2.01
33	0.15	8.50	1.255	0.026	-0.02	-15.70	2.15
34	0.18	8.44	1.257	0.023	0.52	-15.53	2.52
35	0.20	8.31	1.260	0.017	0.01	-15.15	2.30
36	0.40	8.28	1.260	0.016	-0.01	-14.97	3.21
37	0.60	8.62	1.248	0.036	0.05	-15.85	4.40
38	0.80	8.58	1.250	0.033	0.08	-15.74	5.28
39	1.00	8.48	1.254	0.027	0.10	-15.44	6.12

Samples 13, 17, 20, 21, 23, 25 are repeats.



FRW AlCl<sub>3</sub> JAR TEST RESULTS

Dose (mM/L)	Titrants HCl	(mM/L) NaOH	pH	A <sub>1</sub> cm	DOC (mg/L)	Al <sub>d</sub> (mM/L)	Floc note	t <sub>50</sub> (sec)
0	0	0	7.91	.575	10.59	—	—	6.0
.1	1.15	0	5.42	.241	4.89	.0089	2	20.7
.12	.92	0	5.18	.198	3.95	.0073	2	13.
.15	.85	0	4.93	.154	2.94	.0145	2	17.7
.18	.75	0	4.96	.135	2.48	.0133	2	18
.20	.70	0	4.94	.113	1.95	.0107	2	23
.40	.12	0	4.93	.088	1.32	.0141	1	31
.60	0	.40	4.93	.089	1.35	.0496	1	79
.80	0	1.0	4.84	.082	1.17	.0685	1	61
1.0	0	1.6	4.87	.082	1.17	.0696	1	142
0	0	0	7.70	.604	10.95	—	—	5.8
.1	.85	0	5.43	.259	5.28	.0128	—	7.8
.12	.50	0	6.06	.231	4.68	.0009	—	45
.15	.35	0	6.20	.196	3.91	.0015	1	33
.18	.45	0	5.90	.155	2.96	.0022	2	23.5
.20	.40	0	5.92	.150	2.84	.0030	2	19
.40	0	.40	6.16	.121	2.14	.0047	2	24.5
.60	0	.95	6.18	.115	2.00	.0030	2	44
.80	0	1.75	6.34	.115	2.00	.0022	2	55
1.0	0	2.35	6.37	.111	1.90	.0015	2	68
0	0	0	7.70	.613	11.06	—	—	4.9
.1	0	0	6.98	.580	10.66	.1000	1	6.6
.12	0	0	7.00	.447	8.75	.0707	1	6.5
.15	0	.15	7.13	.301	6.13	.0321	1	8.2
.18	0	.30	7.24	.217	4.37	.0062	1	18
.20	0	.35	7.03	.223	4.51	.0033	2	12
.40	0	1.0	7.18	.162	3.13	.0059	2	25
.60	0	1.75	7.50	.160	3.08	.0139	2	43
.80	0	2.35	7.61	.150	2.84	.0138	2	52
1.0	0	3.15	8.13	.166	3.22	.0704	2	—
0	0	0	7.60	.606	10.97	—	—	5.9
.1	0	.5	8.45	.607	10.99	.0944	0	6.5
.12	0	.45	8.39	.562	10.42	.1007	0	6.1
.15	0	.55	8.27	.449	8.78	.0926	1	8.0
.18	0	.60	8.40	.340	6.88	.0790	2	11.3
.20	0	.85	8.30	.363	7.31	.0907	2	7.5
.40	0	1.5	8.51	.564	10.45	.3481	2	4.5
.60	0	2.05	8.24	.204	4.09	.1111	2	38
.80	0	2.80	8.62	.217	4.37	.1704	2	50
1.0	0	3.25	8.43	.217	4.37	.1330	2	55

COMPUTER OUTPUT OF THE PROGRAMME PRECIP  
FOR  $AlCl_3$  JAR TESTS

#	CQAG DOSAGE MMOL/L	PH	HC03 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MU MEQ/L
1	0.10	5.42	0.136	0.000	-0.08	-5.91	1.56
2	0.10	5.43	0.139	0.000	0.03	-5.77	1.31
3	0.12	5.18	0.082	0.000	-0.05	-5.69	1.35
4	0.15	4.93	0.047	0.000	-0.01	-5.16	1.36
5	0.18	4.96	0.051	0.000	-0.01	-5.22	1.35
6	0.20	4.94	0.048	0.000	-0.02	-5.30	1.35
7	0.40	4.93	0.047	0.000	-0.03	-5.18	1.37
8	0.60	4.93	0.048	0.000	-0.03	-4.62	1.90
9	0.60	4.58	0.022	0.000	0.00	-3.78	2.23
10	0.80	4.84	0.039	0.000	0.02	-4.42	2.56
11	1.00	4.87	0.042	0.000	0.02	-4.42	3.16
12	0.12	6.06	0.438	0.000	-0.01	-8.29	1.30
13	0.15	6.20	0.536	0.000	-0.05	-8.51	1.31
14	0.18	5.90	0.339	0.000	-0.04	-7.46	1.31
15	0.20	5.92	0.350	0.000	-0.06	-7.37	1.32
16	0.40	6.16	0.509	0.000	-0.02	-7.86	1.70
17	0.60	6.18	0.525	0.000	-0.11	-6.88	2.33
18	0.80	6.34	0.645	0.000	-0.01	-8.76	3.04
19	1.00	6.37	0.669	0.000	-0.03	-9.02	3.66
20	0.10	7.10	1.095	0.001	-0.13	-10.91	1.36
21	0.12	7.00	1.054	0.001	-0.22	-9.86	1.40
22	0.15	7.13	1.107	0.001	-0.16	-10.72	1.52
23	0.18	7.24	1.143	0.001	-0.10	-11.87	1.64
24	0.20	7.03	1.068	0.001	-0.03	-11.30	1.66
25	0.40	7.18	1.125	0.001	0.05	-11.62	2.31
26	0.60	7.50	1.204	0.003	-0.01	-12.51	3.04
27	1.00	7.61	1.221	0.003	0.61	-12.93	3.95
28	0.10	8.45	1.257	0.023	0.04	-15.52	1.79
29	0.12	8.39	1.259	0.020	-0.07	-15.25	1.79
30	0.15	8.27	1.260	0.015	-0.04	-14.80	1.87
31	0.18	8.40	1.259	0.020	0.07	-15.39	1.95
32	0.20	8.30	1.260	0.016	-0.11	-14.92	2.10
33	0.40	8.51	1.255	0.027	0.29	-15.15	2.96
34	0.60	8.24	1.260	0.015	0.06	-14.56	3.32
35	0.80	8.62	1.248	0.035	0.07	-15.88	4.09
36	1.00	8.13	1.258	0.012	0.03	-14.29	4.44
37	1.00	8.43	1.297	0.023	0.00	-15.21	4.57

Samples 9 and 36 are repeats.

## FRW ALPOL JAR TEST RESULTS

Dose mM/L	Titrants HCl	mM/L NaOH	pH	A <sub>254 nm</sub> 1 cm.	DOC mg/L	AT <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
0	0	0	8.20	.571	10.54	—	—	7.6
.1	1.12	0	5.36	.288	5.87	.0148	2	31.2
.12	1.22	0	4.85	.249	5.06	.0170	2	8.6
.15	1.05	0	5.28	.202	4.04	.0087	2	12.9
.18	1.07	.07	5.22	.175	3.43	.0096	2	14.3
.20	1.15	.05	5.36	.167	3.17	.0105	2	25.6
.40	.80	0	5.52	.113	1.95	.0141	2	32.2
.60	.52	0	5.50	.105	1.75	.0345	1	66.4
.80	.32	0	5.36	.126	2.27	.2667	1	47.3
1.0	.15	0	5.30	.133	2.43	.4100	1	51
0	0	0	7.95	.570	10.53	—	—	7.3
.1	.90	0	5.79	.308	6.27	.0036	1	28
.12	.68	0	6.22	.370	7.44	.0333	1	7.9
.15	.58	0	6.34	.267	5.44	.0182	1	8.6
.18	.75	0	5.94	.217	4.37	.0092	2	9.7
.20	.65	0	5.85	.184	3.63	.0033	2	20.2
.40	.35	0	6.05	.121	2.14	.0006	2	23.6
.60	0	0	6.14	.114	1.97	.0010	1	43.8
.80	0	.30	6.29	.112	1.92	.0009	1	55.4
1.0	0	.65	6.40	.110	1.87	.0009	2	80.9
0	0	0	8.15	.574	10.58	—	—	6.4
.1	.2	0	6.74	.346	7.00	.0090	1	36.4
.12	.15	0	7.09	.305	6.21	.0050	1	44.2
.15	.10	0	7.14	.260	5.30	.0032	1	34.7
.18	0	0	7.23	.252	5.13	.0010	2	10.3
.20	.05	0	6.82	.210	4.22	.0018	2	27
.40	0	.2	6.92	.180	3.54	.0020	2	22.6
.60	0	.48	7.10	.142	2.65	.0022	2	28.2
.80	0	.80	7.07	.125	2.24	.0037	2	48.5
1.0	0	1.10	7.15	.121	2.14	.0044	2	64.1
0	0	0	8.29	.576	10.61	—	—	6.3
.1	0	.15	8.30	.438	8.60	.0437	0	9.3
.12	0	.20	8.22	.504	9.62	.0737	0	6.7
.15	0	.30	8.52	.304	6.19	.0470	0	29.6
.18	0	.32	8.44	.308	6.24	.0456	1	29.4
.20	0	.32	8.25	.288	5.87	.0306	2	24.3
.40	0	.60	8.25	.210	4.22	.0407	2	22.5
.60	0	.88	8.18	.178	3.50	.0389	2	30.6
.80	0	1.25	8.38	.167	3.24	.0622	2	40.5
1.0	0	1.45	8.30	.150	2.84	.0552	2	58.1

COMPUTER OUTPUT OF THE PROGRAMME PRECIP  
FOR ALPOL JAR TESTS

#	COAG DOSAGE MMOL/L	PH	HCO3 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MU MEQ/L
1	0.10	5.36	0.123	0.000	-0.01	-5.60	1.55
2	0.12	4.85	0.041	0.000	-0.03	-5.04	1.63
3	0.15	5.28	0.104	0.000	0.01	-5.72	1.62
4	0.18	5.22	0.092	0.000	-0.03	-5.61	1.70
5	0.20	5.36	0.124	0.000	0.25	-4.91	1.91
6	0.40	5.52	0.172	0.000	-0.05	-5.84	2.16
7	0.60	5.50	0.166	0.000	-0.02	-5.42	2.50
8	0.80	5.36	0.125	0.000	0.50	-4.31	3.34
9	1.00	5.30	0.111	0.000	0.80	-4.03	4.08
10	0.10	5.79	0.286	0.000	0.02	-6.97	1.50
11	0.12	6.22	0.564	0.000	-0.09	-7.21	1.60
12	0.15	6.34	0.655	0.000	-0.11	-7.89	1.65
13	0.18	5.94	0.372	0.000	-0.01	-6.92	1.66
14	0.20	5.85	0.319	0.000	0.12	-7.15	1.63
15	0.40	6.05	0.444	0.000	0.05	-8.40	2.02
16	0.60	6.14	0.508	0.000	0.09	-8.43	2.36
17	0.80	6.29	0.622	0.000	0.04	-8.98	3.04
18	1.00	6.40	0.707	0.000	0.06	-9.36	3.74
19	0.10	6.74	0.939	0.000	0.05	-9.72	1.48
20	0.12	7.09	1.117	0.001	-0.10	-11.36	1.59
21	0.15	7.14	1.136	0.001	-0.10	-11.76	1.64
22	0.18	7.23	1.166	0.001	-0.08	-11.63	1.69
23	0.20	6.82	0.973	0.000	0.03	-10.74	1.64
24	0.40	6.92	1.027	0.001	-0.01	-11.06	2.23
25	0.60	7.10	1.106	0.001	-0.05	-11.71	2.89
26	0.80	7.07	1.096	0.001	0.04	-11.36	3.52
27	1.00	7.15	1.126	0.001	0.06	-11.58	4.17
28	0.10	8.30	1.270	0.016	-0.04	-15.26	1.67
29	0.12	8.22	1.270	0.013	-0.05	-14.70	1.75
30	0.15	8.52	1.265	0.027	0.03	-16.10	1.88
31	0.18	8.44	1.267	0.022	0.02	-15.79	1.96
32	0.20	8.25	1.270	0.015	0.03	-15.20	1.98
33	0.40	8.25	1.269	0.015	0.05	-15.05	2.67
34	0.60	8.18	1.269	0.013	0.10	-14.78	3.22
35	0.80	8.38	1.268	0.021	0.17	-15.36	3.93
35	1.00	8.30	1.269	0.027	0.15	-15.08	4.49

## FRW Algel JAR TEST RESULTS

Dose mM/L	Titants HCl	mM/L NaOH	pH	A <sub>1</sub> <sup>254 nm</sup> 1 cm	DOC mg/L	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
0	0	0	7.87	.580	10.66	—	—	6.3
.1	1.15	0	5.25	.325	6.60	.0067	2	26.2
.12	1.20	0	4.88	.290	5.91	.0083	2	27
.15	1.15	0	5.09	.250	5.09	.0049	2	28.6
.18	1.15	0	5.07	.216	4.35	.0047	2	40.9
.20	1.10	0	5.16	.193	3.84	.0057	2	40.7
.40	1.05	0	5.19	.120	2.12	.0293	2	57
.60	.95	0	5.19	.105	1.75	.0741	2	107
.80	.85	0	5.20	.099	1.60	.0862	1	217
1.0	.80	0	5.13	.096	1.52	.1136	1	100
0	0	0	7.90	.579	10.64	—	—	6.4
.1	1.0	0	5.79	.317	6.44	.0030	2	31.6
.12	1.05	0	5.59	.301	6.13	.0033	2	42.1
.15	.90	0	5.93	.267	5.44	.0012	2	43.5
.18	.85	0	5.99	.236	4.79	.0017	2	37
.20	.80	0	6.10	.221	4.46	.0013	2	40.8
.40	.70	0	6.08	.123	2.19	.0018	2	53.7
.60	.65	0	6.05	.109	1.85	.0010	2	63.4
.80	.50	0	6.03	.102	1.87	.0011	2	125.3
1.0	.32	0	6.12	.102	1.67	.0017	2	188.7
0	0	0	7.75	.575	10.59	—	—	6.4
.1	.25	0	6.89	.484	9.33	.0503	2	6.9
.12	.60	0	6.75	.321	6.52	.0035	1	34.8
.15	.30	0	6.98	.296	6.03	.0044	1	41
.18	.30	0	6.89	.253	5.15	.0025	2	41
.20	.10	0	7.10	.259	5.28	.0022	2	30.7
.40	0	0	7.10	.157	3.01	.0015	2	51.7
.60	0	.05	7.06	.125	2.24	.0015	2	57.5
.80	0	.20	7.12	.119	2.09	.0015	2	77.1
1.0	0	.40	7.24	.119	2.09	.0022	2	74.8
0	0	0	7.80	.582	10.68	—	—	6.6
.1	0	.15	8.70	.532	10.02	.0648	0	6.8
.12	0	.10	8.35	.370	7.44	.0200	1	36.5
.15	0	.12	8.24	.349	7.05	.0263	1	12.0
.18	0	.15	8.47	.315	6.41	.0323	2	23.0
.20	0	.22	8.58	.293	5.97	.0400	2	48
.40	0	.30	8.43	.216	4.35	.0393	2	48
.60	0	.40	8.26	.174	3.40	.0298	2	51.6
.80	0	.50	8.30	.157	3.01	.0393	2	55
1.0	0	.62	8.34	.145	2.72	.0417	2	66.9

COMPUTER OUTPUT OF THE PROGRAM PRECIP  
FOR Algel JAR TEST

#	COAG DOSAGE MMOL/L	PH	HCO3 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MU MEQ/L
1	0.10	5.25	0.096	0.000	0.01	-5.80	1.56
2	0.20	5.16	0.079	0.000	0.03	-5.76	1.80
3	0.40	5.19	0.085	0.000	0.03	-5.07	2.38
4	0.60	5.19	0.085	0.000	0.13	-4.66	2.98
5	0.80	5.20	0.087	0.000	0.16	-4.60	3.51
6	1.00	5.13	0.075	0.000	0.19	-4.40	4.11
7	0.10	6.89	1.002	0.000	-0.08	-9.56	1.58
8	0.20	7.10	1.096	0.001	-0.01	-11.75	1.80
9	0.40	7.10	1.097	0.001	-0.01	-11.90	2.30
10	0.60	7.06	1.082	0.001	-0.05	-11.72	2.86
11	0.80	7.12	1.106	0.001	-0.02	-11.95	3.50
12	1.00	7.24	1.146	0.001	-0.04	-12.24	4.17
13	0.10	5.79	0.280	0.000	-0.04	-7.06	1.56
14	0.20	6.10	0.467	0.000	-0.08	-8.24	1.83
15	0.40	6.08	0.455	0.000	-0.06	-8.01	2.32
16	0.60	6.05	0.437	0.000	-0.10	-8.14	2.84
17	0.80	6.03	0.424	0.000	-0.03	-8.04	3.31
18	1.00	6.12	0.487	0.000	-0.02	-8.12	3.80
19	0.10	8.70	1.245	0.040	-0.03	-16.68	1.75
20	0.20	8.58	1.252	0.031	0.03	-16.40	2.02
21	0.40	8.43	1.257	0.022	0.02	-15.79	2.60
22	0.60	8.26	1.260	0.015	0.05	-15.21	3.18
23	0.80	8.30	1.259	0.017	0.03	-15.24	3.79
24	1.00	8.34	1.259	0.019	0.04	-15.36	4.41
25	0.10	5.59	0.192	0.000	0.00	-6.61	1.60
26	0.20	5.93	0.357	0.000	-0.04	-7.79	1.69
27	0.40	5.99	0.395	0.000	-0.04	-7.79	1.76
28	0.60	4.88	0.043	0.000	0.02	-5.37	1.63
29	0.80	5.09	0.068	0.000	0.02	-5.76	1.68
30	1.00	5.07	0.065	0.018	0.00	-5.76	1.76
31	0.10	8.35	1.260	0.018	0.00	-15.79	1.71
32	0.20	8.24	1.260	0.014	0.01	-15.23	1.80
33	0.40	8.47	1.257	0.024	-0.01	-16.06	1.92
34	0.60	6.75	0.925	0.000	-0.30	-10.17	1.74
35	0.80	6.98	1.046	0.001	-0.14	-10.97	1.74
36	1.00	6.89	1.003	0.000	-0.11	-10.86	1.79

$A_{254 \text{ nm}} / \text{cm}$  / DOC CORRELATION FOR FRW

Sample #	$A_{254 \text{ nm}} / \text{cm}$	DOC mg/L	Regressed DOC mg/L
DW	.065	.09	—
B1	.602	11.25	10.93
2	.421	8.27	8.32
3	.264	5.26	5.38
4	.186	3.64	3.68
5	.536	10.28	10.08
6	.565	10.84	10.46
7	.341	6.81	6.90
8	.421	8.68	8.32
9	.207	4.80	4.15
10	.356	7.56	7.18
11	.119	2.08	2.10
12	.125	2.36	2.25
13	.157	3.28	3.01
14	.259	5.81	5.28
15	.317	7.01	6.45
16	.102	1.60	1.68
17	.096	1.49	1.53
18	.576	11.27	10.61
19	.438	9.34	8.61
20	.240	4.47	4.22
21	.346	6.91	7.0
22	.142	2.90	2.66
23	.308	6.31	6.27
24	.110	1.83	1.84
25	.504	9.11	9.63

APPENDIX A5  
JAR TEST RESULTS FOR FDW



## FDW Alum JAR TEST RESULTS

Dose mM/L	Titrant	mM/L	pH	A <sub>254 nm</sub> 10 cm	DOC mg/L	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
0	—	—	8.05	1.244	3.43	—	—	6.6
.15	.55	0	5.14	.189	.79	.0081	1	10
.20	.40	0	5.19	.185	.77	—	1	21
.40	0	0	4.88	.198	.82	—	1	19.8
.60	0	.55	4.88	.192	.80	.0268	2	23.6
.80	0	1.10	4.95	.187	.78	—	2	26.6
1.0	0	1.65	4.94	.186	.78	.0250	2	38.4
0	—	—	8.05	1.244	3.43	—	—	6.6
.15	.25	0	6.04	.196	.81	—	2	15.9
.20	0	0	6.24	.192	.80	—	2	11.1
.40	.05	.5	6.11	.183	.77	.0005	2	16.0
.60	0	1.0	6.03	.177	.75	.0014	2	25.2
.80	0	1.77	6.30	.181	.76	.0053	2	28.5
1.0	0	2.10	5.88	.173	.73	—	2	35.1
0	—	—	8.00	1.226	3.40	—	—	7.0
.15	0	.35	7.25	.269	1.06	.0061	2	11.6
.20	0	.50	7.27	.250	1.00	—	2	16.1
.40	0	1.05	7.26	.229	.93	.0062	2	16.6
.60	0	1.70	7.41	.224	.91	—	2	23.1
.80	0	2.27	7.34	.213	.87	.0046	2	30.4
1.0	0	2.80	7.14	.207	.85	—	2	35.4
0	—	—	8.00	1.226	3.40	—	—	7.0
.15	0	.58	8.43	.554	1.95	—	2	7.8
.20	0	.78	8.45	.489	1.76	.0891	2	14.2
.40	0	1.35	8.38	.327	1.26	—	2	16.1
.60	0	2.0	8.49	.290	1.13	.0921	2	25.1
.80	0	2.62	8.53	.276	1.09	.0851	2	28.8
1.0	0	3.25	8.51	.264	1.05	—	2	31.3

COMPUTER OUTPUT OF THE PROGRAM PRECIP  
FOR Alum JAR TESTS

#	COAG DOSAGE MMOL/L	PH	HCO3 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MU MEQ/L
1	0.15	5.14	0.058	0.000	-0.03	-5.64	1.27
2	0.60	4.88	0.033	0.000	-0.18	-5.04	2.62
3	1.00	4.94	0.039	0.000	-0.28	-5.17	4.36
4	0.40	6.11	0.368	0.000	-0.12	-8.62	2.16
5	0.60	6.03	0.328	0.000	-0.13	-7.94	2.97
6	0.80	6.30	0.479	0.000	-0.11	-8.21	4.03
7	0.15	7.25	0.888	0.001	-0.00	-11.92	1.58
8	0.40	7.26	0.891	0.001	-0.05	-11.91	2.68
9	0.80	7.34	0.909	0.001	-0.05	-12.31	4.50
10	0.20	8.45	0.972	0.021		-15.53	
11	0.60	8.49	0.973	0.020	0.02	-15.63	3.91
12	0.80	8.53	0.971	0.023	0.05	-15.80	4.82

COMPUTER OUTPUT OF THE PROGRAMME  
ADSPREC FOR Alum JAR TESTS

#	DOSE (mMol/L)	pH	DOC (mg/L)	X/M (mg/mM)
1	0.15	5.14	0.79	19.83
2	0.20	5.19	0.78	14.22
3	0.40	4.88	0.82	8.12
4	0.60	4.88	0.80	5.15
5	0.80	4.95	0.79	3.60
6	1.00	4.94	0.78	2.86
7	0.15	6.04	0.82	17.52
8	0.20	6.24	0.80	13.18
9	0.40	6.11	0.77	6.64
10	0.60	6.03	0.75	4.46
11	0.80	6.30	0.76	3.33
12	1.00	5.88	0.74	2.69
13	0.15	7.25	1.07	17.06
14	0.20	7.27	1.00	12.90
15	0.40	7.26	0.93	6.42
16	0.60	7.41	0.92	4.30
17	0.80	7.34	0.88	3.24
18	1.00	7.14	0.86	2.59
ALD > DOSE				
20	0.20	8.45	1.76	318.74
21	0.40	8.38	1.26	9.27
22	0.60	8.49	1.14	5.95
23	0.80	8.53	1.09	4.15
24	1.00	8.51	1.05	3.07

FDW  $AlCl_3$  JAR TEST RESULTS

Dose mM/L	Titrant HCl	mM/L NaOH	pH	$A_{254\text{ nm}}$ $A_{10}$	DOC mg/L	$Al_d$ mM/L	Floc note	$t_{50}$ (sec)
0	—	—	8.00	1.233	—	—	—	6.9
.15	.55	.05	5.41	.167	—	—	1	8.0
.20	.30	0	5.33	.994	.2930	—	1	7.3
.40	0	.25	5.23	.127	—	—	1	183.4
.60	0	.85	5.12	.119	.0489	—	1	253.7
.80	0	1.40	5.03	.131	—	—	1	185.3
1.0	0	2.05	5.03	.137	.2044	—	1	240.6
0	—	—	8.00	1.233	—	—	—	6.9
.15	.31	0	5.92	.185	—	—	1	14.4
.20	0	0	6.20	.177	.0015	—	1	30.9
.40	0	.57	6.13	.158	—	—	1	54.7
.60	0	1.35	6.20	.154	—	—	1	80.3
.80	0	1.80	6.22	.152	.0001	—	1	84.9
1.0	0	2.47	6.19	.146	.0002	—	1	110.8
0	—	—	7.61	1.235	—	—	—	6.3
.15	0	.32	7.24	.266	.0033	—	2	11.2
.20	0	.51	7.49	.307	—	—	2	—
.40	0	1.11	7.36	.216	.0090	—	2	26.8
.60	0	1.72	7.50	.213	—	—	2	36.3
.80	0	2.40	7.68	.214	—	—	2	45.6
1.0	0	2.98	7.59	.205	.0141	—	2	56.3
0	—	—	7.61	1.235	—	—	—	6.3
.15	0	.70	8.72	.985	—	—	1	7.2
.20	0	.87	8.44	.705	.1411	—	2	11.9
.40	0	1.55	8.56	.475	—	—	2	22.1
.60	0	2.21	8.50	.350	.1976	—	2	28.8
.80	0	2.81	8.51	.305	.2107	—	2	37
1.0	0	3.40	8.46	.277	—	—	2	47.5

COMPUTER OUTPUT OF THE PROGRAMME PRECIP  
FOR  $AlCl_3$  JAR TESTS

#	COAG DOSAGE MMOL/L	PH	HCO3 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MJ MEQ/L
1	0.20	8.44	0.975	0.017	0.05	-15.30	1.86
2	0.60	8.50	0.973	0.021	0.07	-15.35	3.20
3	0.80	8.51	0.972	0.021	0.03	-15.35	3.82
4	0.15	7.24	0.885	0.001	-0.02	-12.16	1.33
5	0.40	7.36	0.911	0.001	-0.02	-12.16	2.12
6	1.00	7.59	0.945	0.002	0.01	-12.84	3.98
7	0.20	6.20	0.414	0.000	-0.01	-8.52	1.01
8	0.80	6.13	0.381	0.000	0.02	-9.40	2.79
9	1.00	6.19	0.415	0.000	0.06	-9.24	3.44
10	0.60	5.12	0.056	0.000	0.11	-4.79	1.97
11	1.00	5.03	0.047	0.000	0.49	-4.06	3.56

COMPUTER OUTPUT OF THE PROGRAMME ADSPREC  
FOR  $AlCl_3$  JAR TESTS

#	DOSE (mMol/L)	PH	DOC (mg/L)	X/M (mg/mM)
1	0.15	5.41	0.71	18.70
2	0.20	5.33	3.00	2.15
3	0.40	5.23	0.57	7.32
4	0.60	5.12	0.54	4.95
5	0.80	5.03	0.58	3.68
6	1.00	5.03	0.61	2.90
7	0.15	5.92	0.78	17.78
8	0.20	6.20	0.75	13.44
9	0.40	6.13	0.68	6.86
10	0.60	6.20	0.67	4.59
11	0.80	6.22	0.66	3.45
12	1.00	6.19	0.64	2.78
13	0.15	7.24	1.06	17.08
14	0.20	7.49	1.20	12.42
15	0.40	7.36	0.89	6.59
16	0.60	7.50	0.88	4.39
17	0.80	7.68	0.88	3.31
18	1.00	7.59	0.85	2.64
ALD	> DOSE			
20	0.20	8.44	2.36	104.25
21	0.40	8.56	1.72	11.45
22	0.60	8.50	1.34	5.49
23	0.80	8.51	1.19	3.89
24	1.00	8.46	1.10	2.91

$A_{10\text{ cm}}^{254\text{ nm}}$  / DOC Correlation For FDW

Sample #	$A_{10\text{ cm}}^{254\text{ nm}}$	DOC mg/L	Regressed DOC mg/L
B30	1.244	3.375	3.43
31	.185	.834	.77
32	.198	.915	.82
33	.196	.847	.81
34	.173	.737	.73
35	.250	1.007	1.00
36	.224	.951	.91
37	.327	1.134	1.26
38	.554	1.741	1.95
40	.985	3.120	2.98
41	.475	1.825	1.72
42	.277	1.178	1.09
43	.213	.886	.87
44	.158	.670	.68
45	.127	.435	.56

APPENDIX A6 BLANK RUNS

## Alum Blank Runs

Dose mM/L	Titrant HCl	mM/L NaOH	pH	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
.1	1.0	0	5.11	.0063	1	19.7
.5	0	0	4.90	.0331	2	22.9
1.0	0	1.40	5.04	.0155	2	31.2
1	.60	0	6.05	.0029	1	13.6
.5	0	.52	6.12	.0012	2	17.1
1.0	0	2.12	6.21	.0037	2	29.9
.1	0	.07	7.15	.0040	2	11.2
.5	0	1.25	7.29	.0032	2	15.7
1.0	0	2.80	7.15	.0022	2	28.7
.1	0	.35	8.19	.0449	1	7.2
.5		2.0	8.83	.2802	2	9.5
1.0		3.15	8.24	—	2	27.1

## COAGULANT IDENTIFICATION: ALUM

#	COAG DOSAGE MMOL/L	pH	HCO <sub>3</sub> MMOL/L	CO <sub>3</sub> MMOL/L	IONIC BALANCE MMOL/L	LOG AL <sub>3+</sub>	MU MEQ/L
1	0.10	5.11	0.071	0.000	-0.05	-5.70	1.50
2	0.50	4.90	0.045	0.000	-0.13	-4.94	2.21
3	1.00	5.04	0.063	0.000	-0.30	-5.42	4.39
4	0.10	6.05	0.436	0.000	-0.03	-7.73	1.47
5	0.50	6.12	0.487	0.000	-0.17	-8.31	2.66
6	1.00	6.21	0.558	0.000	-0.14	-8.05	4.99
7	0.10	7.15	1.122	0.001	-0.06	-11.70	1.55
8	0.50	7.29	1.168	0.002	-0.13	-12.30	3.36
9	1.00	7.15	1.127	0.001	-0.03	-11.86	5.62
10	0.10	8.19	1.269	0.013	-0.01	-14.80	1.82
11	0.50	8.83	1.239	0.057	-0.05	-16.50	4.13

AlCl<sub>3</sub> Blank Runs

Dose mM/L	Titrant HCl	mM/L NaOH	pH	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
.1	.95	0	5.13	.0244	0	9.0
.5	0	0	4.95	.5010	0	6
1.0	0	1.45	4.91	.8905	0	9.1
.1	.55	0	6.16	.0025	0	23.9
.5	0	.65	6.15	.0007	0	107.1
1.0	0	2.2	6.16	.0012	1	142.2
.1	0	.12	7.24	.0039	2	11.9
.5	0	1.32	7.31	.0056	2	38.0
1.0	0	2.85	7.35	.0098	2	55.5
.1	0	.45	8.43	.0678	1	6.8
.5	0	2.72	8.53	.1139	2	26.3
1.0	0	3.30	8.53	.1048	2	48.4

COAGULANT IDENTIFICATION: AlCl<sub>3</sub>

#	COAG DOSAGE MMOL/L	pH	HCO <sub>3</sub> MMOL/L	CO <sub>3</sub> MMOL/L	IONIC BALANCE MMOL/L	LOG AL <sub>3</sub> <sup>+</sup>	MU MEQ/L
1	0.10	5.13	0.074	0.000	0.04	-5.11	1.37
2	0.50	4.95	0.051	0.000	0.89	-3.62	2.72
3	1.00	4.91	0.047	0.000	1.78	-3.33	5.23
4	0.10	6.16	0.511	0.000	-0.06	-8.14	1.33
5	0.50	6.15	0.507	0.000	-0.06	-8.66	1.98
6	1.00	6.16	0.518	0.000	-0.02	-8.41	3.51
7	0.10	7.24	1.151	0.001	-0.04	-12.07	1.44
8	0.50	7.31	1.172	0.002	-0.06	-12.15	2.65
9	1.00	7.35	1.183	0.002	-0.05	-12.04	4.18
10	0.10	8.43	1.268	0.022	0.04	-12.58	1.75
11	0.50	8.53	1.263	0.029	1.00	-15.70	3.55
12	1.00	8.53	1.262	0.029	0.09	-15.72	4.59



## Alpol Blank Runs

Dose mM/L	Titrants HCl	mM/L NaOH	pH	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
.1	1.22	0	5.22	.0663	0	6.5
.5	.65	0	5.23	.4431	0	7.6
1.0	.18	0	5.15	.8774	0	6.5
.1	.75	0	6.14	.0588	0	6.5
.5	.15	0	6.20	.4168	0	8.6
1.0	0	.35	6.08	.4256	0	146
.1	.12	0	7.28	.0013	1	25.5
.5	0	.45	7.33	.0025	1	89.5
1.0	0	1.10	7.26	.0074	1	146.2
.1	0	.20	8.26	.0185	0	11.4
.5	0	.68	8.18	.0251	2	40.9
1.0	0	1.4	8.26	.0308	2	74.5

## COAGULANT IDENTIFICATION A1P01

#	COAG DOSAGE MMOL/L	pH	HC03 MMOL/L	CO3 MMOL/L	IONIC BALANCE MMOL/L	LOG AL3+	MU MEQ/L
1	0.10	5.22	0.090	0.000	0.02	-4.77	1.69
2	0.50	5.23	0.094	0.000	0.96	-3.93	3.21
3	1.00	5.15	0.080	0.000	1.97	-3.52	5.32
4	0.10	6.14	0.498	0.000	-0.08	-6.70	1.56
5	0.50	6.20	0.544	0.000	-0.21	-6.01	2.56
6	1.00	6.08	0.463	0.000	-0.03	-5.59	3.89
7	0.10	7.28	1.163	0.001	-0.11	-12.71	1.54
8	0.50	7.33	1.177	0.002	-0.03	-12.59	2.67
9	1.00	7.26	1.160	0.001	0.02	-11.80	4.19
10	0.10	8.26	1.270	0.015	0.05	-15.47	1.67
11	0.50	8.18	1.269	0.013	0.04	-14.98	2.87
12	1.00	8.26	1.269	0.016	0.14	-15.17	4.44

## Algel Blank Runs

Dose mM/L	Titrant HCl	mM/L NaOH	pH	Al <sub>d</sub> mM/L	Floc note	t <sub>50</sub> (sec)
.1	1.25	0	5.18	.0696	0	7.1
.5	1.0	0	5.21	.3479	0	6.6
1.0	.72	0	5.15	.9343	0	6.5
.1	.75	0	6.22	.0559	1	6.8
.5	.50	0	6.21	.4097	1	6.6
1.0	.18	0	6.19	.9122	1	6.4
.1	.1	0	7.29	.0050	1	38.6
.5	0	.17	7.37	.0034	2	79.1
1.0	0	.48	7.34	.0048	2	104.8
.1	0	.12	8.24	.0280	2	10.2
.5	0	.35	8.09	.0223	2	38.1
1.0	0	.75	8.28	.0404	2	59.1

## COAGULANT IDENTIFICATION Algel

#	COAG DOSAGE MMOL/L	pH	HCO <sub>3</sub> MMOL/L	CO <sub>3</sub> MMOL/L	IONIC BALANCE MMOL/L	LOG Al <sup>3+</sup>	MU MEQ/L
1	0.10	5.18	0.083	0.000	0.07	-4.70	1.75
2	0.50	5.21	0.090	0.000	0.76	-4.01	3.36
3	1.00	5.15	0.080	0.000	2.31	-3.49	6.12
4	0.10	6.22	0.556	0.000	-0.09	-6.98	1.62
5	0.50	6.21	0.553	0.000	-0.23	-6.04	2.91
6	1.00	6.19	0.542	0.000	-0.42	-5.59	4.67
7	0.10	7.29	1.166	0.001	-0.03	-12.16	1.56
8	0.50	7.37	1.186	0.002	0.02	-12.61	2.71
9	1.00	7.34	1.181	0.002	0.09	-12.30	4.24
10	0.10	8.24	1.270	0.014	0.03	-15.21	1.67
11	0.50	8.09	1.267	0.010	0.07	-14.67	2.87
12	1.00	8.28	1.269	0.017	0.17	-15.13	4.48

APPENDIX A7  
COMPUTER PROGRAMMES

Two computer programmes were developed for this work:

(i) PRECIP designed to calculate the activity of the ion  $Al^{3+}$ , from pH data and the ionic strength.

(ii) ADSPREC designed to calculate the loading of the floc, from pH and DOC Data.

Both programmes were written in FORTRAN 77 compatible with VAX Computers (interactive FORTRAN).

A7.1 Programme PRECIP

A7.1.1 Input Sequence

The input sequence is made of two parts:

(i) Inputs related to the quality of the raw water, the type of coagulant used, and the number of samples to be processed.

This includes the Alkalinity of the raw water, which is used for the speciation of the carbonic species, and the calculation of the ionic strength, and the name of the coagulant, which is used for calculating the Sodium, Chloride, and Sulfate contents. These values are used later for the calculation of the ionic strength and/or the Aluminum speciation

itself.

(ii). Inputs related to the individual samples.

This includes the coagulant dosage, the titrant dosages, the final pH and the dissolved Aluminum. The dosages are used to calculate the ionic strength, whereas, the pH and dissolved Aluminum are used to calculate the Aluminum speciation itself.

#### A7.1.2 Computation Sequences

The data are first processed to convert them into molar units, and the ionic strength is initialized to

$$0.5((\text{Na})+(\text{Cl})+4(\text{SO}_4)+(\text{Al}_D))$$

The activity coefficients are then calculated. This point in the programme (address 4) is the upper limit of a loop, closing on a check of the stability of the value of the ionic strength (relative change less than  $10^{-3}$ ). The values of these coefficients are incorporated into the constants of the equations leading to the speciation of Carbonic and Aluminum ions.

A similar inner loop is set for the Sulfate, which stabilizes the value of the concentration of the free Sulfate ion  $\text{SO}_4^{2-}$ , whenever the coagulant name is set to "ALUM". Otherwise, the values of  $\text{SO}_4^{2-}$  and  $\text{AlSO}_4^+$  are set to 0., and the loop is bypassed. This loop ends at the statement addressed 3.

The ionic strength is then calculated, and the loop 4 is closed or opened accordingly. The activity of  $Al^{3+}$  is converted into  $\log_{10}[Al^{3+}]$  for the output sequence, and the ionic balance is calculated.

#### A7.1.3 Output Sequence

The output sequence prints a table recalling the coagulant identification. Each line of the output is then printed as the sample identification number, the dosage and pH, the results of the carbonic speciation, the ionic balance, the  $\log[Al^{3+}]$ , and finally the ionic strength. The major loop is closed at the statement addressed 5, and a new sample is treated.

#### A7.1.4 PRECIP Programme Listing

This listing is presented in the next page.

#### A7.2 Programme ADSPREC

This programme can be considered as the reverse of the programme PRECIP, since it allows to calculate the dissolved Aluminum, from pH and ionic strength related data.

Furthermore, the programme also calculates the floc loading.

The DOC is evaluated by a binomial function of the  $Al_{10}^{254\text{ nm}}$  (function  $DOC(X)$ ).



#### A7.2.1 Input Sequence

The structure of this sequence is very similar to the input sequence of the programme PRECIP. A first subsequence allows to enter the alkalinity and the  $A_{10\text{ cm}}^{254\text{ nm}}$  of the raw water. These data are converted into molar value and mg DOC/L respectively. The next entries are the coagulant identification, the number of samples to be processed, and the average value of  $pK_s (-\log[H^+]^3/[Al^{3+}])$ . The inputs related to individual samples are the coagulant and titrant dosages, the resulting pH and  $A_{10\text{ cm}}^{254\text{ nm}}$ .

#### A7.2.2. Computation Sequence

This sequence converts all the data into molar values, and initializes the ionic strength to 0. Aluminum species are calculated individually from pH values and  $pK_s$ . The presence of Sulfate is treated in the same way as in the programme PRECIP. The carbonate equilibrium is then solved. The ionic strength is then calculated, and checked with respect to its stability. This allows to open or close the loop beginning at the statement address 10.

The dissolved Aluminum is then calculated and checked with respect to the dosage. If  $Al_D$  is greater than the dosage, a message stating this anomaly is printed, and the major loop of the programme resumes (loop 1).

### A7.2.3 Output Sequence

This sequence prints the sample identification number, the coagulant dosage and pH, and the DOC and floc loading. Then the major loop is closed.

### A7.2.4 Programme Listing

The listing is presented in the next page.



```

PROGRAM ADSPREC
REAL M,MU
CHARACTER*5,COAG
DIMENSION XK(15),R(15),Z(15),C(15),AC(15)
DATA (XK(I),I=1,7)/1.02E-3,7.41E-11,0.,6.92E-23,1620.,4.31E-7,
12.41E-17/
DATA(R(I),I=1,10)/9.,5.4,5.4,9.,3.5,5.5,5.4,5.4/
DATA(Z(I),I=1,13)/2.,1.,1.,1.,1.,-1.,-2.,-1.,-2.,0.,-1.,1.,1./
DOC(X)=.090+3.903*X-.978*X*X
FX)=10.*(-.5*ZA*ZASQRT(X))/(1.+33*RA*SQRT(X))
TYPE 101
FORMAT(1X,'Enter RW Alkalinity(mM/L) & A(1cm):',S)
ACCEPT*,ALK,UV
ALK=ALK/1000.
DOC=DOC(UV)
TYPE 102
FORMAT(1X,'Enter Coagulant ID (ALUM,ALCL3,ALPOL,ALGEL):',S)
ACCEPT*,COAG
TYPE 103
FORMAT(1X,'Enter # of samples :',S)
ACCEPT*,NS
PRINT 201
FORMAT(1X,43(' '),.4X,'M',.6X,'DOSE',.6X,'PH',.6X,'DOC',
16X,'X/M',.10X,'(mMol/L)',.9X,'(mg/L)',.3X,'(mg/mM)',
27.3X,'3(-)',.4X,'8(-)',.2X,'4(-)',.3X,'6(-)',.3X,'7(-)')
TYPE 105
FORMAT(1X,'Enter PKs :',S)
ACCEPT*,PKS
XK(3)=10.*(-PKS)
D01,I1=1,N9
D011,I11=1,15
C(111)=0
AC(111)=0.
TYPE 104,11
FORMAT(1X,'Sample #',I3,/,1X,'Enter DOSE,TITH,TITB
1,(mMol/L),PH,A(1cm),')
ACCEPT*,DOSE,TITH,TITB,PH,UV
DOSE=DOSE/1000.
TITH=TITH/1000.
TITB=TITB/1000.
DOSE=DOC(UV)
IF(COAG.EQ.'ALUM')SD04T=1.5*DOSE
IF(COAG.EQ.'ALPOL')TITB=TITB+1.8*DOSE
IF(COAG.EQ.'ALGEL')TITB=TITB+2.5*DOSE
IF(COAG.NE.'ALUM')C(12)=3.*DOSE
C(12)=C(12)+TITH
C(13)=ALK+TITB
M=10.*(-PH)
OM=1.E-14/M
H2=H2*H
H3=H2*H
H4=H3*H
MU=0
D02,I2=1,15
MU=MU+Z(I2)*Z(I2)*C(I2)/2
M=MU
D03,I3=1,10
ZA=Z(I3)
RA=R(I3)
AC(I3)=F(M)
C(11)=ALK/(1.+XK(6)/H/AC(9))+XK(7)/H2/AC(10)
C(10)=C(11)+XK(7)/H2/AC(10)
C(9)=C(11)+XK(6)/H/AC(9)
C(6)=H/AC(6)
C(7)=OH/AC(7)
A=H3/XK(3)
C(11)=A/AC(11)
C(2)=A*XK(11)/H/AC(2)
C(3)=A*XK(3)/H2/AC(3)
C(4)=A*XK(4)/H4/AC(4)
IF(C(8).EQ.0.)GOTO 20
C(5)=A*C(8)*AC(8)+XK(5)/AC(5)
CB=SD04T-C(5)
DIV=ABS(1.-CB/C(8))
IF (DIV.GE.0.001)THEN
C(8)=CB
GOTO 4
ELSE
ENDIF
MU=0
D05,I5=1,13
MU=MU+Z(I5)*Z(I5)*C(I5)/2
DIV=ABS(1.-M/MU)
IF (DIV.GE.0.001) GOTO 10
ALD=0
D06,I6=1,3
ALD=ALD+C(I6)
IF (ALD.GE.DOSE)THEN
PRINT*,('ALD > DOSE ')
GOTO 1
ELSE
ENDIF
ALP=1000.*(DOSE-ALD)
X5M=(DOCO-DOCE)/ALP.
DOSE=1000.*DOSE
FORMAT(1X,2X,I3,4X,F6.2,4X,F5.2,4X,F6.2)
CONTINUE
PRINT 203
FORMAT(1X,43(' '),S)
STOP
END

```