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**Removal of Organic Colour from Natural Surface Waters
by Coagulation and Floc Blanket Clarification,
with an Investigation of the Effects of
the Addition of Kaolin as a Process Aid**

by

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A thesis submitted in partial fulfilment of the requirements for the degree of
Master of Science in the Faculty of Engineering, University of Cape Town.

DECLARATION BY CANDIDATE

I, Brendon Richard Theunissen, declare that this thesis is my own work and has not been submitted for a degree at another university.

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28 AUGUST 2001

DATE

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SYNOPSIS

Background and objectives

In the Southern Cape and Western Cape regions of South Africa, organically coloured natural surface waters are used as the main source of potable water supply (Swartz and De Villiers, 1998). These waters have a characteristic yellow-brown to dark brown colour, which is usually the result of the presence of humic substances - humic, fulvic and humatomelanic acids. The humic substances are derived mainly from the degradation of plants and organic detritus and are leached through the soils of the watershed and transported by the streams and shallow groundwater flow (Aiken and Cotaris, 1995; Amy *et al*, 1992 and Swartz and De Villiers, 1996). Organic colour is not peculiar to South African surface waters, and has been the topic of much research in the United States of America, Great Britain, Europe, Israel and Japan. South African organically coloured waters contain very low concentrations of calcium, alkalinity and carbonate species. The waters are therefore generally aggressive to cementitious material and corrosive to metals. As a result of the characteristic underlying sandy soil in the catchment areas, the waters are also usually very low in turbidity (suspended clay particle content). The organic colour is undesirable in water supplies for a number of reasons; ranging from aesthetics to the humic substances being precursors to potentially carcinogenic disinfection by-products (Edwards and Amirtharajah, 1985).

Coagulation with hydrolysing metal salts is a standard and effective means of removing organic colour (Edwards and Amirtharajah, 1985). The conventional steps utilised in this method of treatment usually include coagulant chemical dosing, rapid mix, flocculation, horizontal flow sedimentation and finally rapid gravity sand filtration. Some treatment plants however, combine the flocculation and sedimentation steps into one unit process, known as floc blanket clarification (Hudson, 1981). Flocs formed by the coagulation of organic colour are typically light, fragile and do not settle well. However, a number of researchers have noted that the strength and settling properties of the organic colour flocs can be improved by the presence of turbidity in the raw water (Edwards and Amirtharajah, 1985 and Tambo and Wang, 1993). Although South African organically coloured surface waters usually have very low turbidities, it is possible that the loading rate (up-flow velocity) in floc blanket clarification of organically coloured waters could be increased by the addition of clay, such as kaolin (Tambo and Wang, 1993 and Gregory *et al*, 1999).

This dissertation presents a review of relevant literature to provide a foundational understanding of the concepts, principles, processes and mechanisms involved firstly in the coagulation of organic colour, and secondly in floc blanket clarification. The dissertation then presents an investigation of the effect of the addition of clay - kaolin - as a process aid, in floc blanket clarification of South African organically coloured natural surface waters.

Coagulation of organic colour

Humic substances are chemically complex macromolecular organic acids, derived from the polymerisation of multivalent organic monomers (Dempsey *et al*, 1984 and AWWA Research Committee on Coagulation, 1979). The speciation of humic substances is dependent on pH, and as a result of the presence of functional groups such as carboxyl and methoxyl, which are at least partly deprotonated at the pH condition of most natural waters, the molecules can be regarded as polyanions which are likely to react with the hydrolysis species of aluminium and other metal cations (Dempsey *et al*, 1984; AWWA Research Committee on Coagulation, 1979, Rebhun and Lurie, 1993; Narkis and Rebhun, 1977 and Hundt and O'Melia, 1988). The stability of the humic substances increases with increasing pH, due to the dissociation of the functional groups (Amy *et al*, 1992 and Edwards and Amirtharajah, 1985), and an extended configuration of the humic macromolecules is expected at higher pH values due to the repulsion of the negatively charged functional groups (AWWA Research Committee on Coagulation, 1979).

Aluminium sulphate, or alum, is a hydrolysing metal salt that has historically been, and still is the most commonly used coagulant for the removal of humic substances in South African and also United States waters (Swartz and De Villiers, 1996; Hundt and O'Melia, 1988 and Letterman *et al*, 1999). This dissertation therefore focusses on the use of aluminium sulphate for the coagulation of humic substances, however similar principles and mechanisms of coagulation apply to other hydrolysing coagulants, such as ferric chloride and ferric sulphate (Amirtharajah and O'Melia, 1990). The solubility of alum and the speciation of the various hydrolysis products, are dependent on pH. The minimum solubility of aluminium hydroxide precipitate occurs at pH 6.3 at 25 degrees Celsius - but this pH of minimum solubility increases with decreasing temperature (Letterman *et al*, 1999). The following species are produced as pH is varied (Letterman *et al*, 1999):

At low pH: positively charged, soluble hydrolysis products and the Al^{3+} aqua-metal ion.

At high pH: negatively charged, soluble $[Al(OH)_4]^-$. This species is tetrahedral, so no further deprotonation can occur.

Due to the fact that the speciation of both humic substances and hydrolysing metal salts is pH dependent, the dominant mechanisms involved in the coagulation of organic colour are also dependent on pH. If the zones of effective coagulation of organic colour are superimposed on an alum solubility diagram (pH versus alum dosage), two predominant zones of removal are identified (Semmens and Field, 1980; Dempsey *et al*, 1984; Dempsey *et al*, 1985; Edwards and Amirtharajah, 1985; Hundt and O'Melia, 1988 and Van Benschoten, 1990b):

Precipitation dominated removal zone: in this zone, which occurs at a pH of 4.5 to 5.0, the concentration of positively charged monomeric aluminium hydrolysis species is relatively high, and the formation of large aluminium polymers and aluminium hydroxide precipitate is not expected (Dempsey *et al*, 1984). Removal in this zone is likely caused by the direct precipitation of humic substances with monomeric aluminium hydrolysis species (Amirtharajah and O'Melia,

1990; Dempsey *et al*, 1984 and Edwards and Amirtharajah, 1985). Coagulation in this removal zone is accomplished over a relatively narrow pH and alum dosage range, and linear stoichiometry between humic substances concentration and required alum dosage is observed (Edwards and Amirtharajah, 1985). The flocs that are formed in this removal zone tend to be small and not well defined, with poor settling characteristics (Dennett *et al*, 1996).

Adsorption dominated removal zone: this removal zone occurs almost entirely within the pH - alum dosage region where precipitation of aluminium hydroxide is expected (Dempsey *et al*, 1984). The removal zone ranges from pH 5.5 to 7.5, with alum dosages that generally exceed about 30 mg/l (as alum) (Edwards and Amirtharajah, 1985 and Hundt and O'Melia, 1988). The humic substances are likely to be removed predominantly by adsorption on aluminium hydroxide precipitate (Dempsey *et al*, 1984 and Randtke, 1988). Van Benschoten and Edzwald (1990b) and Edwards and Amirtharajah (1984) both found greater removals of humic substances in the adsorbance dominated removal zone than in the precipitation dominated zone. Removals may however not be considered optimum, as an increased alum dosage is required to achieve aluminium hydroxide precipitation (Van Benschoten and Edzwald, 1990b). The increased removals may be due to the increased opportunities for interparticle contacts in the solution - due to the presence of voluminous hydroxide precipitate (Edwards and Amirtharajah, 1985). Dennett *et al* (1996) found that the flocs formed in the adsorbance dominated removal zone were larger and settled better than those formed in the precipitation dominated removal zone. Edwards and Amirtharajah (1985) observed that this removal zone has a non-linear stoichiometric relationship for the lower alum dosage boundary, but no upper boundary at all. It is noted that the adsorbance dominated removal zone is larger than the precipitation dominated removal zone. It would therefore be easier to operate a water treatment plant in the adsorbance dominated removal zone, particularly for the low buffer capacity waters found in the Southern Cape and Western Cape regions in South Africa, where slight dosing changes could result in coagulation pH moving outside the optimum required for the precipitation dominated removal zone.

Edwards and Amirtharajah (1985) found that at high humic substance concentrations, such as those found in the Southern Cape and Western Cape regions in South Africa, the two removal zones merge to form a single band of effective removal.

Flocs formed during the coagulation of humic substances are generally light, fragile and do not settle easily (Rebhun and Lurie, 1993 and Swartz and De Villiers, 1998). Relatively large sedimentation tanks therefore need to be provided, to prevent excessive floc carry-over to the filters and consequent short filter runs. The floc characteristics can be markedly improved by the presence of turbidity (clay particles), as these particles serve as nuclei for the formation of large, dense, rapid settling flocs and can result in an improved quality of settled water (Rebhun *et al*, 1969; Rebhun and Lurie, 1993; Mazet *et al*, 1990; Bratby, 1980 and Kuo *et al*, 1988).

A number of studies, such as those by Edwards and Amirtharajah (1985), Dempsey *et al* (1985), Edzwald (1993) and Rebhun and Lurie (1993), have shown that in waters containing both organic colour and clay particles (turbidity), the requirements for coagulation of the humic substances dominate those of the clay

particles. The required coagulant dosage is therefore determined mainly by the concentration of the humic substances, and not the turbidity. This is a result of the greater reactivity and concentration of reacting units of humic substances as compared to the number concentration of clay particles at commonly encountered mass concentrations (Rebhun and Lurie, 1993). The results of these studies of mineral particle effects on coagulant dosage requirements are significant, as they show that it is feasible to add clay particles to low turbidity organically coloured waters, to improve the strength and settling characteristics of the flocs without creating a significantly higher coagulant demand (Edwards and Amirtharajah, 1985).

Floc blanket clarification

Floc blanket clarifiers (FBCs) combine flocculation and settling into one unit (Hudson, 1981), in which the water flows vertically upwards through a fluidised bed of flocs - the floc blanket - which are suspended in equilibrium with the rising flow (Bratby, 1980 and Brown and La Motta, 1971). The micro-flocs (formed after coagulant dosing and rapid mix) that enter the floc blanket clarifier (FBC) aggregate and become entrapped in the floc blanket (Gregory *et al*, 1999 and Brown and La Motta, 1971). The FBCs are usually constructed to provide diverging flow, so that the up-flow velocity decreases with height. As the flow rises in the FBC, a point is reached where the settling velocity of the fluidised suspension exceeds the up-flow velocity, and an interface forms between the suspension and the relatively clear supernatant above (Gregory *et al*, 1999). The clear supernatant is then collected at the surface of the FBC, and directed to the filtration step.

Several mechanisms contribute to the growth of the micro-flocs that enter the FBC, these include:

Peri-kinetic flocculation: particle aggregation resulting from the random thermal motion of fluid molecules. This mechanism is significant for particles less than 1 to 2 μm (Amirtharajah, 1980).

Ortho-kinetic flocculation: particle aggregation induced by fluid shear. This is the predominant flocculation mechanism in conventional flocculation processes (Amirtharajah, 1980 and Letterman *et al*, 1999).

Differential settling: unequal particle settling velocities can cause particle contacts and aggregation. Although this does not contribute greatly to particle growth in conventional flocculation systems, it is a major mechanism in floc blanket clarification (Amirtharajah, 1980 and Letterman *et al*, 1999).

Entrapment: rising small particles are mechanically entrapped, and prevented from passing through the voids between the larger more mature particles in the floc blanket. This is probably the most important mechanism of particle aggregation and growth in floc blanket clarification (Gregory *et al*, 1999; Brown and La Motta, 1971 and Tambo and Hozumi, 1979).

Three main types of settling are possible in suspensions of particles in upward flowing liquid (Gregory *et al*, 1999):

Type 1 and 2 settling: unhindered settling of discrete particles. The suspension may contain

particles with different settling velocities and will have a diffuse interface with the clear liquid. *Type 3 settling*: if the concentration of particles in the suspension is increased, hindered settling takes effect. The particles all settle with the same velocity and the interface of the suspension and the clear liquid becomes distinct.

Type 4 settling: as the concentration is further increased, a point is reached where thickening of the suspension leads to compression settling. The rate of settling becomes dependent on the weight of solids above.

The settling of fluidised floc blankets typically found in FBCs is hydrodynamically similar to Type 3 hindered settling. The individual particle (or floc) behaviour is hindered by the presence of other particles. As a result of the high particle concentration, the free area between particles is reduced, causing greater inter-particle fluid velocities and alteration of flow patterns around the particles. Consequently, the average settling velocity of the particles in the fluidised floc blanket suspension is generally less than that of a discrete particle of similar size (Gregory *et al*, 1999).

The stability of the floc blanket in FBCs is influenced by a number of physical parameters, these include; the inlet conditions and the associated dissipation of excess energy, the efficiency of the collection of the clarified water, the efficiency of the withdrawal of excess floc as the floc blanket grows, the depth of the floc blanket and most importantly, the up-flow velocity.

Experimental investigation

A laboratory scale floc blanket clarification plant was constructed, and raw organically coloured water originating from the top of Table Mountain was obtained from the head of the Constantia Nek Water Treatment Works in Cape Town. A series of experiment runs were then undertaken, with the specific aim being to investigate the effect of various kaolin dosages on the FBC settled water quality, at various hydraulic loading rates (up-flow velocities), and to determine whether up-flow velocity and floc blanket stability can be increased by dosing kaolin. A matrix of results was produced for the various kaolin dosages and FBC up-flow velocities. The kaolin dosages used were 0 mg/ℓ (for the control), 50 mg/ℓ, 100 mg/ℓ and 300 mg/ℓ, which were of comparable magnitude to those used by Tambo and Wang (1993) in a similar investigation in Japan.

Due to the fact that sand filtration would normally follow floc blanket clarification at a water treatment plant, the quality of the settled water from the FBC, with respect to the solids that would need to be removed by filtration, is of primary importance in evaluating the performance of the FBC. The following parameters were therefore measured in the raw water and the settled water:

Turbidity: which relates directly to the quantity of suspended solids that would need to be removed by subsequent filtration.

Apparent colour: which provides a combined measure of organic colour and of any micro-flocs of coagulated colour remaining in the water. The micro-flocs would place a solids load on subsequent filtration, but do not appear as individual particles and are therefore not adequately

quantified by turbidity measurements.

UV absorbance: which is a surrogate parameter for quantifying the amount of humic substances present in the water.

In addition, samples were taken from the floc blanket during each experiment run to determine the concentration profile of the blanket. The time taken to establish the floc blanket in each experiment run was also recorded.

The results indeed indicate that the up-flow velocity (and hence the capacity) of the FBCs could be increased by dosing kaolin. In this investigation the benefits of the kaolin addition, on the settled water apparent colour were noticeable from up-flow velocities of 2.5 m/h upwards, and on settled water turbidity were noticeable from 3.5 m/h upwards. At 5.0 m/h it was not possible to even establish a floc blanket at all if kaolin was not dosed, however the FBC performed relatively well with a kaolin dose of 300 mg/l. In general, the beneficial effect of increasing kaolin dosage became more evident as the up-flow velocity increased.

The results of the measurement of the floc blanket concentration profile for the various experiment runs, indicate that the addition of kaolin allows the floc blanket to remain stable, and Type 3 hindered settling to predominate, at higher up-flow velocities than would otherwise be possible. Within the range tested, the attainable up-flow velocity (at which the floc blanket remained stable) was found to increase with increasing kaolin dosage. Dosing kaolin appears to increase the floc blanket concentration and raise the up-flow velocity at which the floc blanket undergoes a transition from Type 3 hindered settling - where optimum operating conditions are approached - to Type 2 unhindered settling - where flocculation is inefficient. The floc blanket concentration profile results correlate with the settled water turbidity and apparent colour results - the transition from Type 3 hindered settling to Type 2 unhindered settling corresponds to significant increases in turbidity and apparent colour, which are obviously expected to be associated with the decreased stability of the floc blanket.

For the specific raw waters used in this investigation, kaolin doses of 50 mg/l to 300 mg/l could be applied with little effect on the required coagulant dose. This confirms similar findings by other investigators - such as Edwards and Amirtharajah (1985) and Dempsey *et al* (1985) - that the coagulant demand in organically coloured waters is determined by the organic colour content and not turbidity. As the raw water used for this investigation is of similar quality to many of the organically coloured surface waters found in the Southern Cape and Western Cape regions of South Africa, similar doses of kaolin as a process aid are likely to be possible in full-scale FBCs, without an increase in required coagulant dosage. Where organic colour is present in greater concentrations, the kaolin dose could possibly be increased above 300 mg/l without altering the coagulant demand.

Measurement of the time taken to establish a floc blanket in the various experiment runs, indicates that at higher up-flow velocities (2.5 m/h and above), the addition of kaolin causes an increase in the growth rate of the floc blanket, which becomes more noticeable as up-flow velocity is increased. While it is difficult to use these results to predict the effect in full scale floc blanket clarification, it appears that

dosing kaolin would be beneficial in establishing floc blankets from start-up conditions. At lower up-flow velocities however (1.8 m/h and below), it appears that the addition of kaolin weights the floc so that Type 4 compression settling dominates, and the thickening of the floc at the bottom of the FBC causes a reduced floc blanket growth rate.

Conclusions and recommendations

It is difficult to use the results of this investigation to predict the exact results that would be achieved in full-scale floc blanket clarification. However, the results of the investigation indicate that the addition of kaolin can indeed be beneficial in floc blanket clarification of South African organically coloured surface waters. The benefits that may be derived from the addition of kaolin include an increase in the allowable FBC loading rate (up-flow velocity), and, at higher up-flow velocities; increased floc blanket stability, improved flocculation dynamics due to the increased concentration of the floc blanket, and quicker generation of floc blankets at FBC start-up. These benefits could lead to possible savings in the capital expenditure associated with both the construction of new FBC plants, and the postponement of extensions to existing FBC plants to meet growth in water demands.

It is believed that based on the results of this laboratory investigation, it would be worthwhile to investigate the effects of the addition of kaolin in full-scale floc blanket clarification. Such an investigation could possibly produce more absolute results, that could be used to reliably predict the effects of the addition of kaolin on the performance of FBCs.

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LIST OF SYMBOLS

AL _T ratio	Ratio of aluminium ion dosed to suspended particle concentration
CU	Colour unit (equivalent to colour produced by 1 mg platinum/ℓ)
DOC	Dissolved organic carbon
EDL	Electrical double layer
EDLC	Electrical double layer compression
FBC	Floc blanket clarifier
HMS	Hydrolysing metal salts
HU	Hazen units (equivalent to 1 CU)
NOM	Natural organic matter
NTU	Nephelometric turbidity units
POC	Particulate organic carbon
SOC	Synthetic organic chemicals

University of Cape Town

CHAPTER 1

INTRODUCTION

In the Southern Cape and Western Cape regions of South Africa, organically coloured natural surface waters are used as the main source of potable water supply (Swartz and De Villiers, 1998). These waters have a characteristic yellow-brown to dark brown colour, which is usually the result of the presence of humic substances. The humic substances are derived mainly from the degradation of plants and organic detritus and are leached through the soils of the watershed and transported by the streams and shallow groundwater flow (Aiken and Cotsaris, 1995, Amy *et al*, 1992 and Swartz and De Villiers, 1996). The organic colour is undesirable in water supplies for a number of reasons; ranging from aesthetics to the humic substances being precursors to potentially carcinogenic disinfection by-products (Edwards and Amirtharajah, 1985). Organic colour is not peculiar to South African surface waters, and has been the topic of much research in the United States of America, Great Britain, Europe, Israel and Japan.

Coagulation with hydrolysing metal salts is a standard and effective means of removing organic colour (Edwards and Amirtharajah, 1985). The conventional steps utilised in this method of treatment usually include coagulant chemical dosing, rapid mix, flocculation, horizontal flow sedimentation and finally rapid gravity sand filtration. Some treatment plants however, combine the flocculation and sedimentation steps into one unit process, known as floc blanket clarification (Hudson, 1981). In this process the water flows vertically upwards through a fluidised bed of flocs - the floc blanket - which are suspended in equilibrium with the rising flow (Bratby, 1980 and Brown and La Motta, 1971). The micro-flocs (formed after coagulant dosing and rapid mix) that enter the floc blanket clarifier (FBC) aggregate and become entrapped in the floc blanket (Gregory *et al*, 1999 and Brown and La Motta, 1971). The FBCs are usually constructed to provide diverging flow, so that the up-flow velocity decreases with height. As the flow rises in the FBC, a point is reached where the settling velocity of the fluidised suspension exceeds the up-flow velocity, and an interface forms between the suspension and the relatively clarified supernatant above (Gregory *et al*, 1999). The clear supernatant is then collected at the surface of the FBC, and directed to the filtration step.

The up-flow velocity that can be achieved in FBCs treating organically coloured water, is limited by the fact that the flocs formed during the coagulation of organically coloured waters are generally light and fragile and do not settle easily (Rebhun and Lurie, 1993). However, a number of researchers have noted that the strength and settling properties of organic colour flocs can be improved by the presence of suspended clay particles in the raw water - the quantity of suspended particles in the water is usually measured as turbidity (Edwards and Amirtharajah, 1985 and Tambo and Wang, 1993). Interestingly, these researchers have noted that the presence of turbidity does not necessarily require an increased coagulant dosage, and can in fact enhance the mechanisms of coagulation. South African organically coloured surface waters usually have very low turbidities, however, it is possible that the loading rate (up-flow velocity) in floc blanket clarification of organically coloured waters could be increased by the addition of clay, such as kaolin (Tambo and Wang, 1993 and Gregory *et al*, 1999). The benefits derived

from an increase in allowable up-flow velocity, would obviously include possible savings in the capital expenditure associated with both the construction of new FBC plants, and the postponement of extensions to existing FBC plants to meet growth in water demands.

There are a number of floc blanket clarification water treatment plants in the Southern Cape and Western Cape regions of South Africa that treat low turbidity organically coloured waters. However, the effect of dosing clay (adding turbidity) into these waters has not been studied and documented in detail, if at all. It was therefore decided to conduct an investigation of the effect of the addition of clay - kaolin - as a process aid, in floc blanket clarification of South African organically coloured natural surface waters. This dissertation presents the investigation, along with a review of relevant literature to provide a foundational understanding of the concepts, principles, processes and mechanisms involved firstly in the coagulation of organic colour, and secondly in floc blanket clarification

The dissertation is set out in the following format:

Chapter 2: deals with the nature and origin of organic colour in natural surface waters, the various methods used for measuring the quantity of organic colour present in the water, the particular nature of water containing organic colour in South Africa and the reasons for removing organic colour,

Chapter 3: presents an extensive review and synthesis of literature that addresses the coagulation of organic colour. The object of this section is to provide a detailed description of the processes and mechanisms involved in the coagulation of humic substances using hydrolysing metal salts. The influence of clay particles and organic polymers is also addressed,

Chapter 4: describes the concept and the various processes and mechanisms involved in floc blanket clarification,

Chapter 5: describes the experimental investigation, presents the results and a discussion of the results, and finally,

Chapter 6: presents the various conclusions and recommendations.

CHAPTER 2

ORGANICALLY COLOURED SURFACE WATERS

2.1 The Origin and Nature of Organic Colour

Surface waters often contain organic material, which depending on numerous conditions affecting the catchment and aquatic environment, may consist in varying degree of the following:

Natural organic matter (NOM): including humic substances, microbial and cellular exudates, organic debris and detritus, living organisms such as bacteria, zooplankton and algae, and other organic material dissolved into or in suspension in the water from sources such as plant tissue and animal wastes (Edzwald, 1993; Randtke, 1988 and Aiken and Cotsaris, 1995).

Synthetic organic chemicals (SOCs): including pesticides, volatile organic chemicals produced commercially or generated as waste products, and by-products of commercial chemicals added to the water (Randtke, 1988).

The organic material may be in particulate, colloidal or dissolved form, and although no natural cut-off between these fractions exists (Aiken and Cotsaris, 1995), the following broad operational classifications have been used historically:

Particulate organic carbon (POC): which includes matter not passing through a 0.45 μm membrane filter, such as plant debris, microbes and organic substances adsorbed onto inorganic particles (Crozes *et al*, 1995).

Dissolved organic carbon (DOC): including organic material in true solution, and macromolecules and micro-colloidal suspended solids that are small enough to pass through a 0.45 μm membrane filter (Randtke, 1988 and Aiken and Cotsaris, 1995).

In general, DOC is in greater abundance than POC, and accounts for approximately 90 percent of the total organic carbon in most surface waters (Randtke, 1988 and Aiken and Cotsaris, 1995). POC is usually effectively removed under the same conditions of coagulation, sedimentation and filtration as those used to remove inorganic turbidity (clay particles), and it is unlikely that the removal mechanisms are different to those occurring in inorganic turbidity removal (Randtke, 1988). DOC on the other hand, possibly involves different removal mechanisms to those occurring in conventional turbidity removal.

The yellow-brown to dark brown colour found in natural surface waters in many parts of the world is usually a result of the presence of the humic substances component of the NOM. The humic substances are derived mainly from the degradation of plants and organic detritus and are leached through the soils of the watershed and transported by the streams and shallow groundwater flow (Aiken and Cotsaris, 1995; Amy *et al*, 1992 and Swartz and De Villiers, 1996). Research has shown that humic substances contribute from approximately half to most of the DOC, with fractions of up to 90 percent for highly

coloured waters (Edzwald, 1993; Aiken and Cotsaris, 1995; Crozes *et al.*, 1995; Amy *et al.*, 1992; Edwards and Amirtharajah, 1985; Narkis and Rebhun, 1975 and Narkis and Rebhun, 1977). Humic substances are generally the higher molecular weight fraction of the NOM (Randtke, 1988).

The term "humic substances" originated in the field of soil science, and was carried over into the aquatic field as a general term encompassing a wide range of compounds having an essentially similar constitution and many common properties, but differing in molecular weight and the proportion of various functional groups (Hall and Packham, 1965). Humic substances were originally classified by Oden (1919), according to the solubilities of the common fractions. In 1930 this system was slightly modified by Page, to give the most widely used classification system to date (Black and Christman, 1963). This classification system, which consists of (from most soluble to least soluble) fulvic acid, hymatomelanic acid, humic acid, and humus coal, is shown in Table 2.1. Most investigators consider only the fulvic and humic acid fractions, and do not separate the hymatomelanic acid component from the humic acid component (Rebhun and Lurie, 1993; Hall and Packham, 1965; WHO, 1993; AWWA Research Committee on Coagulation, 1979 and Aiken and Cotsaris, 1995). These organic acids are amorphous, chemically complex polyelectrolyte macromolecules, derived from the polymerization of multivalent organic monomers (Dempsey *et al.*, 1984 and AWWA Research Committee on Coagulation, 1979). The colour caused by humic substances is due to conjugated double bonds, that adsorb light (Narkis and Rebhun, 1975). As a result of the presence of functional groups such as carboxyl, methoxyl, phenol, alcohol, chinoid, quinonoid and ketone, which are at least partly deprotonated at the pH condition of most natural waters, the molecules can be regarded as polyanions which are likely to react with the hydrolysis species of aluminium and other metal cations (AWWA Research Committee on Coagulation, 1979; Dempsey *et al.*, 1984; Rebhun and Lurie, 1993 and Hundt and O'Melia, 1988). The stability of the humic substances increases with increasing pH due to the dissociation of the functional groups (Amy *et al.*, 1992 and Edwards and Amirtharajah, 1985), and an extended configuration of the humic macromolecules is expected at higher pH values, due to the repulsion of the negatively charged functional groups (AWWA Research Committee on Coagulation, 1979). Phenol, and particularly carboxyl, appear to be the dominant functional groups in humic substances - their dissociation constants in humic substances have been identified by various investigators as between 8.0 and 8.71, and between 4.23 and 4.9 respectively (AWWA Research Committee on Coagulation, 1979).

In a nuclear magnetic resonance study, Cook and Langford (1998) made the following conclusions about the structure of fulvic and humic acid:

Fulvic acid: consists of (i) relatively large immobile units/moieties that are mainly aliphatic in nature and largely unfunctionalised, (ii) more mobile moieties that are mainly aromatic in nature and are relatively unfunctionalised, and (iii) mobile, highly functionalised moieties that are mainly carbohydrate in nature.

Humic acid: consists of one major immobile unit associated with more mobile functionalised units that are mainly aromatic in nature.

Table 2.1 *Classification of humic substances (Hall and Packham, 1965 and Black and Christman, 1963)*

Group	Definition
Fulvic acid	Soluble in NaOH and mineral acid
Hymatomelanic acid	Soluble in NaOH and alcohol, insoluble in mineral acid
Humic acid	Soluble in NaOH, insoluble in alcohol and mineral acid
Humins (or humus coal)	Insoluble in NaOH and water

In both the fulvic and the humic acid, it was concluded that the carboxyl groups constitute the majority of the functionalisation, although the presence of phenolic groups was also detected. The fulvic acid was found to be much more functionalised than the humic acid. Cook and Langford concluded that due to the complexity of the fulvic and humic acid molecules, it is not possible to provide a simple structural formula for the compounds, although this has been attempted by some researchers.

Table 2.2 shows a summary of the major elements in fulvic and humic acids. Fulvic acids contain more oxygen, but less carbon and nitrogen, and have a higher content of oxygen containing functional groups per unit weight (AWWA Research Committee on Coagulation, 1979). The fulvic acid fraction generally has a lower molecular weight, ranging from 500 to 5 000, than the humic acid fraction which ranges from 5 000 to 500 000 (Rebun and Lurie, 1993 and AWWA Research Committee on Coagulation, 1979). The various operational definitions of the fractions of humic substances are not absolute, and humic substances from any source have a continuous range of solubility, adsorptivity, molecular size and chemical reactivity (Dempsey *et al*, 1984).

Table 2.2 *Elementary analysis of fulvic and humic acids (AWWA Research Committee on Coagulation, 1979)*

Element	Percentage dry, ash-free weight	
	Fulvic acids	Humic acids
C	40-50	50-60
H	4-6	4-6
O	44-50	30-35
N	<1-3	2-6
S	0-2	0-2

There has been a fair amount of debate as to whether humic substances exist in true solution or as colloidal suspensions. Although humic substances do pass through a 0.45 μm membrane filter, a strong case can be made for their colloidal behaviour, particularly in the case of the larger humic acid molecules. Black and Christman (1963) concluded, as a result of electro dialysis and membrane filtration

studies, as well as angular-light-scattering and ultraviolet spectroscopy data; that humic substances exist as colloidal suspensions. Shapiro (1964) suggested that the colloidal properties exhibited were due to complex formation with iron, if present in solution. Hall and Packham (1965) stated that it is likely that humic substances are in true solution in water, but that a proportion of the molecules are sufficiently large to exhibit colloidal properties. The question has often been sidestepped by referring to humic substances as macromolecules which exhibit the properties of both colloids and truly dissolved substances (Randtke, 1988; Bratby, 1980 and AWWA Research Committee on Coagulation, 1979). An importance difference between fulvic and humic acid, is the fact that fulvic acid is "soluble" at pH 1, and is not coagulated at its point of zero charge at pH 2, as would be expected of a colloidal suspension. This is strong evidence that fulvic acids are in true solution (Randtke, 1988). Research on various sources of water has found the fulvic acid fraction to contribute the greater portion, 80-90 percent, of the total humic substances (Narkis and Rebhun, 1977; AWWA Research Committee on Coagulation, 1979 and Black and Christman, 1963). This is likely due to the fact that fulvic acid is more soluble than humic and hynamelanic acid (Black and Christman, 1963). Because fulvic acid generally contributes the majority of humic substances, and there is good reason to believe that fulvic acid is in true solution, it is reasonable to consider humic substances to comprise mainly molecules in true solution (Randtke, 1988).

Over the past 40 years, different authors have described humic substances as both hydrophobic and hydrophilic. With the more recent introduction of chromatographic techniques to concentrate and fractionate NOM, the NOM has been fractionated into hydrophilic acids, bases and neutrals; and hydrophobic acids, bases and neutrals. Humic substances form part of the hydrophobic fraction. Fulvic acid is however more hydrophilic than humic acid; probably due to the higher density of acidic functional groups in the fulvic molecules (Aiken and Cotsaris, 1995; Edzwald, 1993 and Amy *et al*, 1992).

Black and Christman (1963) found that the intensity of the colour due to the humic substances, as measured with a filter photometer, increased with increasing pH. These colour variations were noted to be reversible but not linear. Figure 2.1 shows the results of Black and Christmans' experiments on a number of different water samples.

Narkis and Rebhun (1977) found that the colour intensity of a solution of 1 mg/l of humic acid at pH 8.0, measured in Pt-Co colour units (see Section 2.3), is approximately 10 times greater than that of a 1 mg/l solution of fulvic acid.

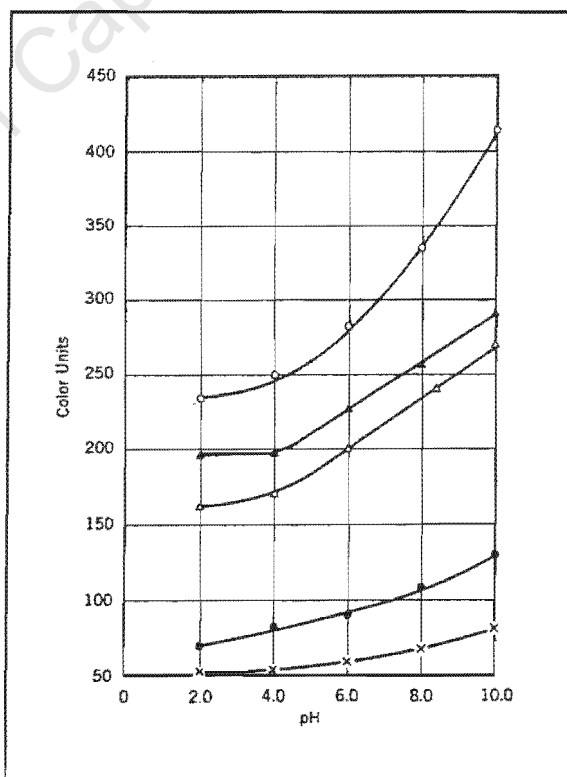


Figure 2.1 The effect of pH on colour of various water samples (Each sample identified by different symbol)(Black and Christman, 1963)

2.2 The Measurement of Organic Colour

The heterogeneous and ill-defined character of humic substances has prevented a method of measuring them directly from being developed (Amy *et al*, 1992). However several "surrogate" parameters used to quantify the humic substances and colour, have been developed as technology has progressed. The most common methods used for quantifying humic substances and organic colour are described below:

Platinum - cobalt units:

This method has traditionally been the most commonly used for the measurement of organic colour in natural waters and is referred to as the standard method in "*Standard Methods for the Examination of Water and Wastewater*" (APHA, AWWA and WPCF, 1989).

A colour standard is produced by preparing a solution of platinum in the form of the chloroplatinate ion. A colour unit (CU) is then defined as the colour produced by 1 mg platinum/l - and is therefore sometimes quoted as mg Pt/l. Various strengths of the standard solution can be made up by diluting the original solution. The coloured water sample and the standards are placed in 50 ml Nessler tubes. The sample is then matched to the nearest standard by looking vertically down the tubes in such a manner that clear light is directed up the tubes (APHA, AWWA and WPCF, 1989).

An adaption of the above method, which reduces the subjectivity resulting from human interpretation, is to prepare a comparative curve of optical density verses CU. This is done by measuring the optical densities of a number of appropriate Pt-Co colour standards, using a filter photometer at a wavelength of approximately 420 nm. The optical density of the colour sample is then similarly measured and the colour rating determined from the comparative curve (Black and Christman, 1963).

As a result of the pH dependency of colour intensity, as discussed in Section 2.1, it has been suggested that colour measurement be standardised at pH 8.3. However, the difficulty of adjusting the pH of South African organically coloured waters, due to their inherent low buffer capacity (see Section 2.3), makes this proposal impractical for routine analysis (Swartz and De Villiers, 1998). The pH at which colour is measured is therefore rarely quoted.

One of the inconveniences of the Pt-Co method, is that the method becomes difficult to use if the hue of the sample varies significantly from that of the standard.

Hazen units:

This method is the most commonly used by authorities controlling water treatment plants in South Africa (Juby and Botha, 1994). The method is very similar to the visual comparison version of the Pt-Co method, however standard coloured glass disks of various intensities are

used instead of a Pt-Co standard. The coloured disks are placed over 50 ml Nessler tubes containing clear water, to which the coloured water sample is compared in a similar fashion to the Pt-Co method. The coloured disks are calibrated in Hazen units (HU), where 1 HU is equivalent to 1 CU (or 1 mg Pt/l) (Juby and Botha, 1994).

Custom made viewing boxes containing their own light source are available. A Nessler tube containing clear water and another containing the coloured water sample are placed in the viewing box. A disk containing various coloured glass standards is rotated over the clear water Nessler tube, until a match is obtained.

As with the Pt-Co method, the Hazen unit method has the disadvantage of being difficult to use when the hue of the sample is significantly different to that of the glass coloured disks. In addition, the measurement is subject to human interpretation. Nevertheless the method provides a quick and easy method of quantifying the intensity of organic colour in natural waters.

With each of the methods described above, either the true colour or the apparent colour, defined as follows, can be measured:

True Colour: the intensity of the colour after all particulate material has been removed, usually by filtration through a 0.45 μm membrane filter.

Apparent Colour: the intensity of the colour before removal of the particulate material. This is usually more intense than the true colour due to particle interference with the measurement process.

The true colour method is obviously preferred, as it is a truer reflection of the colour caused by the humic substances.

Ultraviolet absorbance:

Organic compounds that are aromatic in structure or have conjugated double bonds, absorb light in the ultraviolet (UV) wavelength region. As humic substances contain aromatic moieties, UV absorbance is a good technique for measuring their presence. Humic substances have no characteristic spectra; absorbance usually decreases with increasing wavelength (Edzwald *et al*, 1985).

Since about 1985, much of the literature concerning humic substances has made use of UV absorbance to report the amount of humic substances present in a water. The absorbance is often measured at 254 nm, and reported in absorbance units, although various researchers have used other wavelengths. Rebhun and Lurie (1993) suggest 260 nm (also used by Semmens and Field, 1980). The UV absorbance can be read using a standard spectrometer and requires no chemical standard preparations. The UV absorbance should be measured after filtration through a 0.45 μm filter, to eliminate interference by particulate matter.

The UV absorbance of a particular water increases slightly with increasing pH, but not as dramatically as for colour measured as CU (mg Pt/l). This is illustrated by the results of Black and Christman's investigations (Black and Christman, 1963), where the percentage increase in CU of a water sample as pH increased from 2.0 to 10.0 was 78 percent. The increase in UV absorbance of the same water sample over the same pH variation was approximately 13 percent. Black and Christman also found the increase in UV absorbance with increasing pH to be independent of the wavelength at which the absorbance was measured.

The main advantages of the UV absorbance method are the ease of conducting the measurement and the accuracy of the measurements, which are not subject to human interpretation.

Dissolved organic carbon (DOC):

Another method used in more recent times to quantify organic colour, is the measurement of carbon atoms covalently bonded in organic molecules, that is, the dissolved organic carbon (DOC). This method will also measure non-humic NOM and SOCs, but because the majority of organic carbon in coloured water is often due to humic substances, as described in Section 2.1, the method can be applied in many instances but should be used with caution. Measurement of DOC has the disadvantage of being a more complex procedure than the Pt-Co, Hazen and Absorbance unit methods. As with UV absorbance, DOC should be measured after the water has been filtered by a 0.45 μm filter.

Specific ultraviolet absorbance (SUVA):

The ratio of UV absorbance to DOC concentration, termed specific ultraviolet absorbance (SUVA), can be used as an indicator of the humic substances fraction of the NOM. SUVA is defined as the UV absorbance (at 254 nm) per meter of ultraviolet light path length through the water, per unit of DOC concentration in mg/l - the units of SUVA are $\ell/\text{mg}\cdot\text{m}^{-1}$. Waters with a low humic fraction tend to have SUVAs less than 2 $\ell/\text{mg}\cdot\text{m}^{-1}$, while waters with a high humic fraction have SUVAs between 3 and 5 $\ell/\text{mg}\cdot\text{m}^{-1}$ (Letterman *et al*, 1999 and Edzwald, 1993).

2.3 The Nature of Water Containing Organic Colour in South Africa

Natural surface waters that contain organic colour in South Africa are found mainly in the Southern Cape and Western Cape coastal zones, ranging from Storms River in the east to Table Mountain in the west. Some coloured waters are also found in Mpumalanga, but to a lesser extent (Swartz and De Villiers, 1996). A survey of coloured waters, sampled at the inlet of various water treatment plants in this area, was undertaken by Swartz and De Villiers (1996). A summary of this data is given in Table 2.3. Figure 2.2 shows a map of the survey area, and indicates where the samples were taken. A number of characteristics commonly associated with organically coloured surface waters, and particularly those found in the Southern Cape and Western Cape, are discussed below:

Table 2.3 *Survey of water quality for coloured waters in the Southern Cape and Western Cape coastal zones (Swartz and De Villiers, 1998)*

Sample	Apparent Colour H.U.	True Colour H.U.	UV 300,4 A.U.	DOC mg C/l	Turbidity NTU	Conductivity mS/m	pH	Alkalinity mg/l as CaCO ₃	Calcium mg/l
1 Lower	366	150	2.38	8.0	0.5	5.0	3.2		1.6
Higher	960	886	4.33	25.0	5.3	14.0	5.3	0.8	25.0
2 Lower	322	45			6.9	7.0	3.8	0.0	4.0
Higher	770	487			45.0	55.0	7.7	52.0	32.0
3	300	240		9.9	5.0		5.8	3.3	
4 Lower	160				2.0	8.0	4.1	2.0	4.0
Higher	650				400.0	70.0	6.5	28.0	30.0
5 Lower	160	100		6.6	8.5		5.8	3.0	
6 Lower	30				2.0	7.0	6.6	5.0	2.2
Higher	110				10.0	14.0	6.8	10.0	3.2
7 Lower		20	0.37		3.3	5.3	5.4	0.5	0.8
Higher		140	1.04		10.9	9.1	6.4	3.0	1.9
8 Lower		10	0.26		1.1	3.3	6.5	0.6	0.5
Higher		40	0.48		7.3	7.7	7.6	8.2	1.9
9 Lower		5	0.09		0.9	3.1	6.3	2.0	1.2
Higher		40	0.61		20.0	11.1	8.1	10.5	4.6
10 Lower		120	1.50		0.7	6.3	4.5	0.0	1.0
Higher		240	2.20		2.7	11.0	5.4	1.0	2.4
11 Lower		120	1.70		1.2	5.3	4.3	0.0	1.0
Higher		240	2.60		5.8	10.2	5.3	1.3	2.3
12 Lower	250	185		9.6	4.1	5.0	3.9	0.0	
Higher	680	460			20.0	11.0	5.9	2.0	
13 Lower	500				0.1		3.8	0.0	
Higher	1 100				10.0		4.5		
14	150	120		11.4	0.7		5.1	2.0	
15	350	320		18.6	1.2		5.4	3.5	
16	60				1.2		5.2	6.0	
17 Lower	45				0.8	7.5	5.2	18.0	
Higher	390				25.0	15.5		29.0	
Average	387	198		12.7	20.8	13.6	5.5	7.1	6.6

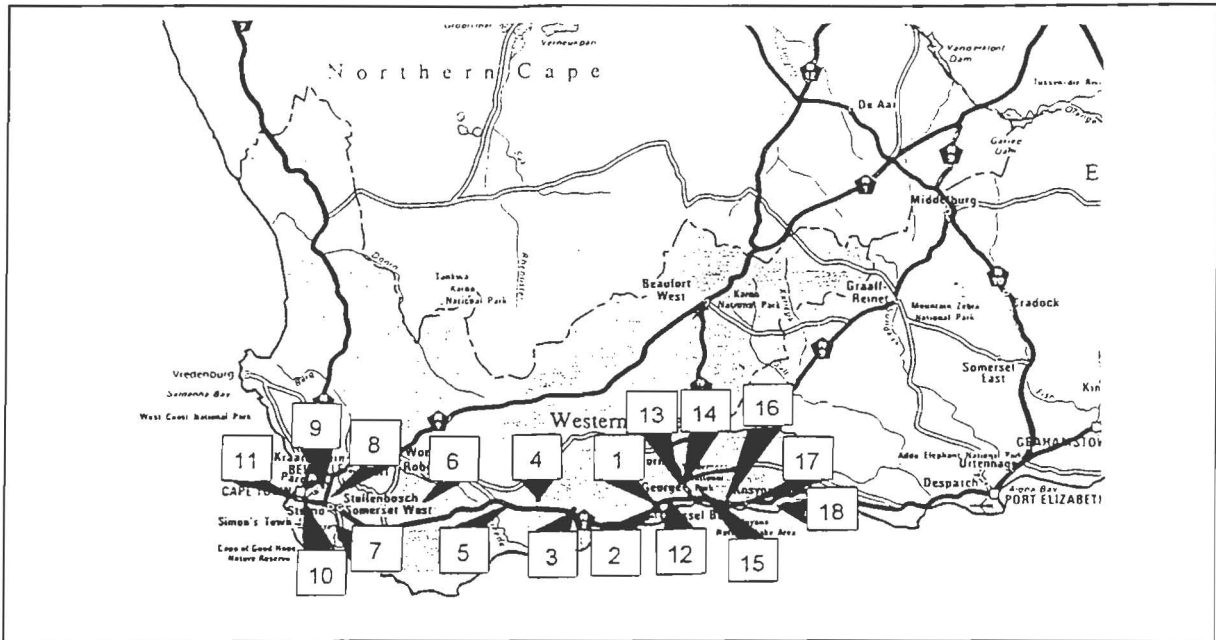


Figure 2.2 Location of water treatment plants surveyed by Swartz and De Villiers (1998)

Colour intensity:

Colour intensity increases where the watershed is underlain by sandy soil, because sandy soils have a low adsorptive capacity. Clayey soils on the other hand have a high adsorptive capacity, due to the greater reactivity and specific surface area of the clay particles. Clayey soils therefore tend to act as a sink for organic matter, storing it until it is decomposed by microorganisms. Generally, the intensity of the organic colour also increases during periods of heavy rainfall, as more humic substances are transported to the streams (Aiken and Cotsaris, 1995).

The catchments for the organically coloured Southern Cape and Western Cape surface waters are predominantly underlain by the sandstone group known as Table Mountain Sandstone. The more intensely coloured waters, especially those found in the George - Mossel Bay area, tend to be significantly more intensely coloured than those recorded in literature for the rest of the world. (Amy *et al*, 1992; Black and Christman, 1963 and Swartz and De Villiers, 1996). This intense colour is ascribed to the Table Mountain Sandstone and to the unique fynbos plant kingdom that is found in the area (Swartz and De Villiers, 1996).

The presence of calcium and magnesium in the water decreases the solubility of higher molecular weight components of the humic substances, through charge suppression (Aiken and Cotsaris, 1995). The lack of these elements in the Cape coloured waters, which tend to be very soft, may also contribute to their high colour.

DOC Concentration:

Generally, waters containing organic colour have an elevated DOC concentration (Letterman *et al*, 1999). A DOC concentration of 2 mg/ℓ may be considered low, a concentration of 10 to 25 mg/ℓ may be considered high, while some waters have extremely high concentrations - up to 60 mg/ℓ (Amirtharajah and O'Melia, 1990 and Letterman *et al*, 1999). The survey of Southern Cape and Western Cape waters, shown in Table 2.3, shows a range in DOC of 5 to 25 mg/ℓ. In another survey of Southern Cape and Western Cape coastal waters, Thebe *et al* (2000) also found DOC to be mainly in the 5 to 25 mg/ℓ range, with one water having a concentration of 40 mg/ℓ.

Aggressive and corrosive nature:

Research has shown two important aspects concerning the dissolution - precipitation dynamics of waters containing humic substances (Mackintosh, 1990):

- The dissolution potential with respect to many metals and minerals, of waters containing humic substances, is likely to be higher than that of humic free waters. This is largely a result of the affinity that humic substances, particularly the carboxyl functional groups component, have for metal ions (Randtke, 1988).
- The humic substances tend to interfere with and frustrate the precipitation of metals and minerals.

Calcium ions are often the most significantly effected by these characteristics, due to the fact that the formation of a protective CaCO_3 skin covering the more soluble Ca(OH)_2 material of cement based water conduits, is impeded (Mackintosh, 1990). This is exacerbated by the low calcium concentrations that occur in the soft Southern Cape and Western Cape coloured waters. The waters in the Cape also tend to be deficient in carbonate species, which worsens the aggressive nature of the water. The Cape organically coloured waters are thus particularly aggressive to cement based materials such as concrete pipes.

Natural waters containing organic colour derive acidity not only from mineral acids such as carbonic acids, but also from the acidic humic substances (Mackintosh, 1990). This acidity naturally affects the pH of the water to the extent that some Southern Cape and Western Cape coloured waters have pH values as low as 3.0 - 3.4 (Mackintosh, 1990). These waters usually have very low or no alkalinity, and tend to be corrosive to metal pipes and fittings, even those that are made from normally corrosion resistant materials such as copper and galvanised steel (Swartz and De Villiers, 1996 and Swartz and De Villiers, 1998). The corrosive nature of the water is increased by the fact that the formation of a protective CaCO_3 skin is inhibited.

Characterisation of organically coloured waters:

The organically coloured waters of the Southern Cape and Western Cape usually have a low total dissolved solids (TDS) concentration and low buffer capacity. This makes accurate measurement of pH difficult. The low buffer capacity of the waters makes accurate adjustment of pH for optimized coagulation difficult. The organic acidity derived from the humic substances interferes with the common equilibrium chemistry of the water (Mackintosh, 1990), leading to the characterisation of water using alkalinity and/or acidity and/or pH being unreliable.

Turbidity:

Finally, the turbidities of the majority of organically coloured waters in the Southern Cape and Western Cape are low (Swartz and De Villiers, 1996), due to the lack of clay particles in the sandy underlying soil. Turbidities of less than 2 Nephelometric turbidity units (NTU) are common. This same characteristic is noted in many of the surface waters in Japan (Ebie and Amano, 1993) and in sources used in a study of various coloured water sources in the United States of America (Black and Christman, 1963).

2.4 The Reasons for Removing Organic Colour

2.4.1 General

Humic substances are not known to be physiologically harmful (Black and Christman, 1963 and AWWA Research Committee on Coagulation, 1979) and no health-based guideline is proposed by the World Health Organisations' "Guidelines for drinking water quality" (WHO, 1993). Nevertheless there are a number of reasons why it is necessary to remove the material - these reasons are briefly discussed below:

Aesthetic:

Most people would obviously prefer a clear, colourless water for domestic use. A dark water would give the impression that the water is not clean and perhaps not healthy. Colours above 15 CU can be detected in a glass of water by most people. A colour of less than 15 CU would be acceptable to consumers, but this value is likely to vary according to local circumstances (WHO, 1993).

Aggression and corrosion:

As discussed in Section 2.3, waters containing humic substances are aggressive to cementitious materials and corrosive to metals

Formation of harmful disinfection by-products:

Humic substances tend to react with chlorine and other oxidants used in the disinfection process, to form "disinfection by-products" (DBPs) which have a potential health risk (Reckhow and Singer, 1984). This matter has been the subject of much research over the last three decades, and is discussed in further detail in Section 2.4.2.

Disinfectant demand:

The reaction of humic substances with chlorine and other oxidants, tends to reduce or nullify the disinfectant properties of the oxidants. A higher than normal disinfectant dose is therefore required for organically coloured water (Najm and Krasner, 1995 and Dempsey *et al*, 1984).

Taste and odour:

The presence of humic substances is often associated with taste and odour which may be considered unpleasant (AWWA Research Committee on Coagulation, 1979 and Juby and Botha, 1994). The taste and odour problem can be exacerbated by the formation of DBPs in the disinfection process (Juby and Botha, 1994).

Industrial requirements:

Many industries require low colour in process water (Research Committee on Coagulation and Research Committee on Color Problems, 1970). An example of such a requirement is in the paper manufacturing industry.

Interference with water treatment processes:

The humic substances foul resins and membranes used for processes such as demineralisation, reducing their exchange and desorption efficiencies (Narkis and Rebhun, 1977). Humic substances may also interfere with activated carbon adsorption (Randtke, 1988 and Dempsey *et al*, 1984).

Nutrients:

The organic humic substances may act as nutrients for bacteria and algae.

Complexation of other elements and compounds:

Colour may combine with and increase the concentration of soluble iron, manganese and lead in waters, and may stabilise their presence by chelation (Research Committee on Coagulation and Research Committee on Color Problems, 1970). Iron and manganese are sometimes present in natural coloured waters and their removal by aeration and sedimentation, or other processes is therefore inhibited (Juby and Botha, 1994, AWWA Research Committee on Coagulation, 1979). The increased solubility of lead, present in coloured waters as a result of industrial waste build up or dissolving of lead containing plumbing fittings, poses a health risk due to the toxicity of the lead (WHO, 1993).

Humic substances also have the ability to adsorb toxic pesticides and insecticides (SOCs), and to possibly transport these chemicals through a water treatment works as humic complexes (Narkis and Rebhun, 1977 and Amirtharajah and O'Melia, 1990).

2.4.2 Carcinogenic by-products of disinfected organically coloured water

Disinfection of water is unquestionably the most important step in the treatment of water for public supply. The destruction of microbiological pathogens - which almost invariably involves the use of reactive, oxidising chemical agents - is essential, and efficient disinfection should never be compromised. However, the chemicals used in the disinfection process are not only powerful biocides, but are also capable of reacting with organic matter in the water to form disinfection by-products (DBPs) with potentially harmful long-term health effects (WHO, 1993). The formation of the DBPs is related to the aromatic carbon content of the water - because humic substances have a high aromatic carbon content, they have a particularly high DBP formation potential (Singer, 1999). Chlorine is the most

commonly used disinfectant. Other major disinfectants include chlorine dioxide, chloramines and ozone, while ultraviolet light and potassium permanganate are used to a very limited extent (Cohn *et al*, 1999).

In 1974, Rook, in the Netherlands, demonstrated that chlorine was responsible for creating trihalomethanes (THMs) in the water treatment process, particularly when it reacts with humic substances (Rook, 1974). These are a group of halogen substituted single-carbon compounds, with the general formula CHX_3 . The four most important members of the group are chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform (WHO, 1993). The brominated THMs are formed when bromide ions present in the water, react with chlorine or ozone, and are converted to hypobromous acid and hypobromite, which in turn react with organic matter to form the THMs (Sketchell *et al*, 1995 and Crozes *et al*, 1995). Chloroform has been found to affect kidney and liver function in humans, to possibly be toxic to developmental and reproductive functions, and is a known animal carcinogen (Cohn *et al*, 1999). An expert panel formed by the International Life Science Institute viewed chloroform as a likely carcinogen to humans, above a certain dose range. The other three THMs are also known animal carcinogens (Cohn *et al*, 1999).

A number of relationships between THM formation potential (THMFP) and organic carbon have been formulated. An example is (Letterman *et al*, 1999):

$$\text{THMFP} = 43.78 \text{ TOC}^{1.248} \quad (2.1)$$

Since Rook's discovery (Rook, 1974), there has been a plethora of research into the formation of DBPs and their associated health effects. A host of other potentially harmful DBPs have been identified, such as haloacetic acids (HAAs), haloketones, haloacetonitriles, aldehydes, haloaldehydes, chloropicrin, cyanogen chloride, chloral hydrate and chlorophenols (Cohn *et al*, 1999 and Krasner *et al*, 1989). THMs, and in particular chloroform are usually by far the most prevalent of the DBPs (Cohn *et al*, 1999 and Van Steenderen *et al*, 1988).

The health hazard associated with the DBPs is not certain, and there has been considerable debate over the significance of the findings of epidemiological studies, such as those undertaken by Morris *et al* (1992) and Cantor *et al* (1978); which have shown a correlation between DBP consumption and cancer (Cohn *et al*, 1999). However, when combined with the data from the numerous animal toxicological studies, the epidemiological studies provide a compelling case for the potential cancer risk to humans.

Although chlorine produces the most DBPs, other disinfectants such as chloramines, chlorine dioxide and ozone also react with source water organics, to produce DBPs (Cohn *et al*, 1999). In some instances, these alternative disinfectants produce other potentially harmful substances, such as chlorite in the case of chlorine dioxide (Crozes *et al*, 1995), and cyanogen chloride in the case of chloramines (Krasner *et al*, 1989) [chloramines have the disadvantage of requiring an extremely long contact time to allow effective disinfection of *Giardia* cysts and viruses (Crozes *et al*, 1995)]. The removal of DBP precursors, such as humic substances, is therefore the most suitable means of reducing the DBP concentration in treated drinking water (Singer, 1999).

CHAPTER 3

COAGULATION OF ORGANIC COLOUR

3.1 Methods Available for Removing Organic Colour

Organic colour caused by humic substances can be removed from water using a number of methods, with varying levels of success and economic viability. Examples of such methods are:

- Membrane filtration (Juby and Botha, 1994 and Taylot and Wiesner, 1999).
- Breakdown of the humic material via intensive oxidation, generally with ozone, or combinations of ozone and hydrogen peroxide or ultraviolet irradiation. The oxidation process is usually followed by membrane filtration or an adsorption process, such as granular activated carbon, to remove the simple short-chain breakdown products of the oxidation process (Singer and Reckhow, 1999 and Swartz and De Villiers, 1998).
- Ion exchange, particularly with macroporous anion exchange resins in the chloride form (Clifford, 1999).
- Coagulation and flocculation, followed by sedimentation, in most instances, and filtration.

Coagulation is by far the most commonly used and researched of these methods. Although it often fails to remove even as much as 50 percent of the NOM present in a water supply, the fraction that causes colour, has the greater THM formation potential, and the greater affinity for hydrophobic SOCs and for toxic metals, is preferentially removed (Randtke, 1988). In general, the higher molecular weight of humic substances allows them to be removed by coagulation more readily than other fractions of NOM. NOM removal by coagulation, of 50 to 80 percent can be expected - the higher efficiency is achieved with waters containing higher humic substance - NOM ratios (Letterman *et al*, 1999 and Edzwald, 1993). Fulvic acid, which is composed of smaller molecules than humic acid, as discussed in Section 2.1, has been observed to be less amenable to removal than the larger humic acid molecules (Croué *et al*, 1993). The following guidelines have been proposed for removal of NOM, based on SUVA (specific ultraviolet absorbance):

SUVA ranging from 3 to 5 $\text{l/mg}\cdot\text{m}^{-1}$: the water has a high humic substances fraction, and relatively high removals of DOC can be expected (50 to 80 percent).

SUVA less than 3 $\text{l/mg}\cdot\text{m}^{-1}$: the water has a low humic substances fraction, and DOC removals of 30 percent or lower should be expected (Letterman *et al*, 1999 and Edzwald, 1993).

As coagulation is usually indispensable in water treatment for the removal of even very low turbidity levels, it is an excellent process for the removal of humic substances and is often effective enough to eliminate the need for additional treatment of organics (Randtke, 1988). Coagulation of organic colour is discussed in greater detail in the remainder of this chapter.

In the field of turbidity removal, the term coagulation is often used to denote the chemical mechanisms involved in colloid destabilisation (Amirtharajah and O'Melia, 1990 and Randtke, 1988). However, with regard to the removal of humic substances; coagulation is more suitably considered to include all reactions, mechanisms and results in the overall process of particle aggregation within a water being treated, including chemical particle destabilisation, precipitation, coprecipitation, and interparticle contacts with associated particle size growth (flocculation) (Amirtharajah and O'Melia, 1990 and Randtke, 1988). The latter terminology is used in this dissertation.

Some excellent investigations of the coagulation of organic colour were undertaken by Black, Packham and their coworkers (Black and Christman, 1963; Hall and Packham, 1965; Packham, 1964 and Black and Willems, 1961). Although much research has been conducted since then, their studies provide much of the foundation for the present understanding of the coagulation of organic colour caused by humic substances (Amirtharajah and O'Melia, 1990). Coagulation is usually accomplished via the following two physical process units:

Rapid mix (or flash mix): a high intensity mixing process of short duration, typically a few seconds, wherein coagulant and pH adjusting chemicals are dosed into the water. The chemicals are distributed evenly in the water, to facilitate in-situ coagulant formation and the various destabilisation and precipitation reactions.

Flocculation: a low intensity mixing process of extended duration, typically 10 to 30 minutes, which facilitates interparticle contacts and particle growth. The larger particles are then more suited to removal by settling.

Rapid mix and flocculation are usually followed by sedimentation and rapid gravity sand filtration. In some instances, dissolved air floatation is used instead of sedimentation, although this is not common. If the humic substance and turbidity levels are low (say colour < 40 CU, turbidity < 12-16 NTU), in-line filtration (rapid mix followed by filtration) or direct filtration (rapid mix followed by flocculation and then filtration) may also be considered (Amirtharajah and O'Melia, 1990 and Randtke, 1988 and Cleasby and Logsdon, 1999).

The coagulation of humic substances has traditionally been accomplished by adding the hydrolysing metal salt coagulant, aluminium sulphate, to the water being treated (Letterman *et al*, 1999). However, over the last decade the spectrum of coagulants used in water treatment has grown substantially; and now includes (Letterman *et al*, 1999 and Hundt and O'Melia, 1988):

- Other aluminum based hydrolysing salts, such as aluminium chloride.
- Ferric iron hydrolysing salts, such as ferric chloride and ferric sulphate.
- Prehydrolysed metal salts, such as polyaluminium chloride.
- Various organic polymers (polyelectrolytes).
- An assortment of chemical mixtures.

Aluminium sulphate, or alum, has historically been and still is the most commonly used coagulant for

the removal of humic substances in South African waters, and also United States of America waters (Swartz and De Villiers, 1996; Hundt and O'Melia, 1988 and Letterman *et al*, 1999). This dissertation will therefore focus on the use of aluminium sulphate (alum) for the coagulation of humic substances, however similar principles and mechanisms of coagulation apply to other hydrolysing coagulants (Amirtharajah and O'Melia, 1990). An understanding of aluminium sulphate in aqueous solution is helpful in examining the mechanisms of coagulation - this topic is discussed in Section 3.2.

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3.2 Aluminium Sulphate in Aqueous Solution

When aluminium sulphate $[Al_2(SO_4)_3 \cdot nH_2O]$ is added to water, the Al^{3+} ion hydrates, forming such strong bonds with the oxygen atoms of six surrounding water molecules, that the oxygen-hydrogen association in the water molecules is weakened, and hydrogen is released into solution (Letterman *et al*, 1999 and Hundt and O'Melia, 1988). A number of positively charged mononuclear hydrolysis products are formed, such as $[Al(H_2O)_6]^{3+}$, $[Al(OH)(H_2O)_5]^{2+}$, $[Al(OH)_2(H_2O)_4]^+$ and $[Al(OH)_4(H_2O)_2]^-$. Although the water molecules are important in determining the behaviour of these species, they are not usually included in the chemical formulae (Letterman *et al*, 1999) - the water molecules will be omitted from the chemical formulae of all hydrolysis species from this point on.

After formation of the mononuclear hydrolysis products, and provided sufficient metal ion exists in the system, hydrolysis can proceed further with the formation of complex polynuclear species, microcrystals and metal hydroxide precipitate (Letterman *et al*, 1999; Hundt and O'Melia, 1988 and Dempsey *et al*, 1984). As a result of the complex aqueous chemistry of aluminium, many researchers disagree about the existence and exact nature of the polynuclear hydrolysed species (Letterman *et al*, 1999; Hundt and O'Melia, 1988 and Van Benschoten and Edzwald, 1990a). However, literature contains convincing evidence of such products, as shown in Table 3.1 (Letterman *et al*, 1999).

Table 3.1 Examples of polynuclear aluminium hydrolysis species (Letterman *et al*, 1999)

Polynuclear species	[OH]/[Al]	Reference
$[Al_8(OH)_{20}]^{4+}$	2.50	Hayden and Rubin (1974)
$[Al_{13}O_4(OH)_{24}]^{7+}$	2.46	Bertsch <i>et al</i> (1986)
$[Al_{14}(OH)_{37}]^{10+}$	2.29	Turner (1976)

Many investigators have proposed that polymers form in a structure analogous to aluminium hydroxide precipitate $[Al(OH)_3]_{(s)}$. As the polymer grows, hexameric rings form and condense, to create a two dimensional sheet. These sheets bind to one another by H-bonding and Van der Waals forces, to eventually form three dimensional amorphous $[Al(OH)_3]_{(s)}$, or gibbsite $[Al_2O_3]$ (Dempsey *et al*, 1984). Sulphate, a tetrahedral polyvalent anion, tends to link OH-Al polymers together in a distorted fashion, to form the solid lattice. The presence of sulphate (from aluminium sulphate) thereby catalyses the rapid formation of aluminium hydroxide precipitate $[Al(OH)_3]_{(s)}$, at lower OH to Al ratios (pH as low as 4.0) than would otherwise be possible. As a result of the distorted formation of the lattice, the precipitate is normally amorphous (Hundt and O'Melia, 1988).

The solubility of aluminium hydroxide precipitate, and the speciation of the various hydrolysis products, are important in optimising coagulant performance and are obviously dependent on pH. The minimum solubility of aluminium hydroxide precipitate occurs at pH 6.3 at 25 degrees Celsius - but this pH of minimum solubility increases with decreasing temperature (Letterman *et al*, 1999). The following

species are produced as pH is varied (Letterman *et al*, 1999):

At low pH: positively charged, soluble hydrolysis products and the Al^{3+} aqua-metal ion.

At high pH: negatively charged, soluble $[\text{Al}(\text{OH})_4]^-$. This species is tetrahedral, so no further deprotonation can occur.

Solubility diagrams are often used to plot the speciation of the hydrolysis products and the solubility of aluminium hydroxide, for different aluminium concentrations and pH values. When plotting these solubility diagrams, the reactions used to explain the activity and formation of the hydrolysis species use electrolyte theory and conventions, which describe single ion activities. Bertsch and Parker (1996) have argued that it is not appropriate to use this theory to explain the activity of large, polyvalent, polynuclear species, and, consequently it is not thermodynamically correct to include polynuclear species in the calculations used to plot these solubility diagrams (Letterman *et al*, 1999). Letterman and Driscoll (1993), Hayden and Rubin (1974) and Van Benschoten and Edzwald (1990a) have reported that the effect of pH on the solubility of freshly precipitated aluminium hydroxide can be accurately predicted using just the aqua-metal ion Al^{3+} , and two mononuclear species; $[\text{Al}(\text{OH})]^{2+}$ and $[\text{Al}(\text{OH})_4]^-$ (Letterman *et al*, 1999). A solubility diagram for amorphous aluminium hydroxide, based on this assumption is shown in Figure 3.1.

The rates at which the various hydrolysis species form, when aluminium sulphate is added to water, depend on pH and the types of ions present in the aqueous solution (Rebhun and Lurie, 1993). Typically, the formation of mononuclear species takes place within 10^{-4} to 1 second, while precipitation of amorphous aluminium hydroxide takes from 1 to 7 seconds. Formation of crystalline aluminium oxide (gibbsite) can take from months to years (Rebhun and Lurie, 1993).

The release of hydrogen ions into solution during the hydration of aluminium, as already described, causes aluminium sulphate to act as an acid. Typically for every 1 mg/l of commercial grade alum that reacts to produce a precipitate of aluminium hydroxide, 0.5 mg/l as CaCO_3 of alkalinity is consumed (Amirtharajah and O'Melia, 1990). The implications of this characteristic of aluminium sulphate are discussed in Section 3.4.4.

The hydrolysis products of aluminium can adsorb on particulate surfaces, such as stabilised colloid suspensions, whilst continuing to hydrolyse. They also react with NOM, particularly the higher

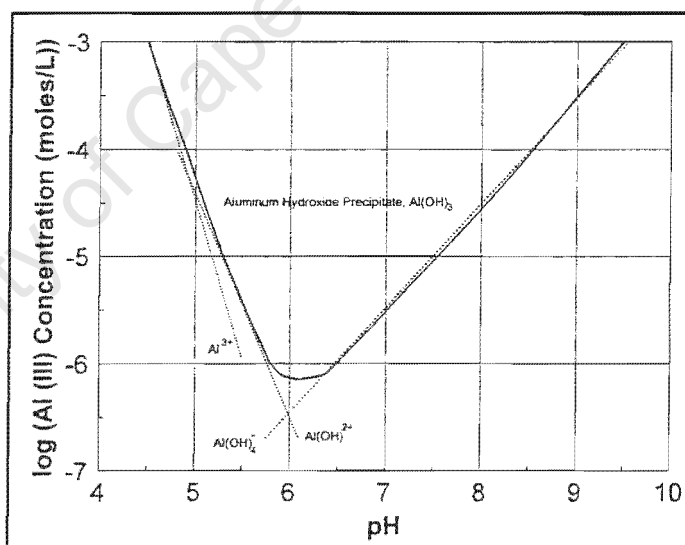


Figure 3.1 Solubility diagram for amorphous, freshly precipitated aluminium hydroxide (Letterman *et al*, 1999)

molecular weight fraction, such as humic substances. Soluble hydrolysis products may bind with NOM functional groups, and positively charged microcrystalline metal hydroxide particles can be destabilised by adsorption of a negatively charged coating of NOM (Letterman *et al*, 1999 and Van Benschoten and Edzwald, 1990a). The aluminium hydrolysis reactions, and the reactions between the various aluminium species and humic substances, are competitive. It is therefore likely that the speciation of the hydrolysis products will differ in the presence of humic substances, although the nature and extent of such differences is not yet understood (Randtke, 1988 and Van Benschoten and Edzwald, 1990a). The mechanisms and reactions of coagulation can be controlled and optimised by adjusting the pH of the water being treated, thereby varying the amount of metal hydroxide precipitate and the concentration of the various hydrolysis species.

Aluminium in drinking water has been implicated as a contributing factor in the occurrence of Alzheimer's disease. The evidence in support of this is not conclusive, and researchers have not been able to either verify or refute the claim. The concentration of aluminium in treated water can however be minimised, by keeping the pH during coagulation near the pH of minimum solubility of aluminium hydroxide (pH 6.0 to 6.5). This practise is observed by the City of Cape Town, who coagulate in the pH range 5.7 to 6.5. Alternatively coagulation can be performed at pH values yielding higher solubility, which may enable more efficient colour removal, with the pH being adjusted suitably after coagulation but ahead of filtration, to precipitate and remove the remaining aluminium - this may however increase the load on the filters (Letterman *et al*, 1999 and Swartz and De Villiers, 1998).

3.3 Mechanisms of Coagulation of Humic Substances

There are three primary mechanisms by which coagulation may possibly remove humic substances (Randtke, 1988). These three mechanisms are discussed below:

Colloid destabilisation:

It is emphasised that colloid destabilisation can only remove particles from an aqueous environment, and not substances in true solution (Randtke, 1988). As it is likely that humic substances are mostly in true solution (see Section 2.1), colloidal destabilisation may have limited relevance with regard to the removal of humic substances. Nevertheless the possibility that at least the humic acid component may indeed be colloidal, and not in true solution (see Section 2.1), warrants the discussion of colloidal destabilisation as a possible means of removing humic substances.

Colloids form stable suspensions in water mainly as a result of surface charge effects, as a result of hydrophilic effects due to bound water at particle surfaces, and also steric effects due to adsorbed macromolecules (Edzwald, 1993). The surface charge on the colloids causes a diffuse cloud of counter-balancing ions to surround each colloidal particle in the suspension, forming an "electrical double layer" (EDL) - the electrostatic repulsion between these EDLs creates an energy barrier which prevents the colloidal particles from approaching within range of the attractive Van der Waals forces. Colloid destabilisation overcomes the energy barrier so that the particles can aggregate (flocculate), and be removed by phase separation. The process is brought about by one of the following four secondary mechanisms (Weber, 1972 and Letterman *et al*, 1999):

Electrical double layer compression (EDLC): is achieved by adding a simple electrolyte such as NaCl to the suspension. The ions of opposite charge to the colloidal particles enter the diffuse EDL and cause it to become compressed. This reduces the energy required to move two colloids of like charge into close contact, where the attractive Van der Waals forces can dominate the electrostatic repulsion. EDLC is not practical for normal water treatment, because the salt concentrations required for destabilisation may approach that of seawater. In addition, the rate of particle aggregation would be relatively slow in most suspensions (Letterman *et al*, 1999, Randtke, 1988).

Adsorption and charge neutralisation: is achieved by adding to the suspension; coagulant compounds that have a strong tendency to adsorb on particle surfaces, and that carry a charge opposite in sign to the net surface charge on the colloids. Examples of such coagulants are cationic polyelectrolytes and the hydrolysis products formed by hydrolysing metal salts, such as aluminium sulphate. These compounds neutralise the charge on the colloids, with consequential destabilisation of the suspension - stoichiometry exists between the coagulant and the suspension. As the strong adsorption effects dominate the electrostatic effects, excess coagulant/counter-ions can be adsorbed on the colloids, resulting in reversal of the net charge

and restabilisation of the suspension (Weber, 1972; Amirtharajah and O'Melia, 1990; Letterman *et al*, 1999 and Dennett *et al*, 1996).

Adsorption and bridging: occurs when segments of a high molecular weight polymer adsorb on more than one colloidal particle, thereby linking the particles together. The polymer molecules are long enough to extend across the electrical double layers of the particles, to overcome the electrostatic repulsion effects. Stoichiometry exists, and the adsorption of excess polymer may lead to restabilisation of the suspension (Letterman *et al*, 1999 and Weber, 1972).

Enmeshment in a precipitate: commonly known as sweep floc, occurs when a hydrolysing metal salt is dosed at concentrations that exceed the solubility product of the metal salt. The colloidal particles become enmeshed in the voluminous precipitate of metal hydroxide - the colloids can actually act as nuclei for the formation of the precipitate. Sweep floc is actually a combination of destabilisation and transport mechanisms, but is normally discussed as a type of particle destabilisation, as it allows the aggregation and settling of colloidal particles (Dennett *et al*, 1996; Weber, 1972 and Letterman *et al*, 1999).

While EDLC is not practical for normal water treatment, the other three mechanisms of colloid destabilisation can and do occur, depending on the specific conditions of treatment and water quality.

Precipitation:

In the context of coagulation, this term is sometimes used to describe any process resulting in the production of solids, including colloid destabilisation. In the context of NOM and humic substances removal, precipitation is more suitably used to describe the conversion of a dissolved substance into a solid, by causing the solubility product of the substance to be exceeded (Randtke, 1988).

The precipitation reactions may follow complexation reactions between the metal and the organic ligands. The organic ligands that are negatively charged cause strong electrostatic based complexation reactions with positively charged aluminium species. When the negative charge is satisfied, precipitation occurs (Edzwald, 1993). Precipitation could also be caused by a shielding of the negatively charged sites on the organic molecules, that causes a contraction and collapse of the molecule, and consequent precipitation (Edwards and Amirtharajah, 1985).

The metal-humate precipitate may in turn be enmeshed in metal hydroxide precipitate, and be included in sweep flocculation (Rebhun and Lurie, 1993 and Crozes *et al*, 1995).

Coprecipitation:

This process is defined as the contamination of a precipitate by an impurity that is otherwise soluble under the conditions of precipitation. Four different types of coprecipitation have been identified by Kolthoff (1932) and Skoog and West (1982) (Randtke, 1988):

Isomorphic inclusion: in which the impurity substitutes into the crystal lattice for a lattice ion of similar size and chemical characteristics.

Nonisomorphic inclusion: in which the impurity appears to be dissolved in the precipitate.

Occlusion: in which an impurity differing in size or chemical characteristics from the lattice ions is adsorbed at lattice sites as the crystals are growing, producing crystal imperfections.

Surface adsorption: in which the impurity is not incorporated into the internal crystal structure, but is adsorbed on the outer surface of the precipitate.

Humic substances do not have the proper size and chemical characteristics to enable them to be incorporated into the lattice structure of metal hydroxides, so isomorphic inclusion is not possible. The metal hydroxides formed during water treatment are usually amorphous and are expected to have a very large surface area. They can be considered to be in the process of crystallising during the entire time that they remain in contact with the water being treated. Soluble humic substances are therefore likely to be coprecipitated primarily by adsorption onto the metal hydroxide surfaces as they form - through occlusion (Randtke, 1988).

Dempsey *et al* (1984) found that one hundred times more humic substances were adsorbed on in-situ formed aluminium hydroxide than on pre-precipitated gibbsite. This seems to support the conclusion that the humic substances are co-precipitated as the hydroxide forms, and not merely on the outer surface of the precipitate. It may also be possible for soluble metal-humate complexes (Al-humate/Al-fulvate), which would form kinetically faster than aluminium hydroxide as discussed in Section 3.2, to be removed by co-precipitation (Dempsey *et al*, 1984 and Rebhun and Lurie, 1993).

Forces responsible for the adsorption on the surface of the metal hydroxide can include Van der Waals interactions, hydrogen bonding, hydrophobic bonding, ionic bonds, ligand exchange and dipole interactions (Crozes *et al*, 1995 and Hundt and O'Melia, 1988).

Metal ion based coagulants, such as aluminium sulphate, can achieve destabilisation of colloidal humic substances by adsorption and charge neutralisation, and can cause the precipitation of metal fulvates and humates. In addition, metal based coagulants can remove humic substances by enmeshment/sweep floc (if any fraction of the humic substances is indeed colloidal) and by coprecipitation. In comparison, organic polymers, such as synthetic cationic polyelectrolytes, do not provide a substrate for enmeshment/sweep floc and coprecipitation. Coagulation by these polymers is therefore limited to adsorption and charge neutralisation, adsorption and bridging, and possibly precipitation of dissolved humic substances (Crozes *et al*, 1995 and Narkis and Rebhun, 1975). Coagulation of humic substances

with metal based coagulants is thus usually more effective than coagulation with polymers, and as a result, metal coagulants are far more commonly used in practice. The remainder of the discussions of humic substances coagulation, will therefore be devoted to that achieved with metal based coagulants.

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3.4 Coagulation of Humic Substances with Hydrolysing Metal Salts

Aluminium sulphate, or alum, has historically been and still is the most commonly used coagulant for the removal of humic substances in South African waters, and also United States of America waters (Swartz and De Villiers, 1996; Hundt and O'Melia, 1988 and Letterman *et al*, 1999). This section will focus on the coagulation of humic substances with aluminium sulphate, however, similar principles and mechanisms of removal apply to other hydrolysing coagulants (Amirtharajah and O'Melia, 1990).

Numerous studies, such as those by Black and Christman (1963), Hall and Packham (1965), Semmens and Field (1980), Dempsey *et al* (1984), Dempsey *et al* (1985), Edwards and Amirtharajah (1985), Hundt and O'Melia (1988), Van Benschoten (1990b), Edzwald (1993) and O'Melia *et al* (1999), have been conducted on the coagulation of humic substances. These have shown a stoichiometric relationship between the concentration of humic substances and the required coagulant dose, at all pH values at which humic substances can be removed by coagulation - although this stoichiometry is sometimes nonlinear (Dempsey *et al*, 1984, Amirtharajah and O'Melia, 1990).

The mechanisms and degree of humic substances removal by coagulation, depends on the nature and dosage of the coagulant, the concentration of the humic substances, the solution conditions (such as pH, hardness and temperature), kinetics and relative rates of the possible reactions, and mixing quality and intensity (O'Melia *et al*, 1999; Rebhun and Lurie, 1993 and Letterman *et al*, 1999). pH is particularly important, as it affects the speciation of the coagulant (as discussed in Section 3.2) and the degree of deprotonation of the humic substances functional groups (Crozes *et al*, 1995). The influence of pH can be viewed in terms of the balance between two competitions:

- Between hydrogen ions and metal hydrolysis products, for organic ligands.
- Between hydroxyl ions and organic anions for metal hydrolysis products.

Generally, increasing pH promotes deprotonation of the humic substances (increasing the negatively charged species) and decreases the charge on metal coagulants. This results in a requirement for a higher alum dosage at higher pH (O'Melia *et al*, 1999). Precipitation of Al-humates requires a coagulant dosage high enough to dislodge the hydrogen ions from the functional groups of the organic molecules. If the pH is too low, the hydrogen ions out-compete the metal hydrolysis products for the organic ligands, and poor removal occurs because some of the organic ligands are not precipitated. At higher pH values, hydroxyl ions are able to successfully compete with humic substances for the available metal ions. Precipitation of aluminium hydroxide occurs, shifting the removal mechanism from precipitation to co-precipitation. As pH increases, the humic substances become more negatively charged due to a higher degree of functional group dissociation, and the coagulating species become less positively charged. Adsorption becomes less favourable and the required coagulant dosage increases (Randtke, 1988). At still higher pH values, the $Al(OH)_4^-$ hydrolysis species dominates, aluminium hydroxide precipitate is reduced due to the increasing aluminium sulphate solubility, and the removal of humic substances is negligible.

Optimum alum dosage and pH conditions for the coagulation of humic substances have been identified by various studies. While the investigators have not been unanimous on the exact optimum coagulation conditions (Dempsey *et al*, 1984), many of the studies, such as those by Semmens and Field (1980), Dempsey *et al* (1984), Dempsey *et al* (1985), Edwards and Amirtharajah (1985), Hundt and O'Melia (1988) and Van Benschoten (1990b), have identified two predominant zones where significant removal of humic substances takes place. These zones are shown on Figure 3.2, plotted on a pH - alum dosage diagram. The shaded areas on this figure denote regions in which at least 20 percent

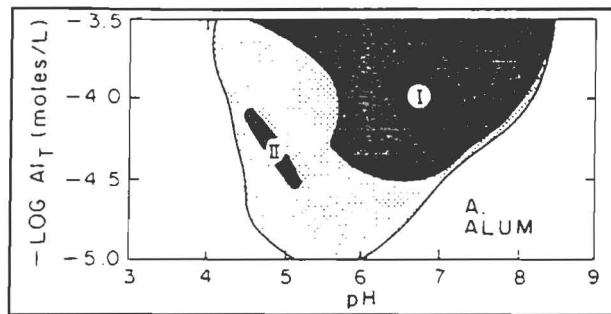


Figure 3.2 *Humic substances removal zones by coagulation [Shaded areas denote regions in which at least 20 percent removal occurs by settling (black) and by 0.20 μm filtration (hashed)] (Dempsey *et al*, 1984)*

removal occurred by settling (black) and by 0.20 μm membrane filtration (hashed). Figure 3.3 shows a similar plot, with a zone of 80 percent and another of 90 percent removal of humic acid by settling, with a superimposed aluminium solubility diagram. Although some authors have argued that organic solutes (such as humic substances) can alter the aluminium solubility (Randtke, 1988), the superimposition of the solubility diagram can give an approximation of the relative dominance of the various aluminium

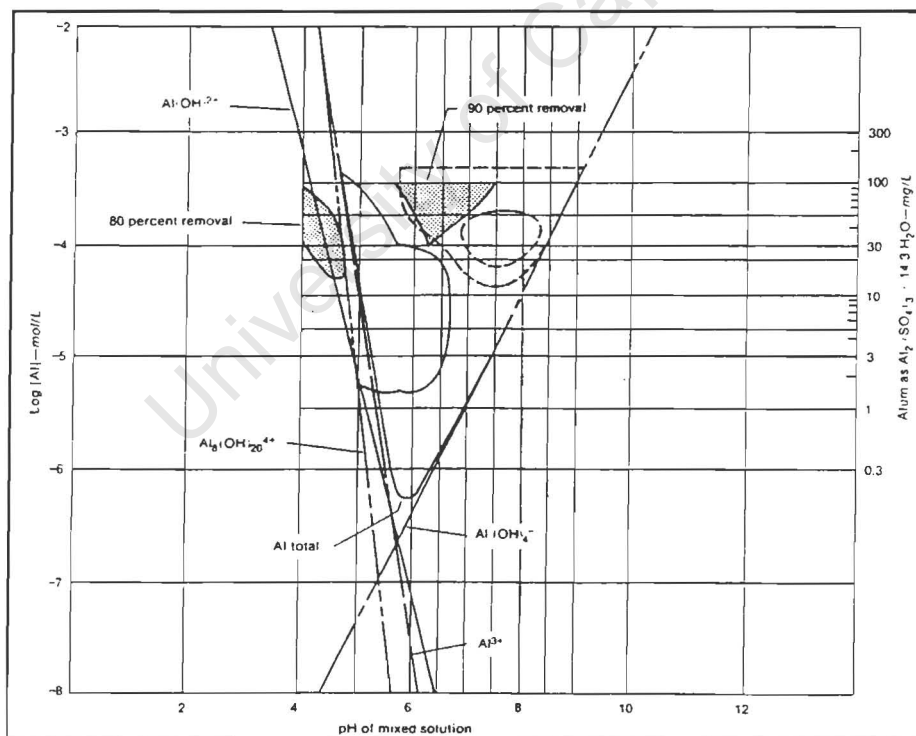


Figure 3.3 *Colour removal zones - initial colour 100-900 CU, turbidity 0 NTU (Edwards and Amirtharajah, 1985)*

hydrolysis species, and consequently, an indication of the possible mechanisms involved in the coagulation of the humic substances in a particular region of the pH - alum dosage plot. The two

predominant removal zones shown in Figures 3.2 and 3.3 are each discussed in greater detail in Sections 3.4.1 and 3.4.2.

3.4.1 Precipitation dominated removal zone

In this zone, which occurs at a pH range of approximately 4.5 to 5.0, the concentration of positively charged monomeric aluminium hydrolysis species is relatively high, and the formation of large aluminium polymers and aluminium hydroxide precipitate is not expected (Dempsey *et al*, 1984). Removal in this zone is likely caused by the direct precipitation of humic substances with monomeric aluminium hydrolysis species (Amirtharajah and O'Melia, 1990; Dempsey *et al*, 1984 and Edwards and Amirtharajah, 1985). If any fraction of the humic substances is colloidal, it would be destabilised by charge neutralisation (Randtke, 1988).

Edwards and Amirtharajah (1985) observed an upper boundary in this removal zone - when aluminium dosages above this boundary were applied, effective removal no longer took place. They attributed this to overdosing and consequent stabilisation of the precipitate particles. This seems to support the idea that removal is facilitated by aluminium monomers and not hydroxide. Coagulation in this removal zone is accomplished over a relatively narrow pH and alum dosage range (Edwards and Amirtharajah, 1985).

Linear stoichiometry between humic substance concentration and required alum dosage is observed in this removal zone. This is illustrated in Figure 3.4, which shows stoichiometric upper and lower boundaries for colour removal at pH 5.0, when the required alum dosage is plotted against initial colour (Edwards and Amirtharajah, 1985).

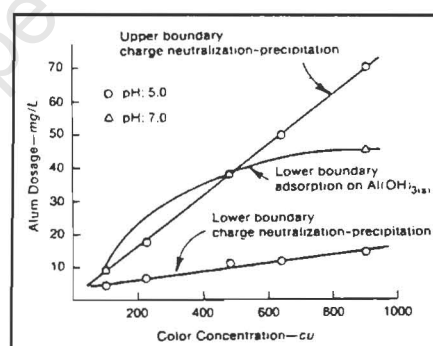


Figure 3.4 *Stoichiometry of colour removal domains (Edwards and Amirtharajah, 1985)*

Dennett *et al* (1996) found the flocs that formed in this removal zone tended to be small and not well defined. They had poor settling characteristics, but were definitely filterable. Rebhun and Lurie (1993) concur with this observation, particularly for waters that are low in mineral content. Coagulation in this zone may therefore be more suited to the direct filtration process (that is; omission of the settling process prior to filtration), provided the humic substance concentration is not too high (Amirtharajah and O'Melia, 1990).

3.4.2 Adsorption dominated removal zone

This removal zone occurs almost entirely within the pH - alum dosage regions where precipitation of aluminium hydroxide is expected, as shown on Figure 3.2 and 3.3 (Dempsey *et al*, 1984). The removal zone ranges from pH 5.5 to 7.5, with alum dosages that generally exceed about 30 mg/l (as alum) (Edwards and Amirtharajah, 1985, Hundt and O'Melia, 1988). The humic substances are likely to be removed predominantly by adsorption on aluminium hydroxide precipitate. The soluble humic

substances fraction would be co-precipitated by occlusion, as discussed in Section 3.3, and any colloidal fraction would be removed by sweep flocculation (Dempsey *et al*, 1984, Randtke, 1988).

Edwards and Amirtharajah (1985) observed that this removal zone has a non-linear stoichiometric relationship for the lower alum dosage boundary, but no upper boundary at all. This supports the notion that the removal mechanism is predominantly adsorption on aluminium hydroxide. Figure 3.4 shows a plot of the lower boundary stoichiometric relationship for adsorption on aluminium hydroxide (Edwards and Amirtharajah, 1985).

Dempsey (1989) concluded that the presence of aluminium hydroxide precipitate, even in large quantities, does not exclude simultaneous reactions with monomeric and polymeric hydrolysis species. Van Benschoten and Edzwald (1990b), Rebhun and Lurie (1993) and Dempsey *et al* (1984), have also proposed that the species adsorbed on the aluminium hydroxide precipitate, may be Al-humate/Al-fulvate complexes. Complexation is defined as the association of humic substances and aluminium species that does not lead to the formation of a separable solid phase (Van Benschoten and Edzwald, 1990b; Dempsey *et al*, 1984). Complexation of humic substances with cationic aluminium hydrolysis species should result in increased adsorption, owing to the decreased electrostatic repulsion between the adsorbent and the adsorbate (Dempsey *et al*, 1984).

Van Benschoten and Edzwald (1990b) and Edwards and Amirtharajah (1984) both found greater removals of humic substances in the adsorbance dominated removal zone than in the precipitation dominated removal zone. Removals may however not be considered optimum, as an increased alum dosage is required to achieve aluminium hydroxide precipitation (Van Benschoten and Edzwald, 1990b). The increased removals may be due to the increased opportunities for interparticle contacts in the solution - due to the presence of voluminous hydroxide precipitate. At very high concentrations of humic substances, interparticle contact opportunities may increase in the precipitation dominated removal zone, and the differences in removals for the two zones may be reduced (Edwards and Amirtharajah, 1985).

Dennett *et al* (1996) found that the flocs formed in the adsorbance dominated removal zone were larger and settled better than those formed in the precipitation dominated removal zone. This removal zone is therefore more suited to the conventional water treatment process; of rapid mix, flocculation, sedimentation, filtration.

Letterman *et al* (1999) give the following description of the removal of NOM (including humic substances) by adsorption: when metal hydroxide begins to precipitate in the presence of NOM, the more hydrophobic, higher molecular weight fraction (such as humic substances) tends to adsorb and coat the colloidal microcrystals as they form. This process creates the significant coagulant demand of waters that contain adsorbable NOM. When the density of the adsorbed NOM is relatively high, the microcrystals will have a net negative surface charge (due to negative organic molecules extending into the solution) and will remain stable and dispersed (steric stabilisation) - resulting in an increase in turbidity. As the hydrolysing metal salt (HMS) dosage is increased, the surface area concentration of the microcrystals increases and the amount of NOM adsorbed per unit area of particle surface decreases. Eventually, at

a higher HMS dosage, there is not enough negatively charged coprecipitated NOM on the hydroxide surfaces to stabilise the positively charged hydroxide precipitate particles, and the suspension becomes unstable, forming flocs that consist of metal hydroxide precipitate and sorbed NOM. The dosage of HMS required to reach this point has been shown by a number of investigators to be proportional to the initial concentration of NOM in the water. At HMS dosages that exceed the coagulant demand, the formation of an unstable (flocculent) precipitate leads to the relatively rapid formation of visible floc. In most cases, the rate of flocculation increases in proportion to the volume concentration of precipitate in suspension.

The description given in the previous paragraph is demonstrated in Figures 3.5a, 3.5b and 3.5c. Figure 3.5a shows a plot of filtered UV absorbance at 254 nm (cm^{-1}) with increasing alum dosage. The plot shows a relatively sharp drop in filtrate UV absorbance as alum dosage is increased. This sharp drop is characteristic of waters containing NOM with a high percentage of humic substances, as opposed to lower molecular weight, more hydrophilic NOM which is not as easily removed by coagulation. The effect of the alum dose on pH is shown on Figure 3.5c. A dose of at least 30 mg/l (as alum) was required for effective removal (corresponding to a pH of about 5.65), with the maximum removal occurring at a dose of 100 mg/l (corresponding to a pH of about 6.85). The range of effective removal therefore falls within the adsorbance dominated zone. Figure 3.5b shows the increase in filtrate turbidity and aluminium concentration with increasing alum dose, that is associated with the stabilised microcrystalline hydroxide precipitate which passed through the membrane filter used in the study. As the alum dosage is further increased the turbidity and aluminium concentration both decrease abruptly, indicating that the suspension of hydroxide particles, with coprecipitated humic substances, has become unstable and filterable flocs have begun to form.

It is noted that the adsorbance dominated removal zone is larger than the precipitation dominated zone. It would therefore be easier to operate a water treatment plant in the adsorbance dominated zone, particularly for the low buffer capacity waters found in the Southern Cape and Western Cape regions in South Africa, where slight dosing changes could result in coagulation pH moving outside the optimum required for the precipitation dominated zone.

Another advantage of operating a water treatment plant in the adsorbance dominated zone concerns the possible risks associated with Alzheimer's Disease, as discussed in Section 3.2. As aluminium solubility is greatly reduced in the adsorbance dominated zone, less aluminium can pass through the filtration stage to the water consumers (Swartz and De Villiers, 1998).

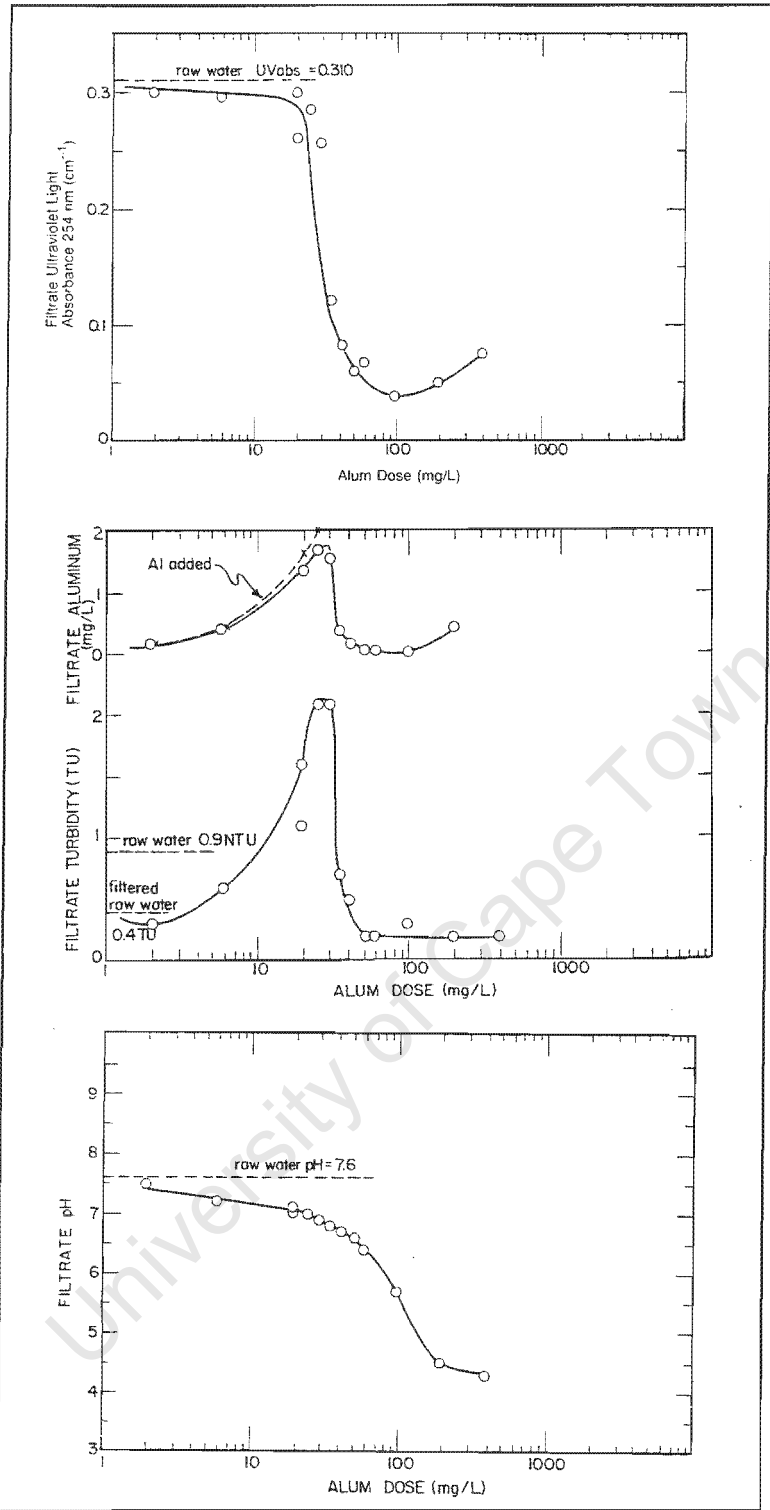


Figure 3.5 Jar test coagulation results - effect of alum dosage on filtrate (a) UV absorbance, (b) aluminium concentration, (c) turbidity and (d) pH (Letterman et al, 1999)

3.4.3 Combination of precipitation and adsorbance removal zones

While more effective humic substances removal generally occurs within the bounds of the two removal zones discussed above, limited coagulation does occur in the intermediate pH range (pH 5.0 to 6.0 depending on the concentration of humic substances and other water quality criteria) - likely by a combination of the two main removal mechanisms (Hundt and O'Melia, 1988 and Amirtharajah and O'Melia, 1990).

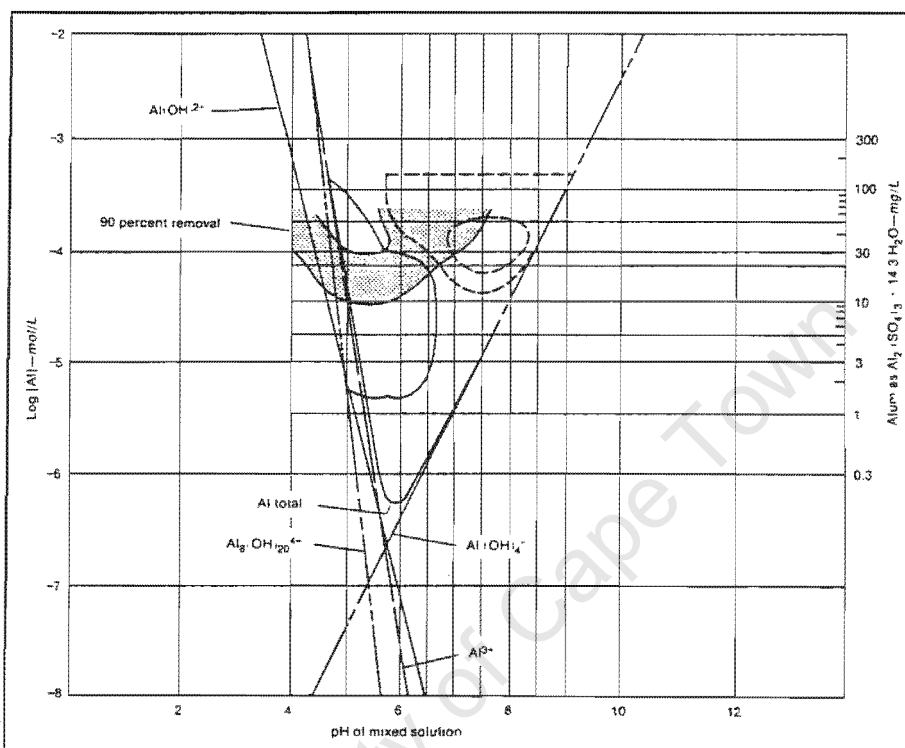


Figure 3.6 Colour removal band - initial colour 450 CU, turbidity 0 NTU (Edwards and Amirtharajah, 1985)

Edwards and Amirtharajah (1985) found that at high humic substance concentrations, such as those found in the Southern Cape and Western Cape regions in South Africa, the two removal zones merge to form a single band of effective removal. Figure 3.6 shows a band of 90 percent removal (by settling and centrifuging), for a water with an initial humic acid concentration of 20 mg/l (corresponding to 450 CU). The 90 percent removal band ranges from pH 4.5 to 7.5, and optimum removal was found to occur in the pH range 4.5 to 5.75. When Edwards and Amirtharajah increased the initial humic acid concentration to 37.5 mg/l (corresponding to 900 CU, which is comparable to the waters found in the Mossel Bay area in South Africa), a similar band of removal was observed - however the pH range for 90 percent removal decreased to 4.0 to 6.5 (as opposed to 4.5 to 7.5 for the lower organic colour concentrations), and the optimum removal zone took place at pH 4.5 to 5.5 (as opposed to 4.5 to 5.75 for the lower concentrations).

3.4.4 The effect of soft, low Alkalinity water on the coagulation of humic substances and the requirement for pH adjustment

Divalent cations such as calcium, can complex with humic substances and reduce their charge, which can result in a reduction in required coagulant dose (O'Melia *et al*, 1999). Hundt and O'Melia (1988) proposed that at higher pH values, such as occur in the precipitation dominated removal zone, calcium occupies sites on the humic substances. Thus aluminium which would normally occupy these sites is still available to remove additional humic substances. At lower pH values, such as occur in the adsorbance dominated removal zone, calcium may cause the humic substances to be more hydrophobic and more readily adsorbed on aluminium hydroxide precipitate. As discussed in Section 2.3, the organically coloured waters found in the Southern Cape and Western Cape regions in South Africa are generally deficient in calcium ions. Humic substances are therefore more difficult to remove from these waters.

The low alkalinities generally associated with the Southern Cape and Western Cape coloured waters were also discussed in Section 2.3. The acidic nature of hydrolysing metal salts, as discussed in Section 3.2, causes a significant drop in the pH of these poorly buffered waters when alum is dosed. A base such as NaOH, Na₂CO₃ or Ca(OH)₂ is therefore normally dosed during coagulation, to supplement the initial alkalinity and control the pH at the optimum required for coagulation (Letterman *et al*, 1999). Considering the beneficial nature of calcium in the coagulation of humic substances, it seems that lime [Ca(OH)₂] is the best suited base for pH control. The addition of the base also prevents elevated concentrations of aluminium from being present in the treated water - as aluminium solubility is greatly increased at low pH (as discussed Section 3.2).

3.5 The Influence of Clay Particles on the Coagulation of Humic Substances

Flocs formed during the coagulation of humic substances are generally light, fragile and do not settle easily (Rebhun and Lurie, 1993 and Swartz and De Villiers, 1998). Relatively large sedimentation tanks therefore need to be provided, to prevent excessive floc carry-over to the filters and consequent short filter runs. The floc characteristics can be markedly improved by the presence of turbidity (clay particles) as these particles serve as nuclei for the formation of large, dense, rapid settling flocs and can result in an improved quality of settled water (Rebhun *et al*, 1969; Rebhun and Lurie, 1993; Mazet *et al*, 1990; Bratby, 1980 and Kuo *et al*, 1988). As waters containing humic substances generally have very low turbidities (as discussed in Section 2.3), there may be merit in adding clay such as bentonite or kaolinite to the water before coagulation is undertaken (Bratby, 1980 and Edwards and Amirtharajah, 1985).

A number of studies, such as those by Edwards and Amirtharajah (1985), Dempsey *et al* (1985), Edzwald (1993) and Rebhun and Lurie (1993) have shown that in waters containing both organic colour and clay particles (turbidity), the requirements for coagulation of the humic substances dominate those of the clay particles. This is a result of the greater reactivity and concentration of reacting units of humic substances as compared to the number concentration of clay particles at commonly encountered mass concentrations (Rebhun and Lurie, 1993). Rebhun and Lurie (1993) reported that in natural waters with the same mass concentrations of clay particles and DOC, the number concentration of humic substances is 4 to 6 orders of magnitude higher than that of the clay particles. They stated that this means greater surface areas and a higher concentration of charges and reaction sites for the humic substances. Dentel (1988) found that a 3.5 mg/l concentration of fulvic acid had approximately the same surface area as a 1 700 mg/l concentration of silica. The cation exchange capacity of clay particles is in the region of 0.1 to 1 $\mu\text{eq}/\text{mg}$ clay, whereas that of humic substances is much higher - 5 to 15 $\mu\text{eq}/\text{mg}$ DOC (Narkis and Rebhun, 1975 and Edzwald, 1993). In addition, humic substances can easily out-compete mineral particles kinetically (Rebhun and Lurie, 1993).

Tambo and Wang (1993) hypothesised that the coagulating chemical reacts preferentially with the humic substances, due to their higher charge density and number concentration. The turbidity particles are then enmeshed in the coagulating colour flocs. As a result, the presence of turbidity has little effect on the optimum coagulant dosage and coagulation pH for an organically coloured water, and a stoichiometric relationship exists only between the coagulant and the humic substances. In addition, Tambo and Wang found that thorough removal of turbidity always took place under conditions of good colour removal.

Dempsey *et al* (1985) found that in normal situations, the concentration of humic substances determines the required coagulant dosage. They concluded that turbidity only influences colour removal by perhaps slightly increasing the coagulant demand and broadening the pH - coagulant dosage zone of removal. Humic substances however, were found to dramatically increase the coagulant dosage required for the removal of turbidity.

Edzwald (1993) studied two vastly different waters in the United States:

The Myrtle Beach Intracoastal Waterway: which is high in humic substances (20 mg DOC/ℓ), relatively low in turbidity (30 NTU) and relatively soft (< 50 mg/ℓ as CaCO₃).

The Missouri River at St. Louis: which is highly turbid (670 NTU), low in humic substances (3 mg DOC/ℓ) and moderately hard (150 mg/ℓ as CaCO₃).

Figure 3.7 shows plots of percentage UV absorbance and percentage turbidity remaining after a series of coagulation jar tests were performed on the two waters, using alum at a constant pH of 7.0. The plots show that a much higher dosage is required for good humic substances and turbidity removal in the water with the high initial humic substances concentration (150 to 175 mg/ℓ, as opposed to 25 to 50 mg/ℓ for the water with the initial high turbidity). Edzwald concluded that this demonstrates dramatically that DOC, and not turbidity, controls coagulation.

Edwards and Amirtharajah (1985) also studied the effects of turbidity (in the range of 27 - 30 NTU) on the coagulation of waters containing humic substances. They found that optimum simultaneous removal of colour and turbidity occurred at ranges of pH and coagulant dosage that are nearly identical to the optimum ranges for water in which turbidity is absent. At low concentrations of humic substances (4 mg humic acid/ℓ), the coagulant dosage (alum) required for colour removal in the presence of turbidity, was slightly lower than that required when turbidity was absent. At higher humic substance concentrations, the coagulant dosage required for simultaneous removal of colour and turbidity was only slightly higher than that necessary for colour removal alone.

The addition of turbidity increases the number of particles and would therefore increase the number of collisions, thus improving flocculation kinetics in the lower pH range (where voluminous metal hydroxide does not precipitate). At higher pH, the clay particles may provide nucleation sites, thus accelerating the precipitation of metal hydroxide (Edwards and Amirtharajah, 1985).

Figure 3.8 shows the colour removal zones for a water containing a low concentration of humic substances (4 mg humic acid/ℓ, corresponding to 100 CU), with no turbidity present. This can be compared to Figure 3.9, which shows the removal zones for a water containing the same concentration

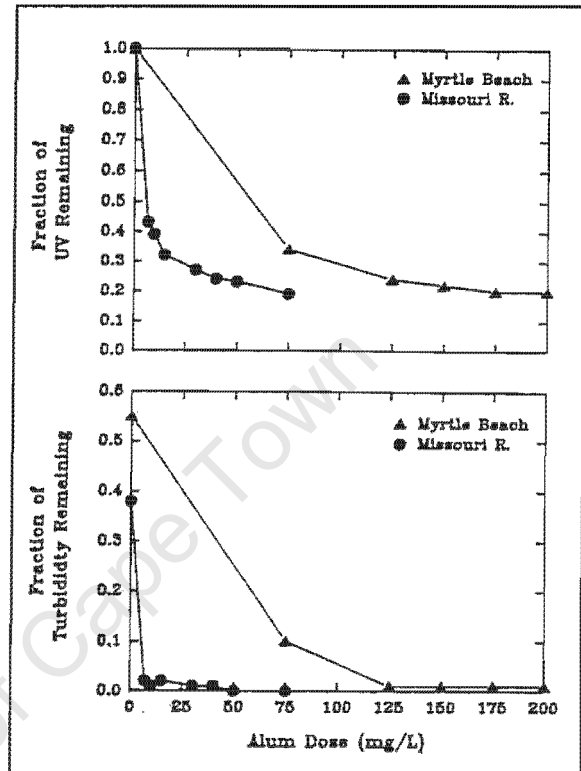


Figure 3.7 Jar test coagulation results - comparison of water with high humic substances concentration versus water with high turbidity (Edzwald, 1993)

of humic substances, but with turbidity present (27 - 30 NTU). The figures show that it is easier and more economical to coagulate a water with turbidity at these levels, than a water with humic substances alone, because:

- Broader zones of pH and coagulant dosage are possible - which agrees with the conclusions of Dempsey *et al* (1985).
- Lower dosages of coagulants can possibly be used.

Tambo and Watanabe (1979) derived a floc density function. They found that the ratio of aluminium ion dosed to suspended particle concentration (they termed this the ALT ratio), greatly affects floc density: as the ALT ratio decreases, the floc density at a particular floc size increases. Therefore, increasing the turbidity of waters containing humic substances would result in an increase in floc density, as the coagulant demand remains relatively constant.

The results of these studies of clay particle effects on coagulant dosage requirements are significant, as they show that it is feasible to add clay particles to low turbidity organically coloured waters, to improve the strength and settling characteristics of the flocs without creating a significantly higher coagulant demand (Edwards and Amirtharajah, 1985).

3.6 Organic Polymers (Polyelectrolytes)

Polymer coagulants used in water treatment are high molecular weight synthetic organic compounds, also known as polyelectrolytes. These compounds tend to adsorb on the surfaces of most particles in aqueous suspension. The polymers consist of chains of subunits, called monomers, which can be linear, branched or cross linked. The number and type of monomer can be varied in manufacture, to produce a wide variety of different polyelectrolytes (Letterman *et al*, 1999).

The monomers may have a positive or negative charge - polymers with predominantly positive monomers are termed cationic polyelectrolytes, while those with a predominance of negative monomers are termed anionic polyelectrolytes. In some cases, though not all, charged sites are formed by ionisation reactions, and the charge on the polyelectrolyte is a function of the solution pH. Nonionic polyelectrolytes are those with no charged sites, or a negligible tendency to develop them in solution (although the term polyelectrolyte is not strictly correct in this case, it is still commonly used in describing nonionic polymers) (Letterman *et al*, 1999).

There is concern over the health implications of the use of polyelectrolytes in potable water, and stringent limits have been placed on the use of these substances in many countries - Switzerland and Japan do not permit the use of polyelectrolytes at all (Letterman *et al*, 1999).

Polyelectrolytes can be used for two different purposes in the coagulation of humic substances. These are each discussed briefly below:

Primary coagulant polyelectrolytes:

As discussed in Section 3.3 cationic polymers can cause coagulation of humic substances by adsorption and charge neutralisation, adsorption and bridging, and possibly by the precipitation of dissolved humic substances (Crozes *et al*, 1995 and Narkis and Rebhun, 1975). Relatively low molecular weight (<500 000) cationic polymers are generally used for this purpose (Letterman *et al*, 1999). The polyelectrolytes react stoichiometrically with the humic substances, and the high cation exchange capacity of the humic substances can result in a relatively high polyelectrolyte dosage requirement. Better coagulation is achieved at low pH where the degree of dissociation of the humic substances is decreased, resulting in a lower coagulant demand (Narkis and Rebhun, 1977).

As polyelectrolytes do not produce a voluminous hydroxide precipitate (as do hydrolysing metal salts) which increases the particle number concentration, they cannot cause enmeshment/sweep floc and coprecipitation, and the rate of particle aggregation may be too small to produce large settleable flocs in a reasonable time (Bratby, 1980 and Letterman *et al*, 1999). This is important in the coagulation of low turbidity organically coloured waters where there are no mineral particles to act as nuclei or to weight the flocs. The relatively poor settling characteristics of the floc produced, and the high coagulant demand (with associated health implications) results in

limited use of polyelectrolytes as primary coagulants in the removal of humic substances. These polyelectrolytes may be more suited to the direct filtration process, provided that the humic substances concentration is not too high (Letterman *et al*, 1999).

Flocculent aid polyelectrolytes:

Flocculent aid polyelectrolytes are generally anionic or nonionic and have a relatively high molecular weight - up to 1 000 000. Most are made with the acrylamide monomer and are known as polyacrylamides (Amirtharajah and O'Melia, 1990 and Letterman *et al*, 1999). Because of their high molecular weight and therefore appreciable length, the polymers are able to bridge or interconnect particles in larger agglomerates. These flocculent aids are added to the coagulation process to increase the size and strength of the flocs (Letterman *et al*, 1999). The dosages applied are usually low and can therefore comply with the health regulation requirements. Flocculent aids are particularly useful in strengthening and weighting the fragile and light flocs characteristic of the coagulation of organic colour.

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CHAPTER 4

FLOC BLANKET CLARIFICATION

4.1 The Concept of Floc Blanket Clarification

As discussed in Section 3.1, the conventional steps utilised in the removal of organic colour are: coagulant chemical dosing, rapid mix, flocculation, sedimentation and finally filtration. The floc blanket clarification process combines two of these steps, namely flocculation and sedimentation, into one process unit (Hudson, 1981). The water being treated is fed into the floc blanket clarifier (FBC) once it has been dosed with coagulation chemicals and has passed through the rapid mix step - these first two steps initiate the formation of micro-flocs. In the FBC the water flows vertically upwards through a fluidised bed of larger mature flocs - the floc blanket - which are suspended in equilibrium with the rising flow (Bratby, 1980 and Brown and La Motta, 1971). FBCs are usually constructed to provide diverging flow, so that the up-flow velocity decreases with height. The micro-flocs that enter the FBC aggregate and become entrapped in the floc blanket (Gregory *et al*, 1999 and Brown and La Motta, 1971). As the flow rises in the FBC, a point is reached where the settling velocity of the fluidised suspension exceeds the up-flow velocity, and an interface forms between the suspension and the relatively clear supernatant above. This interface is distinct in a well designed and operated FBC (Gregory *et al*, 1999). The clear supernatant is then collected at the surface of the FBC and directed to the filtration step.

As floc particles accumulate in the floc blanket, the volume occupied by the suspension tends to increase, and the upper surface of the floc blanket rises. In order to maintain a mass balance of solids entering and leaving the unit, the level of the floc blanket is controlled, usually by decanting the floc via a submerged weir (Gregory *et al*, 1999; Mackrle, 1965 and Brown and La Motta, 1971). The decanted floc is then thickened via quiescent settling in some form of hopper, before being withdrawn to a solids handling facility such as a centrifuge or sludge lagoons.

A number of other names have been used for the floc blanket clarification process, these include: sludge blanket clarification, contact flocculation, solids contact up-flow sedimentation and solids contact clarification. Figure 4.1 shows an example of a pair of typical FBCs - a proprietary unit produced by Paterson Candy, Int. Ltd. (Bratby, 1980). The various components can be seen, such as the inlet at the bottom of the clarifier, a suspended hopper for decanting and thickening floc from the blanket, and the clear water collection troughs.

The combination of the flocculation and settling steps in one unit leads to decreased capital costs, providing the process is suited to the application. The operating costs are generally low as the power requirements are minimal, although some proprietary items do include mechanical stirrers. Some of the variants of the floc blanket clarification process have no mechanical equipment that needs maintenance.

Apart from the potential savings in construction costs, there are a number of other advantages of FBCs over conventional flocculation - sedimentation units. These include (Kawamura, 2000):

- The existence of a high concentration of large mature floc in the floc blanket, which causes efficient clarification and allows the required duration of flocculation to be shortened (Tambo and Hozumi, 1979). This is due to the seeding effect of the mature flocs and the improved flocculation due to small flocs being entrapped in the floc blanket.
- The reduced size of the site required for the treatment plant infrastructure.
- Simple sludge (from the floc blanket) removal.
- Capability of delaying degradation of the clarified water quality in the case of temporary improper coagulant dosage or even a short interruption of the coagulant feed, due to the buffering effect of the floc blanket.

There are however, also a number of disadvantages (Kawamura, 2000):

- Compared to conventional flocculation - sedimentation FBCs require more stringent operational control.
- There is a rapid loss in efficiency during hydraulic and solids overloading and hydraulic shock loading. This leads to carry-over of floc particles and overloading of the filters.
- Diurnal temperature fluctuations can induce hydraulic instability and carry-over of floc particles. This is particularly noticeable in the afternoon hours - it has been hypothesised that absorption of infrared rays from the sun produces density currents at the surface of the blanket (Amirtharajah, 1980).
- Difficulties are experienced in starting up the process and producing a floc blanket.

The floc blanket clarification process emerged in the field of water treatment in India in about 1932 (Gregory *et al*, 1999), and has become particularly popular in Europe (Amirtharajah, 1980). Since then much work has been done to attempt to understand the various mechanisms that govern the process, by workers such as Ives (1968), Mackle (1965), Tesarik (1967), Miller *et al* (1966) and Gregory *et al* (1999), in Europe, by Brown and

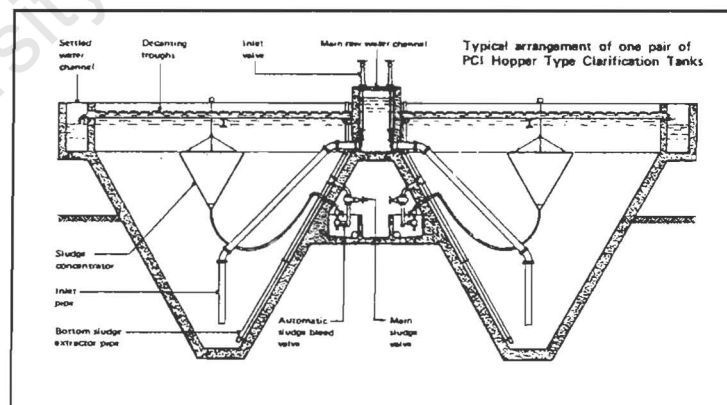


Figure 4.1 Example of floc blanket clarifiers (Bratby, 1980)

La Motta (1971) in the United States and by Tambo and Wang (1993) in Japan. Some of the principles pertaining to floc blanket clarification are discussed in greater detail in the following sections.

4.2 Particle Growth and Aggregation in Floc Blanket Clarification

Once the micro-flocs enter the FBC with the inlet flow, several mechanisms contribute to their growth into larger settleable particles which can be separated from the water - these include:

Peri-kinetic flocculation: particle aggregation resulting from the random thermal motion of fluid molecules. This mechanism is significant for particles less than 1 to 2 μm (Amirtharajah, 1980).

Ortho-kinetic flocculation: particle aggregation induced by fluid shear. The shear, or mixing intensity, is measured as the root-mean-square-velocity gradient, commonly referred to as the velocity gradient (G). The velocity gradient has the units s^{-1} , and may be calculated from the following widely used equation (Camp and Stein, 1943):

$$G = \left(\frac{P}{V\mu} \right)^{1/2} \quad (4.1)$$

where P = power dissipated in the water
 V = volume of water in the unit
 μ = absolute viscosity of water

Ortho-kinetic flocculation is the predominant flocculation mechanism in conventional flocculation processes (Amirtharajah, 1980 and Letterman *et al*, 1999).

Differential settling: unequal particle settling velocities can cause particle contacts and aggregation. Although this does not contribute greatly to particle growth in conventional flocculation systems, it is a major mechanism in floc blanket clarification (Amirtharajah, 1980 and Letterman *et al*, 1999).

Entrapment: rising small particles are mechanically entrapped, and prevented from passing through the voids between the larger more mature particles in the floc blanket. This is probably the most important mechanism of particle aggregation and growth in floc blanket clarification (Gregory *et al*, 1999; Brown and La Motta, 1971 and Tambo and Hozumi, 1979).

The fluid - particle system in the floc blanket is amenable to analysis as a turbulent field (Amirtharajah and O'Melia, 1990 and Amirtharajah, 1980). The dimensionless product of velocity gradient (G), retention time (t) and floc volumetric concentration (Φ - defined as the volume of floc per unit volume of fluidised suspension), is widely recognised as being a measure of the effectiveness of the ortho-kinetic flocculation process (Gregory *et al*, 1999). For dilute suspensions, such as those encountered in conventional flocculation - sedimentation, optimum ortho-kinetic flocculation conditions are generally considered only in terms of the dimensionless product Gt (Amirtharajah, 1980; Gregory *et al*, 1999 and Ives, 1968). For flocculation prior to horizontal flow sedimentation basins; Camp (1955) found satisfactory performance of conventional flocculators to occur at velocity gradients from 20 to 74 s^{-1} , and Gt values between 2×10^4 and 2×10^5 . In the case of floc blanket clarifiers, the velocity gradient is usually less than in conventional flocculators, and the value of Gt is only about 2×10^4 (Gregory *et al*, 1999 and Brown and La Motta, 1971). However, the greater volumetric concentration in the concentrated

floc blanket contributes to flocculation by enhancing the probability of inter-particle collisions. Optimum flocculation conditions are therefore better represented by the product of $Gt\Phi$ (Ives, 1968 and Gregory *et al*, 1999).

Ives (1968) developed an expression for $Gt\Phi$, where a series of infinitely small horizontal layers are integrated across the depth of the floc blanket. This was simplified by Amirtharajah (1980) as follows (in this case adapted for a square pyramidal shaped FBC):

$$\sum_{L_t}^{L_u} G_L \Phi_{L_t} t_L = \frac{L_u^2}{2} \left[\frac{\gamma_s - \gamma}{Q\mu f^{9/2}} \right]^{1/2} F \left(\frac{L_u}{L_t} \right) \quad (4.2)$$

- where L_u = length of one side of the floc blanket at the upper blanket surface
 L_t = length of one side of the floc blanket at the lower blanket boundary
 t_i = liquid retention time at the level L
 γ_s, γ = specific weights of floc and water respectively
 f = shape factor for the floc = 2.78 for alum and ferric floc according to Bond (1960)
 F = function of L_u/L_t according to Ives (1968)

Ives (1968) suggested a range for $Gt\Phi$ of 60 to 120, and this parameter can therefore be used in the design of FBCs (Amirtharajah, 1980).

Excessive velocity gradient values should not be allowed as shear and breakup of the flocs will occur. Fair and Geyer (1954) proposed a limit of 100 s^{-1} , however, the actual limit would depend largely on the characteristics of the flocs being produced, the type of coagulant dosed and the addition of flocculent aid polyelectrolytes. The nature of the flocs are also influenced by the magnitude of the velocity gradient - with smaller, denser flocs forming at high velocity gradients, and larger less dense flocs forming at lower velocity gradients (Hudson, 1965 and Amirtharajah and O'Melia, 1990). Generally, tapering of the velocity gradient (from initial higher values) in flocculation processes improves the settling characteristics of the flocs. The higher velocity gradient regions cause rapid transformation of primary particles into high density flocs, and the subsequent lower velocity gradient regions cause the build-up of progressively larger flocs for better settling, whilst limiting floc breakup (Amirtharajah and O'Melia, 1990).

In FBCs, the decrease in up-flow velocity with rising flow facilitates a natural tapered flocculation process (Ives, 1968). However, maximum velocity gradients of only 2.5 s^{-1} are feasible in FBCs, and it is therefore possible that the shearing of flocs may not be as important as in conventional flocculation systems. The velocity gradient in a floc blanket can be calculated by combining Equation 4.1 with expressions for the power dissipated by turbulence and by drag on the floc particles. Ives (1968) found the power dissipated per unit volume by turbulence to be negligible compared to the contribution of

particle drag. He developed the following expression for the velocity gradient G_L at level L , in a conical shaped FBC with side walls sloped at 63° to the horizontal:

$$G = \left[\frac{4(\rho_s - \rho)gQ}{\mu\pi L^2} \right]^{1/2} \left[\frac{1}{s} - \frac{4Q}{s\pi v_p L^2} \right]^{3/4} \quad (4.3)$$

where v_p = settling velocity of a typical single floc particle
 ρ_s, ρ = mass densities of the floc and the water respectively

Ives's finding that turbulence has an insignificant contribution to the velocity gradient indicates that poor flocculation would take place in an up-flow clarifier without a floc blanket. This is indirectly confirmed by the fact that difficulties are usually experienced in establishing a floc blanket at FBC start-up conditions (Ives, 1968) - especially when low turbidity water is being treated. When a FBC is started, particles accumulate slowly at first, but then at an increasing rate due to the enhanced flocculation and entrapping effects of the growing blanket. Eventually a maximum accumulation rate is reached, which is limited by the particle characteristics and the up-flow velocity of the water (Gregory *et al*, 1999). According to Amirtharajah (1980), in low turbidity water, the difficulties experienced in establishing a floc blanket can be ameliorated by dosing clay into the water to increase the number of particles and the potential for particle collisions (Amirtharajah, 1980).

Another implication of the dominance of particle drag effects in ortho-kinetic flocculation, is that flocculation will improve as the depth of the floc blanket is increased (Ives, 1968). This is confirmed by the findings of Miller *et al* (1966), although the returns were insignificant after about 2.5 m. Miller's results are presented in Figure 4.2, which shows a graph of effluent turbidity versus floc blanket depth.

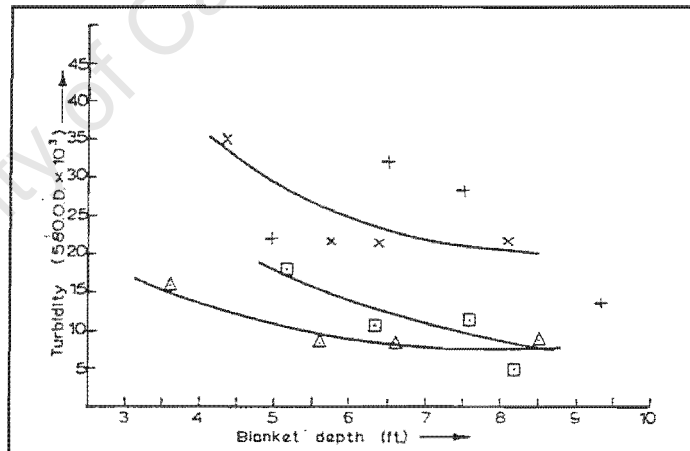


Figure 4.2 Variation of FBC effluent turbidity with floc blanket depth (Miller *et al*, 1966)

4.3 Sedimentation in Floc Blanket Clarification

At high particle concentrations in a suspension, individual particle behaviour is hindered by the presence of other particles. With increased particle concentration, the free area between particles is reduced, causing greater inter-particle fluid velocities and alteration of flow patterns around the particles. Consequently, the average settling velocity of the particles in a concentrated suspension is generally less than that of a discrete particle of similar size (Gregory *et al*, 1999).

The product of the settling velocity of the suspension and the mass concentration, is the solids mass flux (F_m) - relative to the upward flow of the water. An equivalent relationship holds for the floc volumetric concentration (Φ), which defines the solids volume flux, or blanket flux (F_v) (Gregory *et al*, 1999):

$$F_v = v_s \Phi \quad (4.4)$$

where v_s = settling velocity of the suspension
 Φ = floc volumetric concentration

The relationship between solids mass flux and concentration is shown in Figure 4.3, and is complicated because v_s is affected by concentration. The relationship can be divided into the following four regions, as indicated on Figure 4.3 (Gregory *et al*, 1999):

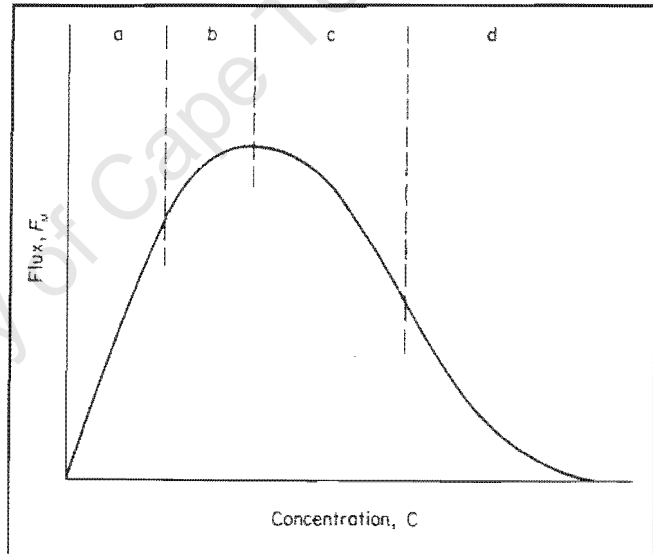


Figure 4.3 Typical relationship between flux and concentration of a suspension (Gregory *et al*, 1999)

Region (a), Type 1 and 2 settling: unhindered settling of discrete particles occurs, and flux increases in proportion to concentration. The suspension contains particles with different settling velocities and has a diffuse interface with the clear liquid above.

Region (b), Type 3a settling: with increasing concentration, hindered settling takes effect, and eventually the maximum flux is reached. In this region the particles all settle with the same velocity and the interface of the suspension and the clear liquid becomes distinct.

Region (c), Type 3b settling: further increase in concentration reduces the flux because of the associated reduction in v_s . The suspension continues to settle homogeneously.

Region (d), Type 4 settling: at the point of inflection in the flux - concentration curve, the concentration reaches a point where thickening can be regarded to start leading ultimately to compression settling. The rate of settling becomes dependent on the weight of solids above.

Tesařík (1967) and Brown and La Motta (1971) showed that the floc blanket behaves as a fluidised bed, where fluidisation is hydrodynamically similar to hindered, or Type 3 settling. Richardson and Zaki (1954) derived the following widely accepted empirical relationship to describe hindered settling of rigid particles (Amirtharajah, 1980 and Gregory *et al*, 1999):

$$v_s = v_p E^n = v_p (1 - \Phi)^n \quad (4.5)$$

where E = porosity of the suspension
 n = power value dependent on the Reynold's Number of the particle
 v_p = terminal settling velocity of an individual particle from the suspension in unhindered flow (i.e. absence of the effect of surrounding particles)

The relationship was adapted to flocculent suspensions by Gregory (1979) by the inclusion of correction factors to adjust for effective volume, to account for particle distortion and compression. The adjusted relationship is as follows:

$$v_s = v_p k_1 (1 - k_2 \Phi^*)^r \quad (4.6)$$

where Φ^* = half-hour settled floc volume (the volume occupied by the floc after a sample of the suspension has been placed in a 1 l measuring cylinder and allowed to settle for 30 minutes, expressed as a fraction of the total volume of the sample). Φ^* tends to range from 0.16 to 0.20.
 k_1, k_2, r = constants representing the system.

Based on extensive floc blanket data, Gregory *et al* (1999) proposed that Equation 4.6 be simplified to the following, for high alkalinity organically rich water, and other waters that produce similar floc quality:

$$v_s = v_p (1 - 2.5\Phi^*) \quad (4.7)$$

Using the settling velocity data for v_p given in Table 4.1, Equation 4.7 can be applied to the design of FBCs.

Table 4.1 *Settling velocities (v_p) for floc particles (Amirtharajah, 1980)*

Floc type	Range of settling velocities, v_p , at 15° C	
	<i>mm/s</i>	<i>m/h</i>
Fragile floc, colour removal with alum	0.61 - 1.22	2.2 - 4.4
Medium floc, algae removal with alum	0.20 - 0.30	0.7 - 1.1
Strong floc, turbidity removal with alum	0.24 - 0.35	0.9 - 1.3
Strong floc, lime-soda softening	0.24 - 0.35	0.9 - 1.3
Crystalline floc, CaCO ₃ granules	0.40 - 0.66	1.4 - 2.4

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4.4 Prediction of Optimum Floc Blanket Clarification Operating Conditions

Figure 4.4 shows a plot of various relationships governing the settling dynamics in FBCs (Gregory *et al*, 1999). The relationships show that settled water quality deteriorates rapidly (point A) as increasing up-flow velocity causes the floc concentration (point B) to decrease below the concentration at maximum flux (point C). Conversely, little improvement in settled water quality is likely to be gained by decreasing up-flow velocity so that the concentration is greater than that at maximum flux (to the left of points A and B). This is because for concentrations greater than that at maximum flux, inter-particle distances are small enough for entrapment to dominate the clarification process (Gregory *et al*, 1999).

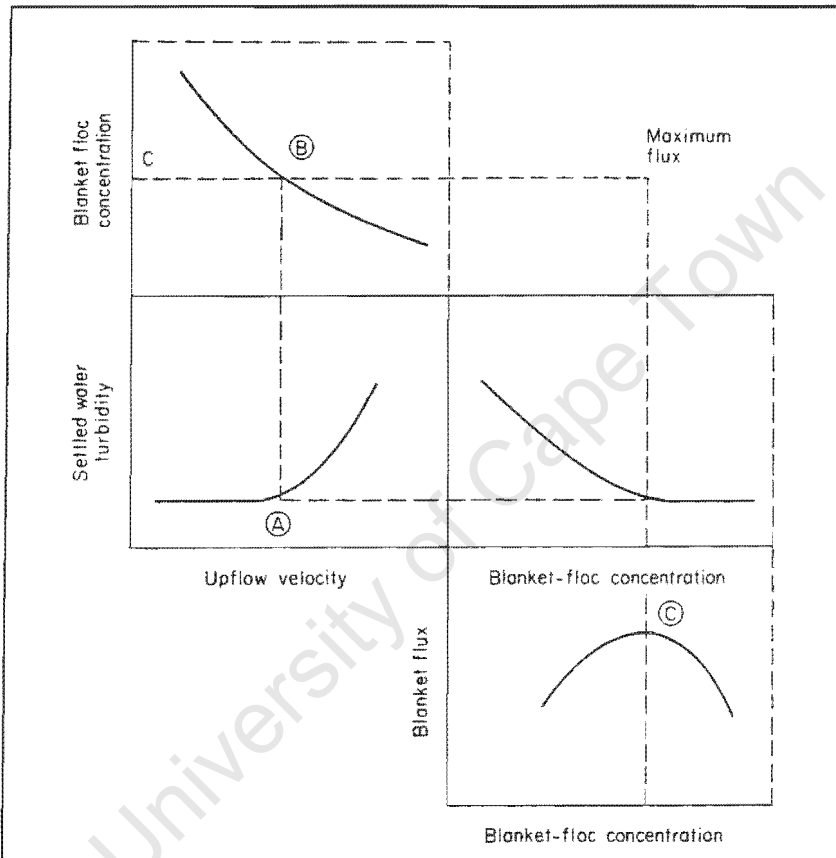


Figure 4.4 Typical relationships between clarified water quality and floc blanket concentration, up-flow velocity and floc blanket flux (Gregory, 1979)

As increasing up-flow velocity causes the concentration to decrease below that at maximum flux, inter-particle distances increase, and the motion of particles becomes more intense. Some of the larger particles may not survive the higher shear rates that develop and smaller particles may avoid entrapment and escape from the floc blanket. Consequently, maximum flux conditions represent possible optimum design and operating conditions (Gregory *et al*, 1999).

The limit of up-flow velocity has been expressed in terms of v_p by some investigators. Bond (1965) noted that the blanket interface remained clearly defined at an up-flow velocity up to about $0.5v_p$, that slight

“boiling” of the blanket surface occurred above $0.55v_p$, and that clarification deteriorated notably at about $0.65v_p$. Tambo *et al* (1969) found that a floc blanket is stable for up-flow velocities less than $0.7v_p$, and very unstable at velocities less than $0.8v_p$. Gregory (1979) found that the floc blanket - clear water interface was sharp up to the point of maximum flux, which he found to occur at about $0.5v_p$ (with a Φ^* value of about 0.20), and that it was very difficult to maintain a blanket above $0.75v_p$ (Gregory *et al*, 1999).

It is emphasised that the performance of the floc blanket process, and indeed any flocculation - sedimentation process, is affected primarily by the chemical coagulation conditions. If these conditions are not maintained at the optimum, the process will be inefficient no matter how carefully it is designed.

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4.5 The Effect of Physical Variables on Floc Blanket Behaviour

The stability of the fluidised floc blanket directly affects the efficiency of solid - liquid separation in FBCs. The most detrimental phenomenon affecting floc blanket instability, is the formation of currents which disturb uniform distribution of flow (Mackrle, 1965). Tesařík (1967) showed that the diverging flow in a FBC is by nature unsteady and not radial. Currents due to hydrodynamic instability conditions will therefore always be present in fluidised beds, and cannot be entirely removed (Mackrle, 1965).

Instability currents can originate from many kinds of disturbances, such as non-uniform floc size distribution. The floc particles in the upper part of the blanket may accumulate to such dimensions that they might not be maintained in suspension by the upward flow, and may start to settle. By this action a descending current is formed. However any downward stream inevitably causes a consequent upward stream - when such an upward stream reaches the top of the blanket, it causes eruptions of floc at the blanket - clear water interface. These eruptions, which can also be caused by instability currents resulting from other factors, are a common site in FBCs (Mackrle, 1965). The flocs are thrown far up into the clear water zone, before receding again possibly as a result of currents and the sudden decrease in floc concentration with an associated increase in hindered settling velocity (Tesařík, 1967). The floc blanket therefore appears to boil as portions of the surface periodically rise and fall again. If the eruptions rise too high, flocs overflow into the clarified water collection troughs and are passed on to the filters. If the instability conditions are pronounced, the efficiency of the separation process is greatly reduced and filters runs will become short and inefficient. On the other hand, if the instability conditions in the FBC are curtailed, a stable floc blanket can be maintained even at relatively high up-flow velocities (Mackrle, 1965).

A number of the physical parameters that can affect the behaviour of FBCs are discussed in the following sections:

Inlet conditions:

The inlet flow into the FBC generally has a high velocity and is very turbulent. As this energy is partly dissipated in the concentrated floc blanket, excess energy can significantly increase instability of the blanket (Mackrle, 1965). It is therefore essential that the inlet is designed to control the momentum of the incoming water, to avoid streaming and boundary separation (Ives, 1968).

Any irregularity in the distribution of the water entering the floc blanket zone may also cause a great deterioration of the solid - liquid separation efficiency. Mackrle (1965) hypothesised that due to the relatively high velocity of the incoming flow, any irregularity is readily propagated through the entire floc blanket, increasing the magnitude of instability currents that are naturally present in the FBC. Tesařík (1967) stated that vortices are formed at the inlet and move upward in the flow direction. Although these vortices are dissipated in the viscous floc blanket, some may reach the blanket surface and cause eruptions.

The inlet conditions are therefore critical in controlling floc blanket stability (Mackrle, 1965). Marckrle (1965) found the slot distribution system to be the most effective. In this system, uniform distribution of the inlet flow to the FBC is provided by a narrow inlet slot (Mackrle, 1965). This can be accomplished by allowing the flow to enter the FBC through an inverted funnel (or pyramidal hopper depending on the shape of the FBC) - the slot is formed between the floor of the FBC and the lip of the funnel. The width of the slot should be optimised to control the momentum of the flow.

Clarified water collection:

Above the floc blanket is a zone of relatively clear water, which is usually collected by a series of horizontal troughs which are perforated by orifices or have overflow edges along their length. This collection system must be uniform, and be designed to prevent interference with the relatively uniform flow in the floc blanket (Ives, 1968). If this is not done, floc will be drawn up and into the collection troughs by streaming currents.

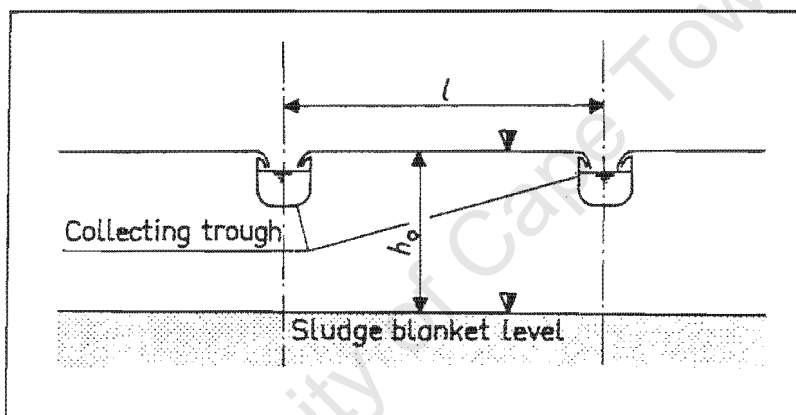


Figure 4.5 Arrangement of clarified water collection troughs (Tesařík, 1967)

Tesařík (1967) used potential theory analysis to show that the clear water zone should have a minimum depth equal to half the spacing between collection troughs - with regard to Figure 4.5, $h_0 > \frac{1}{2} \times l$. In any event, it is advisable that a supernatant depth of at least 1 m be allowed, to prevent carry-over and to act as a buffer zone (Gregory *et al*, 1999).

Floc withdrawal:

Bond (1960) showed that in a fluidised suspension with an expanding cross section, the maximum concentration will occur at the top of the suspension. The level of the continuously growing floc blanket should therefore be controlled at or near the surface of the floc blanket. Floc withdrawal at any other level would be inefficient (Ives, 1968).

Removal of the floc is usually accomplished by a submerged weir, over which excess floc flows into a sludge thickening hopper. It is advisable that the submerged weir is symmetrical within

the FBC, to prevent uneven currents occurring as the sludge is withdrawn (Ives, 1968). This can be accomplished either by suspending a hopper in the centre of the FBC, as shown on Figure 4.1, or by providing a submerged peripheral weir as is done on some proprietary FBCs.

Mackrie (1965) proposed that in order to prevent density currents that form in the sludge thickening hopper as the floc settles, from reaching and disturbing the floc blanket, a small controlled flow should be drawn continuously from the sludge thickening hopper. This would provide a homogenous sedimentation condition for separation of the floc from the upward flow, and reduce the possibility of density current formation.

Floc blanket depth:

The beneficial effect of increased floc blanket depth on flocculation efficiency and consequently on solid - liquid separation efficiency was discussed in Section 4.2. However, it is also possible that deeper beds help dampen out the turbulence created by the inlet conditions (Miller *et al*, 1966). The floc blanket *effective depth*, defined as the total volume of the floc blanket divided by the depth of the blanket, usually ranges from 2.5 to 3.0 m (Miller *et al*, 1966).

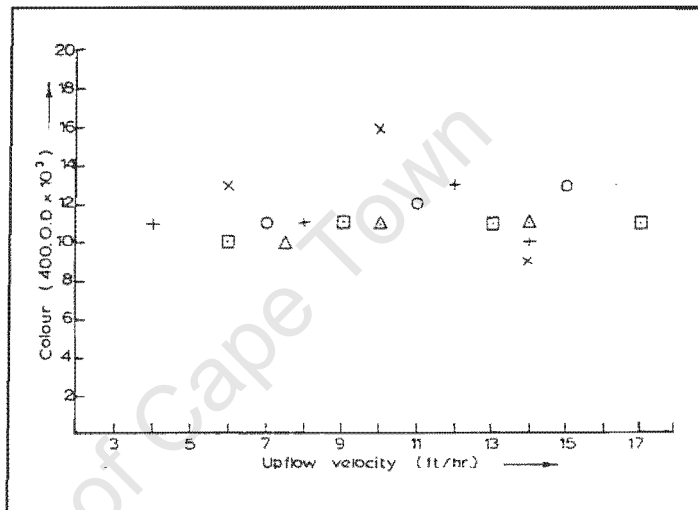


Figure 4.6 Variation of filtered FBC effluent colour with up-flow velocity (Miller *et al*, 1966)

Up-flow velocity:

The allowable up-flow velocity is very much dependent on the type of water being treated. Floc produced by coagulating clay-bearing water generally settles much faster than that produced by coagulating water with little mineral turbidity, and settling characteristics may be improved by the addition of flocculent aid polyelectrolytes (Gregory *et al*, 1999 and Miller *et al*, 1966). As the up-flow velocity approaches and exceeds the practical maximum, increasing quantities of floc will be carried over to the filters. Three factors can contribute to the increase in carry-over with increasing up-flow velocity (Miller *et al*, 1966):

- As the up-flow velocity is raised, it will exceed the settling velocity of an increasing proportion of the floc blanket.
- Greater attrition, or floc break-up, will occur as a result of increased turbulence. This will result in a higher proportion of small flocs, although some of these may be re-

flocculated.

- The escape of small flocs from the floc blanket is likely to be easier at higher up-flow velocities, due to the increased porosity in the blanket.

An interesting finding by Miller *et al* (1966), was that organic colour removal (after floc blanket clarification and filtration) is independent of up-flow velocity, as illustrated in Figure 4.6. This illustrates that the chemical reactions and interactions required for the removal of organic colour occur quickly, and are independent of flocculation efficiency. Good flocculation is however required to remove the particles created in the coagulation of organic colour.

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CHAPTER 5

EXPERIMENTAL INVESTIGATION OF THE EFFECTS OF THE ADDITION OF KAOLIN AS A PROCESS AID IN FLOC BLANKET CLARIFICATION OF ORGANICALLY COLOURED SURFACE WATERS IN SOUTH AFRICA

5.1 Introduction

Beneficial effects of the presence of clay particles (turbidity) in the coagulation of organically coloured waters were discussed in Section 3.5. Also, in Section 4.2, dosing of clay to facilitate the improvement of flocculation dynamics in FBCs was discussed.

Tambo and Wang (1993) undertook a study of floc blanket clarification of organically coloured waters in the presence of turbidity. They found that the efficiency of the floc blanket clarification process could be significantly enhanced by adding kaolinite (a type of clay) particles. The density of the flocs produced was significantly increased, and the process was operated successfully at up-flow velocities as high as 18 m/h, whereas maximum up-flow velocities of about 1 to 2 m/h are more common in floc blanket clarification of low turbidity coloured waters. In agreement with the findings of numerous other researchers, as discussed in Section 3.5, Tambo and Wang found that the optimum coagulation dosage and pH conditions are determined by the organic colour concentration, regardless of the coexisting clay particles. Tambo and Wang achieved optimum results when the colour (CU) - clay concentration (mg/l) ratio was 1:1.

The beneficial effect of turbidity in the floc blanket clarification process was also noted by Gregory *et al* (1999). They suggested that clay should purposely be added to low turbidity waters to increase the floc density and the settling velocity of the floc blanket.

There are a number of floc blanket clarification water treatment plants in the Southern Cape and Western Cape regions of South Africa, that treat low turbidity organically coloured waters. However, the effect of dosing clay (adding turbidity) into these waters has not been studied and documented in detail, if at all. Considering the possible benefits of the presence of turbidity, such as broader zones of pH and coagulant dosage for effective coagulation, possible lower coagulant dosage requirements, easier start-up of the FBCs, improved floc blanket settling dynamics with associated higher allowable loading rates (up-flow velocities), and most importantly, possible savings in the capital expenditure associated with both the construction of new FBC plants, and the postponement of extensions to existing FBC plants to meet growth in water demands, it seems appropriate that the effects of the presence of turbidity be investigated.

A laboratory scale FBC and associated equipment was therefore constructed, and a series of experiments

undertaken to investigate the effect of the addition of kaolin (clay) as a process aid, in floc blanket clarification of South African organically coloured surface waters. The specific aim of the experiments was to investigate the effect of various kaolin dosages on the settled water quality at various hydraulic loading rates (up-flow velocities) in the FBC, and to determine whether the up-flow velocity and floc blanket stability could be increased by dosing kaolin.

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5.2 Methodology

5.2.1 Raw water

Raw water for the investigation, originating from the dams on top of Table Mountain was obtained from the head of the Constantia Nek Water Treatment Works, and was delivered to the laboratory by the City of Cape Town Fire Department. As the water storage volume at the laboratory was limited, the water supply had to be replenished on a number of occasions and the same batch of water could therefore not be used for all the experiments - the water quality was nevertheless fairly consistent.

The raw water quality was typical of the soft, low alkalinity, high organic colour, low turbidity surface waters found in the Southern Cape and Western Cape of South Africa. The general range of the water quality was as follows:

UV absorbance: from 0.74 to 0.85 absorbance units/centimetre (at 260 nm).

Colour: from 175 to 210 CU.

Turbidity: from 0.8 to 1.0 NTU.

Alkalinity: approximately 0.

Total hardness: approximately 10 mg/l as CaCO₃.

5.2.2 Experimental setup

A schematic process flow diagram of the experimental apparatus is shown in Figure 5.1, and a description of the experimental setup and the various components of the apparatus is given below:

Storage tanks:

A series of storage tanks, including one 2 500 ℓ and three 1 000 ℓ high density polyethylene (HDPE) tanks were used to store the raw water. In addition, a 10 000 ℓ plastic portable swimming pool was used to replenish the HDPE tanks.

Flow control and pipework:

In order to eliminate the effect of changing levels in the storage tanks, the flow from the storage tanks was directed through a 10.5 ℓ polyvinylchloride (PVC) constant head tank. The constant head in the main compartment of this unit, from which the flow to the FBC was drawn, was achieved by providing a 700 mm wide weir over which water flowed constantly (the variation in head over the weir was negligible). The water that over-flowed the weir was collected in a 1 000 ℓ fibreglass over-flow tank, from where it was pumped back to the storage tanks.

Depending on the required flow, the raw water flow rate was measured using either a Metric 10E or a Metric 10 rotameter type flow meter (operating range approximately from

100 ml/minute to 600 ml/minute, and 400 ml/minute to 2 000 ml/minute respectively), which was mounted downstream of the constant head tank.

The water was conveyed from the storage tanks to the constant head tank via 20 mm diameter HDPE piping. 12.5 mm nominal diameter surgical tubing was used to convey the water from the constant head tank to the FBC, and from the FBC to waste.

A pinch clamp installed immediately upstream of the flow meter was used to control the flow rate through the FBC.

Chemical dosing:

After flow measurement, kaolin, base for pH adjustment, primary coagulant and a flocculent aid polyelectrolyte were dosed respectively into the pipe conveying the feed water. Two adjustable speed CFP 4/8 peristaltic pumps, manufactured by the University of Cape Town Civil Engineering Department workshop, were used to dose the chemicals. The pumps were equipped with multiple tube manifolds, and could therefore dose a number of chemicals at once. Kaolin slurry, and the base, coagulant and flocculent aid solutions were prepared in 20 litre plastic reservoirs, covered to prevent contamination. A paddle mixer was built and used to mix the chemical reservoirs while preparing the solutions. One peristaltic pump was used to dose the kaolin, coagulant and flocculent aid - the concentration of the kaolin slurry, and the coagulant and flocculent aid solutions was prepared to ensure that the correct concentration was dosed into the water. A separate pump was used to dose the base - the speed of this pump was adjusted to achieve the required coagulation pH.

Rapid mix:

A length of chain (approximately 1 000 mm long, with 12 mm wide by 22 mm long links) was installed in the pipe after each chemical dose point, to induce turbulence and provide a rapid mix of the chemicals into the water.

pH measurement:

pH was monitored using a Hanna Instruments HI 8417 pH meter, in conjunction with a HI 1912B combination pH electrode. The electrode was mounted in a purpose made in-line chamber, installed downstream of the alum dose point, so that the coagulation pH could be monitored instantly and continuously. The pH meter calibration was against Hanna Instruments N.B.S. buffer solutions; nominally pH 4.01 and pH 7.01 (HI 7004 and HI 7007 respectively). The instrument was calibrated before every experiment. Once the experiment was completed, the pH electrode was cleaned in 0.1 molar HCl solution, thoroughly rinsed with distilled water and then stored in a solution of KCl.

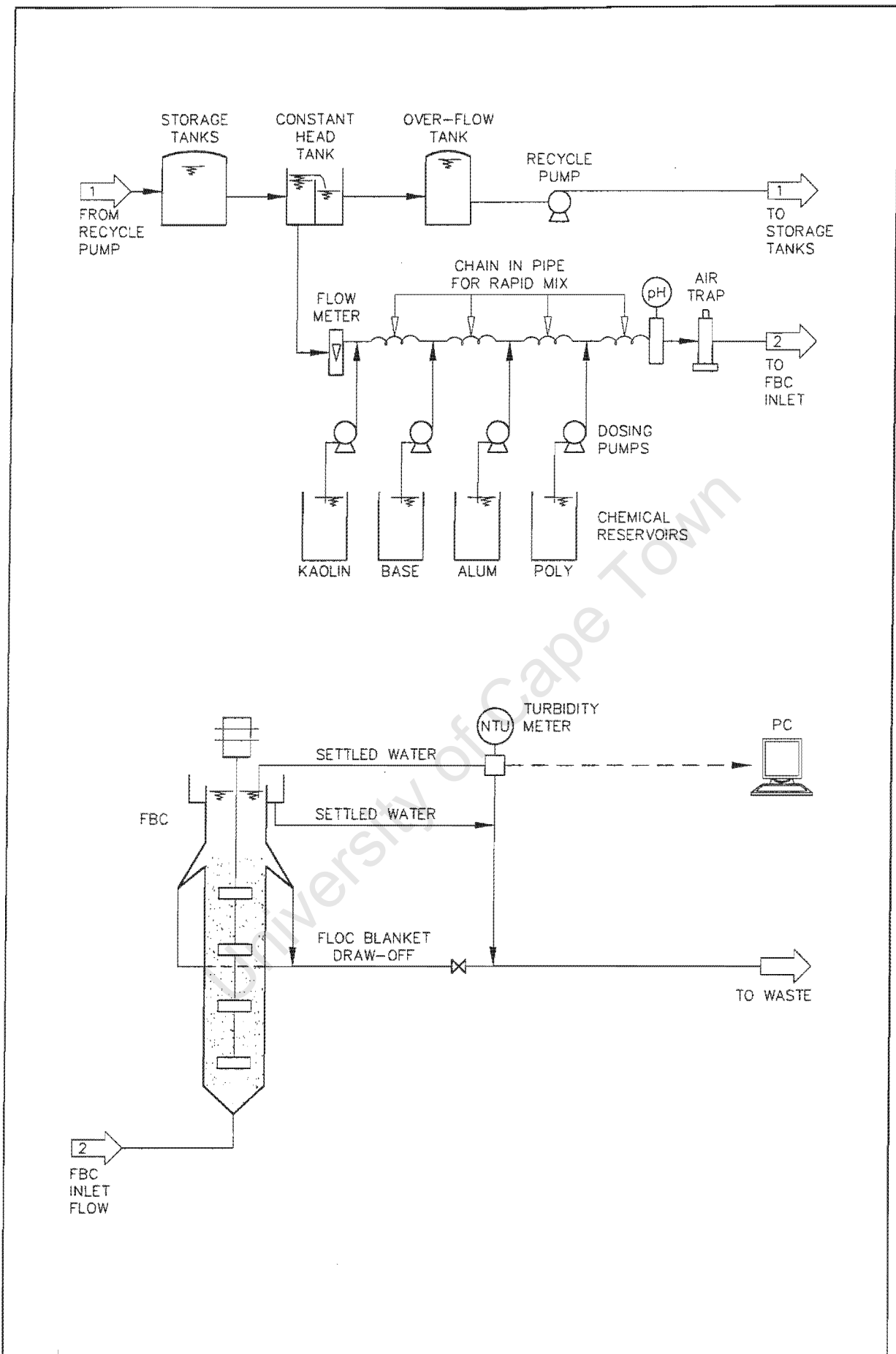


Figure 5.1 Schematic process flow diagram of the experimental apparatus

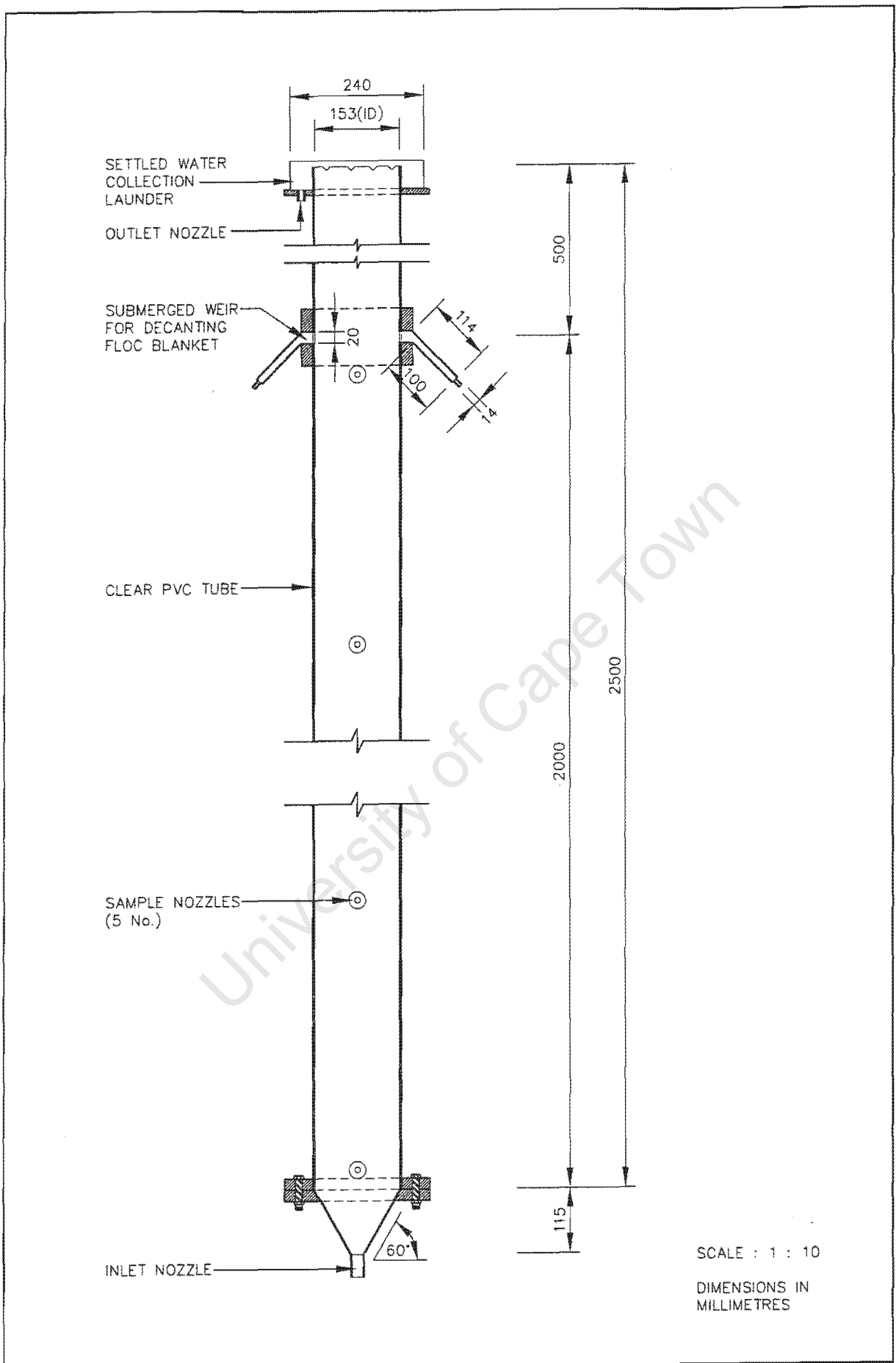


Figure 5.2 Flocculation clarifier used for the investigation

Air removal:

A purpose made air trap was installed downstream of the pH meter, to remove air caught in the pipework at the start of each experiment, and prevent the air from causing air-locks in the inlet pipe or from disturbing the floc blanket.

Floc blanket clarifier (FBC):

The water was then directed into the bottom of the FBC, a drawing of which is shown on Figure 5.2. The FBC consisted principally of :

An inlet cone: to facilitate gradual transition of the flow cross sectional area from that of the inlet pipe to that of the FBC.

The main body of the FBC: which was constructed from a 150 mm nominal diameter clear PVC tube, 2 500 mm long.

A submerged weir: which was placed 2 m above the top of the inlet cone, and was used to control the height of the floc blanket. Floc and water that overflowed the submerged weir was drained to waste. This flow was controlled with a pinch clamp installed on the drainage pipe.

Five sample ports: evenly spaced along the length of the FBC between the inlet and the submerged weir. These were used to decant samples of the floc blanket, so that the floc concentration could be measured.

A v-notch over-flow weir and launder: which were used to collect the settled water evenly around the periphery of the FBC.

A slow paddle stirrer: which turned at approximately 5.5 rpm and was used at the start-up of each experiment. The paddle stirrer had 4 individual paddle blades (50 mm deep by 100 mm wide) on a central shaft. The blades were spaced evenly between the FBC inlet and the submerged weir.

The settled water collected in the launder was discharged to waste.

Turbidity measurement:

An Orbeco-Hellige Turbidimeter was used to monitor the turbidity of the settled water from the FBC. A constant stream of settled water was siphoned from the top of the FBC and passed through a purpose made sample vial, which was placed in the turbidimeter sample vial socket. A 0 to 10 volt signal from the turbidimeter, proportional to the turbidity reading, was read into a personal computer using a PC 30B data input card. This enabled the settled water turbidity reading to be recorded every second. The data sets were then condensed and averaged to a single reading for each 60 second interval, using a computer program written in True Basic. These data sets could then be processed in a normal computer spreadsheet. The turbidimeter was calibrated using an Orbeco-Hellige formazin suspension Nephelometric turbidity standard (based on the

United States of America Environmental Protection Agency standard methods). The same turbidimeter was used to measure the raw water turbidity - in this case individual water samples were measured (instead of using the continuous reading method).

5.2.3 Experimental procedure

A series of experiment runs were undertaken, with the aim of producing a matrix of results for various kaolin dosages and FBC up-flow velocities. The various kaolin dosages used were 0 mg/l (for the control), 50 mg/l, 100 mg/l and 300 mg/l, which were of comparable magnitude to those used by Tambo and Wang (1993) in a similar investigation in Japan.

Before starting each experiment run, the FBC was emptied, the solutions of the various chemicals and the kaolin slurry were prepared, the pH meter and turbidimeter were calibrated, and if necessary the peristaltic pump tubing was replaced. The raw water flow was then started, but discharged to waste before entering the FBC. This allowed time to ensure that the dosing pumps were set correctly, that the correct raw water flow rate was being achieved and that all air was removed from the pipework.

Once the equipment was operating properly, the flow was directed into the FBC, and the FBC paddle stirrer switched on for an initial period equal to two FBC hydraulic retention times. The paddle stirrer provided a gentle shear to aid the formation of flocs and seed the floc blanket. Once the paddle stirrer was switched off, the flocs settled, condensed and formed a floc blanket (the extent of the settling and formation of the floc blanket was dependent on the loading of the FBC). As the experiment run progressed, the volume of floc grew and the surface of the floc blanket rose vertically. Once the surface of the blanket reached the submerged weir, a relatively "steady state" was attained. The experiment run was then terminated, once the various samples had been taken. The time taken for the surface of the floc blanket to reach the submerged weir, from the moment that the paddle stirrer was switched off, ranged from 0.5 to 30 hours.

The predominance of organic colour coagulant demand over that of turbidity, was dealt with in Section 3.5. In accordance with the findings of the various studies discussed in this section, it was decided to determine the required coagulant demand according to the organic colour concentration, independently of the kaolin dosage used. The City of Cape Town Scientific Services Division has undertaken significant test work to determine the most suitable pH and alum dosage required for the optimisation of the Constantia Nek Water Treatment Works. As this water treatment works utilises FBCs, and uses the same raw water as that used for this investigation, it was decided to use the pH and alum dosage regime recommended by the City of Cape Town. Their recommendation was 0.97 mg Al/l per UV absorbance unit (as measured through a 10 mm light path, at a wavelength of 300 nm), at a pH of 5.8. This dosage regime would likely plot in a pH - alum dosage solubility diagram in the band where effective coagulation of organic colour (in waters with a high concentration of organic colour) takes place by a combination of precipitation and adsorption, as described in Section 3.4.3. The City of Cape Town recommended the coagulation pH of 5.8 to minimise the amount of aluminium allowed in solution in the treated water - the implication of aluminium as a contributing factor in Alzheimer's disease was

discussed in Section 3.2. Due to the relatively consistent water quality of the different batches of raw water used in the experiments, the range of the required alum dosage for the different batches of raw water was fairly narrow (7.5 to 8.6 mg Al/l). The variation in alum dosage was therefore considered to have a relatively insignificant effect on the performance of the FBC. The details of the chemicals dosed were as follows:

Base for pH adjustment: reagent grade sodium hydrogen carbonate [NaHCO₃] produced by Saarchem (Pty) Ltd. The base dosage was adjusted (by adjusting the speed of the dosing pump) to give a coagulation pH of 5.8 (measured after the chemical dosing and rapid mix steps).

Primary coagulant: reagent grade aluminium sulphate (alum) [Al₂(SO₄)₃·15H₂O] produced by Saarchem (Pty) Ltd.

Flocculent aid: Magnafloc LT20, a potable water grade, high molecular weight nonionic polyacrylamide. A dose of 0.1 mg/l was used in accordance with common practise at full scale water treatment works, to increase the size, strength and weight of the flocs.

5.2.4 Parameters measured during each experiment run

Once the FBC paddle stirrer had been switched off, samples of the settled water were taken at regular intervals. The following parameters were measured in the raw water and in the settled water samples:

Apparent colour: was measured in Hazen Units (where 1 HU = 1 CU = 1 mg Pt/l) using a Lovibond 1000 Comparator. The principle of operation for this unit is described in Section 2.2

UV absorbance: was measured at a wavelength of 260 nm as recommended by Rebhun and Lurie (1993), using a Unicam 8625 spectrometer. The light path length in the sample vials was 10 mm. The UV absorbance of the raw water was also measured at a wavelength of 300 nm, so that the UV absorbance - alum dosage relationship recommended by the City of Cape Town could be used (as described in Section 5.2.3).

Turbidity: the logging of the settled water turbidity, as described in Section 5.2.2, was started when the FBC paddle stirrer was switched off. The raw water turbidity was measured when each batch of water was delivered to the laboratory.

Once the surface of the floc blanket reached the submerged weir, a 100 ml sample was taken from each of the five sample ports, so that the concentration profile of the blanket could be determined. Each sample was placed in a crucible, weighed (using a Mettler AE 200 mass balance) and oven dried for 24 hours at 105 degrees Celsius. The crucibles were then weighed again, and the solids concentration for each of the samples determined.

The floc blanket growth was also recorded, starting from the moment the FBC paddle stirrers were switched off.

5.3 Results and Discussion

5.3.1 Turbidity and apparent colour

Due to the fact that sand filtration would normally follow floc blanket clarification at a water treatment plant, the quality of the settled water from the FBC, with respect to the solids that would need to be removed by filtration, is of primary importance in evaluating the performance of the FBC. Settled water turbidity is a common means of monitoring the performance of FBCs, as it relates directly to the quantity of suspended solids that would need to be removed by filtration. A further load is placed on the filtration step by micro-flocs of coagulated colour, which do not appear as individual particles and are therefore not adequately quantified by turbidity measurements. These micro-flocs do however strongly influence apparent colour (Edwards and Amirtharajah, 1985) - this parameter is consequently also useful in quantifying the load that would be placed on subsequent filtration. It was therefore decided that the turbidity and apparent colour of the settled water would provide a suitable means of quantifying the performance of the FBC, and the load that would be placed on a subsequent sand filtration step. The turbidity and apparent colour results of the various experiment runs are can be summarised in two simple graphs, which are each discussed in turn below:

Turbidity versus up-flow velocity graph:

Figure 5.3 shows a graph of settled water turbidity (at steady state as defined in Section 5.2.3) plotted against the up-flow velocity in the FBC, where a separate plot is shown for each kaolin dosage used. For all kaolin dosages the plots show a steady increase in settled water turbidity as up-flow velocity is increased towards 3.5 m/h. The turbidity of the 300 mg/ℓ kaolin dosage plot is slightly higher than those of the other kaolin dosage plots over this range - this may be the result of the coagulant demand of the kaolin at this elevated dosage becoming significant in comparison to that of the organic colour. Below an up-flow velocity of 2.5 m/h, the difference in turbidity for the various kaolin dosages used is erratic and no clear trend is observed - the results in this range of up-flow velocities were more likely influenced by temperature differences and perhaps other minor experimental inaccuracies (these may also have been responsible for the out-lying result at 1.0 m/h for a kaolin dosage of 100 mg/ℓ). At 3.5 m/h however, the influence of the kaolin begins to become evident. At this up-flow velocity the turbidity is reduced proportionally (non-linearly) to the kaolin dosage (with the exception of the 300 mg/ℓ kaolin dosage). At 5 m/h, the effect of the kaolin is far more dramatic and the 300 mg/ℓ kaolin dosage produced a substantially lower turbidity (20 NTU) than those of the lower kaolin dosages (40 NTU and 55 NTU for 100 mg/ℓ and 50 mg/ℓ kaolin dosages respectively). If no kaolin was dosed, it was not possible to even generate a floc blanket at all at 5 m/h. The turbidity produced in the case of the 300 mg/ℓ kaolin dose is of a similar order to the range of turbidities produced at up-flow velocities of 3.5 m/h and lower (which ranged up to approximately 15 NTU). However, the turbidities of the lower kaolin dosages at 5.0 m/h are several times greater than those achieved at up-flow velocities of 3.5 m/h and lower.

Apparent colour versus up-flow velocity graph:

Figure 5.4 shows a graph of settled water apparent colour (at steady state as defined in Section 5.2.3) plotted against the up-flow velocity in the FBC, where a separate plot is shown for each kaolin dosage used. As with the turbidity results, the apparent colour increases steadily with increasing up-flow velocity. The results for the different kaolin dosages become evident at a lower up-flow velocity than was observed for the turbidity results. Apart from a few out-lying results (which may be influenced by temperature differences and perhaps other minor experimental inaccuracies), the apparent colour is reduced by increasing kaolin dosage. This difference is noticeable from an up-flow velocity of 1.8 m/h, but becomes far more evident at higher up-flow velocities. At 3.5 m/h, the apparent colour for a zero kaolin dose rises to 130 HU, almost double that of a 50 mg/l kaolin dose (which yielded an apparent colour of 70 HU). At 5.0 m/h, the apparent colour for a kaolin dosage of 300 mg/l is 70 HU. This is well within the range of apparent colour results achieved at lower up-flow velocities (which ranged up to 75 HU, excluding the result for zero kaolin dosage at 3.5 m/h). However, the apparent colour results for kaolin dosages of 100 mg/l and 50 mg/l at 5.0 m/h, are 175 HU and 300 HU respectively. These values are substantially higher than the range of apparent colour results achieved at lower up-flow velocities.

In both the turbidity versus up-flow velocity and apparent colour versus up-flow velocity graphs, the beneficial effect of dosing kaolin is more evident at higher up-flow velocities. This can be further demonstrated by plotting the results of settled water turbidity and apparent colour (at steady state) against kaolin dosage, with different plots for the various up-flow velocities. These two graphs are shown in Figures 5.5 and 5.6 respectively and are discussed below:

Turbidity versus kaolin dosage graph:

In this graph (Figure 5.5), at up-flow velocities of 3.5 m/h and lower, there is no obvious trend to the turbidity results with increasing kaolin dosage (the turbidities at a kaolin dosage of 300 mg/l are slightly higher than at lower dosages, but this may be the result of the coagulant demand of the kaolin at this elevated dosage becoming significant in comparison to that of the organic colour, as proposed in the discussion of the turbidity versus up-flow velocity graph). At 5.0 m/h however, a clear trend is evident, and the turbidity is reduced markedly with increasing kaolin dosage. At a kaolin dose of 50 mg/l, the 5.0 m/h turbidity of 55 NTU is approximately four times greater than the next highest turbidity of 14 NTU. At a kaolin dose of 300 mg/l however, the 5 m/h turbidity is brought down to 20 NTU, which is similar in magnitude to the turbidity results for the lower up-flow velocities.

Apparent colour versus kaolin dosage graph:

In this graph (Figure 5.6), a trend to decreasing settled water apparent colour with increasing kaolin dosage is evident for up-flow velocities of 1.8 m/h and above. The trend is however far

more obvious at the higher up-flow velocities, and at 5 m/h is quite dramatic. At a kaolin dose of 50 mg/ℓ, the 5 m/h apparent colour of 300 HU is over four times greater than the next highest apparent colour of 70 HU. At a kaolin dose of 300 mg/ℓ however, the 5 m/h apparent colour is reduced to 70 HU.

It is noted that most of the settled water turbidities for the various experiment runs, particularly at the higher up-flow velocities, are greater than would be acceptable for settled water in a conventional water treatment plant. Unfortunately the duration of the experiment runs in this investigation had to be limited, due to the limited amount of raw water available. It is likely that at full scale operation, there would be time for the floc blanket to stabilise and mature more thoroughly. In addition, full-scale FBCs generally allow for significantly deeper floc blankets than was possible with this investigation. These factors would likely provide for more effective growth and entrapment of the small flocs, and the inlet turbulence would be dampened to a greater extent (Miller *et al*, 1966). It is therefore proposed that the turbidity and apparent colour results for the settled water should not be seen as absolute values that would correspond to full-scale FBCs. Instead, the results simply indicate the relative benefit that may be derived from dosing kaolin, in the operation of FBCs.

The turbidity and apparent colour results for the various experiment runs indicate that the addition of kaolin does indeed improve the performance of the FBC, particularly at the higher up-flow velocities. The benefits of the kaolin addition on settled water apparent colour are noticeable from 2.5 m/h upwards, and are noticeable on settled water turbidity from 3.5 m/h upwards. At 5.0 m/h it was not possible to even establish a floc blanket at all if kaolin was not dosed, however the FBC performed relatively well with a kaolin dose of 300 mg/ℓ. It therefore appears that the up-flow velocity, and hence the capacity, of the FBC can be increased by dosing kaolin.

5.3.2 UV absorbance

In Figure 5.7, the percentage UV absorbance remaining in the settled water (at steady state as defined in Section 5.2.3) for the various experiment runs is plotted against up-flow velocity. Generally, the percentage UV absorbance remaining is fairly constant, and is not effected either by up-flow velocity or kaolin dosage. This confirms the findings of other investigations, as discussed in Section 3.5; that the coagulant demand in organically coloured waters is determined primarily by the organic colour content and not by turbidity. The percentage UV absorbance remaining for the 300 mg/ℓ kaolin dosage plot, is however elevated slightly higher than the plots for the lower kaolin dosages. As mentioned in Section 5.3.1, it is possible that at this elevated kaolin dose, the coagulant demand of the kaolin begins to become significant. A separate batch of water was used for the 300 mg/ℓ kaolin dose experiment runs - this may also have had some influence on the result. Considering that the raw water used for this investigation is of similar quality to much of the organically coloured surface water in the Southern Cape and Western Cape of South Africa, similar doses of kaolin as a process aid are likely to be possible in full-scale FBCs. Where organic colour is present in greater concentration, the kaolin dose could possibly be increased above 300 mg/ℓ without altering the coagulant demand.

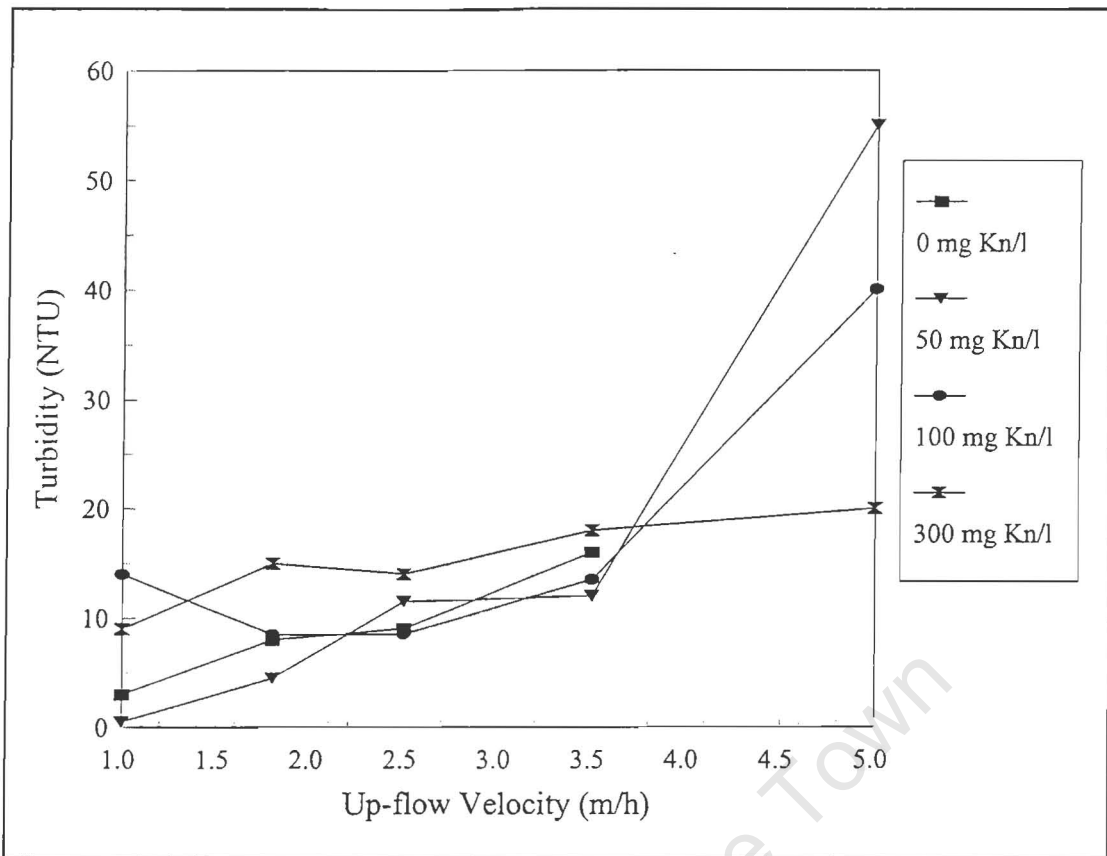


Figure 5.3 FBC settled water - turbidity versus up-flow velocity

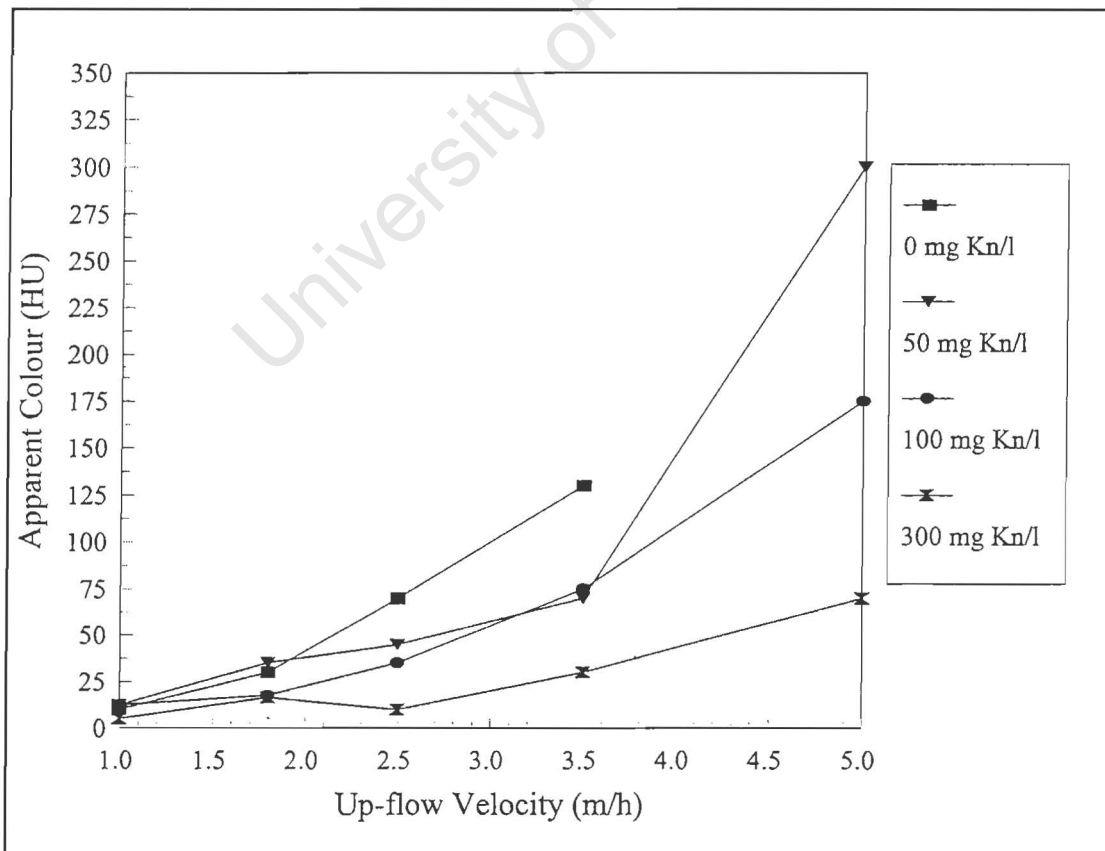


Figure 5.4 FBC settled water - apparent colour versus up-flow velocity

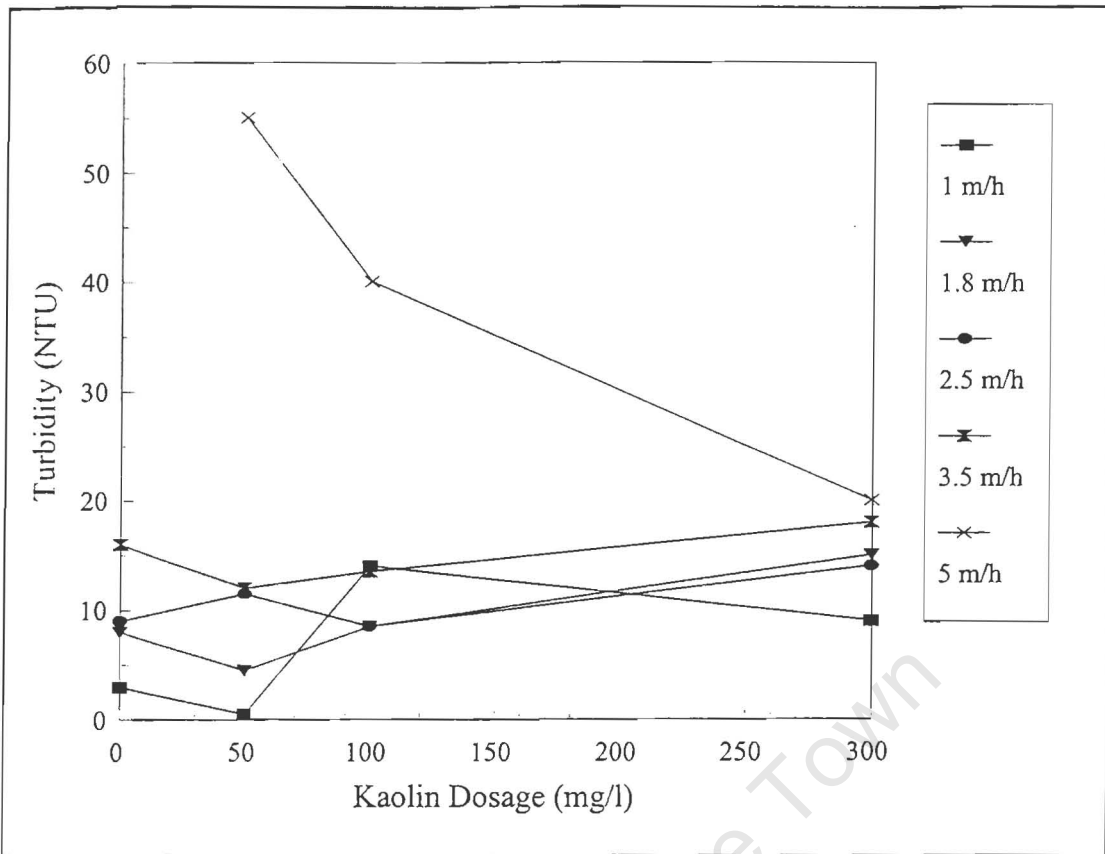


Figure 5.5 FBC settled water - turbidity versus kaolin dosage

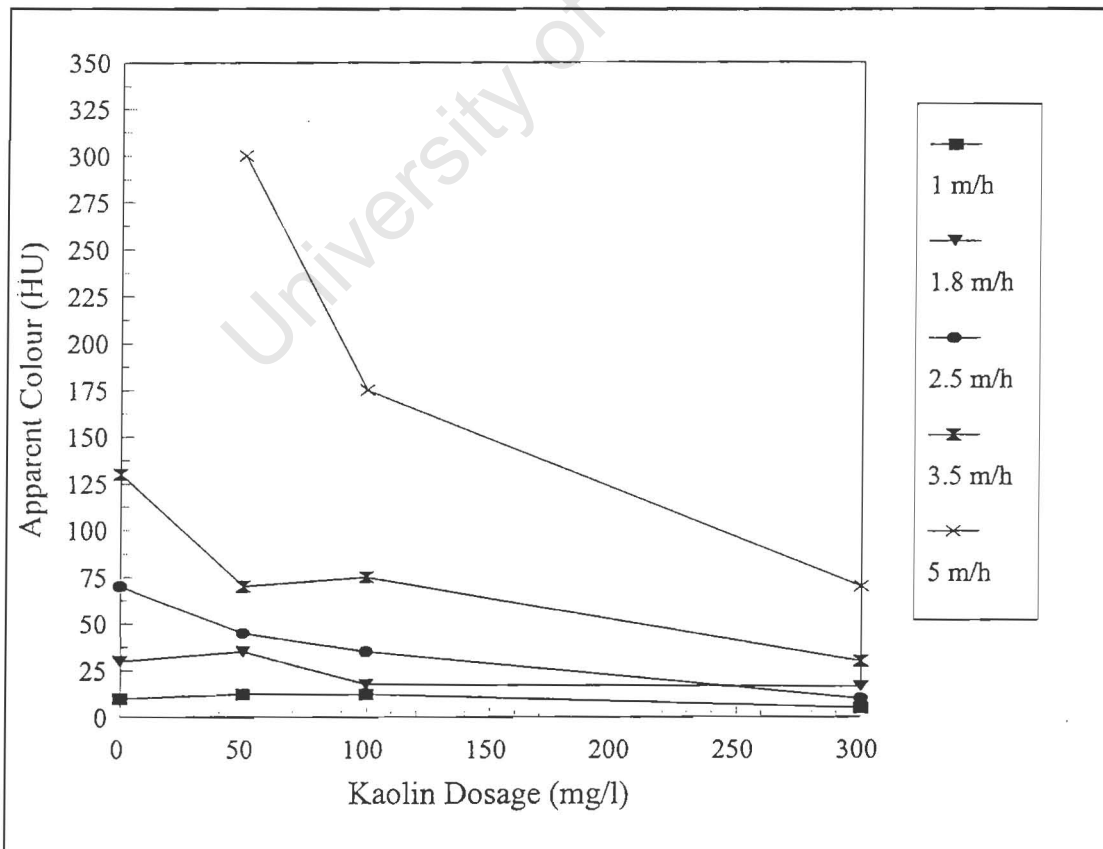


Figure 5.6 FBC settled water - apparent colour versus kaolin dosage

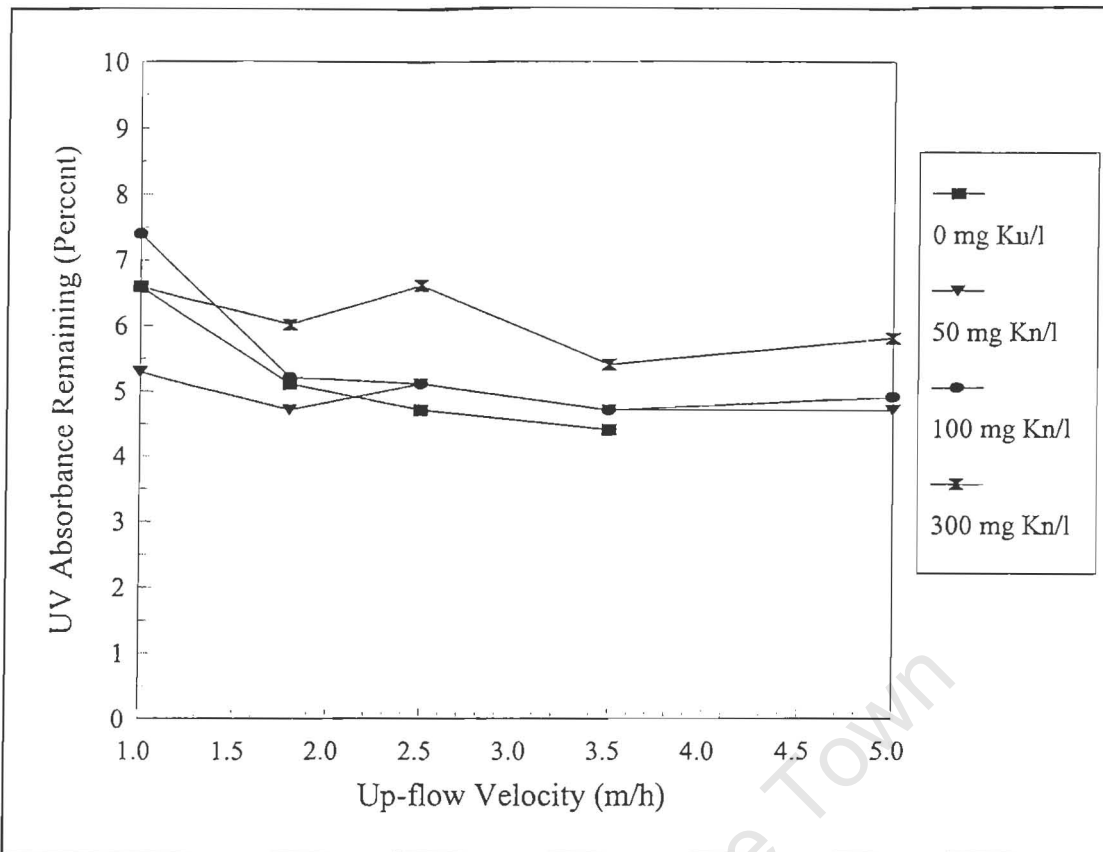


Figure 5.7 FBC settled water - percentage UV absorbance remaining

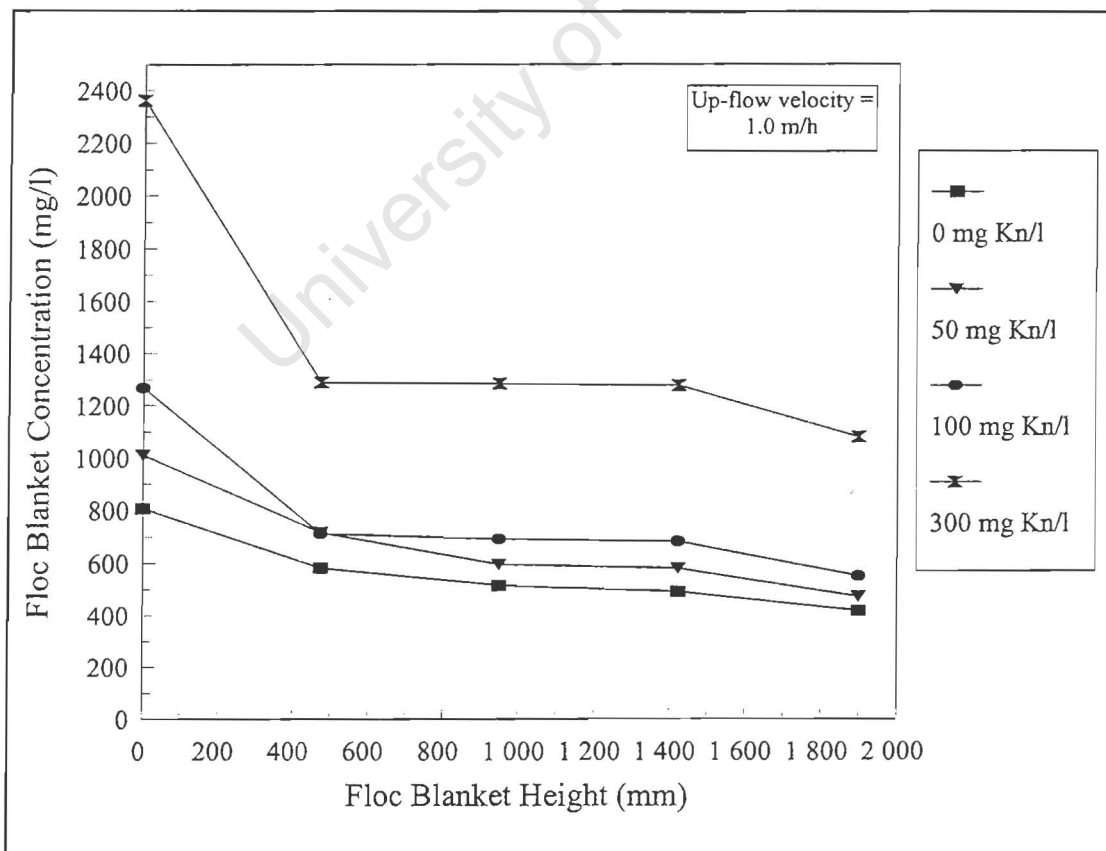


Figure 5.8 Floc blanket concentration - up-flow velocity = 1.0 m/h

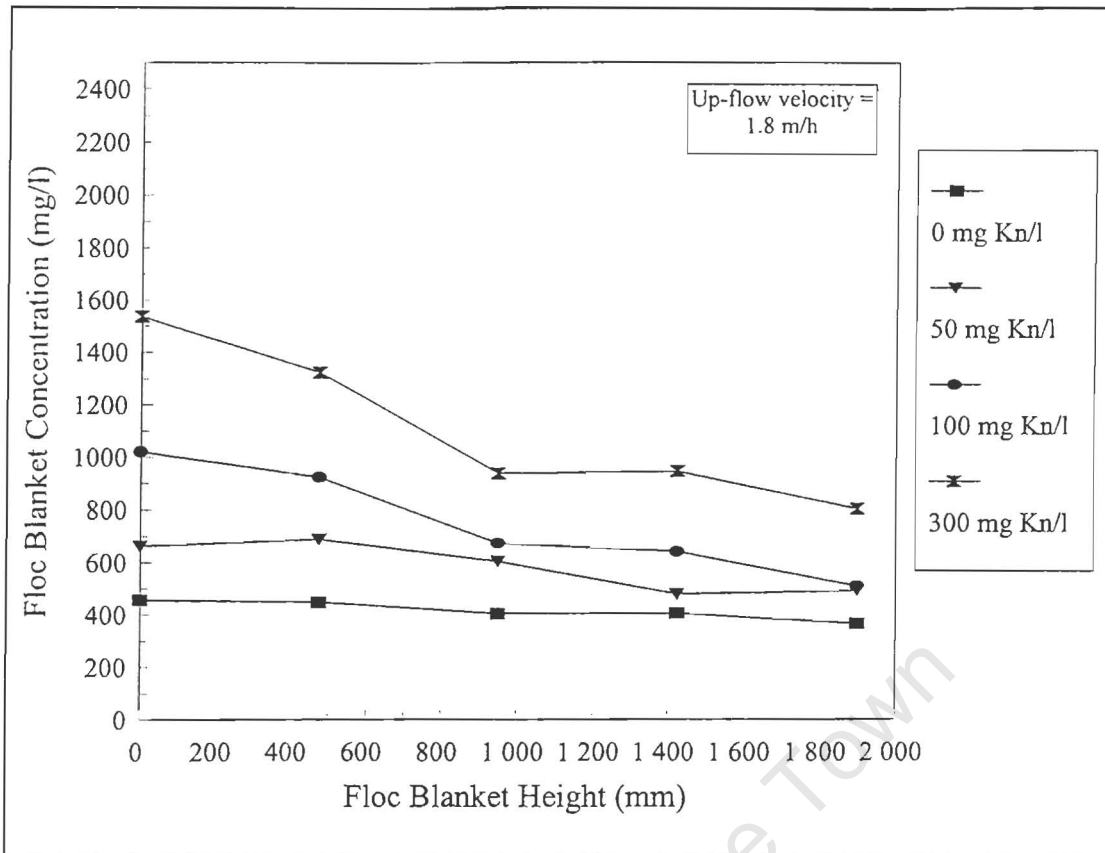


Figure 5.9 Floc blanket concentration - up-flow velocity = 1.8 m/h

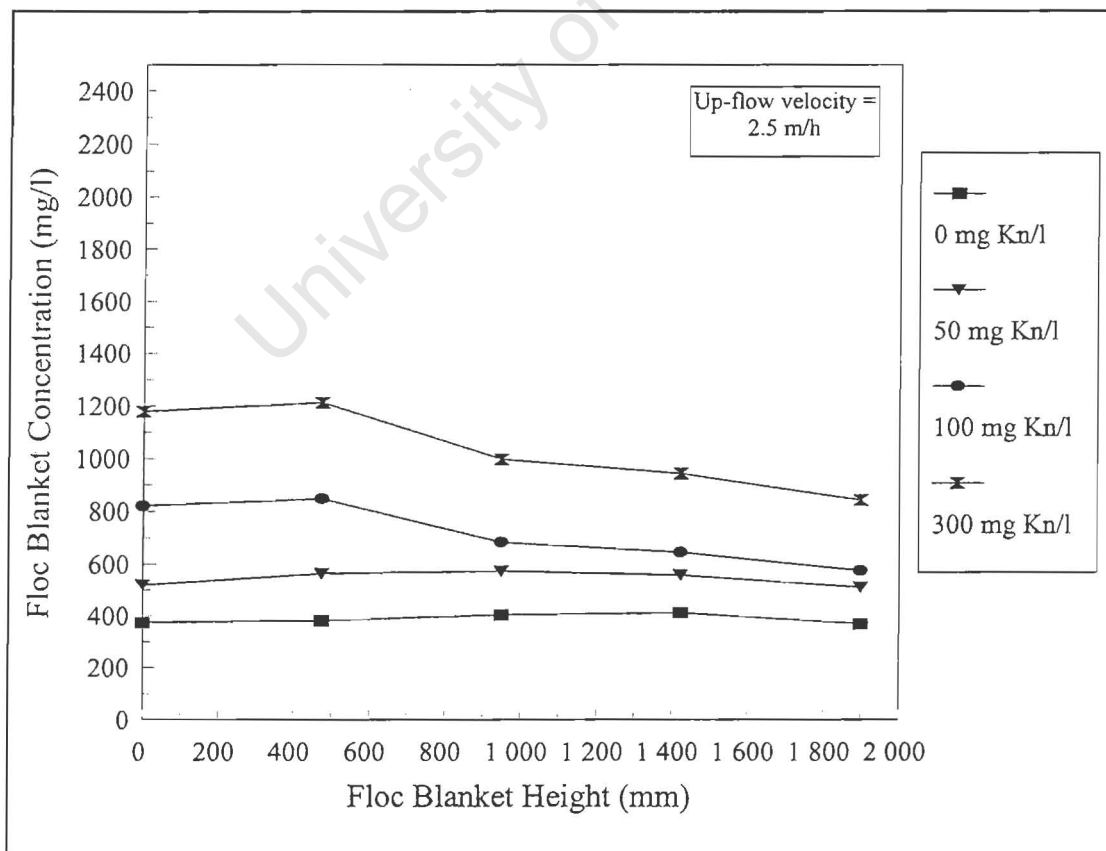


Figure 5.10 Floc blanket concentration - up-flow velocity = 2.5 m/h

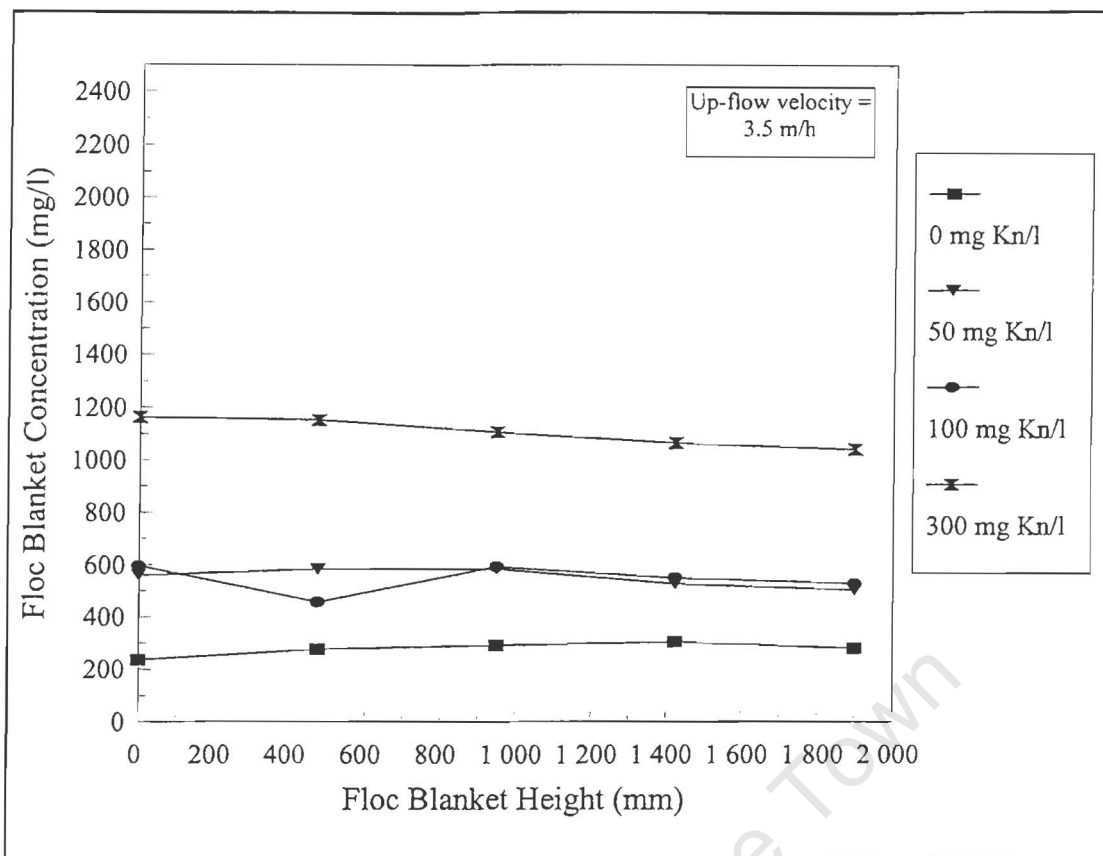


Figure 5.11 Floc blanket concentration - up-flow velocity = 3.5 m/h

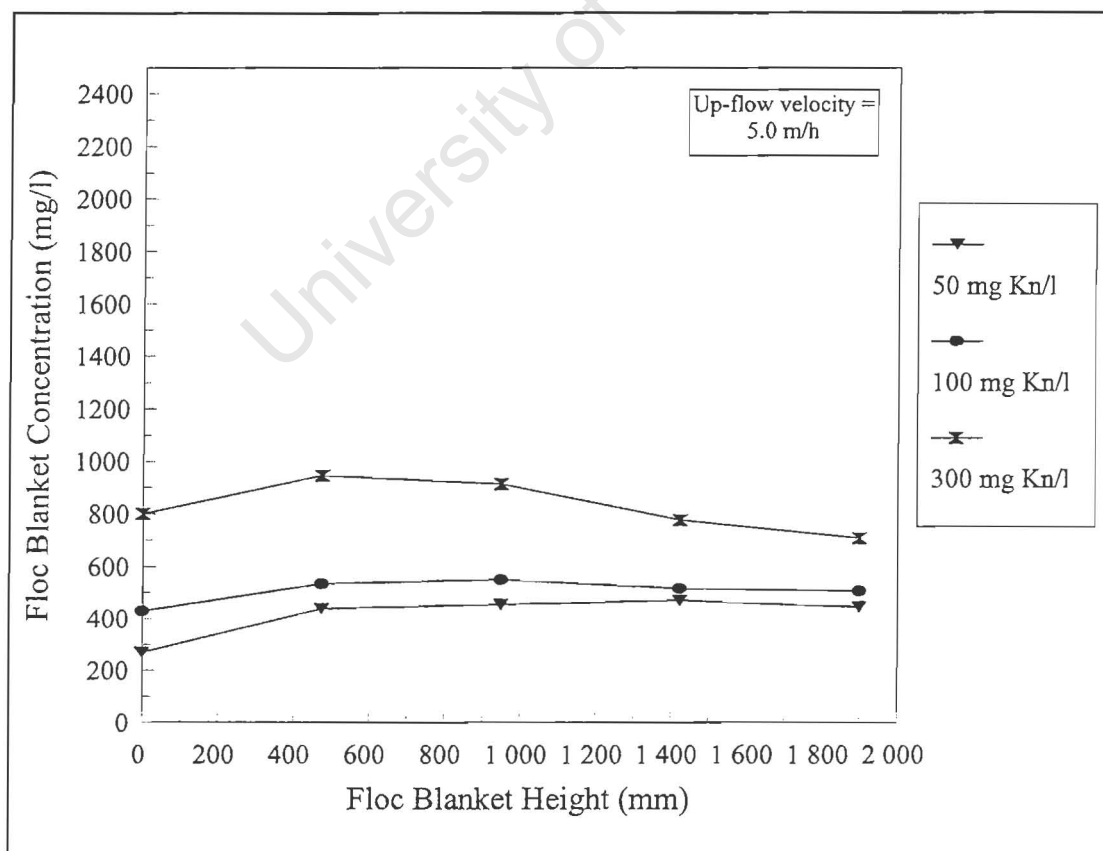


Figure 5.12 Floc blanket concentration - up-flow velocity = 5.0 m/h

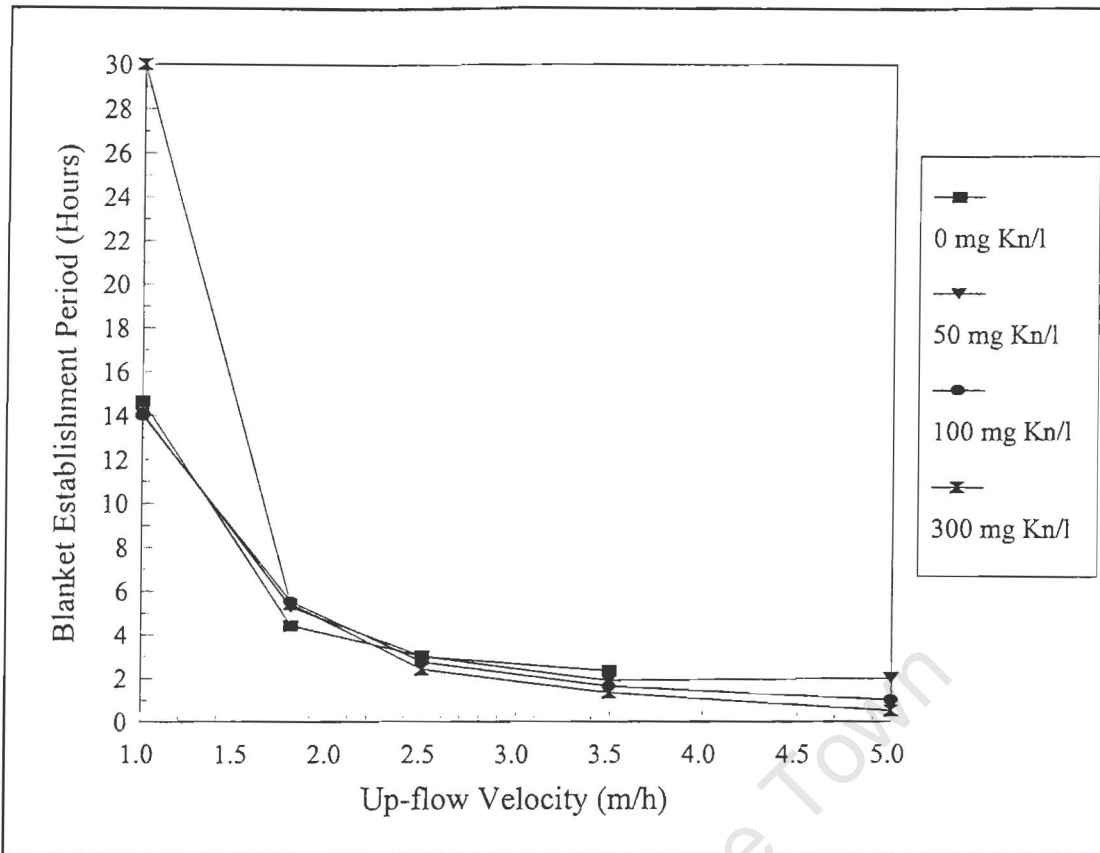


Figure 5.13 Floc blanket establishment period (time taken for floc blanket to reach steady state as described in Section 5.2.3)

The fact that the percentage UV absorbance remaining is not affected by up-flow velocity, indicates that if the coagulant dose is correct, coagulation of the organic colour and formation of flocs that can be removed by filtration through a 0.45 μm membrane filter will take place, irrespective of the up-flow velocity. At higher up-flow velocities however, the flocculation in the FBC becomes less effective and the micro-flocs will not grow sufficiently large enough for them to be settled from the water. These micro-flocs may even pass through subsequent sand filtration.

At all kaolin dosages used, there was a slight decrease in percentage UV absorbance remaining as up-flow velocity increased from 1.0 m/h to 1.8 m/h. It is not clear what caused this. It is possible that at the lower flow rate, inaccuracies in coagulant dose were more noticeable, or the rapid mix intensity was insufficient or other inaccuracies were more noticeable.

5.3.3 Floc blanket concentration

Figures 5.8 to 5.12 show plots of the floc blanket concentration profile against floc blanket height for the various experiment runs. A separate graph is shown for each of the up-flow velocities used in the experiment runs (i.e. 1.0 m/h, 1.8 m/h, 2.5 m/h, 3.5 m/h and 5.0 m/h). In each of the graphs, a separate plot is shown for each kaolin dosage used.

In the 1 m/h graph shown in Figure 5.8, the plots show a decreasing concentration towards the top of the

floc blanket. At this low loading rate it appears that Type 4 compression settling as described in Section 4.3 is prevalent. The low up-flow velocity allows the concentration to increase and thickening of the floc appeared to occur in the lower portion of the FBC.

In the 1.8 m/h graph shown in Figure 5.9, the same trend is observed, however the concentrations are generally lower than those observed at 1.0 m/h. In addition the average slope for the zero kaolin dose plot is flattened. It appears that in the zero kaolin dose case, thickening is no longer significant and the decreased concentration causes the floc blanket to transform from Type 4 compression settling, to a fully fluidised bed with Type 3 hindered settling. As described in Section 4.4, the solids flux in the floc blanket approaches a maximum within the Type 3 settling zone, with the optimum operating conditions being achieved at maximum flux.

In the 2.5 m/h graph shown in Figure 5.10, the trend of decreasing concentration towards the top of the floc blanket is again observed for kaolin dosages of 100 mg/ℓ and 300 mg/ℓ. The concentrations for all the plots have reduced in comparison to those observed at 1.8 m/h. It appears that the floc blankets for both the zero and the 50 mg/ℓ kaolin dosages have become fully fluidised and Type 3 hindered settling is dominant.

At 3.5 m/h, as shown on Figure 5.11, only the 300 mg/ℓ kaolin dose plot shows significant evidence of thickening. The 50 mg/ℓ and 100mg/ℓ kaolin dose plots are both fairly flat, and the floc blankets in these cases appear fully fluidised and dominated by Type 3 hindered settling. In the zero kaolin dose case, the concentration profile now increases slightly with increasing blanket height. It appears that the concentration of the floc blanket has decreased to the point where Type 2 unhindered settling of discrete particles occurs, and the solids flux has decreased from the maximum achieved in the Type 3 settling zone. The inter-particle distances in the floc blanket have increased, and entrapment and growth of smaller particles is no longer efficient. As described in Section 4.4, this indicates that the up-flow velocity is too high for the zero kaolin dose case, and the FBC is over-loaded - this is indeed confirmed by the turbidity and apparent colour results discussed in Section 5.3.1.

At 5.0 m/h, as shown in Figure 5.12, the 300 mg/ℓ kaolin dose plot is again the only one that shows significant evidence of thickening. In all cases there was an increase in concentration from a blanket depth of 0 to a depth of 500 mm - this may be due to the increased turbulence at the entrance to the FBC at the increased flow. The 100 mg/ℓ kaolin dose plot is still fairly flat (apart from the bottom of the blanket), and it appears that Type 3 hindered settling is still significant. In the case of the 50 mg/ℓ kaolin dose plot, it appears that the floc blanket is dominated by Type 2 unhindered settling, and the FBC is over-loaded - this bears good relation to the turbidity and apparent colour results discussed in Section 5.3.1.

These floc blanket concentration profile results indicate that the addition of kaolin allows the floc blanket to remain stable, and Type 3 hindered settling to predominate, at higher up-flow velocities than would otherwise be possible. Within the range tested, the attainable up-flow velocity was found to increase with increasing kaolin dose. Dosing kaolin appears to increase the floc blanket concentration and raise the up-

flow velocity at which the floc blanket undergoes a transition from Type 3 hindered settling - where optimum operating conditions are approached, to Type 2 unhindered settling - where flocculation is inefficient.

5.3.4 Floc blanket growth rate

In Figure 5.13 the floc blanket establishment period (time taken for the floc blanket to grow and reach steady state as described in Section 5.2.3) for the various experiment runs is plotted against up-flow velocity, with a different plot for each kaolin dose used.

At an up-flow velocity of 5.0 m/h the growth rate of the floc blanket is increased with increasing kaolin dose. The 2 hour floc blanket establishment period at a kaolin dose of 50 mg/ℓ is reduced to 1 hour at 100 mg kaolin/ℓ and ½ hour at 300 mg kaolin/ℓ - a 300 mg/ℓ kaolin dose reduced the 50 mg/ℓ kaolin dose period by 75 percent.

At 3.5 m/h the increase in floc blanket growth rate with increasing kaolin dose is again observed, although the trend is perhaps not as pronounced. In this case the 2.3 hour floc blanket establishment period at zero kaolin dose is reduced to 1.9 hours at 50 mg kaolin/ℓ, to 1.6 hours at 100 mg kaolin/ℓ and finally to 1.3 hours at 300 mg kaolin/ℓ - a 300 mg/ℓ kaolin dose reduced the zero kaolin dose period almost by half.

At 2.5 m/h the trend is still observed, although less obvious than at 5.0 m/h and 3.5 m/h. In this case both the zero and the 50 mg/ℓ kaolin dosages had a 3 hour floc blanket establishment period. This period was reduced to 2.8 hours at 100 mg kaolin/ℓ and to 2.4 hours at 300 mg kaolin/ℓ - a 300 mg/ℓ kaolin dose reduced the zero kaolin dose period by 20 percent.

At the lower up-flow velocities of 1.8 m/h and 1.0 m/h, the effect of dosing kaolin on the floc blanket establishment period is erratic and no clear trend is observed. At 1.0 m/h, a kaolin dose of 300 mg/ℓ actually causes a marked decrease in the floc blanket growth rate - the floc blanket establishment period of 30 hours is double that of the approximately 14 hours observed for the lower kaolin dosages. It appears that at the lower up-flow velocities (1.8 m/h and below), the addition of kaolin weights the floc so that Type 4 compression settling dominates, and the thickening of the floc at the bottom of the FBC causes a reduced floc blanket growth rate.

From the above results it is clear that at higher up-flow velocities (2.5 m/h and above), the addition of kaolin causes an increase in the growth rate of the floc blanket, which becomes more noticeable as up-flow velocity is increased. While it is difficult to use these results to predict the effect in full scale floc blanket clarification, it appears that dosing kaolin may be beneficial (particularly at higher up-flow velocities) in establishing floc blankets from start-up conditions.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

An experimental investigation was conducted into the effect of the addition of clay (kaolin) as a process aid, in floc blanket clarification of South African organically coloured natural surface water. The specific aim of the experiments, was to investigate the effect of various kaolin dosages on the settled water quality at various hydraulic loading rates (up-flow velocities) in the FBC, and to determine whether up-flow velocity and floc blanket stability can be increased by dosing kaolin.

The results indeed indicate that the up-flow velocity (and hence the capacity) of FBCs can be increased by dosing kaolin. In this investigation the benefits of the kaolin addition, on the settled water apparent colour were noticeable from up-flow velocities of 2.5 m/h upwards, and on settled water turbidity were noticeable from 3.5 m/h upwards. At 5.0 m/h it was not possible to even establish a floc blanket at all if kaolin was not dosed, however the FBC performed relatively well with a kaolin dose of 300 mg/ℓ. In general, the beneficial effect of increasing kaolin dosage became more evident as the up-flow velocity increased.

The floc blanket concentration profile results indicate that the addition of kaolin allows the floc blanket to remain stable, and Type 3 hindered settling to predominate, at higher up-flow velocities than would otherwise be possible. Within the range tested, the attainable up-flow velocity (at which the floc blanket remained stable) was found to increase with increasing kaolin dosage. Dosing kaolin appears to increase the floc blanket concentration and raise the up-flow velocity at which the floc blanket undergoes a transition from Type 3 hindered settling (where optimum operating conditions are approached), to Type 2 unhindered settling (where flocculation is inefficient). The floc blanket concentration profile results correlate with the settled water turbidity and apparent colour results - the transition from Type 3 hindered settling to Type 2 unhindered settling corresponds to significant increases in turbidity and apparent colour, which are obviously expected to be associated with the decreased stability of the floc blanket.

For the specific raw waters used in this investigation, kaolin doses of 50 mg/ℓ to 300 mg/ℓ could be applied with little effect on the required coagulant dose. This confirms similar findings by other investigators, as discussed in Section 3.5, that the coagulant demand in organically coloured waters is determined by the organic colour content and not by turbidity. As the raw water used for this investigation is of similar quality to many of the organically coloured surface waters found in the Southern Cape and Western Cape regions of South Africa, similar doses of kaolin as a process aid are likely to be possible in full-scale FBCs, without the need to increase coagulant dose. Where organic colour is present in greater concentrations, the kaolin dose could possibly be increased above 300 mg/ℓ without altering the coagulant demand.

The floc blanket establishment period results indicate that at higher up-flow velocities (2.5 m/h and above), the addition of kaolin causes an increase in the growth rate of the floc blanket, which becomes more noticeable as up-flow velocity is increased. While it is difficult to use these results to predict the effect in full scale floc blanket clarification, it appears that dosing kaolin would be beneficial in establishing floc blankets from start-up conditions. At lower up-flow velocities however (1.8 m/h and below), it appears that the addition of kaolin weights the floc so that Type 4 compression settling dominates, and the thickening of the floc at the bottom of the FBC causes a reduced floc blanket growth rate.

It is difficult to use the results of this investigation to predict the exact results that would be achieved in full-scale floc blanket clarification. However, the results of the investigation do indicate that the addition of kaolin can indeed be beneficial in floc blanket clarification of South African organically coloured surface waters. The benefits that may be derived from the addition of kaolin include an increase in the allowable FBC loading rate (up-flow velocity), and, at higher up-flow velocities; increased floc blanket stability, improved flocculation dynamics due to the increased concentration of the floc blanket, and quicker generation of floc blankets at FBC start-up. These benefits could lead to possible savings in the capital expenditure associated with both the construction of new FBC plants, and the postponement of extensions to existing FBC plants to meet growth in water demands.

It is believed that based on the results of this laboratory investigation, it would be worthwhile to investigate the effects of the addition of kaolin in full-scale floc blanket clarification. Such an investigation could possibly produce more absolute results, that could be used to reliably quantitatively predict the effects of the addition of kaolin on the performance of FBCs.

CHAPTER 7

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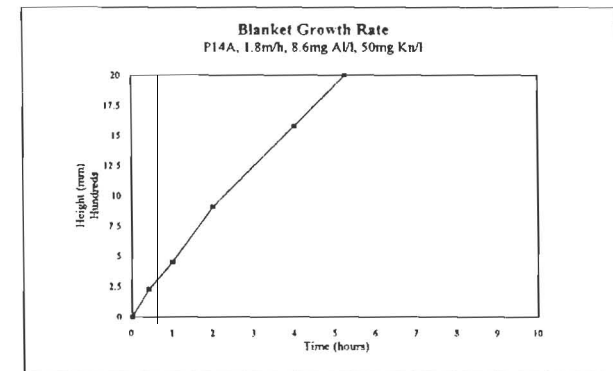
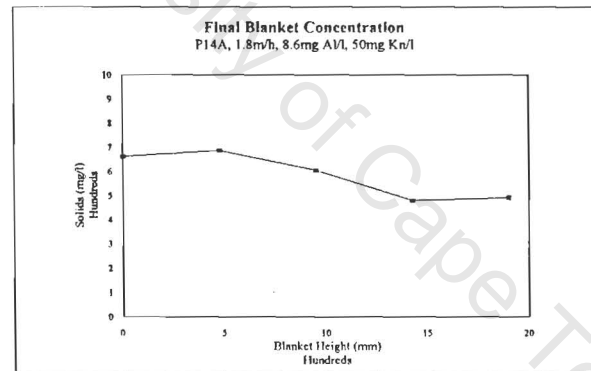
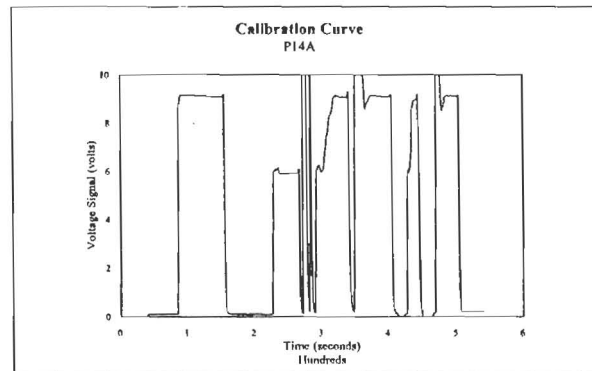
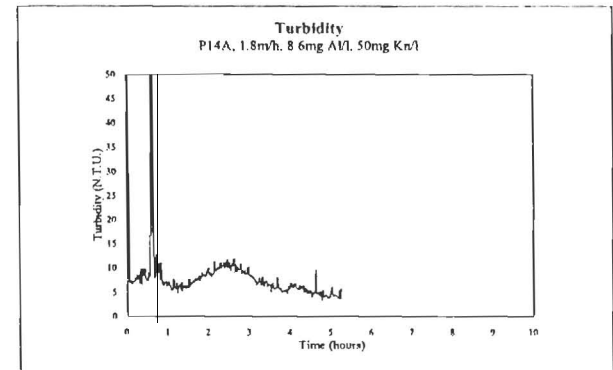
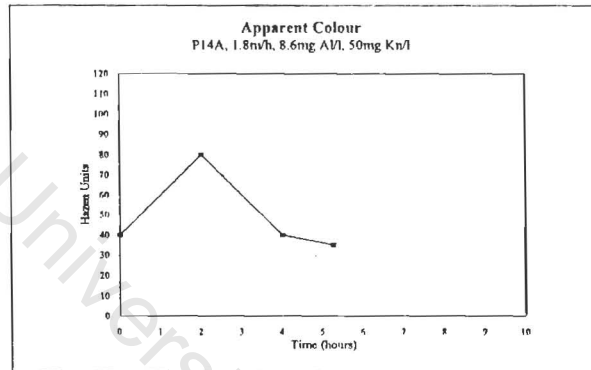
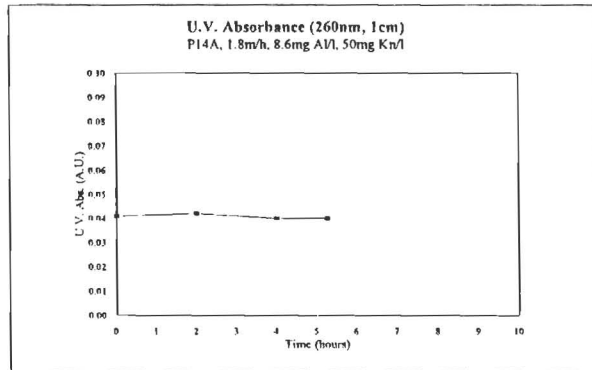
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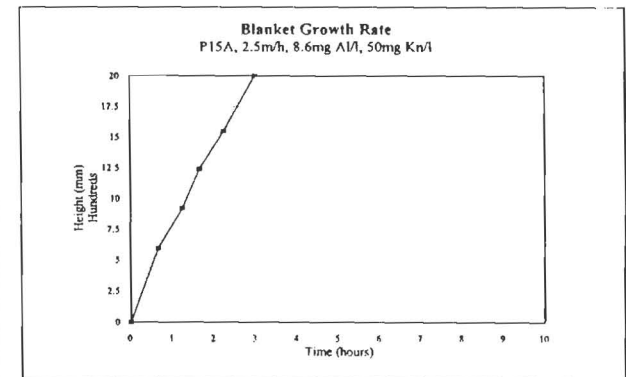
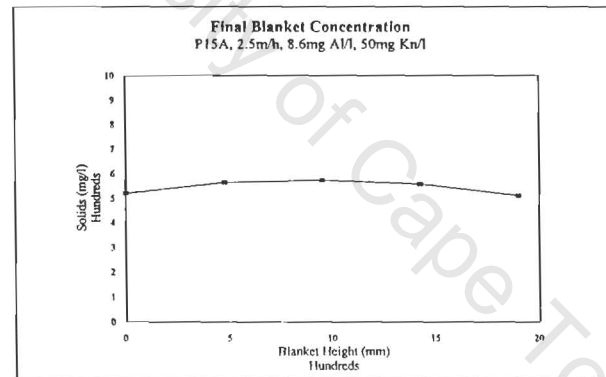
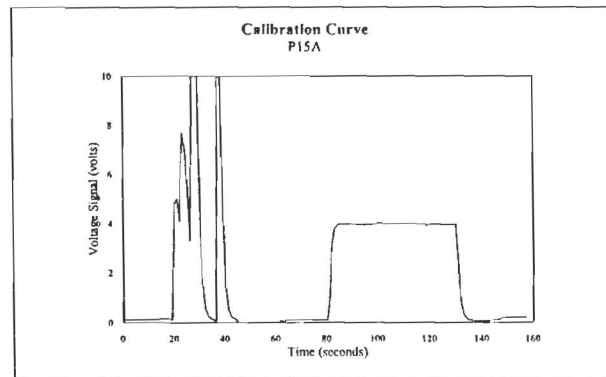
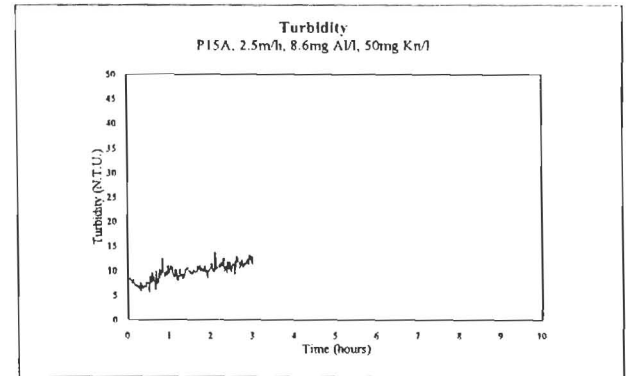
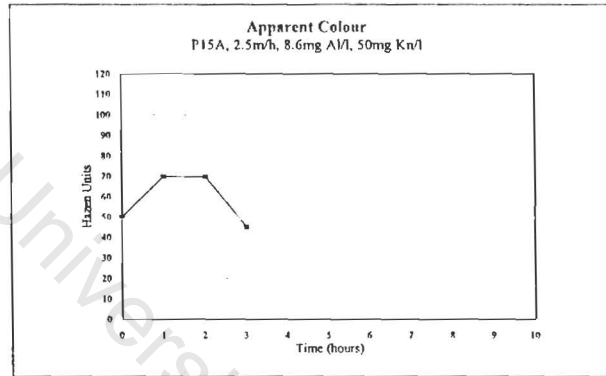
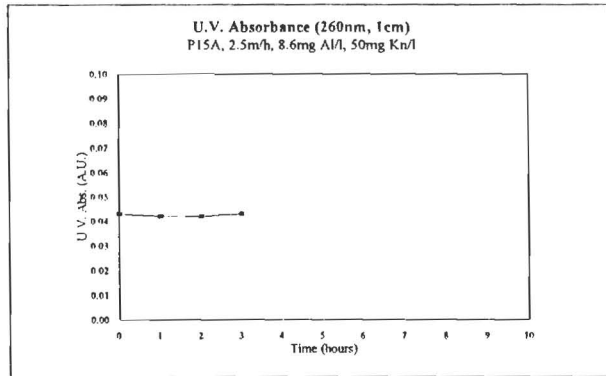
APPENDIX
EXPERIMENT RESULTS

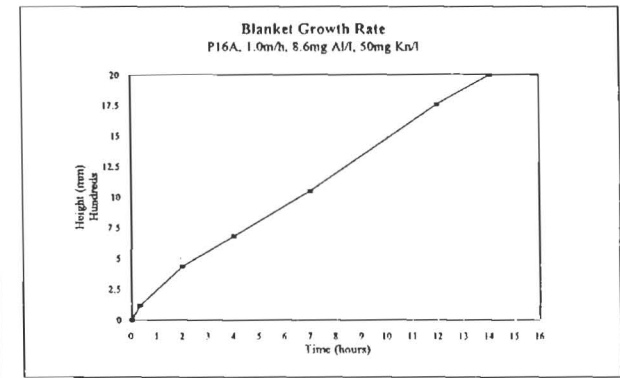
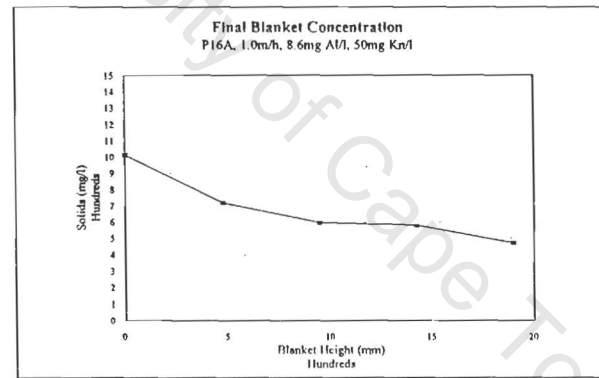
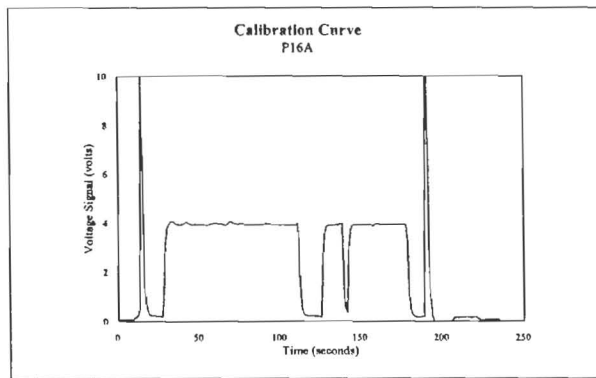
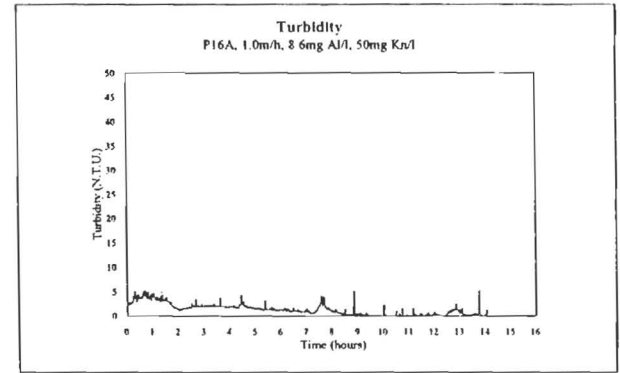
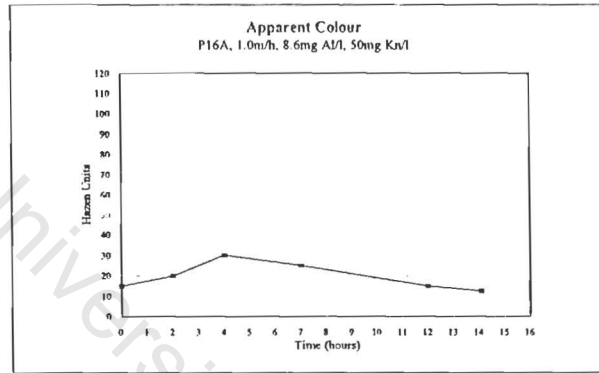
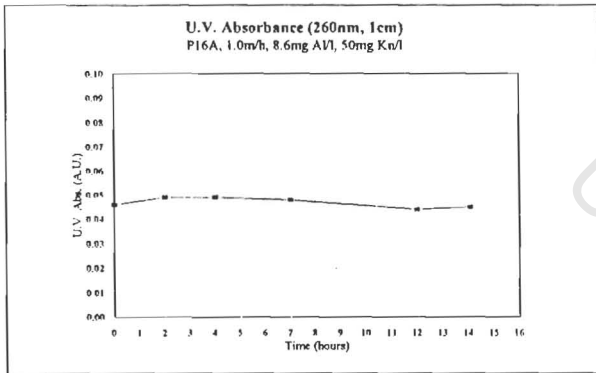
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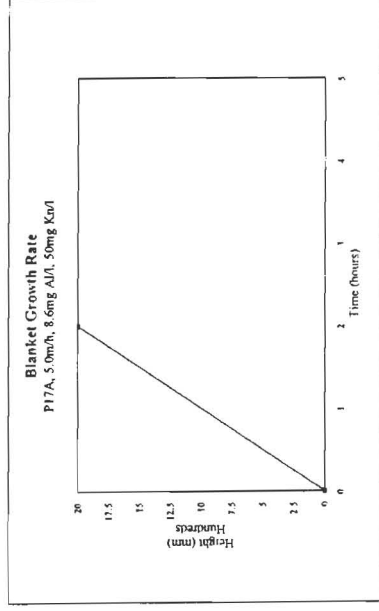
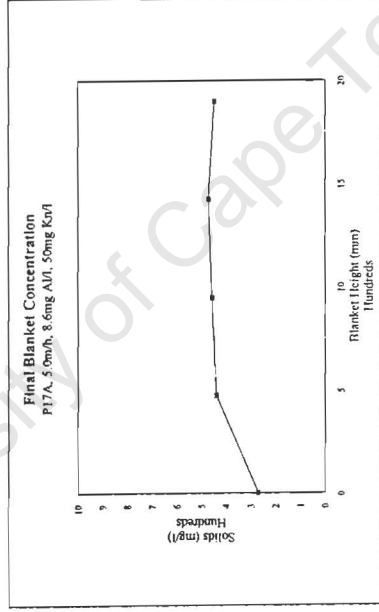
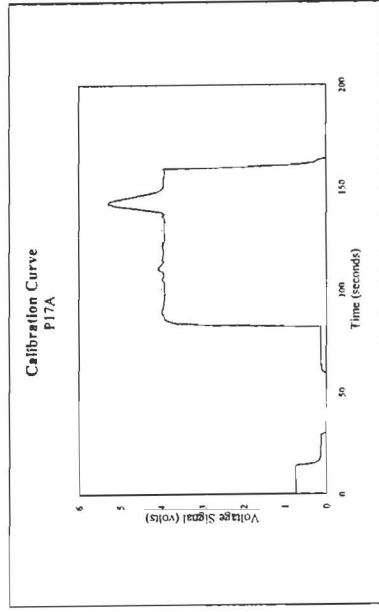
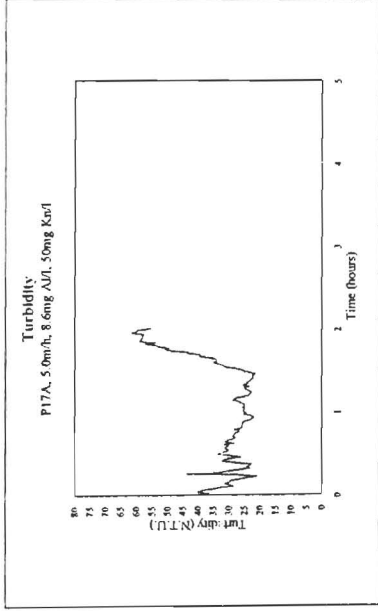
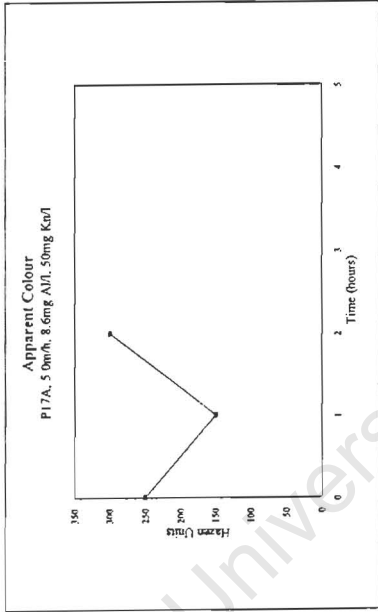
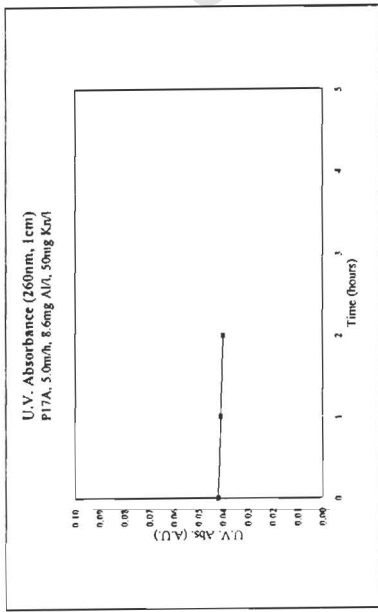
EXPERIMENT SUMMARY

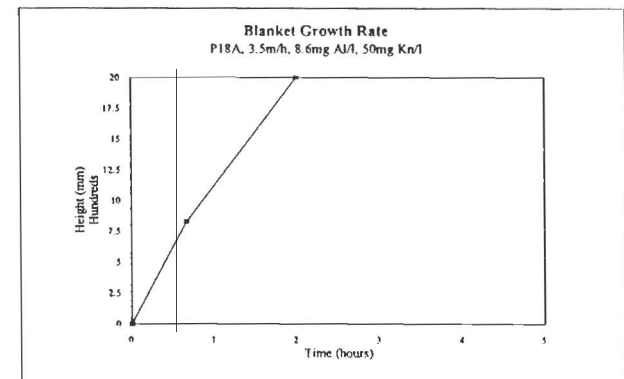
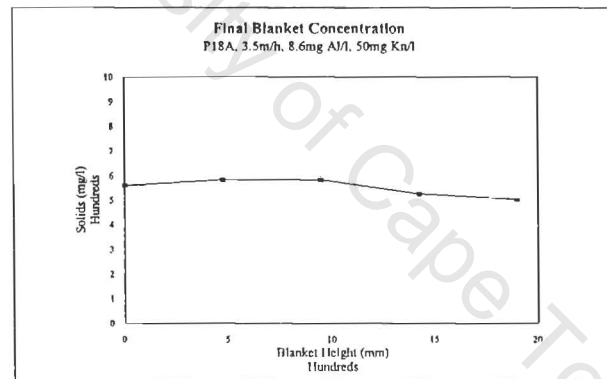
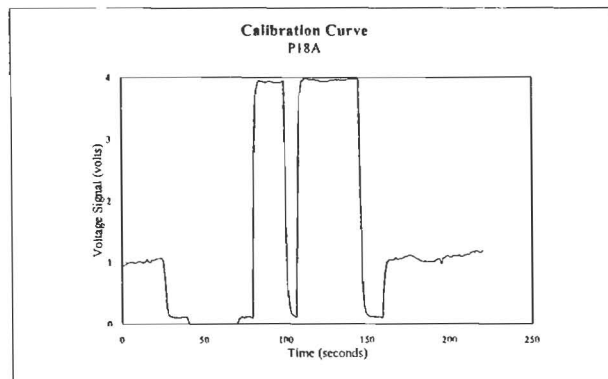
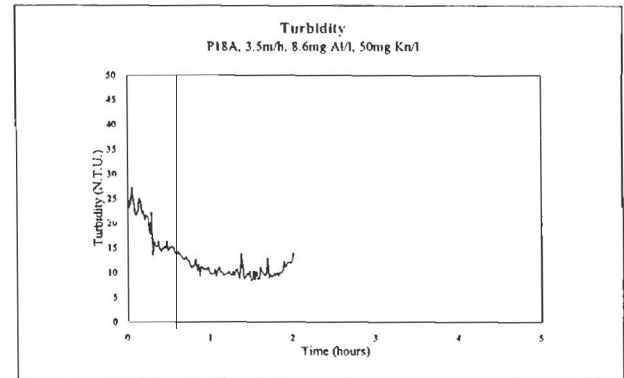
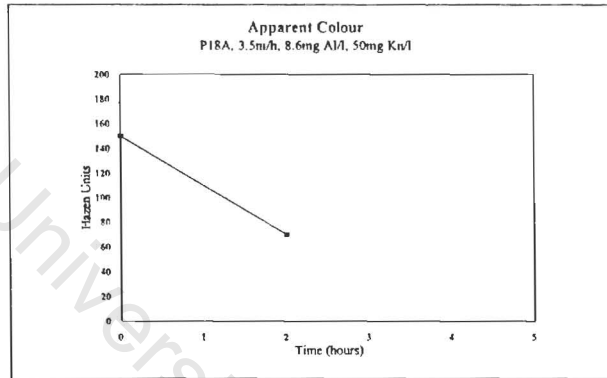
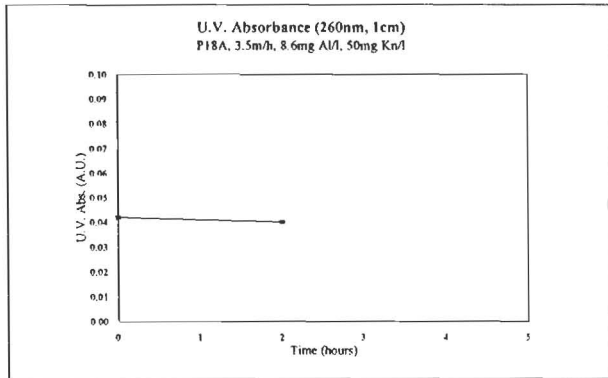
Hydraulic Loading Rate	Parameter	Kaolin Dose			
		0mg Kn/l	50mg Kn/l	100mg Kn/l	300mg Kn/l
1.0	Exp. No.	P30A	P16A	P33A	P29A
	Water Batch	2B	2B	4	3
	Raw Water UV Abs (260 nm @ 1 cm)	0.845	0.845	0.758	0.739
	Raw Water Apparent Colour (HU)	210	210	200	175
	Raw Water Turbidity (NTU)	0.8	0.8	0.8	1.0
	Raw Water Temperature (Degrees Celcius)	18.0	16.5	16.0	19.5
	Alum Dose (mg Al/l)	8.6	8.6	8.6	7.5
Polyelectrolyte Dose (mg/l)	0.1	0.1	0.1	0.1	
1.8	Exp. No.	P22A	P14A	P32A	P27A
	Water Batch	2B	2B	2B	3
	Raw Water UV Abs (260 nm @ 1 cm)	0.845	0.845	0.845	0.739
	Raw Water Apparent Colour (HU)	210	210	210	175
	Raw Water Turbidity (NTU)	0.8	0.8	0.8	1.0
	Raw Water Temperature (Degrees Celcius)	18.0	16.5	16.0	16.5
	Alum Dose (mg Al/l)	8.6	8.6	8.6	7.5
Polyelectrolyte Dose (mg/l)	0.1	0.1	0.1	0.1	
2.5	Exp. No.	P21A	P15A	P31A	P26A
	Water Batch	2B	2B	2B	3
	Raw Water UV Abs (260 nm @ 1 cm)	0.845	0.845	0.845	0.739
	Raw Water Apparent Colour (HU)	210	210	210	175
	Raw Water Turbidity (NTU)	0.8	0.8	0.8	1.0
	Raw Water Temperature (Degrees Celcius)	17.5	17.0	17.5	17.5
	Alum Dose (mg Al/l)	8.6	8.6	8.6	7.5
Polyelectrolyte Dose (mg/l)	0.1	0.1	0.1	0.1	
3.5	Exp. No.	P23A	P18A	P19A	P24A
	Water Batch	2B	2B	2B	3
	Raw Water UV Abs (260 nm @ 1 cm)	0.845	0.845	0.845	0.739
	Raw Water Apparent Colour (HU)	210	210	210	175
	Raw Water Turbidity (NTU)	0.8	0.8	0.8	1.0
	Raw Water Temperature (Degrees Celcius)	16.5	17.0	17.5	17.0
	Alum Dose (mg Al/l)	8.6	8.6	8.6	7.5
Polyelectrolyte Dose (mg/l)	0.1	0.1	0.1	0.1	
5.0	Exp. No.		P17A	P20A	P25A
	Water Batch		2B	2B	3
	Raw Water UV Abs (260 nm @ 1 cm)		0.845	0.845	0.739
	Raw Water Apparent Colour (HU)		210	210	175
	Raw Water Turbidity (NTU)		0.8	0.8	1.0
	Raw Water Temperature (Degrees Celcius)		19.0	17.0	18.0
	Alum Dose (mg Al/l)		8.6	8.6	7.5
Polyelectrolyte Dose (mg/l)		0.1	0.1	0.1	

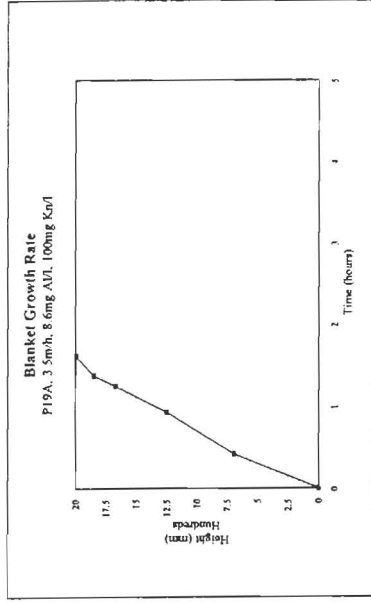
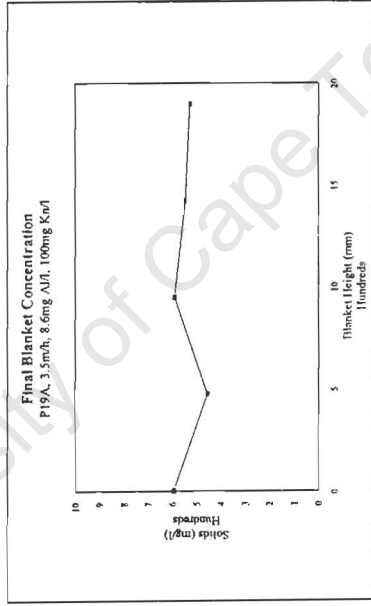
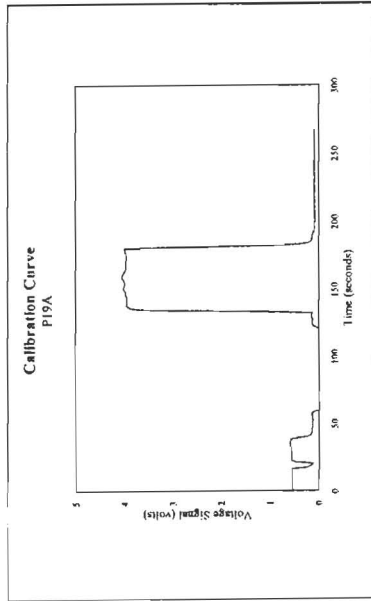
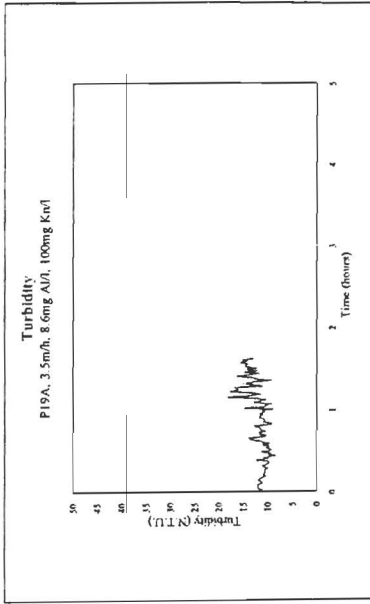
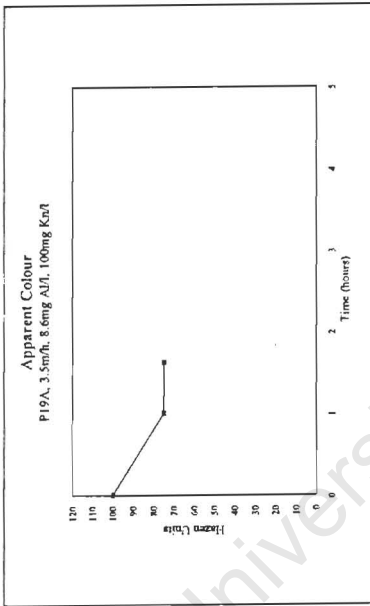
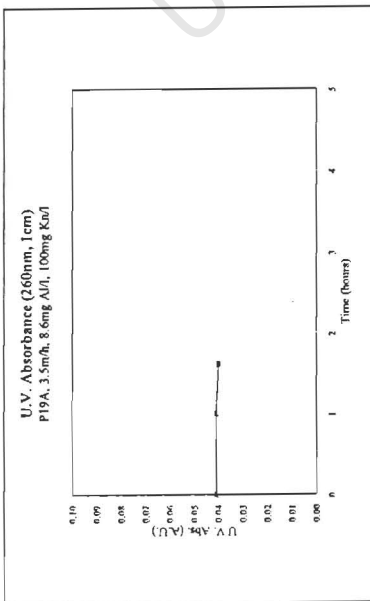


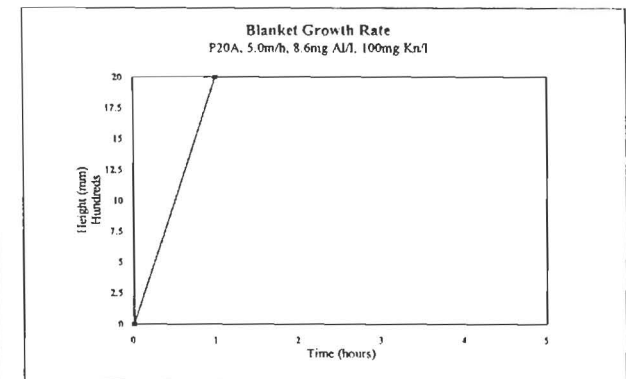
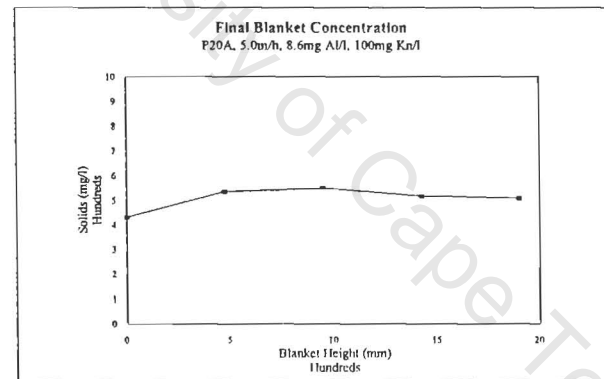
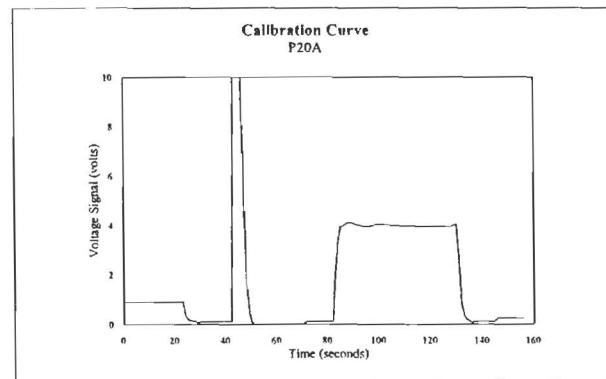
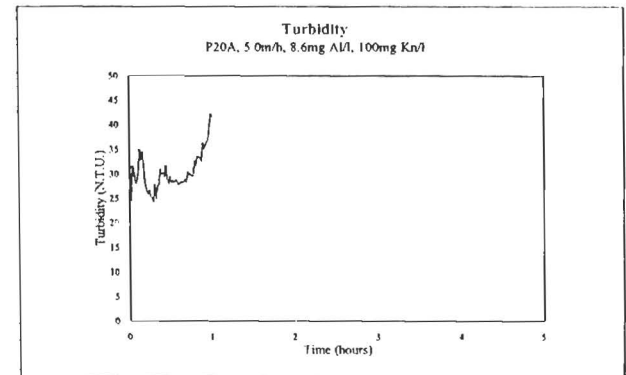
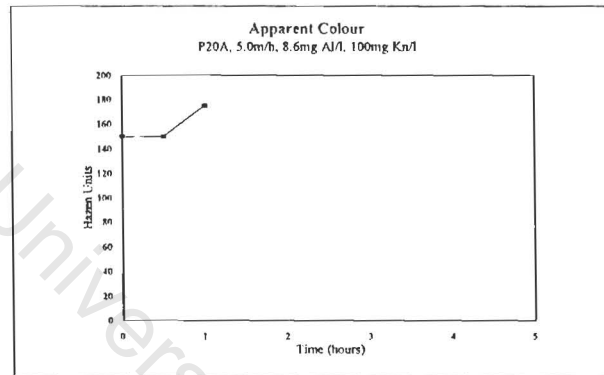
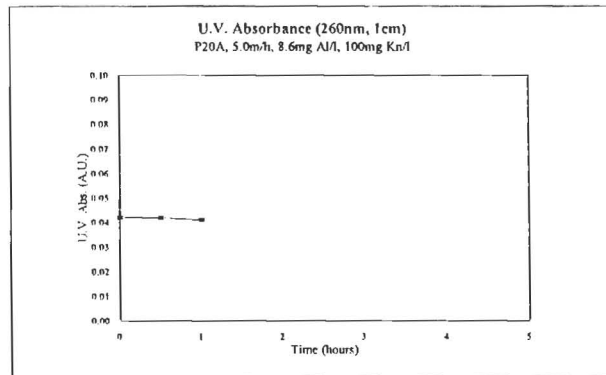


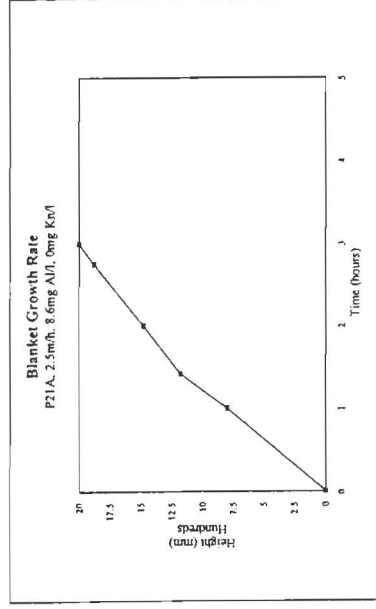
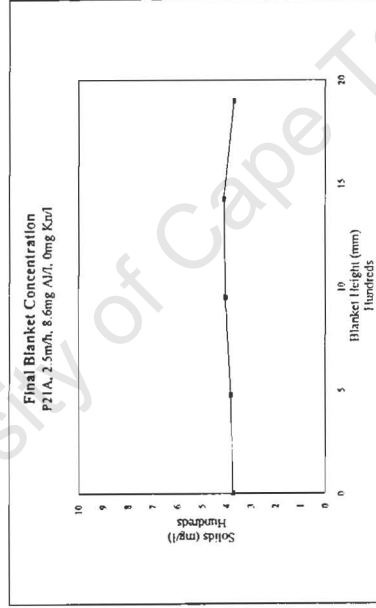
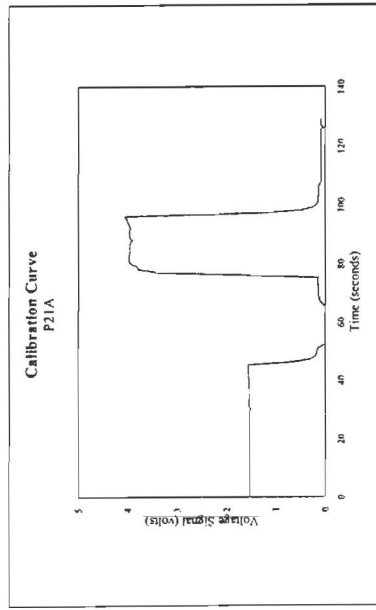
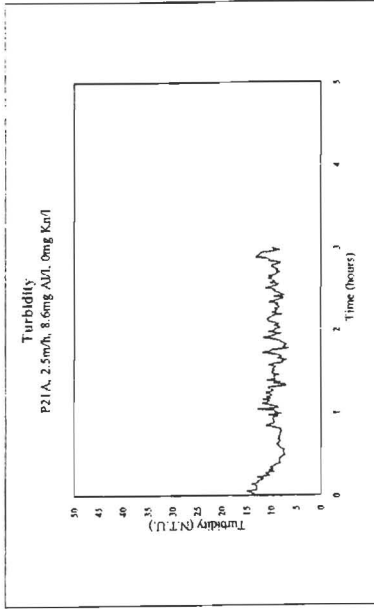
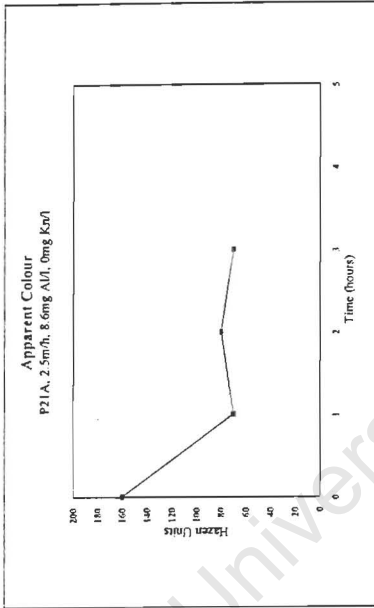
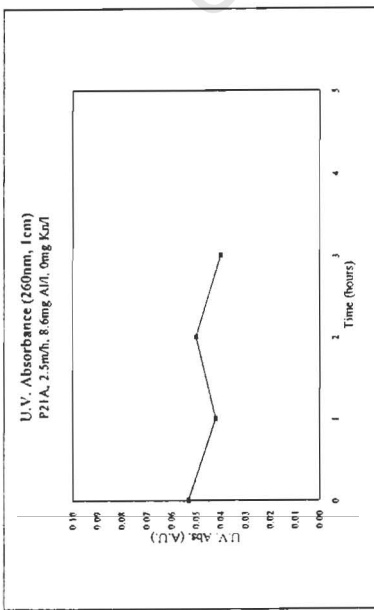


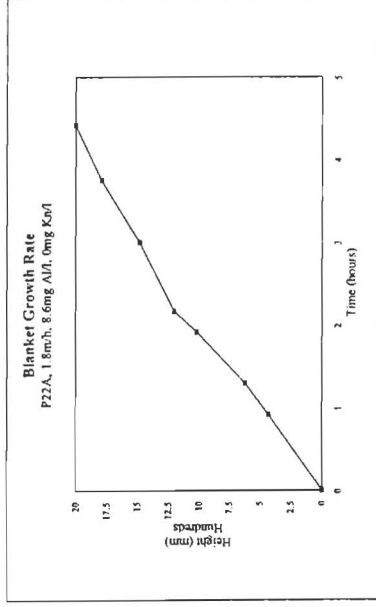
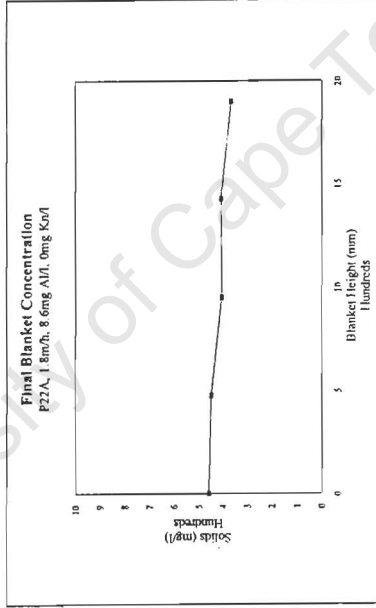
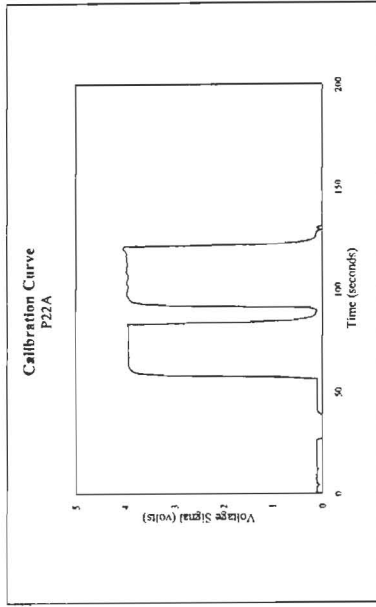
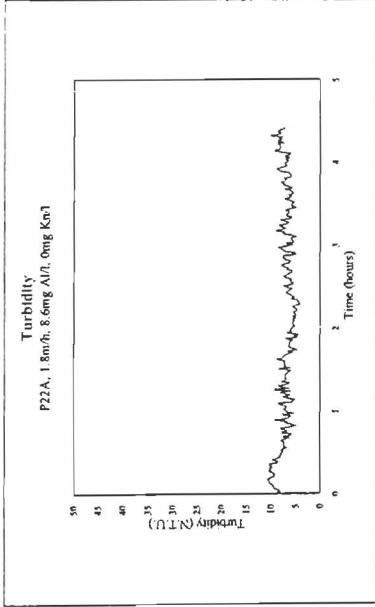
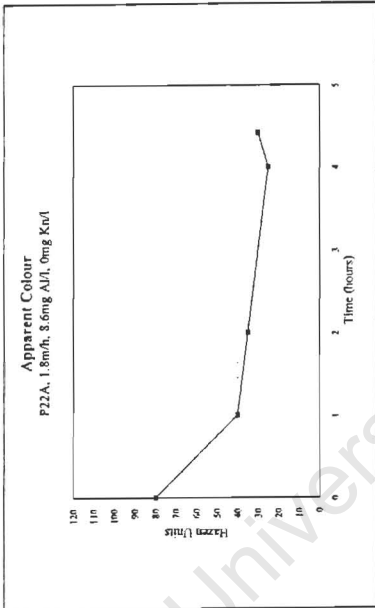
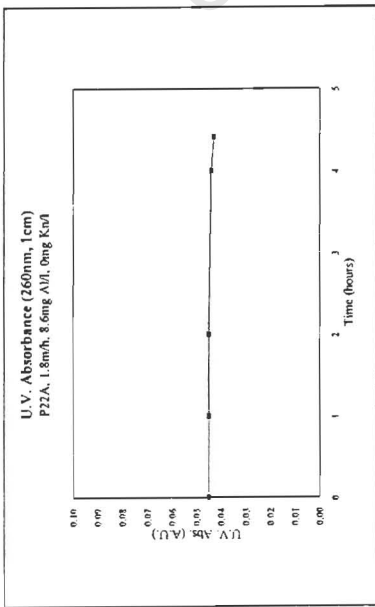


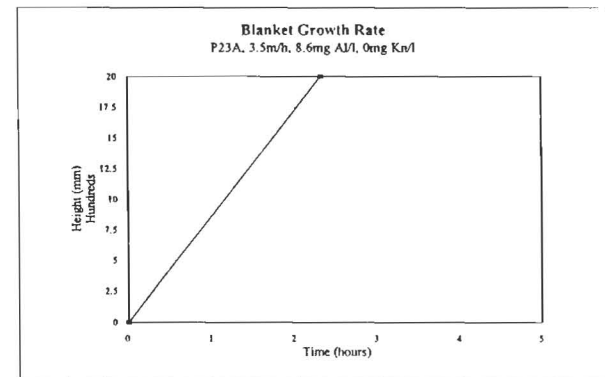
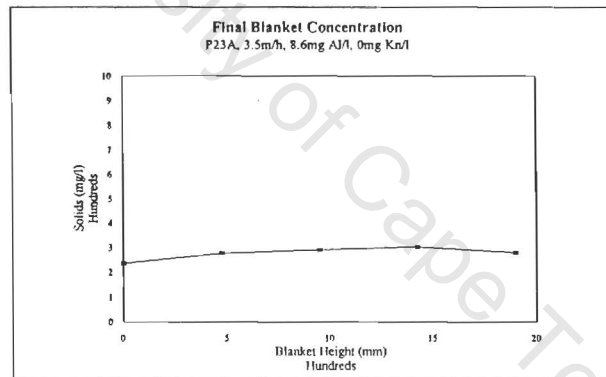
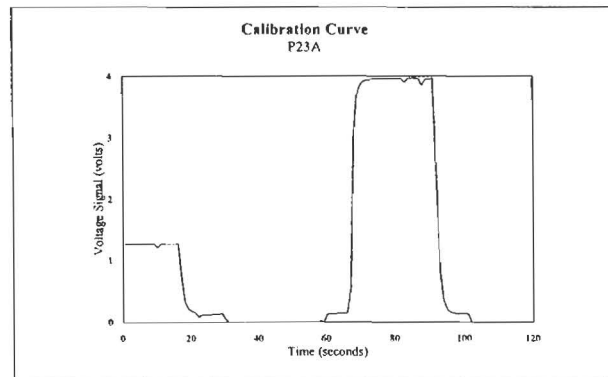
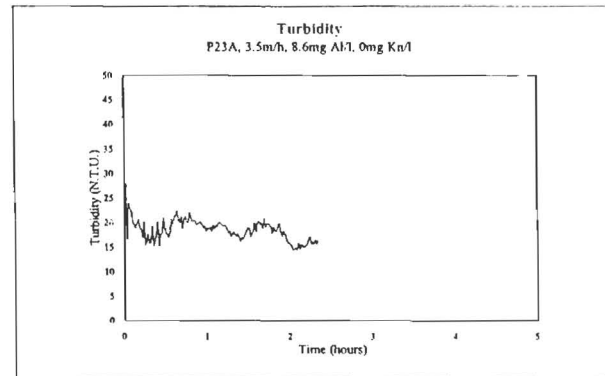
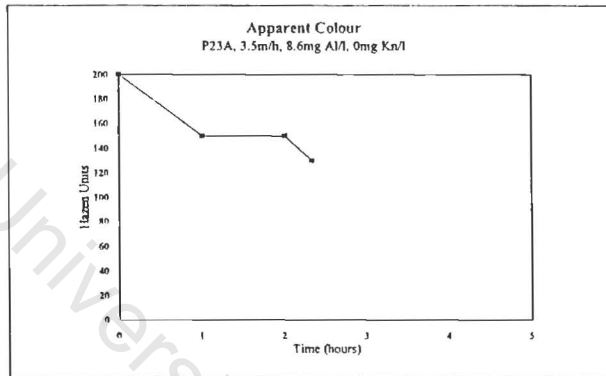
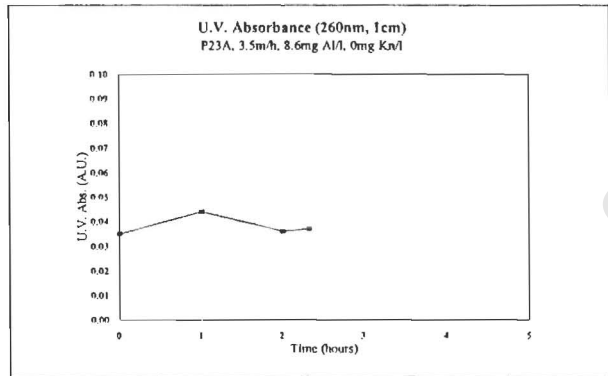


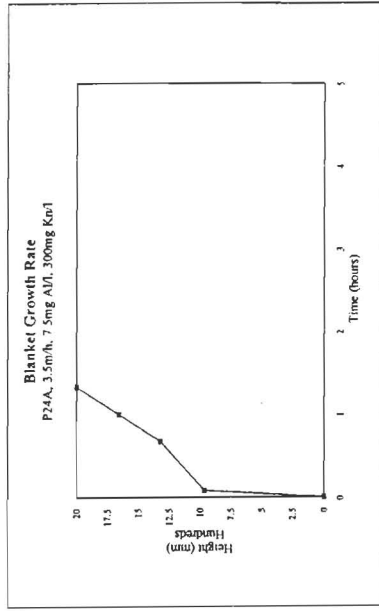
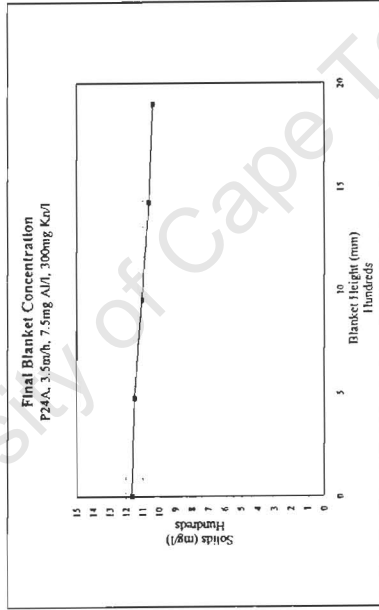
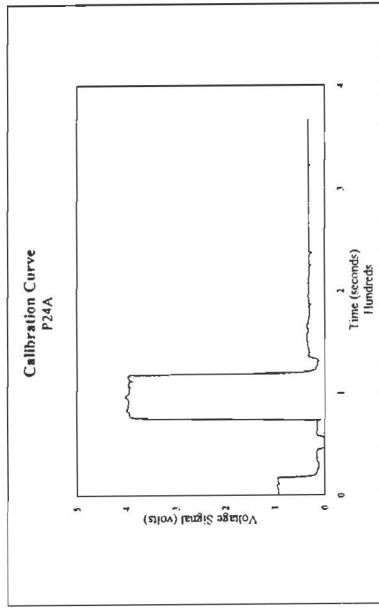
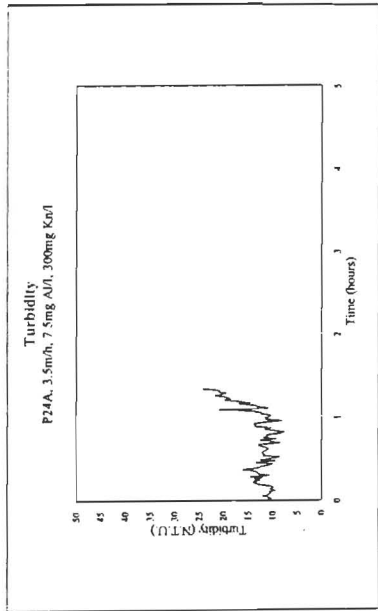
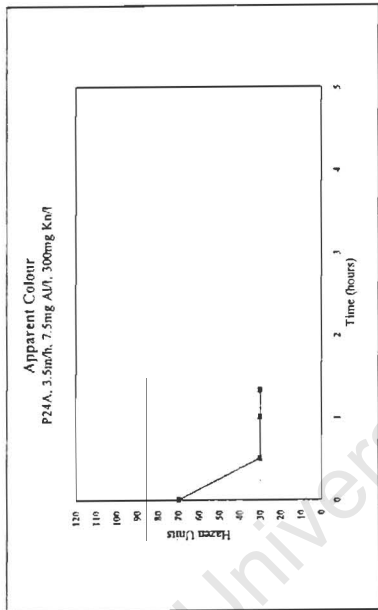
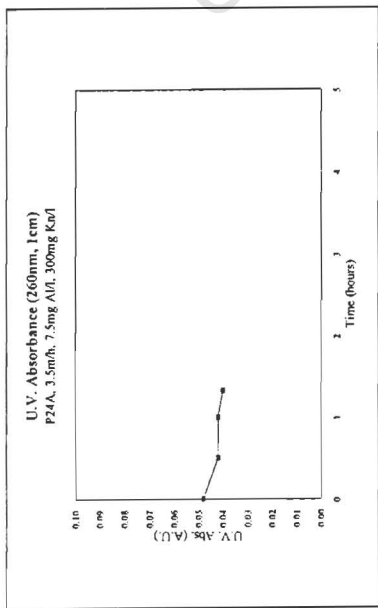


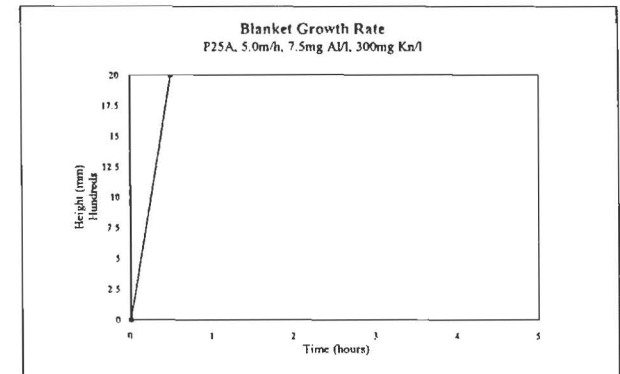
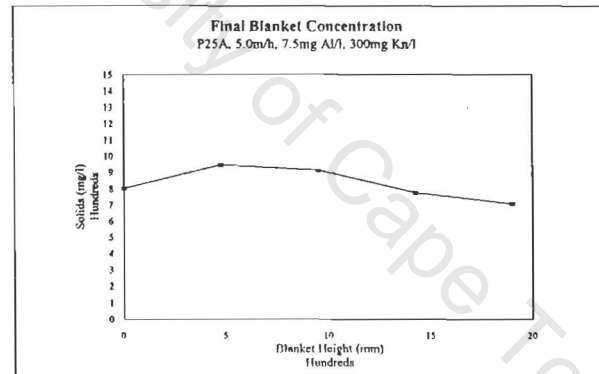
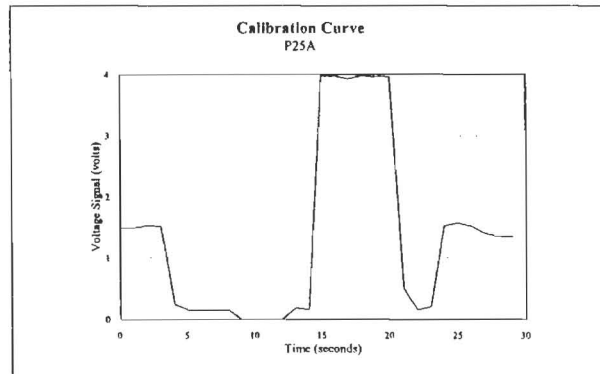
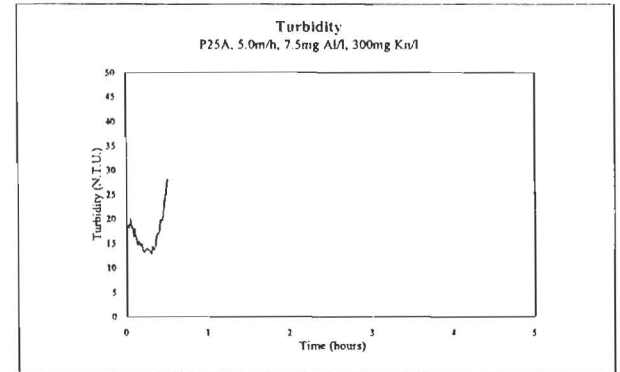
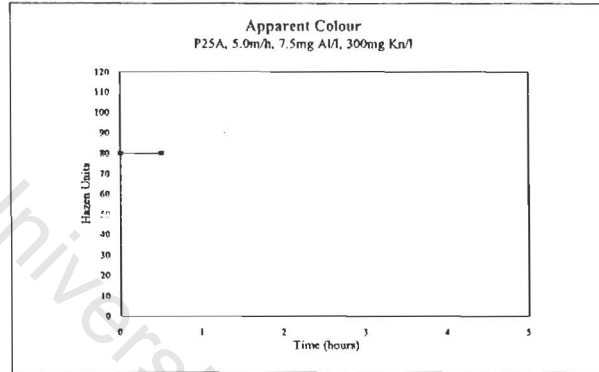
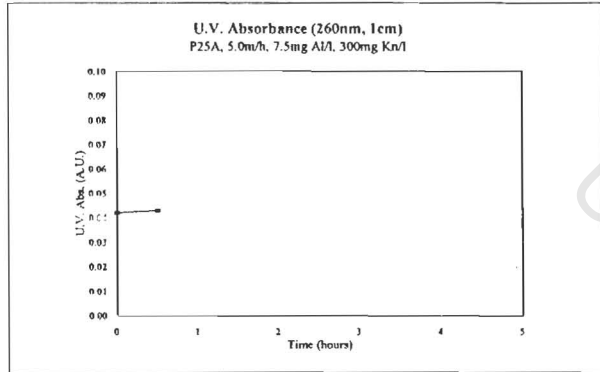












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