THE USE OF COMPRESSIVE RHEOLOGY TOOLS TO DETERMINE THE DEWATERING PROPERTIES OF SELECTED SEWAGE SLUDGES

by

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ABSTRACT

Wastewater treatment produces sludge which is usually dewatered prior to disposal to reduce disposal costs. This work used compressive rheology tools to accurately measure the dewatering properties of selected sewage sludges with a focus on sludge produced by Autothermal Thermophilic Aerobic Digestion (ATAD). Sludges were sampled from a 500 litre ATAD pilot-plant at Killarney Co. Kerry, and from wastewater treatment plants in Australia, Ireland, Germany and Luxembourg. The project aims to outline the dewatering properties of these sludges and to determine some of the factors which govern wastewater sludge dewatering.

The theoretical basis of this work was the phenomenonological solid-liquid separation theory of Buscall and White (1987). The gel-point, compressibility, and permeability have been established as the fundamental physical properties that determine suspension dewaterability. However, until recently, the experimental determination of these properties for wastewater sludges (which exhibit atypical behaviour) was limited due to theoretical and experimental constraints. Recently, new qualitative and quantitative methods based upon the Buscall and White (1987) approach to dewatering characterisation have been developed, and have been successfully applied to wastewater sludges (Stickland, 2005). In this study these methods were applied to ATAD sludges for the first time. Filtration, settling and centrifugation tests were used to measure the material characteristics of several ATAD sludges, some of which were conditioned using polymeric flocculants and inorganic coagulants.

All wastewater treatment sludges which were investigated in this work exhibited non-traditional filtration characteristics, forming highly networked suspension at low solids concentrations. Such sludges are impermeable and highly compressible.

A 500 litre ATAD pilot-plant was commissioned as part of this research. Thickened waste activated sludge was used as the feedstock for the ATAD pilot-plant. In retention time trials, temperatures of 60 °C were achieved during digestion. The pilot-plant achieved 47% volatile solids removal on a 10 day retention time. Digested sludges obtained from the ATAD pilot-plant had very poor dewatering properties at 7 day and 10 day retention times, and it also had an exceptionally high optimum polymer dose rendering it unsuitable for dewatering.

Furthermore, ATAD sludge was obtained from the post-process storage tanks at Killarney WWTP, and from treatment plants in Germany and Luxembourg. In pressure-filtration tests, these ATAD sludges were shown to dewater to similar solids concentrations to anaerobic sludges for pressures ranging from 2kPa to 400kpA. However, in the case of the ATAD sludges obtained from Killarney WWTP the quantities of polymeric flocculant required to achieve satisfactory dewatering were high. The sludges obtained from treatment plants in Germany and Luxembourg showed markedly better dewatering properties than the Killarney ATAD, and this may have been due to the feed sludge to these treatment plants having a higher proportion of primary sludge than at Killarney WWTP which was operated solely on a feed of waste-activated sludge.

Investigations into the factors influencing ATAD dewatering showed that the optimum polymer dose correlated strongly with negatively charged biopolymeric material in the solution phase. A proportion of this material consisted of proteins and polysaccharides which were released as a function of digestion time during batch trials. These substances may accumulate in solution because of cell lysis effects and the erosion of extracellular polymers from sludge flocs during digestion.

Finally, the conditioning of ATAD sludge with ferric sulphate was shown to improve dewatering properties in terms of permeability but reduced the compressibility of the sludge.

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NOMENCLATURE

Roman

A	mass of crucible and sample (g)
A_{cyl}	cross-sectional area of filtration chamber (m^2)
B	mass of crucible (g)
C	mass of crucible and sample before drying test (g)
D	mass of crucible and ashed sample
$D(\phi)$	solids diffusivity ($m^2\ s^{-1}$)
E_1	fitting parameter
E_2	fitting parameter
E_3	fitting parameter
F_d	hydrodynamic drag force
F_g	gravitational force
G	gravitational field
h	suspension height (m)
$h(-)$	normalised suspension height (h/h_0)
h_0	initial suspension height (m)
h_d	sectioning depth (centrifugation scrape-test)
h_f	final suspension height
$(K_d)_T$	digestion decay constant at temperature (T)
$(K_d)_{20}{}^{o}{}_C$	digestion decay constant at 20 °C
m_{liq}	mass of filtrate expelled in filtration test
P	pressure (Pa)
p_1	compressive yield stress fitting parameter
p_2	compressive yield stress fitting parameter
p_s	particle pressure
$P_{os}(\phi)$	particle osmotic pressure
P_T	degree-day product

$P_y(\phi)$ Compressive yield stress (Pa)

$r(\phi)$ hindered settling factor (-)

$R(\phi)$ Hindered settling function (Pa s m^2) ($R(\phi) = (\lambda/V_p r(\phi))$

t time, time of filtration (s)

t_0 initial filtration time (s)

T temperature (^oC)

$u(\phi)$ settling velocity

V specific filtrate *volume*

V_p particle volume (m^3)

Greek

α specific cake resistance

α_m specific mass filter cake resistance

α_p particle diameter

β^2 filtration parameter (m^2 s^{-1})

ε void fraction

ϕ solids volume fraction (-)

ϕ_{av} average final solids volume fraction (-)

ϕ_{cp} maximum packing density (-)

ϕ_g gel-point (-)

ϕ_0 initial solids volume fraction (-)

ϕ_∞ final equilibrium solids volume fraction (-)

η liquid viscosity (Pa s)

$\kappa(\phi)$ dynamic compressibility

Δh change in height of suspension

ΔP applied compressive step or pressure drop (Pa)

$\Delta\rho$ solid-liquid density difference (kg m^{-3})

λ Stoke's settling coefficient (Pa s m)

θ	temperature coefficient
θ_d	retention time (days)
ρ_f	fluid density (kg m^{-3})
ρ_s	solid density (kg m^{-3})

CHAPTER ONE: INTRODUCTION

1.1 Background

Industrial and municipal wastewater treatment processes produce a mixture of solid and liquid waste, or sludge, that must be managed. The effective treatment and disposal of this material poses a significant challenge. In Ireland, in accordance with EU policy, land application of sludge which has been treated to specific standards is the preferred method of disposal (Bartlett and Killilea, 2001). Reducing the water content of sludge using solid-liquid separation operations generally decreases the cost of disposal. The optimisation of sludge dewatering characterisation techniques, and process conditions in dewatering unit processes, is a challenge for the wastewater treatment industry today.

A research study was carried out where novel experimental techniques were applied to selected sewage sludges to describe sludge dewatering properties in terms of the rate of dewatering and extent of dewatering under a compressive force. The techniques are based upon the compressive rheology theory of Buscall and White (1987) and have only recently been successfully applied to highly compressible and permeable materials such as sewage sludges (Stickland, 2005). The techniques employed were a combination of batch settling, centrifugation, and pressure-filtration tests. These were used to determine sludge properties in terms of the following material-dependent parameters: the

compressive yield stress, $P_y\phi$, which defines the compressibility of a suspension and the hindered settling function, $R(\phi)$, which quantifies the permeability of a suspension.

In this research study the primary application of these characterisation techniques was to sludge produced by a process known as autothermal thermophilic aerobic digestion, ATAD, which is one of the specified treatment options of preference for municipal sludge under Irish legislation (Fehily, Timony & Co., 1999) The ATAD process is a high-rate aerobic digestion process occurring at elevated temperatures (> 45°C), with the majority of the heat energy within the process being imparted by the metabolic activities of the microbial biomass under conditions of intensive aeration. A drawback of the ATAD process is a final product which has poor dewatering properties. The underlying causes of these poor dewatering properties are not fully understood but are thought to include small particle size (Forster, 2002). However, ATAD sludge has never before been characterised using compressive-rheology characterisation techniques.

A unique experimental set-up was devised at Killarney wastewater treatment plant in Ireland. The set-up combined a 500 L ATAD pilot-plant, producing sludge under controlled conditions, with experimental tools that were used to characterise the resulting sludge dewatering properties in compressive-rheology terms. Furthermore, ATAD sludge resulting from a number of European ATAD plants was also characterised. In addition to ATAD sludges, these tools were used to characterise several other sewage sludges, including anaerobic sludges, and waste-activated sludges. Potential sludge conditioning processes (to improve dewatering) such as enzymatic addition, freeze-thaw conditioning,

and conditioning using a combination of inorganic coagulants and polymeric flocculants were also evaluated for the first time using compressive-rheology tools.

1.2 Objectives of the Research

There were several research objectives formulated as part of this research study.

The primary research objectives were to use recently developed experimental tools to characterise ATAD sludge according to the compressive-rheology theory of Buscall and White (1987) with the overall aim of optimisation of the ATAD process for dewatering. The ATAD process was to be investigated under controlled conditions, through which parameters such as retention time could be manipulated and subsequent changes in ATAD sludge dewatering could be assessed using the dewatering characterisation methodologies. To achieve these research objectives a number of sub-tasks were designed and undertaken as follows:

- Commissioning of a custom-built air-driven filtration rig (compression-permeability cell) at the University of Melbourne, and using it in experiments validating the use of compressive-rheology tools in the characterisation of conditioned and unconditioned anaerobic sludges.
- Commissioning of a custom-built 500 litre ATAD pilot-plant to digest waste-activated sludge at Killarney WWTP, and operating it under different process conditions.

- Refinement of filtration-rig experiment methodologies at Killarney WWTP.
- The selection of full-scale ATAD plants in continental Europe running under different process conditions for sampling of further ATAD sludges.
- The use of experimental tools (batch settling and pressure-filtration, and optimum polymer dose analysis) to provide data for the compressive-rheology characterisation of ATAD sludge resulting from the full-scale treatment plant at Killarney, the product storage tanks at Killarney, and from the European ATAD plants.
- The selection and investigation of physicochemical factors which may influence ATAD dewatering.

A number of secondary research objectives were developed from the results of the primary research objectives and they in turn were investigated as part of this research.

The use of a combination of batch settling and pressure filtration experiments alone were shown to be inadequate to provide compressive data across a full range of solids concentrations, and compressibility and permeability functional forms needed to be extrapolated across a critical solids range for which no data existed. To counter this, a centrifugation settling technique first described by Green (1997) was applied to sludges to provide data within this region. Furthermore, investigations into physicochemical factors affecting ATAD dewatering and the characterisation of ATAD sludges which had been stored for a prolonged period of time identified a solution fraction of biocolloidal material (proteins and polysaccharides) which

corresponded positively with poor ATAD dewatering. A number of subsequent experimental objectives were devised which incorporated the centrifugation methods into dewatering analysis, and the analysis was expanded to include sludge resulting from anaerobic digestion. These objectives are outlined below:

- Validation of the centrifugation methods by characterisation of flocculated and unflocculated anaerobic sludges.
- Determination of the effect of storage on anaerobic sludges in terms of the quantity and composition of solution biopolymeric material and dewatering properties.
- Determination of the effect of novel conditioning mechanisms such as freeze-thaw conditioning and enzymatic addition on anaerobic and waste-activated sludges.

Finally, further investigations into ATAD dewatering were conducted using batch digestion to determine time-dependent changes in dewatering properties within the process. The use of inorganic coagulants in conjunction with long-chain polyelectrolytes in ATAD conditioning was also investigated.

1.3 Thesis Outline

This thesis aims to develop an understanding the dewatering behaviour of sewage sludges, and in particular sludge resulting from the ATAD process. It is broken down into

8 Chapters including this introductory Chapter. Chapter Two provides a comprehensive review of the literature pertaining to the research. Chapter Three provides a complete description of the materials and experimental methodologies which were used in the research. Chapters Four – Seven divide the research which was conducted into four discrete sections, in which related experiments are described, the results presented, and discussions and conclusions drawn. These chapters are outlined below:

Chapter Four describes the commissioning and operation of the ATAD pilot-plant in terms of digestion dynamics. Process performance is analysed in terms of total solids, volatile solids removal, and chemical oxygen demand (COD) removal while operating on different retention times.

Chapter Five introduces compressive-rheology experimental techniques and their validation and application to mesophilic anaerobic sludges at the University of Melbourne and ATAD sludges at Killarney. Investigations of physicochemical factors affecting sludge dewatering properties are also described.

Chapter Six describes the application of centrifugation characterisation techniques to anaerobic sludges, enzymatically modified anaerobic sludge and freeze-thaw conditioned waste-activated sludge. Experiments are described which quantified the effect of refrigerated storage on sludge dewatering properties and the composition and quantity of biopolymers in solution.

Chapter Seven introduces the centrifugation characterisation techniques to ATAD sludges. Post-storage ATAD sludges are characterised and along with sludge resulting from ATAD batch digestions (to determine digestion time-dependent effects on ATAD sludge dewatering).

Finally, Chapter Eight summarises the results. Key findings of the research are outlined, measured against the research objectives, and the impact of these findings on current theory is discussed, followed by a summary of potential future work.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This Chapter provides a summary of the key literature related to the theory and experimental methodology used in the research study. It is divided into five sections. Section 2.1 introduces the activated sludge process, secondary sludge treatment processes, the Biosolids concept, and the relevant Irish and European legislation which govern wastewater treatment. Section 2.2 describes the ATAD process and its use as a municipal sludge treatment technology. Important parameters for the evaluation and process control of ATAD systems are outlined. Section 2.3 focuses on sewage sludge dewatering properties. There is a subsection dealing specifically with the dewatering of ATAD sludges. This section considers the difficulties associated with sewage sludge dewatering from various perspectives, ranging through the physico-chemical to the biological parameters which impact dewatering. Section 2.4 examines dewatering theory with respect to sewage sludge dewatering, and appraises the various experimental methods available to researchers to determine the dewaterability of sewage sludges. The compressive-rheology theory of Buscall and White (1987) is also reviewed in the fourth section. Finally, Section 2.5 provides a summary of the previous four sections and outlines the issues that this research study addresses.

2.1.1 The activated sludge process and the need for sludge treatment.

The activated sludge process is the most common suspended-growth process used for the biological treatment of municipal wastewater sludge (Metcalf *et al.*, 2001). While many variations of the activated sludge process exist, the process has changed little in its fundamentals since its initial inception by Ardern and Lockett (1914). The basic premise of the process is the stabilisation of a waste under aerobic conditions. It typically consists of an aeration stage in which a flocculated biomass, suspended in the wastewater, (usually known as mixed liquor suspended solids) removes carbonaceous organic matter from the wastewater. This matter is then utilised it in the production of cell tissue and oxidised end products including carbon dioxide and water. The aeration stage is followed by a settling stage. The effluent wastewater (supernatant) from the process overflows from the top of the settling unit and is either discharged or subjected to tertiary treatment (Metcalf *et al.*, 2001).

In the settling stage, activated sludge settles by gravity and the resulting supernatant has typically >99% suspended solids removed (Metcalf *et al.*, 2001). The formation of biological flocs assists the settleability of activated sludge. The biological and physico-chemical characteristics of flocs are the primary factors governing the settleability of activated sludge. Investigations into the underlying mechanisms and the microbes involved in the formation of flocs have been at the forefront of activated sludge research in recent years (Forster, 1985; Jin, 2003; Sponza, 2003).

Substrate conversion by microbes leads to a net gain of biomass during the settling stage. Typically, a percentage of this excess sludge is returned to the aeration stage. This portion is known as return-activated-sludge (RAS) (Metcalf *et al.,* 2001). A percentage of settled sludge is also wasted intermittently. This prevents accumulated solids from contaminating the system effluent. This portion is known as waste-activated-sludge (WAS). WAS is a concentrated sink for the wide variety of compounds which enter the wastewater treatment system, and, as such, WAS is a very difficult product to treat and manage satisfactorily (Vesilind and Spinosa, 2001). At the same time it is an organic material with excellent fertiliser properties which, if contaminants can be removed or managed, should, in line with best cradle to cradle environmental management, be beneficially reused in agriculture. Problems associated with the minimisation, treatment and beneficial re-use of WAS have become one of the biggest challenges facing wastewater engineers in recent times, as international legislation increasingly imposes increasingly strict criteria on its quality and management practices (Campbell, 2000). Figure 2.1 gives a schematic of a typical activated sludge process.

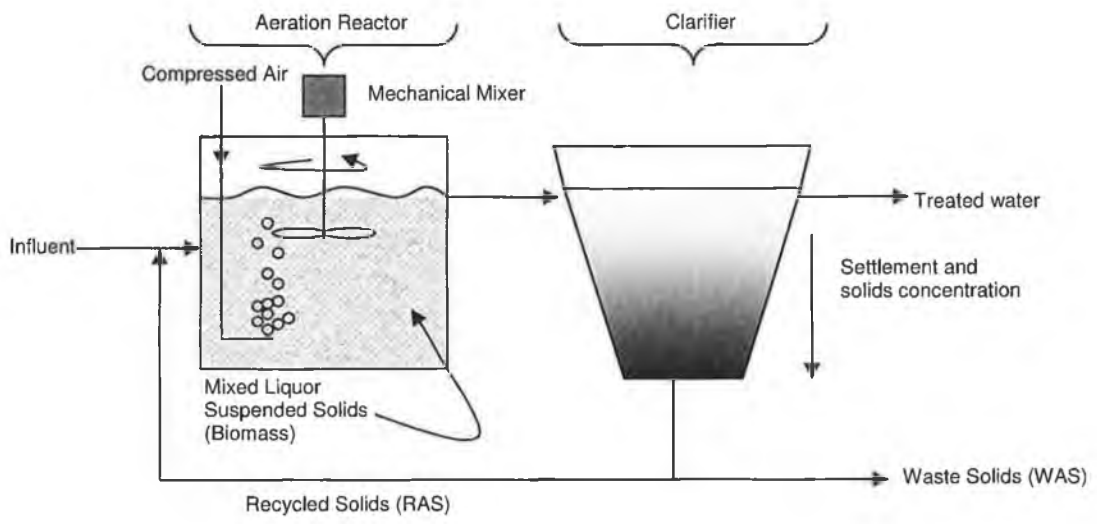


Figure 2.1 Schematic of a typical activated sludge process

2.1.2 Definition of Biosolids

The treatment and reuse of sludge can account for as much as 50% of the total wastewater treatment costs (Rulkens, 2003). The volume of sewage sludge produced globally is set to increase markedly in the coming years. This is a result of the practice of wastewater treatment expanding quickly in both developed and developing countries (Odegaard, 2004). Concurrent with this growth in sludge production are increasingly rigorous legislative criteria on sludge disposal and reuse, and a growing environmental awareness amongst the public (most notably in developed countries).

The phrase 'sewage sludge' evokes negative connotations of an odorous, toxic and pathogenic material. 'Biosolids' is a term which was conceived by the Water Environment Federation of the United States (WERF) and has since gained widespread

acceptance as a term for sewage sludge which has been treated to a specific standard and can be beneficially reused in some way (Vesilind and Spinosa, 2001). The term Biosolids is intended to favourably present a product (treated sludge) by overstepping the negative connotations associated with the untreated product that have developed over time.

The Code of Good Practice for the Use of Biosolids in Agriculture (Fehily, Timoney & Co., 1999) defines biosolids as:

> '*the organic by-product of urban wastewater treatment which, by being treated to reach an approved microbial standard, can be used as fertiliser in agriculture*' (Fehily, Timoney & Co. 1999)

This is the definition which is adopted in this thesis.

2.1.3 The role of dewatering in sludge treatment and management

In recent times the focus of much of the research in the area of sludge management (in decreasing desirability) is:

(i) Sludge minimisation

(ii) Treatment and re-use as Biosolids

(iii) Endpoint solutions such as landfill and incineration

Dewatering is generally applied as part of option (iii) to reduce handling costs but it is also sometimes employed as part of option (ii) depending on the process in question. Technically, dewatering of sludge is not a minimisation technology and, in this thesis sludge minimisation technologies are referred to as those resulting in solids reduction at source while dewatering is defined as a sludge concentrating process as according to Odegaard (2004).

The application of Biosolids (as opposed to untreated sewage sludge) directly to land is practiced and encouraged as part of Local Authority sludge management plans in Ireland. This is permitted provided that sludge has been treated to the standard of a *Class A Biosolid* as specified by The Code of Good Practice for the Use of Biosolids in Agriculture (Fehily, Timoney & Co. 1999). Current (and future) public concerns and stricter legislation are likely to lead to a reduction in the volume of sludge which is deemed suitable for land application in Ireland. Dewatering is a control element of many handling and reuse/disposal options, and there is therefore a need for understanding and optimisation of dewatering processes.

2.1.4 Biosolids in Ireland

European Union legislation governing wastewater treatment and subsequent sludge management has evolved rapidly in the past twenty years. The implementation of this legislation into Irish law has greatly changed wastewater treatment practice in Ireland. It has led to increased sludge production, due to the mandatory requirement of secondary

wastewater treatment for all towns with a population equivalent (p.e.) greater than 200, and, in addition, has set rigid criteria for the treatment and beneficial reuse of this sludge. Moreover, under the Waste Management Act (1996) regional sludge management plans must be prepared by all Local Authorities, ensuring that sludge management options are assessed on a case by case basis with respect to nutrient loading (Fehily, Timoney & Co., 1999).

EC Directive 86/278/EEC (On the Protection of the Environment and in Particular the Soil when Sewage Sludge is Used in Agriculture) was brought into Irish legislation under (S.I.) 183 of 1991 (1991). The Directive prohibited the spreading of untreated sludge on the land (as was typically the case in Ireland at that time). The Directive also specifies maximum permissible limits for pathogenic organisms, heavy metals and nutrients which can be applied to land. Directive 86/278/EEC is an EU standard which can be employed more strictly on a local basis (Matthews, 2001). The Directive sought to encourage the use of sewage sludge in agriculture, and to regulate its use in such a way as to prevent harmful effects on soil, vegetation animals and man.

EC Directive 91/271/EEC (Concerning Urban Wastewater Treatment) introduced into Irish legislation under (S.I.) 419 of 1994 (1994), specified mandatory secondary sludge treatment for all towns with a population greater than 200. The Dumping at Sea Act (S.I) 14 of 1996 (1996) prohibited the dumping at sea of municipal sludges after 1999.

In view of the number of stakeholders affected by the legislation outlined above, it was perceived that there was a need to publish guidance manuals in order to comprehensively integrate and present the legislative specifications in an accessible manner. The Department of The Environment and Local Government (DOELG) commissioned a number of documents. These included a baseline audit of non-hazardous sludge produced in Ireland and sludge management 'Codes of Good Practice'. The two most important documents which were published were *The Inventory of Non-Hazardous Sludges in Ireland* (Fehily, Timoney & Co., 1998) and *The Code of Good Practice for the Use of Biosolids in Agriculture* (Fehily, Timoney & Co. 1999).

The Inventory of Non-Hazardous Sludges in Ireland (Fehily, Timoney & Co., 1998) was published to help meet the requirement of Local Authorities to prepare waste management plans for their functional areas, as specified under Section 22 of The Waste Management Act (1996). The publication provides:

- A non-hazardous sludge inventory on a county, regional and national basis
- An assessment of current methods in use for the recovery/disposal of sludge in Ireland
- Evaluation of options for the cost-effective and environmentally sound treatment, recovery and disposal of such sludges jointly or separately

The *Code of Good Practice for the Use of Biosolids in Agriculture* (Fehily, Timoney & Co., 1999) was published to provide guidelines for Biosolids producers and users. The

code addresses the relevant legislation and provides a comprehensive overview of Biosolids management, from treatment through to land application. Specified in the Code are the following treatment alternatives for the production of a pasteurised Biosolids product.

- Mesophilic anaerobic digestion with pre/post sanitation (mean retention time of 12 days at 35 °C, plus retention at >70 °C for 1 hour)
- Thermophilic anaerobic digestion (mean retention time of 2 days at >55 °C, or 4 days at 50 °C)
- Thermophilic aerobic digestion (where all sludge is subject to a temperature greater than 55 °C for at least 4 hours and mean retention time of 7 days)
- Composting (windrows or aerated piles)
- Alkaline stabilisation
- Thermal drying

The final product is considered pasteurised when it meets the following criteria, which have been adopted from the definition of a *Class A Biosolid* according to US EPA Rule 503 regulations (US EPA, 1993).

- A microbial standard of faecal coliforms <1000 Most Probable Number (MPN) per 4g dry solids
- Salmonella sp. <3 MPN per 4g of dry solids
- Enteric viruses <1 per 4g of dry solids

- Viable helminth ova <1 per 4g of dry solids

The Code also recommends that the following organic pollutants: polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins/dibenzofurans (PCDD/F), polyaromatic hydrocarbons (PAH), and nonylphenol are monitored in Biosolids once every 1-5 years (depending on the population equivalent of the treated wastewater). While acknowledging that the respective wastewater legislation does not set limits regarding these compounds, the Code recommends their inclusion in certificates of biosolids analysis as a precautionary measure to further ensure the safety of the end product. The European Commission has produced a Sludge Working Document that specifies limits for these organic pollutants (http://ec.europa.eu/environment/waste/sludge/pdf/sludge_en.pdf) which will be worked into a later revision of Directive 86/278/EEC.

The Waste Management (Use of Sewage Sludge in Agriculture) Regulations (1998) set limits on the heavy metals content of sludge applied to land (Table 2.1).

Table 2.1 Maximum permissible values of heavy metals contained in sludge applied to land as set out in the Waste Management (Use of Sewage Sludge in Agriculture) Regulations (1998)

Parameters	***Maximum Values (mg/Kg)***
Cadmium	1
Copper	50

Parameters	*Maximum Values (mg/Kg)*
Nickel	30
Lead	50
Zinc	150
Mercury	1

Table 2.1 (continued)

Of the specified treatment processes the following are currently being utilised to produce a Class A *Biosolid* product in Ireland:

- Mesophilic anaerobic digestion with pre/post sanitisation (Navan, Ringsend and Oberstown)
- Thermophilic Aerobic Digestion (Killarney)
- Alkaline Stabilisation (Carlow)
- Thermal Drying (Ringsend)

2.2 Autothermal Thermophilic Aerobic Digestion

2.2.1 Introduction

This section describes the ATAD process in terms of microbiology and engineering aspects. ATAD dewatering is dealt with separately in Section 2.3.

The thermophilic digestion range involves temperatures from 45 °C to 60 °C (Cheremisinoff, 1996). From an engineering point of view, LaPara and Alleman (1999) defined a thermophilic process as any activated sludge process operating at a temperature exceeding 45 °C. Autothermal Thermophilic Aerobic Digestion (ATAD) is an activated sludge process operating at thermophilic temperatures. The majority of the system's heat is generated by the metabolic activities of the respiring thermophiles as they degrade available substrate (Bitton, 2005). The aerobic digestion process consists of two steps, the direct oxidation of biodegradable matter, and endogenous respiration, where cellular material is oxidised. The aerobic process in the absence of nitrification is illustrated in Equation. 2.1.

$$C_5H_7NO_2 + 5O_2 \rightarrow 5CO_2 + 2H_2O + NH_3 + energy \qquad (2.1)$$

Some researchers have argued that the exact 'aerobic' nature of many ATAD reactors is questionable. Anoxic and anaerobic conditions may be prevalent to some extent in many operating reactors (Eloff *et al.*, 2000). Traditionally, detention times required for thermophilic treatment have been significantly shorter than those found in mesophilic processes. This is due to the higher biodegradation rates. LaPara and Alleman (1999) reported that, in general, substrate utilisation rates are 3-10 times greater during thermophilic aerobic treatment than those observed in analogous mesophilic processes. However, recent experimental results have disputed that this is necessarily the case (LaPara *et al.*, 2000a; Lapara *et al.*, 2001) as degradation rates in thermophilic systems were found to be relatively constant throughout the temperature range 25 °C to 65 °C,

with thermophilic cultures less adept than mesophiles at simultaneously utilising multiple substrates.

Early investigations into thermophilic aerobic digestion reported high biodegradation rates, low levels of dissolved oxygen in the aeration basin, and poor bacterial settling qualities (LaPara and Alleman, 1999). Autothermal operation was first reported by McNary *et al.* (1956) during a pilot-scale study of a high strength citrus wastewater. The first full-scale treatments at thermophilic temperatures are reported to have occurred accidentally when aerobic reactors treating high strength wastes experienced temperature shifts into the thermophilic realm (LaPara and Alleman, 1999).

Full scale ATAD processes have been in operation in Europe since 1977. The first full-scale plant was commissioned in Vilsbiburg in Germany in 1977 (LaPara and Alleman, 1999). ATAD plants are now in use across Europe and, following recognition by the US EPA, many ATAD facilities are now in operation in the US and Canada. It is estimated that 35 ATAD systems are operating on the North American continent (Metcalf *et al.*, 2001). Killarney Wastewater Treatment Plant is the only facility which employs ATAD for the treatment of municipal secondary sludge in Ireland.

The Water Environmental Research Federation (WERF) recently classified ATAD as an established process for the treatment of sludge, as opposed to innovative or embryonic (Kelly, 2003). However, many fundamental operating parameters such as pH, temperature and retention time have not been successfully related to system performance

and, in such studies as they have, the comparisons have been somewhat contradictory (LaPara and Alleman, 1999). The poor understanding of system parameters is coupled with a limited knowledge of the microbes found in ATAD systems; their lifestyles and functions.

2.2.2 Microbiology

Micro-organisms which inhabit high temperature environments are defined as thermophiles if optimum growth temperatures are greater than 45 °C (Amend and Shock, 2001). Thermophiles can then be further subdivided into the following categories: thermotolerant, facultative thermophilic, moderate thermophilic and extremely thermophilic, depending on optimal temperatures for growth. Little is known about the microbial populations supported by ATAD reactors. Research in the area has been hindered by difficulties associated with isolating thermophilic cultures, though it is reported that *Bacillus* and *Bacillus*-like organisms have been isolated (LaPara and Alleman, 1999). Sonnleitner and Fiechter (1983) stated that the active thermophilic microflora in aerobic thermophilic sludge is quite homogenous in nature and consists nearly entirely of thermophilic neutrophilic *Bacilli* of which more than 95% have been identified as *Bacillus stearothermophilus*.

New molecular techniques which allow study of bacterial diversity in wastewater treatment systems in a culture-independent manner are now allowing researchers to profile microbial dynamics in thermophilic systems in greater detail. Most of these

techniques are based on the genes encoding ribosomal RNA, such as fluoresecence in situ hybridisation (FISH) and length heterogeneity analysis of polymerase chain reaction-amplified DNA (LH-PCR) (Tiirola *et al.*, 2003, Wagner *et al.*, 2002). These techniques which have been broadly applied only in the past decade are demonstrating that many of the suggested model organisms which are thought to play key roles in the microbiologically-driven processes in wastewater treatment systems are of minor importance *in situ*, and other organisms, which are not yet culturable, are of greater importance (Wagner *et al.*, 2002).

In an aerobic thermophilic biofilm process, Tiirola *et al.* (2003) used LH-PCR as a technique and found that *Bacillus spp.* were not present in significant numbers and only dominated following upset process conditions such as alkaline shock. They suggested that the tendency of *Bacillus spp.* to sporulate and short retention times favoured the bacteria in extreme conditions.

Piterina *et al.* (2006) investigated the thermotolerant and thermophilic bacteria community present in sludge sampled from Reactor 2A at Killarney ATAD plant by analysis of a clone library constructed of ATAD community 16S rDNA genes. They found that thermophilic *Bacillus,* and *Paenibacillus* species were dominant. In a small number of cases they detected phylotypes which clustered obligate anaerobes in the low G+C gram-positive *Clostridia* and *Peptostreptococcaceae* divisions. It was postulated that the presence of these anaerobes within the ATAD system may be indicative of anoxic zones.

Brock (1986) described an early theory of thermophiles proposed by Allen (1950). This theory suggested that thermophilic micro-organisms are able to grow at high temperatures because they rapidly replace the cell material that is destroyed at thermophilic temperatures by active metabolism. However, subsequent research has shown that thermophilic growth is based on the thermostability of the cell components (Brock, 1986).

In the case of the ATAD process, a comprehensive description of microbial dynamics with proposed model organisms has yet to be developed. Considering the relatively recent increase in, and availability of, molecular characterisation techniques, which are superior to traditional culture methods, this is an area worthy of investigation. By using PCR techniques, Lapara *et al.* (2001) correlated microbial community structure with COD removal efficiency in a thermophilic aerobic digestion (TAD) reactor which was treating a pharmaceutical wastewater. They found that the number of distinct bacterial communities declined as a function of increasing temperature. This decline correlated with a reduced ability to remove soluble COD. It suggested that thermophilic populations are not well adapted to utilising complex substrates.

There are very few reports in the literature of studies comparing variation in the microbial flora between different ATAD plants or of the impact of specific species on process performance. Hence, conclusions cannot be drawn on whether there is significant variation in microbial communities at different operating temperatures, at different

retention times, or of microbes selectively favoured by different substrates. This is an area worthy of future research.

2.2.3 Substrate metabolism and enzymatic activity

It is widely reported that proteolysis is the major enzymatic activity occurring during aerobic thermophilic digestion. Bomio (1990) reported that no other enzymatic activities are detectable in the thermophilic treatment of WAS. It has been demonstrated that thermophilic bacterial culture supernatants are capable of hydrolysing various soluble proteins (Kim *et al.*, 2002). *Bacillus spp.* are known to produce heat-stable extracellular proteases which degrade vegetative bacterial cells. Ponti *et al.* (1995a) and Bomio (1990) established a relationship between increased aeration, proteolytic activity and nitrogen reduction.

Ugwuanyi *et al.* (2004) investigated cellulolytic and amylase activity in the thermophilic digestion of a model agricultural waste. Their results appeared to contradict Bomio (1990) but they argued that they, in fact, supported the work insofar as the activity required for the breakdown of the principal polymer in the waste stream appears quickly during digestion. In the case of potato peelings, this was amylase activity, the principal carbon source being starch; for WAS it was protease activity as the principle carbon source was protein.

In view of the reported enzymatic activity of thermophilic populations, two-stage systems have been investigated. In such two-stage systems, sludge is subjected to thermophilic aerobic digestion followed by mesophilic aerobic or anaerobic digestion on the basis that solubilisation during the thermophilic creates a nutrient rich substrate for the subsequent mesophilic stage (Borowski and Szopa, 2007; Suvilampi *et al.*, 2003). For two-stage thermophilic aerobic-mesophilic anaerobic the retention time in the thermophilic stage can be as short as 24 hours (Borowski and Szopa, 2007). This ensures that little sludge stabilisation occurs in the first step, but rather is a pre-treatment step in which solubilisation of complex substrates occurs (acidification). The mesophilic anaerobic step has a significantly longer retention time (8-15 days), however, this is still shorter than the retention time in typical single-stage mesophilic anaerobic digestion regimes. The shorter retention time results from the large quantity of soluble products made available by the pre-treatment step.

Borowski and Szopa (2007) conducted a series of laboratory-scale experiments comparing dual-digestion of municipal sewage sludge with anaerobic digestion. For the dual digestion system a thermophilic aerobic digester operated at 55 ± 2 ^{o}C with a working volume of 7 L was used for the pre-treatment step, followed by a temperature controlled anaerobic digester operated at 35 ± 1 ^{o}C of 7 L working volume as the secondary treatment step. A second anaerobic digester also of 7 L working volume was used as the control. Under optimal conditions, the dual digestion system reduced overall digestion time by 30% in comparison to the control single stage anaerobic digestion (the digestion end-point was determined when biogas evolution became negligible).

In an earlier study by Lapara *et al.* (2001), a two stage thermophilic-mesophilic aerobic system (50 °C – 30 °C) was investigated and compared with a two stage mesophilic-mesophilic (30 °C – 30 °C) aerobic system to treat a pharmaceutical wastewater containing high levels of sulphate. They found that there was a higher level of residual soluble COD in the effluent from the thermophilic-mesophilic system than from the mesophilic-mesophilic system. They postulated that thermophilic-mesophilic system produced recalcitrant soluble microbial products during the thermophilic step. However, as the waste streams investigated in this study differed from those investigated by Borowski and Szopa (2007), and, furthermore, the mesophilic step was aerobic digestion as opposed to anaerobic the results of the two studies cannot be directly compared.

2.2.4 Process Parameters

The following sections give an overview of the current knowledge base of the ATAD process in terms of some key process control parameters: temperature, COD removal, pH and oxygen requirements.

2.2.4.1 Temperature

Early studies of the ATAD process at bench scale determined that the temperature at which biological activity peaked was 45 °C (Streebin, 1968). This was on the basis of specific oxygen utilisation rate (SOUR) measurements. Milenko and Zupancic (2002)

found that traditional aerobic models do not hold at thermophilic temperatures. They also argued that biodegradation rates increase to a maximum at 50 °C, and then decline, as the low solubility of oxygen in sludge at temperatures above 50 °C cannot meet microbial oxygen demand. LaPara and Alleman (1999) put forward contradictory findings to those of Milenko and Zupancic (2002) showing that several researchers have concluded that the effects of temperature on oxygen transfer in ATAD systems is virtually negligible as low solubility at high temperatures is offset by improved overall mass transfer rates due to decreased viscosity and diffusivity.

Various contradictory values have been quoted in the literature as the optimum temperature for substrate removal in thermophilic aerobic digestion; 50 °C (Rudolfs and Amberg, 1953), 55 °C (Hunter *et al.*, 1966; Milenko and Zupancic, 2002), 58 °C (Surucu, 1975), and as low as 30 °C (Visvanathan and Nhien, 1995). It is important to note that these researchers were using different variations of thermophilic aerobic digestion, ranging from fixed filters to suspended biomass, and that the types of substrate being degraded also differed. The *Arrheinus* equation (Equation 2.2) describes the effect of temperature on the rate constant (Droste 1997).

$$(K_d)_T = (K_d)_{20^0C}\,\theta^{T-20} \qquad (2.2)$$

Where

$(K_d)_T$ is the digestion decay constant at any temperature

$(K_d)_{20\,^oC}$ is the digestion decay constant at 20 °C

θ is the temperature coefficient, which generally ranges from 1.020 to 1.1 for different biological treatment processes (Droste, 1997; Metcalf *et al.*, 2001)

T is temperature in ^{o}C

This equation predicts a linear increase in digestion rate in accordance with an increase in temperature.

According to Mihaltz *et al.* (2003) the fundamental mathematical modelling of thermophilic digestion has been neglected in the literature and traditional activated sludge models cannot be extended into the thermophilic zone. As a more suitable alternative, they proposed a dual-substrate kinetic model which also takes into account the probability of thermophilic cells/spores in the feed evolving into active biomass. Their model predictions showed a good fit with reported experimental results.

Gomez *et al.,* (2007) presented a new and comprehensive mathematical model for ATAD digestion. The model separated the ATAD reactor into two completely mixed volumes, these being the liquid and the gaseous phases. The model was made up of two sub-models; a mass balance model and an energy balance model. Included in the model were biochemical transformations based on the standard Activated Sludge Models of the International Water Association. They used the model to simulate ATAD reactor performance in two separate scenarios: ATAD as the first step in a dual digestion system operating on a 5 day retention time and; ATAD as a single-stage sludge treatment

operating on a 10 day retention time. The models results were not validated by comparison to experimental results.

Lapara *et al.*, (2001) found that the extent of soluble COD removal in a batch reactor treating a pharmaceutical wastewater declined as temperature increased by an average of 60mg/L per °C. Their experiments were conducted at temperatures ranging from 30 °C to 70 °C with temperature being raised in 5 °C increments. They found that temperature served as a selective pressure for bacterial community development during aerobic digestion. At temperatures approaching 60 °C this selective pressure is likely to reduce the efficiency of the biomass being able to utilise multiple substrates. LaPara and Alleman (1999) also stated, that, in the case of ATAD, the physico-chemical and biological characteristics are so different from those of the activated sludge process, that the knowledge base from conventional operations is not applicable to the ATAD process. However, many textbooks and papers make the assumption that simple models based on the *Arrheinus* equation can be applied to the ATAD process (Droste, 1997; Kelly and Mavinic, 2003). A more rigorous approach to modelling the relationship between ATAD digestion rates and temperature is therefore required. Evidently, temperature of operation is a fundamentally important variable in the consideration of the ATAD process, and yet, as pointed out by Ugwuanyi *et al.* (2004), despite many empirical reports on the effect of temperature of operation on the ATAD process it has yet to be quantified in an appropriately rigorous manner

The degree-day product (Droste, 1997; Mavinic and Koers, 1979) is an empirical relationship between sludge retention time and temperature which has been proposed to account for the effect of retention time on various kinetic functions such as substrate utilisation and pathogen inactivation and reduction. Equation 2.3 describes the degree-day product

$$P_T = \theta_d \times T \qquad (2.3)$$

Where

θ_d is retention time in days and

T is temperature in °C

Mavinic and Koers (1979) found, that in laboratory and field-scale studies at temperatures ranging between 5 and 20 °C, the amount of digestion achieved attained a maximum at a P_T equal to 250°-*d*. The degree-day product can also be used to assess guideline temperature and subsequent retention time values in situations such as where pasteurisation is a necessity for an ATAD system (Murthy *et al.*, 2000). For instance, in the case of an ATAD process required to operate at a retention time of 5 days at 50 °C (a P_T of 250°-*d*), the same system would only have to operate at a retention time of 4.2 days when operating at a temperature of 60 °C in order to maintain a P_T of 250°-d.

Several time-temperature equations are outlined in the US EPA Biosolids Rule 503 regulations. These equations are used to calculate the minimum retention times required

in the thermophilic treatment of Biosolids to achieve a Class A product. The equations take into consideration the solid-liquid nature of the Biosolids being heated, along with the particle size and how particles are brought into contact with heat. For Biosolids with TS of 7% (w/w) or less, equation 2.4 is used.

$$D = \frac{50,070,000}{10^{0.14t}} \qquad (2.4)$$

Where D is the time required (days) and t is the temperature in degrees Celsius. It is also stipulated that the temperature of the Biosolids must be at 50 °C or higher and that the contact time at that temperature must be at least 30 minutes.

2.2.4.2 Total COD Removal

In a TAD reactor, operating between 62 and 64 °C, Ponti *et al.* (1995b) showed that the rate of Chemical Oxygen Demand (COD) removal increased as a function of the COD content of the feed, and suggested that at loading rates of 20 kg COD m^{-3} or less, the degradative efficiency of the biomass was compromised. Conversely, a decrease of the bacterial degradative efficiency resulting from higher organic contents in the feed was not observed; they concluded that concentrations of up to 60 kg COD m^{-3} can be used without affecting degradative processes.

Thermophiles have been shown to be poorly adept at utilising multiple substrates (LaPara *et al.*, 2000a) and thermophilic cultures also exhibit poor cell membrane integrity under substrate depleted conditions (LaPara *et al.*, 2001). LaPara *et al.* (2000b) found that

growth yields in thermophilic biotreatment were similar to those in analogous mesophilic processes. These findings contradict some of the purported benefits of operating the ATAD process; these being rapid biodegradation rates coupled with low growth yields.

2.2.4.4 pH

Alkaline conditions typically predominate in ATAD reactors, with the pH of the reactor contents ranging between 8 and 9.5 (Ponti *et al.*, 1995b; Eloff *et al.*, 2000; Ugwuanyi *et al.*, 2004). The high pH found in ATAD reactors is thought to be linked to the ammonification of proteinaceous material in the sludge (Ponti *et al.*, 1995b). It is extensively reported that nitrifying bacteria are not found in sludge at thermophilic temperatures (LaPara and Alleman, 1999; Ugwuanyi *et al.*, 2004). Mineralization of organic nitrogen releases nitrogen in the form of NH_4^+ which is of benefit as it raises the nutrient value of the sludge for land application. Ponti *et al.* (1995a) found, at lower aeration rates, nitrogen reduction was reduced due to lower metabolic rates, as measured by proteolytic activity. Eloff *et al.* (2000) noted that free ammonia stripping is prevalent in ATAD reactors. This is due to the equilibrium chemistry of the NH_4^+-NH_3 couple favouring the gaseous NH^3 phase at thermophilic temperatures. In the absence of nitrifying bacteria, this stripping is the only mechanism by which significant quantities of ammonia are removed during the ATAD process.

There are very few data in the literature relating to the relationship between pH and digestion performance. Both LaPara and Alleman (1999) and Ugwuanyi *et al.* (2004)

remarked that no thorough studies have investigated this important parameter. Baudet *et al.* (1990) found that thermophilic biofilms deteriorated as the pH of reactions increased to 8.5 in an investigation of thermophilic aerobic digestion of pig slurry. Thermophiles found in ATAD reactors have been shown to be neutrophilic in nature (Sonnleitner and Fiechter, 1983).

As a process control parameter, pH is useful as an indicator of upset conditions in an ATAD process. The presence of anaerobic or anoxic conditions leads to pH depression due to the production of fermentation products such as VFAs (Chu *et al.*, 1994).

2.2.4.5 Oxygen requirements

It has been suggested that ambient dissolved oxygen levels of 0.5 mg/L are acceptable in ATAD systems. At thermophilic temperatures, oxygen solubility drops to 4 mg/L (Eloff *et al.*, 2000) Such low oxygen levels, coupled with the high oxygen uptake rates which are thought to exist at ATAD temperatures, characterise a system which may contain anoxic zones. Tiirola *et al.* (2003) reported that *Clostridium* and other facultative anaerobes have been shown to be present as viable cell forming units in ATAD systems, and Piterina *et al.* (2006) also reported the presence of obligate anaerobes in sludge treated by ATAD, but whether these microbes thrived in the ATAD environment or simply passed through the system was not clear.

2.2.5 ATAD design and engineering

2.2.5.1 Traditional ATAD Design

Many currently operating ATAD reactors are retrofitted mesophilic aerobic reactors (LaPara and Alleman, 1999). However, most recently commissioned ATAD reactors have been conceived and designed to operate at ATAD temperatures exclusively. Reactor sizes are generally smaller than those in analogous mesophilic systems. This is due to increased throughput, resulting from shorter retention times. ATAD systems can be operated in continuous, batch or semi-batch modes. Retention times vary significantly, as do size, temperature of operation, methods of aeration and foam-control employed. Most ATAD systems used for secondary sludge digestion are operated in a flexible multi-tank configuration. Ultimately, the number of reactors that are used will depend on the hydraulic loading. For instance, in areas where large fluctuations in feed occur (such as in resort areas) three or more reactors may be required to cope with changing influent loading on a seasonal basis such as at Killarney WWTP. In multiple tank configurations, the first reactor can be used as a balancing tank, and the subsequent reactor levels can then be controlled by hydraulic displacement as sludge is pumped in (Stentiford, 2002). Typically, semi-batch systems, such as at Killarney WWTP, are fed once per day, with the feed sludge being pumped in over a period of approximately 1 hour. This allows for the biomass to be in held at thermophilic temperatures for 23 hours.

In situations where a single reactor is used, and a pasteurised end product is required, true batch operation is required. Similarly, in situations where semi-continuous and

continuous treatment is utilised, multiple tank configurations are required to provide plug-flow conditions required to achieve pasteurisation.

2.2.5.2 Aeration

Several types of aeration equipment are used in ATAD reactors. These include circular aerators, turborators, spiral aerators, Venturi pump aerators and diffused air systems (Kelly, 2003). It has been suggested that the use of diffused-air systems results in lower shear-rates within ATAD reactors, producing a sludge which is less disperse and more amenable to dewatering (Staton *et al.,* 2001). However, little published data is available to validate these claims.

2.2.5.3 Foaming

Foaming often occurs in ATAD reactors, but most reactors are now equipped to deal with foam problems using mechanical foam cutters. Some researchers suggested that the presence of a certain level of foam can serve as an insulating factor in ATAD reactors (Kelly and Mavinic, 2003). However, excessive foam is problematic and could only be considered an insulation benefit in a situation where an ATAD reactor was open to the atmosphere. Foaming is thought to be most prevalent at a transitional stage following feeding, and is reportedly linked to the lysis products of mesophilic cells which act as surfactants (Kelly and Mavinic, 2003). Chemical foam-block agents can be used to help reduce foam in ATAD reactors.

2.2.5.4 Second generation ATAD

Recently, so-called 'second generation' ATAD reactors have been developed. These differ from traditional models in the following ways. Only one large tank is used, and air is supplied via a diffused air method which also incorporates foam control. In second generation ATAD, Oxidation-Reduction Potential (ORP) is used to indirectly measure the microbial oxygen demand. Oxygen demand has been shown to be highest during a 'burn' period following feeding (Staton *et al.*, 2001). ORP measurements are employed as a feedback control mechanism. This allows the rate of aeration to be scaled back during periods of less intense microbial oxygen demand, thus cutting operational costs. Due to their recent development, apart from the manufacturer's specifications of the system, very little operational data are available relating to the performance of second generation ATAD systems.

2.3 Sewage Sludge Dewatering

2.3.1 Introduction

The field of sewage sludge dewatering incorporates the interest of a range of disciplines from engineering, chemistry and biology. This section identifies and discusses the principal factors which are thought to control dewaterability of sewage sludge. The fundamental filtration and compressibility theories which are used to model the physical properties of the sludge are also introduced and appraised.

Sewage sludges are markedly more difficult to dewater than inorganic sludges, and often exhibit permeability which is orders of magnitude lower than typical inorganic sludges (Kapur *et al.*, 2002). However, the dewatering devices (belt filter presses and centrifuges) employed, and the methods of conditioning which are used to dewater sewage sludges are similar to those utilised with inorganic sludge, so there is an element of overlap in theory and in the experimental literature, especially in the fundamental modelling of dewatering.

2.3.2 Water distribution in sewage sludge

The distribution of water in sewage sludge is an important consideration in dewatering investigations. Of particular interest is the evaluation and quantification of the properties of water which is available for removal in dewatering unit operations. It is generally accepted that sewage sludges are amongst the most difficult sludges to dewater (Stickland *et al.,* 2003). Sewage sludge, whether it be waste activated sludge, anaerobic sludge, ATAD sludge, or otherwise, is a complex mixture of bacteria, extracellular polymeric substances and other organic and inorganic substances. The most notable component of sewage sludge is water which usually accounts for over 97% of the sludge content. Though sewage sludges, in general, are highly compressible substances, compression times are exponentially longer than those exhibited by inorganic sludges. This is due to their exceptionally low permeability and gel-like nature (La Heij *et al.*, 1996; Wu *et al.*, 2001; Kapur *et al.*, 2002). Furthermore, anaerobically digested, aerobically digested, and ATAD digested sludges all exhibit different behaviour in terms of floc-morphological,

chemical and biological characteristics, and hence, dewaterability (Novak and Park, 2003). An understanding of water distribution in sewage sludge is helpful in describing filtration and expression dynamics.

2.3.2.1 Bound and free water

Due to the presence of solids, all water within the sludge does not have similar properties in terms of vapour pressure, viscosity and density (Katsiris and Kouzeli-Katsiri, 1987; Vesilind and Hsu, 1997). Hence, researchers have categorised water present in sewage sludge into two broad categories 'free water' and 'bound water' (Vesilind and Hsu, 1997; Lee and Wang, 2000; Vaxelaire and Cezac, 2004). The 'free water' is considered to be the water which is not influenced by solid particles and the 'bound water' is considered to be the water whose properties are modified due to the presence of solids. It is generally accepted that all of the 'free water' can be removed by mechanical means, though there are contradictory reports regarding the force required to remove it. Smollen, (1990) proposes that all 'free water' can be removed from an activated sludge by a moderate stress (vacuum filtration under 5×10^4 Pa for 30 minutes), while Lee (1995) concludes that high pressures (usually larger than 28 MPa) are necessary to extract all the 'free water' within an activated sludge. Vesilind further subdivides water held in activated sludge into four types (Vesilind and Hsu, 1997):

- Free water, which freezes at normal temperature

- Interstitial water, which freezes at lower temperatures, due to a high dissolved solids content
- Vicinal water, which is associated with solid surfaces and freezes only at very low temperatures
- Water of hydration, which does not enter the ice crystal phase and which can only be removed from the sludge by thermal means

Of these four types, interstitial, vicinal and water of hydration are often grouped together under the heading 'bound water'

Vaxelaire and Cezac (2004) noted that this classification does not take into account a large amount of water which is trapped within the polymer network, and Mikkelsen and Keiding (2002) introduced another term 'water holding' to describe surface bound water and osmotic water as well as water trapped within this polymer network. In a separate paper, Keiding and co-workers (2001) argued against concepts of 'bound water' and 'free water', and proposed instead that the colligative properties of sewage sludges; such as boiling point elevation, freezing point depression, osmotic pressure and water activity can be used to describe sewage sludge dewatering behaviour. They noted swelling effects in extra-cellular polymer networks of sewage sludge, which resulted from the osmotic pressure difference between these polymer networks and the surrounding bulk water. When this was taken into account, they showed that the expression step in sewage sludge dewatering represented the deswelling of these networks. Keiding and Rasmussen (2003) proposed a simple filtration model based on the Carmeny-Cozen equation in which the

driving force is the difference between the applied external pressure and the osmotic pressure of the filter-cake. They successfully used the model and predict with some accuracy the filtration behaviour of a sewage sludge.

2.3.2.2 Measurements of bound water

Several methods are proposed in the literature for the measurement of 'bound water'. These measurements are based on the premise that 'bound water' exhibits different chemical properties to 'free water' and the amount of 'bound water' in a given sample can be quantified according to these properties. The use of a dilatometer was considered by Colin and Gazbar (1995). The dilatometer measures 'bound water' as that which does not freeze at -20 ^{o}C. The 'free water', which freezes, displaces a volume of indicator fluid and from the total water concentration (measured by drying overnight at 103 ^{o}C). The 'bound water' content can then be established. Drying tests were also used in the literature to determine water properties within sewage sludge. In a drying test, a curve is plotted displaying the evolution of the evaporation flux versus the mean moisture content of the sludge cake (Vaxelaire and Cezac, 2004).

Other methods used to determine water distribution in sludge include, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) tests, and also, mechanical strain tests including filtration, expression and centrifugation tests. There are numerous drawbacks associated with all of these tests and Vaxelaire and Cezac (2004) concluded that no one technique is preferable to the others, and also warned that interpretation of

results reported in the literature should be approached cautiously, as reported experimental conditions vary. For example, Lee (1995) performed drying tests at 40 °C and Chen *et al.* (1997) do the same at 80 °C. Vesilind and Hsu (1997) conducted dilatometric measurements at -8°C, and Colin and Gazbar (1995) did similar tests at -20 °C.

Vaxelaire and Cezac (2004) concluded that perhaps the most useful and straightforward method of determining at least the water which can be removed by mechanical means, are the mechanical strain tests, such as C-P cells, which can be used to evaluate the upper limits of various conventional dewatering devices. The C-P cell is discussed in greater detail in section 2.4.

2.3.3 Extracellular Polymeric Substances (EPS)

2.3.3.1 Definition

Extracellular polymeric substances (EPS) is a general term for a wide variety of substances which are produced by micro-organisms. The substances include polysaccharides, proteins, nucleic acids, lipids and other polymeric compounds which have been found to occur in the intracellular space of microbial aggregates. The total mass of EPS (EPS and water trapped within the EPS matrix) has been shown to account for up to 80% of the solid mass of activated sludge (Frolund *et al.*, 1996). Li and

Ganczarczyk (1990) found that EPS formed the third biggest fraction in activated sludge after microbial cells and water.

As is suggested by their name, EPS are found at, or outside, the micro-organism cell surface. In activated sludge systems, the majority of micro-organisms live in aggregate communities such as films or flocs. The EPS matrix serves several functions. It provides a stable living environment for the micro-organisms which is resistant to desiccation, biocides and other harmful effects. It also aids in the adsorption of substrate particles by accumulating nutrients, and is involved in enzymatic activities aiding solubilisation of substrate. The EPS trap and bind organic materials in close proximity to the bacterial cell. Hydrolytic enzymes, also localised close to the cells, hydrolyse the sorbed organic matter. This allows for the efficient uptake of low-formula-weight hydrolysis products by reducing diffusion loss of products to the surrounding water.

The EPS effectively forms a matrix within which the micro-organisms are embedded. This allows them to live in high density symbiotic communities. In some respects, EPS can be considered the backbone or exoskeleton of activated sludge flocs. The methods by which EPS help to form floc-structures are not fully understood, but it is thought that a combination of surface charge and the hydrophobicity of EPS is an important parameter controlling floc formation (Sponza, 2003).

2.3.3.2 Protein and polysaccharide fractions of EPS

Proteins and polysaccharides have been shown to account for up to 70% of the total extracellular organic carbon in an activated sludge (Dignac *et al.*, 1998). However, there is little consensus in the literature as to the relationship between these two substances and which, if either, exerts the most control on floc properties. For instance, much of the research has focussed exclusively on the polysaccharide fraction of EPS (Forster, 1971; Jorand *et al.*, 1995; Sponza, 2003) and for many years carbohydrate was considered the main component of EPS in pure cultures. However, more recent work in wastewater treatment plants suggested that protein is also a very important, if not more important constituent of EPS. Liu and Fang (2002) found that 41.3% of EPS extracted from a methanogenic sludge was composed of proteins. Other researchers have also found that the quantity of extracellular proteins exceeds that of extracellular polysaccharides in activated sludge (Urbain *et al.*, 1993; Jorand *et al.*, 1995; Higgins and Novak, 1997a; Mikkelsen and Keiding, 2002; Garnier *et al.*, 2005).

Garnier *et al.* (2005) used a combination of size-exclusion chromatography and infrared micro-spectroscopy to investigate the molecular weight and properties of EPS found in an activated sludge. Their results suggest that the protein fraction can be subdivided into two types, which vary mainly in the length of associated alkyl chains and in ester/acidic functionalities. Type A had short alkyl chains, while Type B had notably longer alkyl chains. Protein sizes ranged from 45-670 kilo Daltons (kDa). Polysaccharides were of a smaller size <1 kDa and were present in smaller amounts. Notable also, was the presence

of a third family of compounds, proteins of a low molecular weight associated with polysaccharides. They postulated that these polysaccharide-associated proteins may be the same lectin-like protein that Novak and Park (2003) believed to play a key role in bioflocculation.

Differences in the protein/polysaccharide ratio in activated sludge resulting from different treatment systems would be expected to vary widely. This could be due to differences in lifestyles and hence dietary and waste profiles of the populations being treated, variations in industrial wastewaters treated, and the differing activated sludge treatment methods which are being employed.

2.3.3.3 Soluble and bound EPS

Lapsidou and Rittmann, (2002) identified two schools of thought regarding the classification of solution biopolymers. They named these the "EPS school of thought" and the "soluble microbial product (SMP) school of thought". The 'EPS school' subdivided EPS into the following two categories:

- Bound EPS (sheaths, capsular polymers, condensed gel, loosely bound polymers, and attached organic material)
- Soluble EPS (soluble macro-molecules, colloids and slimes)

The 'SMP school' argued that the fraction referred to as soluble EPS by the 'EPS school' was actually SMP, and researchers accounted for this by referring to it as 'soluble' EPS. Because the 'EPS school' only focussed on EPS and active biomass, they assumed that some of the EPS was soluble.

2.3.3.4 EPS extraction and recovery

When considering the EPS content of sludge it is important to note that composition of extracted EPS may be different to EPS which within the sludge sample. A lot of research regarding EPS focuses on extracted EPS, which is easier to study. However, as there is no universal EPS extraction method, it is very difficult to meaningfully compare and interpret published results (Liu and Fang, 2002).

Wilén *et al.* (2003) found a significant compositional difference between an activated sludge EPS fraction studied *in situ* and the compositional make-up of EPS extracted from the same sludge. This suggests that examining the chemical composition of undisturbed sludge flocs, as opposed to examining the extracted EPS, may provide more useful information about flocculation. They concluded that it may be insufficient or even inaccurate to characterise the polymeric material and its impact on flocculation properties based on extracted EPS alone, mainly due to the low extraction efficiency and difficulties involved in the EPS characterisation.

2.3.4 The role of EPS in sludge dewatering

As one of the principal components of sewage sludge, research has focussed on the precise role of EPS in sludge dewaterability. EPS has been shown to affect charge density and flocculating ability and hence, dewatering characteristics. Mikkelsen and Keiding (2002) found that the quantity of proteins and humics in sludge EPS correlated well with floc charge, while the EPS polysaccharide did not. They also found that sludge with a high EPS content exhibited strong floc structure which was characterised by a low degree of dispersion and low shear sensitivity. These findings contrast with traditional colloidal theory which predicts increased dispersion and reduced floc strength when electrostatic repulsion is increased. They postulated that polymer related forces are more likely to govern floc structure, and in particular the potential role of EPS protein in floc structure. The work of Lapsidou and Rittmann (2002) similarly found that protein played an important role in floc structure. They stated that due to the high content of negatively charged amino acids, proteins are more involved than sugars in electrostatic bonds with multivalent cations. This is a key factor in stabilising aggregate structure.

Liao *et al.* (2002) found that floc surface properties are the most important factor governing bioflocculation, while the EPS quantity is more important in controlling the settleability of the sludge. They examined the theory that large volumes of EPS have a negative effect on the compressibility of sludge and they found a significant correlation between total EPS and the sludge volume index (SVI). Reasons for this could include:

- Steric forces arising from the EPS
- The EPS may form a dense gel which prevents the expression of water from gel pores
- A complex and hydrated EPS within the floc matrix which has the capacity to retain water

They also suggested that increasing sludge retention time (SRT) could have a positive effect on activated sludge filterability, and on the density of sludge flocs. Sludges at high SRTs (16-20 days) displayed a tightly bound and smooth EPS matrix, with few loose bacterial cells. They believed that the relative importance of inter-particle interactions changes with lengthening SRT. Ionic interactions and hydrogen bonds were found to be more important at lower SRTs, while other mechanisms related to the composition and arrangement of EPS, and the more hydrophobic nature of flocs, took precedence at higher SRTs. Finally, they proposed a model to describe the complete floc structure.

Mikkelsen and Keiding (2002) also concluded that bound EPS aids settleability. They stated that sludges with a higher extractable EPS concentration have a tendency to form larger flocs and thus have good filterability. However, dewaterability as expressed by caked dry matter (CDM) of the filter cake was found to worsen as a function of increased EPS content. They believed that reduced dewaterability was caused by an increase in interstitial water within the floc. Low EPS sludges show good dewaterability in terms of CDM but these sludges are prone to blinding problems (in dewatering unit operations) due to a high degree of dispersion.

Neyens *et al.* (2004) argued that the effect of EPS on sludge dewatering is ambiguous. They pointed out that increased levels of EPS may initially aid in sludge dewaterability because of an increase in flocculation due to polymer entanglement. However, once a certain level of sludge flocculation has been attained, further increases in EPS become detrimental to sludge dewaterability, due to the highly hydrated nature of EPS retaining water within the sludge matrix. This counteracts the benefits of its flocculant properties.

Wilén *et al.* (2003) examined the influence of the chemical constituents of activated sludge and EPS on the surface properties of flocs. The role of EPS was found to be very important in bioflocculation. Since most of the EPS contains a heterogeneous mixture of functional groups, it was suggested that flocs can bind by hydrophobic interaction, protein-polysaccharide interaction, hydrogen bonding and ionic interaction. They found that surface charge was governed by more complicated factors than previously thought, and that the protein content of EPS had the strongest influence on floc surface properties.

Sponza (2003) noted that the settling efficiency of flocs depends on their surface characteristics and the EPS composition of bacterial cells, and that the nature of the influent wastewater, rather than process operating conditions has the biggest impact on the EPS composition.

A proper understanding of the role of EPS in the dewaterability of sludge and hence the optimisation of EPS levels to a point which best aids dewaterability could be of major

benefit to plant managers seeking to lower dewatering costs. This could be achieved by altering feedstock composition or otherwise manipulating operating conditions.

A number of workers have considered the possibility of manipulating digestion conditions to optimise EPS content. Spinosa and Lotito (2003) attributed high SVI to lower hydrophobic and more negatively charged surface properties of sludge flocs. Sponza (2003) also related low SVI to large amounts of EPS in sludge samples.

Chen *et al.* (2004) investigated improving sewage sludge dewaterability by reducing EPS content. They found that a combined pre-treatment of sulphuric acid and a surfactant markedly improved sludge dewaterability, in the case of both the centrifugation tests and filtration tests. This improvement was thought to be a direct result of the action of the surfactant on surface EPS, causing it to be reduced.

Houghton and Stephenson (2002) determined that the use of a high carbohydrate feed had a significant impact on the extractable EPS content and dewaterability of anaerobically digested sludge. A high extractable EPS content correlated with increased CST. This impact was not related to the size distribution of the particles. In their studies they found that a calculated EPS yield of 17.2 mg/g suspended solids appeared to be necessary for optimum sludge dewaterability. They believed that optimisation of sludge dewaterability by controlling EPS yield is an area worthy of further study

While it is evident that EPS is an important factor governing activated sludge dewatering behaviour in terms of settling, it is soluble/colloidal EPS, or solution biopolymers that are thought to play the most important role in the dewatering of digested sludges such as ATAD and anaerobic sludges. During digestion, these negatively charged biopolymers are released into solution as a result of erosion of the activated sludge floc structure and cell lysis. These substances are widely thought to have a negative effect on dewatering properties of digested sludges (Murthy *et al.*, 2000; Zhou *et al.*, 2003).

2.3.5 The role of cations in sludge dewatering

Various studies have sought to determine the true role of cations in sludge flocculation and subsequent dewatering operations. Much of this work has focused on the ratio between monovalent/divalent cations and their importance in the structure of the EPS matrix. In general, bioflocs such as those found in activated sludge systems have a net negative charge which is a result of functional groups present on the EPS (Sobeck and Higgins, 2002). Because of this net negative charge, the role of cations in bioflocculation is thought to be important, and it has been well studied (Higgins and Novak, 1997b; Cousin and Ganczarczyk, 1998; Sobeck and Higgins, 2002; Novak *et al.*, 2003).

A number of theories have been put forward to describe the role of cations in sludge flocculation. These include DLVO theory, named after its developers, Derjaguin, Landau, Verwey, and Overbeek (Adamson, 1990), alginate theory (Bruus *et al.*, 1992), and divalent cation bridging theory (Tezuka, 1969; Sobeck and Higgins, 2002). Sobeck and

Higgins (2002) postulated that the cation divalent bridging theory best explains the process of cation-induced bioflocculation.

Sobeck and Higgins (2002) believed that discrepancies and contradictions found in earlier studies of the role of cations in sludge flocculation may have resulted from the use of batch tests as opposed to continuous flow reactor studies. They suggested that sludges with a higher proportion of monovalent cations to divalent cations exhibit weaker floc structure, and are therefore more susceptible to floc breakage in conditions of high shear. Studies by Novak and co-workers have confirmed this (Murthy *et al.*, 2000; Novak and Park, 2003). They concluded that operators of activated sludge systems should try to lower the ratio of monovalent to divalent cations to improve floc properties and treatment performance.

Their work also proposed that different types of biopolymer are digested under aerobic and anaerobic digestion respectively (Novak and Park, 2003). Anaerobic digestion resulted in the release of a relatively larger proportion of proteinaceous material into solution and aerobic digestion resulted in the release of a higher proportion of polysaccharides. They suggested that cations are involved in two different binding mechanisms in sludge flocs. Lectin-like proteins are linked to polysaccharides by calcium and magnesium ions, and this is the portion thought to be degraded by aerobic digestion. A different portion of protein is thought to be retained by iron in flocs. Iron is reduced during anaerobic digestion. This releases a greater volume of protein into solution than in aerobic digestion, leading to a much greater polymer demand for anaerobic sludge. They

suggested that both aerobic and anaerobic digested sludges exhibit increasingly deteriorating dewaterability as a function of retention time. Zhou *et al.*, (2003) found that this was not the case for ATAD sludge, and, after a short period of time in which dewatering properties deteriorated rapidly, further digestion had little effect on ATAD dewatering properties, perhaps suggesting that the initial heat-shock effects might be a significant factor in poor ATAD dewatering.

Novak noted that an increase in the potassium ion in solution is an indicator of cell lysis during digestion. However, this was not shown to occur during either anaerobic or aerobic sludge digestion. The implication of this was that much of the biopolymer released into solution was EPS resulting from the floc rather than intracellular substances (Novak *et al.*, 2003). No similar studies have been carried out for ATAD sludge. If it is assumed that ATAD results in extensive lysis of microbes in the feed sludge, then it is conceivable that longer SRTs would result in a sludge with better dewatering properties as some of this material is re-assimilated into the biomass.

2.3.6 Conditioning

2.3.6.1 Introduction

Sludge dewatering operations require the separation of liquid and solid phases in a relatively short period of time. To achieve this, a conditioning step is usually required to make the sludge more amenable to dewatering. Conditioning can be effected either by

physical means (eg freeze-thaw conditioning) or chemical means (addition of chemical flocculants and coagulants). Chemical conditioning is the preferred process in most wastewater treatment plants.

2.3.6.2 Chemical conditioning

The terms 'coagulant' and 'flocculant' are often used to describe the substances used in sludge conditioning. Both inorganic coagulants and polymeric flocculants are used. Coagulants are substances which are added to colloidal suspensions to bring about aggregation of the dispersed, charged solid phase by charge neutralisation, thus allowing it to settle out of solution. Flocculants are substances which can also effect charge neutralisation of colloidal material, but are distinguished from coagulants by the manner in which they serve as bridges between colloidal particles (Dentel, 2002).

Harbour *et al.* (2001) noted that the addition of polymer to water treatment, industrial and mineral sludge did not result in any increase in compressibility or in the final solids that could be achieved at a specific pressure. Many plant operators would disagree with this statement, but it should be noted that most dewatering operations do not proceed to equilibrium, so perceived improvements in the ultimate final solids achievable are often in fact a result of improved permeability (a quicker rate of dewatering).

Inorganic coagulants, most commonly salts of multivalent cations (such as $FeCl_5$ and $Ca(OH)_2$), effectively reduce the surface charge of solids, allowing solids particles to

aggregate and settle out of solution. This is known as 'patch flocculation' (Dentel, 2002). Inorganic coagulants are not commonly used in sewage sludge dewatering for a number of reasons. The volume of such salts required to successfully condition a sludge can increases the final caked dry matter (CDM) of a sludge by as much as 40%. This is in contrast to a volume increase of <1% for a typical organic polymer. Flocs resulting from the use of such coagulants are generally more susceptible to shear effects than those resulting from organic polymers. However, for ATAD sludge, there has been an increase in their use recently. Metal salts combined with varying amounts of organic polymer have been employed in many American WWTPs (Kelly and Mavinic, 2003). However, the volumes of such metal salts which are used vary markedly from plant to plant (Holbrook *et al.*, 2000). According to Kelly and Mavinic (2003) most ATAD plants in the USA have significantly cut dewatering costs by employing a combination of inorganic coagulants and polymeric flocculants. A study using ATAD Biosolids from three separate treatment plants in the USA; College Station (Texas), Princetown (Indiana), and Titusville, Florida (Murthy, 1998), found that the use of inorganic coagulants (alum and ferric chloride) in conjunction with cationic polymers significantly reduced conditioning costs.

It is thought that ATAD digestion results in a large amount of intracellular biopolymers being released into solution due to the lysis of mesophilic bacteria in the feed sludge and subsequent endogenous respiration (Zhou *et al.*, 2002). The exceptionally high levels of soluble COD, and protein and polysaccharides reportedly found in ATAD centrate reflect this (Murthy *et al.*, 2000; Zhou *et al.*, 2002). These biopolymers become dispersed in solution, and exert a significant conditioning demand on any flocculant used to condition ATAD sludge before flocculation occurs. Murthy *et al.* (2000) showed that the use of

inorganic coagulants as a pre-treatment step before the addition of high weight cationic polymers effectively sweeps up a lot of this colloidal detritus, thus reducing the optimal polymer dose. The resulting filtrate from sludge conditioned in this manner exhibited lower amounts of soluble COD and solution biopolymers than the sludge conditioned solely by high weight polymers. A rough economic model based on original conditioning costs of several American ATAD facilities show that conditioning costs could be brought in line with those of similar sized anaerobic treatment plants. However increased handling costs (transportation, storage, and disposal) were not taken into account (Murthy *et al.*, 2000)

2.3.6.3 High weight polymeric flocculants

High weight polymeric flocculants are frequently used as part of sewage sludge dewatering processes. Cationic polymers are generally employed as they combine charge neutralisation with bridging mechanisms. However, anionic polymers are also used in some cases (Dentel, 2002). The most frequently used flocculants are polymers derived from the acrylamide monomer. 100% acrylamide, the non-ionic homopolymer (derived from a single monomer species) is an effective flocculant, but its activity is usually enhanced by co-polymerisation (Owen *et al.*, 2002). Co-polymerisation can be utilised to introduce functional groups that have an affinity for a specific mineral phase or to provide charged groups that allow the polymer to take on an extended configuration in solution.

Polymers for use in sludge treatment are generally available in three physical forms: dry, liquid and emulsion. The choice of polymer is dependent on the type of sludge being treated, and handling costs etc. Liquid or emulsion polymers are generally preferable due to difficulties, such as dust effects and particle agglomeration, involved in adequately making up dry polymer solutions. ZETAG 7867, which is used at Killarney WWTP is an emulsion product. The polymer is synthesised in an inverse emulsion (typically water droplets in a mineral oil). Dilution leads to inversion, releasing the polymer into the bulk water. Liquid emulsion polymers allow for a much lower viscosity than would be found in a water based solution at equal concentration.

Selecting the correct polymer for a sludge dewatering process can be quite empirical. This is due in part to the secrecy with which chemical companies guard critical information regarding specific polymer properties. In the case of ZETAG 7867 information on the percentage of active product, the amount of charge, the molecular weight and the amount of cross-linkage could not be obtained.

For polymer selection, jar tests are commonly used (Metcalf *et al.,* 2001). A known volume of polymer is transferred to a known volume of sludge undergoing agitation of a quantified shear. Empirical tests which are employed in polymer selection include the capillary suction time (CST) test, and the specific resistance to filtration (SRF). Sludge zeta potentials are often measured in polymer selection too. It is important that conditions during polymer evaluation at bench scale (eg sludge concentration, polymer age, and mixing conditions) are representative of the full-scale process in question. Figure 2.2 is a

typical dose-response curve displaying taken from Johnson *et al.* (2000) showing CST vs. polymer dose (dry weight) for an inorganic sludge.

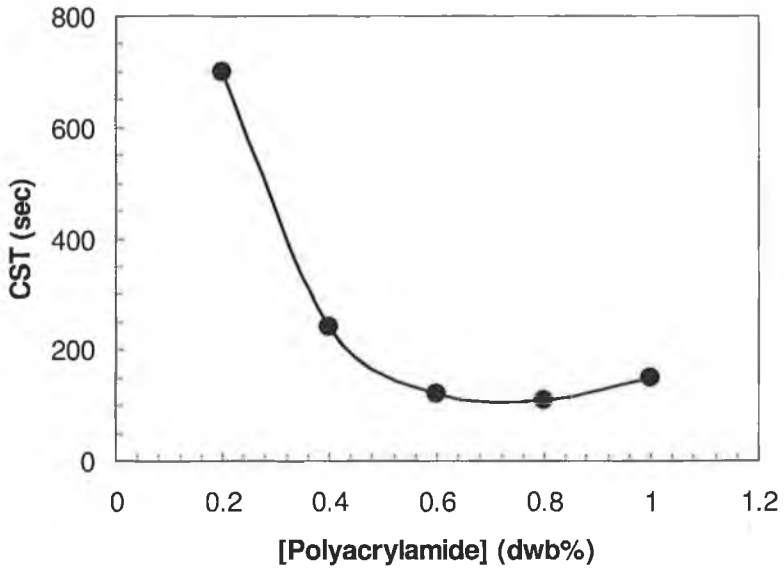


Figure 2.2 A typical dose-response curve displaying CST vs. polymer dose for an inorganic sludge

The curve illustrates that beyond a certain concentration the introduction of additional polymer will not contribute further to significant decreases in sludge filterability. Instead, dewatering characteristics are adversely affected by sterically restabilising sludge particles in solution and increasing the effective viscosity of the filtrate (Johnson *et al.*, 2000).

Dentel (2002) proposed the use of both streaming current and on-line viscosity measurements of the filtrate resulting from dewatering processes as an indicator of polymer overdosing and underdosing. It was established that there is statistically significant correlation between minimum filtrate viscosity and optimum polymer dose.

2.3.6.4 Polymer Aging

It is possible that many wastewater treatment plants are overdosing polymer. This is due to an inadequate period of time being allowed for polymer ageing. High weight polymeric flocculants need at least several hours or even as much as three days to hydrate in solution. Recent work by Owen *et al.*, (2002) has shown how polymer effectiveness is a strong function of ageing time. The effectiveness of a cationic polymer reached an optimum 73 hours after stock solution preparation. Sludge flocculation using a polymer solution which had been aged for one hour solution required 75% more polymer. While the work conducted by Owen *et al.* (2002) focused on changes in polymer effectiveness over a period of hours, other researchers have demonstrated that the effectiveness of polymer solutions decline as a function of age, albeit following an initial period of improvement. This has been variously attributed to microbial decay (Chmelir *et al.*, 1980), chemical changes (Haas and MacDonald, 1972), or what is thought to be most likely reason, conformational changes (Klein and Westerkamp, 1981). In the case of conformational changes, the polymer initially takes on an extended conformation. Over time, the effect of water attacking intra-polymer hydrogen bonds, leads to a more stable and compact coil.

Most flocculant suppliers do not advise users on suitable ageing times for polymer products and it is noteworthy that many sludge treatment plants are making up polymer solutions almost immediately before contact with the feed sludge. Process design incorporating suitably sized tanks for polymer solution to age sufficiently could save substantial amounts of money for plant operators.

2.3.6.5 Effects of polymers on sludge digestion

In sludge treatment processes such as ATAD, it is often necessary to use polymeric flocculants to thicken the feed sludge to a sufficient solids concentration to increase treatment efficiency. The effects of residual polymers on sludge digestion are not fully understood. No investigations into possible effects of high weight polymers on ATAD digestion or subsequent dewatering are present in the literature. Several investigations into the effects of these substances on anaerobic digestion have come to differing conclusions. Chu *et al.* (2003) investigated the effects of a non-ionic, anionic and cationic polymer in anaerobic wastewater sludge digestion. None of the polymers studied were found to have a toxic effect on the anaerobic system. However, in the case of the cationic polymer, digestion rate declined significantly following six days of digestion. It was concluded that this polymer was responsible for large flocs which were resistant to structural disintegration and the decline in degradability was attributed to mass transfer resistance due to substrate being trapped within the floc.

2.3.6.6 Effects of shear on polymer demand

Shear effects in dewatering devices (such as filter presses and centrifuges) and in polymer feeding and sludge feeding systems can influence polymer demand. For example, Novak (2002) described a series of tests in a screw press facility from which it was demonstrated that an in-line flow-meter imparted such shear to the process that polymer doses were nearly double what they would normally be expected to be. Vesilind (1979) described a 'standard stirring device' which incorporates a fixed mixing speed (1000 rpm) provided by a small mixing bar in a 250 ml beaker. 100 ml of sludge is added to the device and flocculated sludge is added. Mixing times of 10, 40 and 100 seconds are used to generate shear. Experiments by Spinosa *et al.* (1987) with the 'standard stirring device' found that different polymers performed better at different shear values (as a function of time) on the same sludge. This illustrates that shear is a very important factor to take into account when selecting a polymer for a specific dewatering process.

2.3.7 ATAD Dewatering

2.3.7.1 Introduction

As Stentiford (2002) noted, information relating to the efficiency with which ATAD sludge can be dewatered depends on whether one receives this information from process operators or process suppliers. Reports on the dewaterability of ATAD sludge vary from 'readily dewaterable' (Eloff *et al.*, 2000) to 'poor' (Murthy *et al.*, 2000). ATAD sludge

sampled from several North American treatment plans exhibited quite varied polymer demands (Murthy, 1998). It has been noted that ATAD sludge will dewater to a high cake solids concentration that compares favourably with analogous mesophilic sludges (Eloff *et al.*, 2000), however, this is not of much use to plant operators if the volume of conditioning chemicals and the time-frames involved are unreasonable.

Overall, there is very little information available on ATAD dewaterability in the literature and it may be an area that is not perceived to be promising in terms of fruitful research. While the underlying factors governing ATAD dewaterability are not fully understood, some assumptions can be made regarding the factors which govern ATAD dewaterability in ATAD reactors:

- A lack of floc forming organisms at thermophilic temperatures
- The high shear rates found in typical ATAD reactors resulting in a disperse sludge.
- The presence of large volumes of intractable biopolymers in the solution-phase of the ATAD sludge resulting form the cell lyses of mesophilic organisms

Zhou *et al.* (2002) found that, at lab-scale, ATAD digestion resulted in an almost immediate decline in sludge dewaterability, resulting in small flocs. Novak *et al.* (2003) found that, in the case of mesophilic aerobic digestion a gradual reduction in dewaterability was found to correlate with digestion time. However, in the case of ATAD, an immediate and pronounced lysis effect released intracellular material into

solution following contact of the cold feed sludge with the respiring biomass. Zhou *et al.* (2002) also found that the ATAD digestion of secondary sludge at 60 °C resulted in a more readily dewaterable sludge in terms of CST than digestion at 55 °C. They believed that the temperature of operation coupled with floc size were the most important variables governing the dewaterability of ATAD sludge. High temperatures were thought to result in the release of biopolymers into solution, of which, protein was shown to correlate with poor dewaterability. However, why these lysis effects were more pronounced in their effects on dewaterability at 55 °C than 60 °C was not clear. Zhou *et al.* (2002) also reported that, in a controlled experiment, it was demonstrated that sludge resulting from a thermophilic reactor exhibiting high shear rates (resulting from mechanical mixing of the sludge at 1,550 rpm) had an S-CST (CST corrected for solids) of 197 s/L/g, and a second sludge resulting from a reactor exhibiting lower shear (resulting from a diffused air arrangement), had an S-CST of 56 s/L/g. This implied that the high shear rates found within most ATAD reactors may have a negative impact on dewatering properties. The first published data from so called 'second generation ATAD reactors', which utilise diffused-air systems, have also reported more readily dewaterable end-products (Scisson, 2003).

It has been noted that ATAD sludge is not a highly flocculated substance, and hence it is expected that the sludge will attain high CDM content over periods of prolonged filtration due to the lack of a water-retentive EPS matrix. Mikkelsen and Keiding (2002) found that a high degree of sludge dispersion increased the cake dry matter content (CDM) in filtration, however the resulting increase in SRF (specific resistance to

filtration) meant that filterability and CDM were inversely related. They suggested that the high degree of dispersion found in thermophilic sludges may be related to specific microbial species, or to specific compounds which were not identified in their studies. It is also likely that the high degree of dispersion could be due to the high shear rates and turbidity associated with intensive hydration, high viscosity, and convection currents found in ATAD systems.

Post process cooling is considered necessary to achieve ATAD Biosolids consolidation. A minimum of 20 days detention may be necessary for cooling and thickening to offset the convection effects which hinder settling at higher temperatures. In some installations, where heat exchangers are used to extract heat from the ATAD biosolids, post-process cooling/thickening tanks sized for 1-3 days are adequate (US EPA, 1993) At Killarney WWTP post-process cooling of ATAD Biosolids occurs in four large post-process storage tanks on site.

2.3.7.2 High conditioning costs of ATAD

Murthy *et al.* (2000) outlined the optimum polymer dose for several ATAD sludges resulting from North American ATAD facilities. The values quoted varied significantly from 85 to 285g/kg DS. These values are exceptionally high. The difference in the figures suggests that the end product of the ATAD process is variable in terms of its dewaterability, and care should be taken when estimating conditioning costs of ATAD sludge based on previously quoted data in the literature.

Experience from full scale operations shows that ATAD results in deterioration of sludge dewatering properties, and hence increased conditioning costs are incurred in ATAD systems. Estimates of conditioning chemicals required vary from 2-3 times more than typical mesophilic systems (Stentiford, 2002) to 3-10 more (Murthy *et al.*, 2000). This once again suggests a system which is poorly understood. Thorough characterisation of ATAD sludge dewatering properties is essential for treatment plants where dewatering is a required step.

It has been claimed that ATAD sludges can attain higher cake solids concentrations following centrifugation and filtration than sludges resulting from mesophilic processes (Kelly and Mavinic, 2003). While this may be true if ATAD sludge were allowed to reach equilibrium solids concentrations in a centrifuge or belt filter press, the time required to reach such concentrations could be orders of magnitude greater than that for a better flocculated mesophilic sludge. In terms of desirable solids content of the end product, 20% (w/w) cake solids content is a reasonable goal for most plant operators.

Murthy *et al.* (2000) reported that, concurrent with a decrease in dewaterability of several sludges as they underwent ATAD digestion, the ratio of monovalent/divalent cations in the solution-phase changed in favour of monovalent cation concentration. They proposed that the divalent cation concentration decreased due to precipitation effects. The pH range of ATAD reactors is typically in the range of 8.3 to 8.8 allowing calcium carbonate to precipitate. They reported polymer demands up to 175g/L when polymeric flocculant is

used on its own for conditioning purposes. These results suggested that excessive polymer demand is linked to the presence of high concentrations of monovalent cations in solution. They found that an increase in the degree-day product also led to an increase in proteins/polysaccharides and COD in solution. Notably, they postulated that solution protein is the most critical type of biopolymer in dictating polymer demand and this is reflected in work done by Zhou *et al.*, (2002). Murthy *et al.* (2000) also found that, for an ATAD sludge, ferric chloride was useful in removing some solution protein and leading to improvements in sludge dewaterability. They presented theoretical operating costs for employing a dual conditioning system combining the addition of ferric salts and polymeric flocculant which suggested that it is the economically favourable option for ATAD plant operators when compared to stand-alone use of polymeric flocculants. However, the corrosive nature of such salts and the increased weight of the final product resulting from their addition (up to 40% heavier) somewhat compromises the purported benefits of conditioning ATAD sludge in such a manner (Zhou *et al.*, 2003).

Agarwal *et al.*, (2005) showed that a fraction of substances in the solution-phase of ATAD sludge (sampled from several full-scale treatment plants) were positively charged, reducing the effectiveness of cationic conditioners in treating ATAD sludge. These results were surprising as the general consensus in the literature is that negatively charged substances are the controlling factor in ATAD dewatering properties. The results generated by Agarwal and co-workers suggested that a dual conditioning step, in which negatively charged conditioning agents are combined with positively charged ones, would better serve to flocculate such ATAD sludges. Indeed, they applied such a method

to an ATAD sludge and reduced the minimum CST which was obtainable. One possible source of this positively charged fraction may be residual polyelectrolyte resulting from the pre-ATAD thickening step.

Forster (2002) argued that the most significant factor influencing ATAD dewatering properties is small particle size. The small particle size is due to the small size of thermophilic organisms and a lack of flocs in ATAD sludge. The lack of flocs is either due to the intensive shearing regime required to aggressively aerate most ATAD reactors, or due to the fact that floc-forming organisms are not prevalent at thermophilic temperatures.

2.3.7.3 Conclusions

There is no consensus on the causes of poor dewaterability in ATAD sludge in the literature. It is evident that ATAD presents an extreme environment, where a biomass of limited diversity exists in conditions of high shear and high temperature, conditions too extreme for the existence of traditional floc-forming microbes. It is also evident that the subject of ATAD dewaterability is an area very much neglected in the literature.

2.4 Sludge dewatering characterisation methods

2.4.1 Introduction

Dewatering theory is a wide and multi-disciplinary field. This section gives and overview of the experimental methods available to researchers wishing to characterise the dewatering properties of sewage sludges, and some of the limitations associated with the most widely used methods. Dewatering theory is also introduced, with a summary of the most widely used approaches to model settling and filtration. The final part of the section provides an in-depth review of the compressive-rheology theory of Buscall and White (1987) and the experimental methods which used to extract the key parameters required for modelling sludge dewatering behaviour.

2.4.2 Characterisation Techniques

Several experimental methods are available to researchers looking to describe the dewatering characteristics of sludge. The most commonly cited methods in the literature are the capillary suction time (CST) test and the specific resistance to filtration (SRF). Both of these methods prove useful in providing empirical filtration data for a sludge at a specific solids concentration. However, little worthwhile data can be extrapolated from them in terms of fundamental sludge dewatering properties across a range of solids concentrations. The use of a Compressibility-Permeability (C-P) cell is superior to these methods and can provide fundamental information relating to sludge dewatering behaviour in terms of compressibility and permeability. However, its cost and long testing times compromise its use in the field. These three experimental methods and some limitations associated with their use are outlined below.

2.4.3 Capillary suction time (CST)

The CST apparatus is perhaps the most widely used method of gauging sludge 'dewaterability' in the literature (Lee, 1994; Smiles, 1998). The method involves the use of a capillary suction apparatus (CSA) developed by Gale and Baskerville (1967). The CSA consists of a sludge cylinder that rests on a filter (usually Whatman No 17 chromatography paper) which serves as the slurry reservoir. The capillary suction of the paper sucks out the filtrate from the sludge while a cake is formed inside the cylinder. The filtrate radiates outward from the centre of the filter. The time it takes for the wet front to travel between two concentric circles of fixed radii is known as the 'capillary suction time' of the sludge.

Its ease of use in terms of time, labour and interpretation of results have assured the popularity of the CST method, and it is useful as an empirical tool to determine the 'filterability' of a sludge at a given solids concentration. However, CST results are dependent on the instrument being used and the initial solids concentration of the sludge. Hence, it is not meaningful to compare CST results from separate research (Vesilind, 1988). Additionally, Johnson *et al.* (2000) have shown that large errors are associated with the use of CST at low solids concentrations. To address these problems, a number of workers have developed methods which have elevated the results attained from the CST device to independence of experimental conditions by incorporating an instrument constant, and correcting for solids concentration of the sludge (Lee, 1994; Vesilind and Ormeci, 2000). However, the validity of such methods has been called into question

(Smiles, 1998). He states that the CST should be treated as an empirical test rather than one which permits careful analysis, and, ultimately, constant pressure-filtration tests, which provide sorptivity and water content pressure relations simply and without ambiguity, must be preferable.

Furthermore, the CST test cannot give any information beyond 'filterability' at a specific solids concentration. For instance, it provides no information on compressibility, or the solids concentration achievable at a given pressure. Harbour *et al.* (2001) also discussed drawbacks associated with the CST test. They noted that the CST test only gives an indication of filtration rate at one (generally low) solids concentration and concluded that sludges with similar CST values may have very different dewatering properties as measured by other more rigorous methods.

Pan *et al.* (2003) reasoned that the CST is an unrealistic measurement to determine sludge characteristics, as no pressure is applied, and overdosing of conditioning polymers as a result of CST measurement have been reported (Wu *et al.*, 1997). Ultimately, the CST is a useful indicator in routine process control to measure 'filterability' of a sludge at a given solids concentration, but caution should be exercised in its use in determining 'dewaterability'.

2.4.4 Specific Resistance to Filtration (SRF)

The specific resistance to filtration (SRF) has several important advantages over other tests for measuring sludge dewaterability. Two of these are its purported independence of sludge suspended solids concentration and its translatability from one laboratory to another (Christensen and Dick, 1985). It is noted that, at low solids concentrations, the SRF of a flocculated sludge is a strong function of suspended solids concentration, but becomes relatively independent at high solids concentrations. Care must be taken in SRF tests that the SRF is calculated from the portion of the curve which is linear and uninfluenced by solids concentration. Furthermore, care must also be taken in assuming the translatability of SRF results from different investigators, as different methods may be in use in different labs (Christensen and Dick, 1985).

Harbour *et al.* (2001) believed that the data obtained from the SRF method is determined by the starting volume fraction of the sludge, and cake thickness, and therefore sludges with different starting concentrations or solids loading cannot be directly compared.

SRF and CST are not mutually suitable for describing dewaterability of differing sludges being subjected to different dewatering techniques. For example, Al-Muzaini and Hamoda (1999) pointed out that SRF is not a viable parameter to estimate how well a sludge will dewater under centrifugal acceleration. Pan *et al.* (2003) also noted that the dewaterability of a sludge in a centrifugation process is best described by CST values and SRF is a practical index for filter press dewatering.

2.4.5 The C-P Cell

Ruth (1946) introduced the compression permeability (C-P) cell for measuring the porosity and specific resistance of a suspension as functions of applied pressure. C-P cells are now used to obtain values to determine dewatering parameters for utilisation as inputs to various dewatering models including those which have been developed from the theory of Buscall and White (1987). The principle of the C-P cell is that the sludge sample to be tested is confined in a compression cell with a permeable membrane at one or both ends and is then subjected to uniaxial compressive force. Hence, behaviour such as cake formation, filtration and compression can be described using various analytical techniques. The major drawback associated with the C-P cell is the long characterisation times (up to 3-4 weeks) associated to collect a complete set of data for a specific sludge. In the case of sewage sludges, which are biological in nature, these long characterisation times could theoretically lead to changes in sludge properties due to microbial activity over the testing period (Wu *et al.*, 2001)

Most of the literature pertaining to the use of C-P cells describes the characterisation of inorganic sludges which are not as susceptible to property changes due to microbial activity. For example, kaolin, alumina and clay suspensions have been extensively characterised in this manner (Harbour *et al.*, 2001; Kapur *et al.*, 2002). Recent attempts to address the time problem have led to modified C-P cells and data logging and extrapolation techniques which can measure both filterability and compressibility simultaneously (La Heij *et al.*, 1996; Usher *et al.*, 2001). However, it must be noted that the C-P cell can only give such data for the specific pressure applied during the test. In

the case of inorganic sludges, Usher *et al.* (2001) described a multiple stepped pressure filtration test which can accurately determine both compressibility and permeability parameters across a range of solids concentrations from low solids (input to a dewatering process) to high solids (output from a dewatering process).

The data which is obtained from a C-P cell, is usually used to define the following dewatering parameters; specific cake resistance, porosity, and a compressive pressure, as defined by the classical work of Tiller and co-workers (Tiller, 1955).

La Heij *et al.* (1996) used a C-P cell to obtain parameters for a model to predict the filtration behaviour of an activated sludge. They found that the time at which equilibrium is reached is independent of the filtration-expression pressure. They also found that the total dewatering time increased with the square of the cake thickness. Wu *et al.* (2001) investigated activated sludge behaviour in a C-P cell. They described a marked difference in dewatering properties between high pressure and low pressures, and postulated that, for the sludge which they studied, there existed a threshold pressure between 25kPa and 50kPa, beyond which cake structure collapsed and there was extensive cake compression. They demonstrated this by showing data displaying cake thickness reduction of 10% at 25kPa and cake thickness reduction of over 90% at 50kPa. They also found that extensive compression at higher pressures prolonged the time required to reach equilibrium by a factor of 3 to 5.

2.5 Dewatering Theory

2.5.1 Introduction

Solid-liquid suspensions, such as sewage sludges, are described as discrete particles or solids suspended in a continuous fluid. In flocculated suspensions, the solids phase forms a network which is also continuous. In order to formulate a description of solid-liquid separation, the interactions between the solid and liquid phases (the fluid drag) and between the particulates (the network strength) must be understood. In general, dewatering theories describe the effect of an applied pressure (mechanical, gravitational or centrifugal) on the particle and fluid pressures in terms of the compressibility and permeability of the suspension, where the compressibility is a measure of the equilibrium extent of dewatering and the permeability gives a measure of the rate of dewatering.

Up until the late twentieth century, solid-liquid separation theories developed in two parts, filtration or consolidation modelling and sedimentation modelling. Filtration modelling is traditionally based on descriptions of the flow of liquid through packed beds. Filtration theory has developed from the work of Darcy (1856) through to the conventional filtration theory of Ruth (1946) and Shirato (1964).

Sedimentation theory has developed in parallel to filtration theory. Stokes first derived an expression for the terminal settling velocity of a single spherical particle in laminar flow.

The Kynch (1952) approach to modelling particle sedimentation is the most widely applied method in the literature.

Traditionally, Kynchian batch settling analysis is used to model thickeners, and Darcy's approach to model filters. The Kynchian theory fails to incorporate bed compression in thickening, while Darcy's law is less accurate for compressible materials (Stickland, 2005).

A sewage sludge characterisation method developed at the University of Melbourne is based on a mathematical theory of dewatering of flocculated suspensions developed by Buscall and White (1987). Subsequent work has applied the theory to constant pressure filtration (Landman and White, 1994; Landman *et al.*, 1997). The theory is based on two material dependent, solids concentration independent, fundamental parameters. These are the hindered settling function, $R(\phi)$, (which characterises the permeability of a sludge) and the compressive yield stress $P_y(\phi)$ (which characterises the compressibility of a sludge). A third parameter, the diffusivity $D(\phi)$, is a combination of the previous two parameters and is used to give an overall characterisation of sludge dewaterability. A brief overview of the underlying theory, its application to filtration, and finally characterisation methods used to derive the fundamental data for analytical analysis are described below.

The Buscall and White approach to the problems of solid/liquid separation has been termed compressive rheology. It is a fluid mechanical approach to uniaxial yielding and

subsequent consolidation of networked particles under a compressive force. The main criterion to be satisfied for measurement of the fundamentals of compressive rheology is that a sufficient particle concentration exist in the system such that inter-particle interactions cause a continuous network to form and this network is subjected to uniaxial compression (de Kretser *et al.*, 2002). The particle network has an integral strength which, as is the case in the shear of concentrated suspensions, must yield for deformation to occur. The field of compressive rheology is concerned with the subsequent expulsion of fluid from the network after yielding, leading to an increase in the concentration of the particle network via consolidation and dewatering. Two important considerations are therefore, the strength of the network, $P_y(\phi)$, and the rate at which liquid escapes from the network during consolidation $R(\phi)$. Due to the interdependence of networked and un-networked suspensions a number of techniques are required to measure these parameters from dilute to fully networked.

2.5.2 Hindered settling function (R(ϕ))

ϕ is the solid volume fraction of the sludge which is simply the volume of solids per total volume of sludge. Figure 2.3 illustrates settling in a homogenous suspension which is un-networked and has a uniform solids concentration ϕ_0.

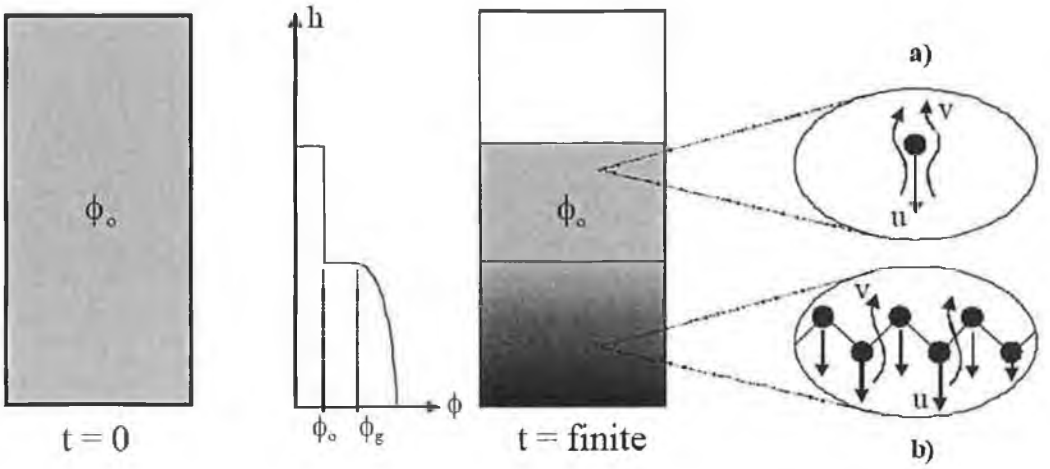


Figure 2.3 Settling in a homogenous suspension which is un-networked and has a uniform solids concentration ϕ_0 (based on a schematic in deKretser *et al.*, 2002)

At some finite time, the suspension will have settled under gravity forming a sediment which has a concentration gradient from a maximum at the base to a point known as the gel-point ϕ_g which is the solids concentration at the interface of the sediment bed above which is a clear liquid region. Figure 2.3 displays the forces acting on a single particle with a settling velocity u and a displacement of fluid causes fluid motion in the opposite direction v. The major forces acting on this particle (ignoring diffusional motion) will be the hydrodynamic drag force, F_d, and the gravitational or buoyancy force, F_g, which can be balanced according to Buscall and White (1987) to give Equation 2.5:

$$(u-v)=\frac{\Delta\rho_g V_p}{\lambda\eta\alpha_p} \qquad (2.5)$$

Where $\Delta\rho$ is the density difference between the solid and the liquid phases, g is the gravitational field, V_p is the volume of the particle and λ is the Stokes settling coefficient, η is the liquid viscosity and α_p is the particle diameter. If the particle concentration is increased in the free settling region, hydrodynamic interactions between particles also increase leading to a deviation from Stokes settling behaviour (Figure 2.3b). These interactions can be accounted for by a volume fraction dependent hindered settling factor $r(\phi)$. Landman and White (1997) define $r(\phi)$ through the following equation for the settling velocity, $u(\phi)$

$$u(\phi)=\frac{u_0(1-\phi)}{r(\phi)} \qquad (2.6)$$

The hindered settling factor defines both the forces acting on a solid moving through a liquid in a dilute suspension, or, in the case of a concentrated sediment, it defines the movement of liquid through a networked solids and as such is inversely related to a Darcian permeability; $r(\phi)$ has the following properties: as $\phi \rightarrow 1$, $r(\phi) \rightarrow \infty$, and as $\phi \rightarrow 0$, $r(\phi) \rightarrow 1$. In the Buscall and White approach, it is useful to define a hindered settling function $R(\phi)$, as $r(\phi)$ is difficult to extrapolate from experimental data. The difficulty in defining $r(\phi)$ is a result of $r(\phi)$ being invariably linked to λ/V_p. Given that most real industrial systems that are encountered are poly-disperse, the fact that the actual

characteristic size of an aggregate or a floc in an interacting system is seldom known, and that the aggregates or flocs are of unknown shape, it is more convenient to simply measure the entire quantity $\lambda/V_p r(\phi)$ experimentally, and this is known as the hindered settling function $R(\phi)$ with units Pa s m^{-2} (Usher *et al.*, 2001)

2.5.3 Compressive Yield Stress ($P_y(\phi)$)

A networked suspension will display an integral strength. The network strength term is related to the particle pressure P_s which equates to the elastic strength in the particle network for flocculated or coagulated systems or to the osmotic of the particles, $P_{os}(\phi)$ for stable particle systems, or systems at concentrations below the gel point. Stable particle suspensions will consolidate to form dense beds approaching ϕ_{cp} (the maximum packing density), which is 0.64 v/v for spherical particles. However, for a suspension of particles interacting with an attractive net energy (e.g. through electrostatics or bridging flocculation), such as for a sewage sludge, the particle pressure must be measured by a physically measured network strength, which depends on the local volume fraction of solids, ϕ. This strength is defined as the compressive yield stress $P_y(\phi)$ (Buscall and White, 1987). An element of the network will remain in its original concentration, ϕ, until an applied stress, ΔP, is applied to the network at which point the network will collapse irreversibly, particle consolidation will occur and the local volume fraction, ϕ, will increase. $P_y(\phi)$ can only be traced in a regime where ϕ is greater than ϕ_g and has the following properties $P_y(\phi) \rightarrow \infty$ where ϕ for $\phi \rightarrow \phi_{cp}$. For $\phi < \phi_g$, the particle concentration

is too small to allow a particle network to develop and $P_y(\phi)$ is zero. The following equation describes the dynamics of consolidation (Buscall and White, 1987);

$$\frac{D(\phi)}{Dt} = \begin{cases} 0, P_s < P_Y(\phi) \\ \kappa(\phi)[P_s - P_y(\phi)], P_y(\phi) \end{cases} \qquad (2.7)$$

$D(\phi)/Dt$ is the material derivative of the local concentration, and $\kappa(\phi)$ is a rate constant called the dynamic compressibility. This equation formally states that the network resists compression if $P_s<P_y(\phi)$, but collapses if $P_s>P_y(\phi)$. The basic consolidation equations of Buscall and White (1987) present a complete theory for solid/liquid separation dynamics and have been applied to the modelling of several dewatering operations including centrifugation, thickening, and filtration (Howells, 1990; Landman and White, 1997; Landman, 1999)

2.5.4 Diffusivity

Landman and White (1997) described a further dewaterability parameter, the diffusivity $D(\phi)$. The diffusivity is related to $R(\phi)$ and $P_Y(\phi)$ according to the following equation;

$$D(\phi) = \frac{dP_y(\phi)}{d(\phi)} \frac{(1-\phi)^2}{R(\phi)} \qquad (2.8)$$

$D(\phi)$ can be interpreted as a diffusion coefficient combining $P_y(\phi)$ and $R(\phi)$ and, broadly speaking, a material exhibiting a low $D(\phi)$ will dewater at a faster rate than a material with a higher $D(\phi)$. The overall governing equation for constant pressure filtration is given by a second order non-linear partial differential equation:

$$\frac{\partial \phi}{dt} = \frac{\partial}{\partial z}\left[D(\phi)\frac{d\phi}{dz} - \phi\frac{dh}{dt} \right] \qquad (2.9)$$

The left handed side of the above equation describes the change in concentration with time due to the compressive force described by the right hand side. This theory has been successfully used to model constant-pressure filtration (Landman and White, 1997) and these models have been used to predict optimum filter throughput, taking into account such variables as initial suspension height, initial suspension concentration, and filtration time. Landman and White (1997) concluded that the optimum throughput was acquired when handling time was equal to filtration time.

2.5.5 Relationship of (Buscall and White, 1987) parameters to Tiller and Shirato models

The classic filtration work of Tiller (Tiller, 1955; Tiller 1975) characterised sludge permeability according to a specific cake resistance, α, and sludge compressibility according to a solids pressure p_s. The main differences between these parameters and those described by Buscall and White are that they are not material dependent and are

defined from within the modelling domain of filtration. p_s is normally referred to in a void fraction versus pressure relationship, p_s vs. ε (void fraction). Specific cake pressure is reported as a function of applied pressure of which it is an implicit function, defined by the mechanical conditions in question, rather than as a function of solids concentration, of which $R(\phi)$ is an explicit function, under all conditions. This approach also precludes the existence of α under non-networked conditions, once again differing from the approach of Buscall and White (1987). However the parameters described by Tiller and co-workers can easily be related to those of Buscall and White, according to the following equations, allowing a wealth of published data to be translated and interpreted (deKretser *et al.*, 2002). A mass specific cake resistance is related to the hindered settling function according to:

$$\alpha_m = \frac{R(\phi)}{(1-\phi)\rho_s \eta} \qquad (2.10)$$

and a volume specific cake resistance according to:

$$\alpha_v = \frac{R(\phi)}{(1-\phi)\eta} \qquad (2.11)$$

Where ρ_s is the solids density and η is the liquid viscosity. The ρ_s vs. ε relationship of Tiller and Shirato is identical to $P_y(\phi)$ (deKrester *et al.*, 2002).

2.5.6 Experimental determination of dewatering parameters

2.5.6.1 Introduction

A number of techniques are available to experimentally determine the above parameters to characterise sludge dewaterability, or to determine them as inputs into dewatering models. deKrester *et al.* (2002) noted that several researchers have determined these parameters for the high volume fractions associated with pressure filtration and argued that simple power law curve-fits cannot neglect data at low volume fractions, which can be obtained from batch settling and low speed centrifugation. A complete protocol has been developed at the University of Melbourne, combining batch settling tests, C-P cell tests and analytical software, to produce curve fits for $R(\phi)$, $P_Y(\phi)$ and $D(\phi)$ from the gel point to the high volume fractions associated with pressure filtration. However, it should be noted that these models have so far only successfully been utilised to satisfactorily predict the filtration behaviour of traditional sludges, which exhibit long periods of cake formation, followed by a short compression regime. As noted before, sewage sludge is highly compressible and exhibits filtration behaviour which is difficult to model, primarily because, during the compression regime, equilibrium is rarely (if ever) achieved.

2.5.6.2 The C-P cell and batch settling

The above parameters are often measured in the high solids regime associated with pressure filtration using a C-P cell and in the low solids regime using batch settling tests. In a filtration test, filtration time, t, is quadratic with the specific filtrate volume, V,

during the cake formation period, followed by a logarithmic dependency during cake compression. $R(\phi)$ is determined from the equilibrium height (the point at which $P_Y(\phi) = \Delta P$ for an applied pressure, P)

Traditional sludges (Figure 2.4a), which are generally inorganic in nature (for example a zirconia suspension) typically show long periods of cake formation followed by short periods of cake compression and are easily characterised by multiple stepped filtration tests (Usher *et al.*, 2001). However, sewage sludges are highly compressible and show very short cake formation periods, followed by a long compression period (Figure 2.4b). This makes the characterisation of sewage sludge by the theory outlined above very difficult for a number of reasons. In terms of $R(\phi)$ measurements, the linear portion of the t versus V^2 curve is too short to extrapolate useful data (in effect, the sludge network begins compressing almost immediately). In terms of $P_Y(\phi)$ measurements the compression regime is too long and the results are compromised by evaporation effects and biological activity within sludge

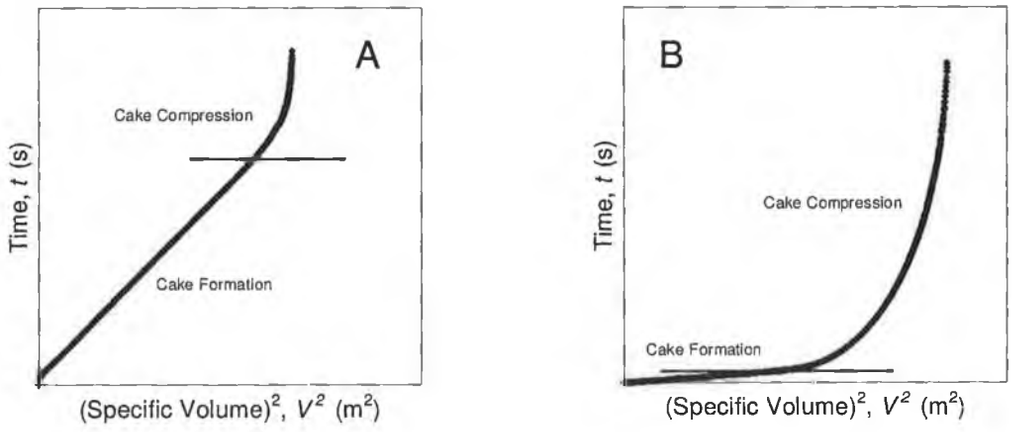


Figure 2.4 Filtration: Time versus filtrate volume^2 for A (an inorganic sludge) and B (biosludge).

The rheological properties of sewage sludge outlined above are thought to be intimately linked to the micro-organisms present and their associated digestion and lyses products. Extracellular polymeric substances (EPS) are a mixture of proteins, polysaccharides, lipids and humic substances, and can be up to 80% of sludge biomass (Nielsen *et al.*, 2003). It is very likely that the EPS quantity and quality are the most important factors influencing sewage sludge dewaterability (Nielsen *et al.*, 2003; Wilén *et al.*, 2003). The question then arises whether sewage sludge can be successfully characterised according to the dewatering theory of Buscall and White (1987). A 'biosludge characterisation protocol' has been developed by Stickland (2005). This protocol addresses the problems associated with characterising sewage sludges according to the Buscall and White approach and is outlined in Chapter 3.

2.5 Summary

Autothermal thermophilic aerobic digestion (ATAD) is increasingly seen as a viable technology to produce a Class A biosolid product according to Irish, EU and US legislation. However, a drawback of the ATAD process is that it produces a sludge which is difficult to dewater and exhibits a high conditioner demand. Several factors have been identified which may be controlling the poor dewatering properties of ATAD sludge. These are: a lack of floc forming organisms at thermophilic temperatures; high levels of soluble and colloidal biopolymers in the solution-phase of the sludge (principally proteins and polysaccharides) and the high shear rates resulting from the intense aeration required in ATAD systems.

To better understand the dewatering properties of ATAD sludge and hence, optimise the process for dewatering, suitable characterisation techniques are required. Characterisation techniques such as the capillary suction time (CST) test and specific resistance to filtration (SRF), are widely applied in the literature and in industry, but whilst useful in predicting dewatering trends, these methods do not readily assist in the design and optimisation of dewatering devices from first principles.

A complete biosludge characterisation protocol based on the compressive rheology theory of Buscall and White (1987) has recently been developed at the University of Melbourne. This protocol has been used to characterise sewage sludges in terms of two material-dependent dewatering parameters, the compressive yield stress, $P_y(\phi)$, which

characterises the compressibility of sludge and the hindered settling function, $R(\phi)$, which characterises the permeability of the sludge. The parameters are determined experimentally by a combination of batch settling, centrifugation, and filtration tests, creating functional forms for these parameters ranging from low solids concentrations to high solids concentrations. The use of this biosludge characterisation protocol to characterise ATAD sludge is a very useful method for quantifying ATAD dewaterability in a unique and unequivocal manner.

CHAPTER 3: MATERIALS AND METHODS

3.1 Introduction

In this Chapter, the materials and experimental methods which were used in this research are outlined. In Section 3.2, the materials and reagents which were used in the work are set out. The pilot-plant which was used at Killarney wastewater treatment plant (WWTP) is also described. In Section 3.3 the experimental methods employed as part of this research are described. These include the methods which were used for physico-chemical analysis of the sludges, flocculation procedures, and optimum polymer dose determination. Finally, in Section 3.4, the biosludge characterisation protocol which was used to characterise sewage sludges is described.

3.2 Materials and Reagents

3.2.1 Analytical reagents

Analytical reagents used in this study were obtained from Sigma-Aldrich and Reagecon and were of at least analytical grade. Table 3.1 summarises the properties of the principal analytical reagents which were used in the experimental work. Distilled water was used in all cases where solutions were prepared for analysis.

Table 3.1 Analytical reagents used as part of this research

Reagents	*Grade/Purity*	*Supplier*
α-glucosidase from *Saccharomyces cerevisiae*	5000 U/g[1]	Sigma-Aldrich
Bisbenzimede H 33258	10 mg/ml	Sigma-Aldrich
BSA (lyophilised powder)	≥ 98%	Sigma-Aldrich
Cellulase from *Aspergillus* sp.	≥1000 U/g[2]	Sigma-Aldrich
COD reagent (premixed); sulphuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), disilver (1+) sulphate, mercury sulphate ($HgSO_4$).	Ag_2SO_4 (0.1 - 1%) H_2SO_4 (60-70%) $K_2Cr_2O_7$ (0.1-1%) $HgSO_4$ (0.1-1%)	Reagecon
Copper sulphate (pentahydrate) ($CuSO_4.5H_2O$)	≥ 98%	Sigma-Aldrich
DNA standard (calf thymus DNA)	1 mg/ml	Sigma-Aldrich
Ferric (III) chloride ($FeCl_3$)	Analytical grade, 97%	Sigma-Aldrich
Ferric (III) sulphate ($Fe_2(SO_4)_3.xH_2O$	Analytical grade, 97%	Sigma-Aldrich
Flourescent Assay Buffer (100 mM Tris HCl, pH 7.4, with 10mM EDTA and 2 M Nacl)		Sigma-Aldrich
Folin-Ciocalteau's phenol reagent		Sigma-Aldrich
Glucose ($C_6H_{12}O_6$)	99.5%	Sigma-Aldrich
Phenol (C_6H_5OH)	99.5%	Sigma-Aldrich
Potassium sodium tartrate ($KOCOCH(OH)CH(OH)COONa \cdot 4H_2O$)	> 99%	Sigma-Aldrich
Potassium sodium tartrate ($KOCOCH(OH)CH(OH)COONa \cdot 4H_2O$)	> 99%	Sigma-Aldrich
Protease from *Bacillus* sp.	≥500 U/g [3]	Sigma-Aldrich

[1] 1 unit (U) is the amount of enzyme which hydrolyzes 1 µmol p-nitrophenyl-β-D-glucopyranoside per minute at pH 4.0 and 37 °C; may contain α- and β-glucosidase

[2] 1 unit (U) is the amount of enzyme which will liberate 1.0 µmole of glucose from cellulose in 1 hr at pH 5.0 at 37 °C (2 hr incubation time).

[3] 1 unit (U) is the amount of enzyme which hydrolyzes 1 µmol of L-Ieucine-p-nitroanilide per minute.

Reagents	*Grade/Purity*	*Supplier*
Protease from *Aspergillus oryzae*	≥16 U/g	Sigma-Aldrich
Sodium carbonate (Na_2CO_3)	>99%	Sigma-Aldrich
Sodium chloride (NaCl)	≥99.5%	Sigma-Aldrich
Sulphuric acid (H_2SO_4)	95 – 98%	Sigma-Aldrich
ZETAG 7867[4]	50% active product	Ciba Chemicals
ZETAG 7587[5]	Not available	Ciba Chemicals

Table 3.1 (continued) Analytical reagents used as part of this research

3.2.2 Sludges sampled

Wastewater treatment sludges were sampled from several treatment plants in Ireland, Luxembourg, Germany and Australia as set out in Table 3.2.

Table 3.2 Sludges sampled

Sludge Type	*Sludge Source*
Autothermal thermophilic aerobic digestion (ATAD)	Killarney WWTP
	Pilot-plant reactor, Killarney, operated on WAS from Killarney WWTP
	Herbrechtingen, Germany
	Uebersyren, Luxembourg

[4] A high molecular weight polyacrylamide of medium charge which was supplied in liquid emulsion form.
[5] A high weight molecular polyacrylamide of high charge. Supplied in MICROBEAD form, which is non-dusting, free-flowing and completely soluble in water.

Sludge Type	*Sludge Source*
	Schwarmstedt, Germany
Mesophilic anaerobic digestion (MAD)	Luggage Point, Australia Carrum, Australia Mt. Martha, Australia MAD reactors, University of Melbourne, operated on WAS from Carrum WWTP
Waste activated sludge (WAS)	Killarney WWTP Carrum, Australia

Table 3.2 (continued) Sludges sampled

3.2.3 Sludge storage

The majority of the analysis conducted at Killarney was performed on fresh sludge samples. In the case of sludges transported from overseas for analysis, and in the case of the MAD sludges studied in Australia, samples which were stored were placed in refrigerated conditions (<5 ^{o}C) within 4 hours of sampling, and were not stored for more than two weeks, except where stated (e.g. in the time-dependent colloidal change experiments).

3.2.4 ATAD pilot-plant

To provide ATAD sludge under controlled conditions, an ATAD pilot-plant reactor was designed and built by *Fuchs Gas Und Wassertechnik GMBH*, Mayen, Germany and was commissioned at Killarney WWTP (Figure 3.1). The reactor consisted of a stainless steel cylindrical tank, with a flat bottom. This tank was insulated with polyurethane foam, and covered with aluminium sheets. The usable volume of the tank was 500 litres. A level sensor showed the volume of sludge within the tank. Aeration and mixing of the tank's contents was provided by one centrally installed circulation aerator which rotated at 1400 rpm. The circulation aerator consisted of a 3-phase motor, a conical coupling with air entry openings, and a hollow shaft with an impeller at its end. As air entry ports, 8 boreholes with threads were provided. Typically, 4 boreholes were closed with screws. Airflow could be adjusted by opening or closing additional boreholes. In ATAD digestion it is usual for a strong and thick foam layer to develop. The depth and density of foam must be controlled. A foam controller was operated continuously during digestion. The foam controller consisted of a 3-phase motor with a shaft, which was covered by the exhaust pipe work. The shaft was equipped with agitator blades, which separated the liquid from the gas phase of the foam. The pilot-plant was also fitted with a control panel which gave a digital readout of reactor temperature, ambient temperature, and operation hours for the foam controller and the circulation aerator. Two TINYTAG data loggers were located inside the control panel box, and these could be connected to a computer by a data wire, with TINYTAG software used to download the temperature data. The pilot-plant was operated outdoors at Killarney WWTP.

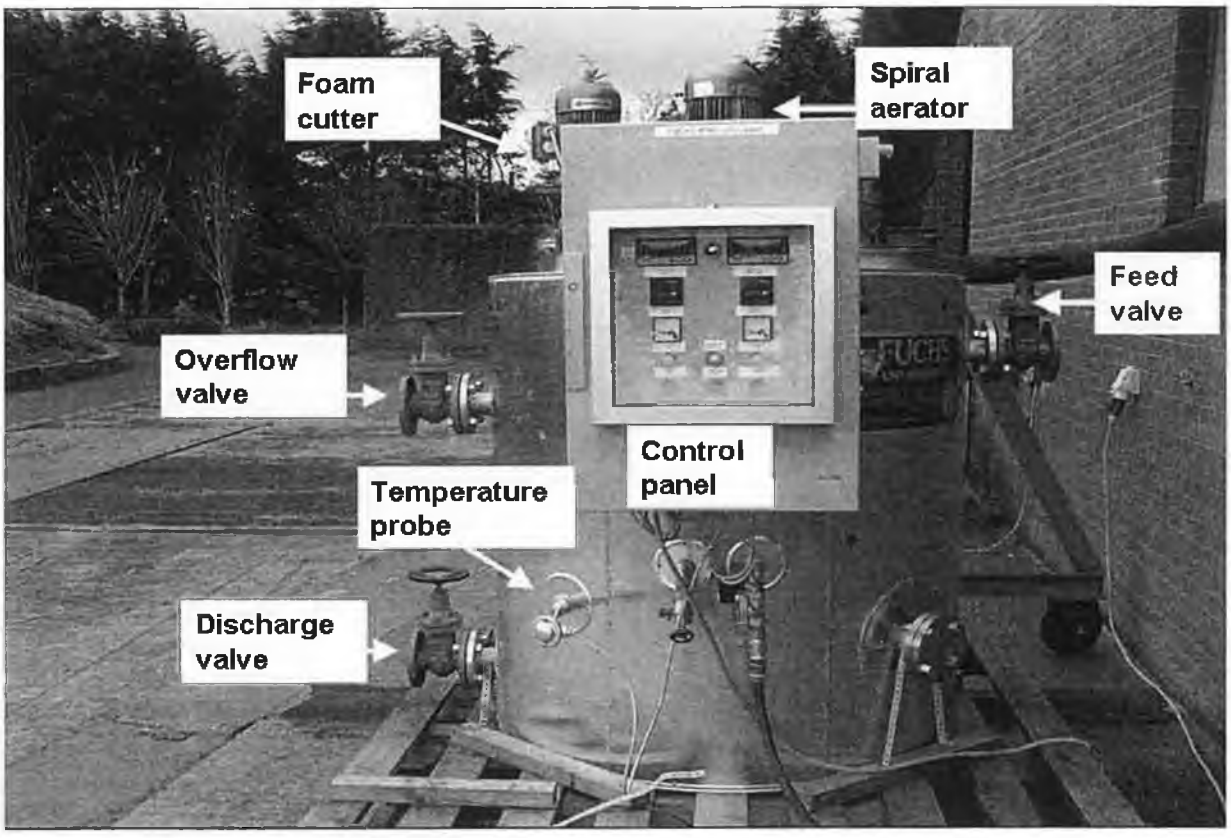


Figure 3.1 ATAD pilot-plant reactor at Killarney WWTP.

3.2.5 Laboratory scale anaerobic digesters

Two lab-scale anaerobic digesters were designed and operated at the University of Melbourne. The digesters consisted of 5 litre glass bottles which were sealed using rubber stoppers and glycerine. A schematic of the digesters is shown in Figure 3.2. The reactors were placed in a temperature controlled water bath, which was fabricated from a fish-tank and a circulatory heater. Magnetic stir-plates were placed under the fish tank and large egg-shaped magnetic stirrer-bars were used to stir the reactor contents. In each reactor, three boreholes in the rubber stoppers were used as an influent port, an effluent port and a gas exhaust. Two water traps were designed, which consisted of inverted measuring cylinders (of a volume of 1 litre) fastened to retort stands. These were semi-submerged in a tank of water and were used to collect gas produced by the reactors.

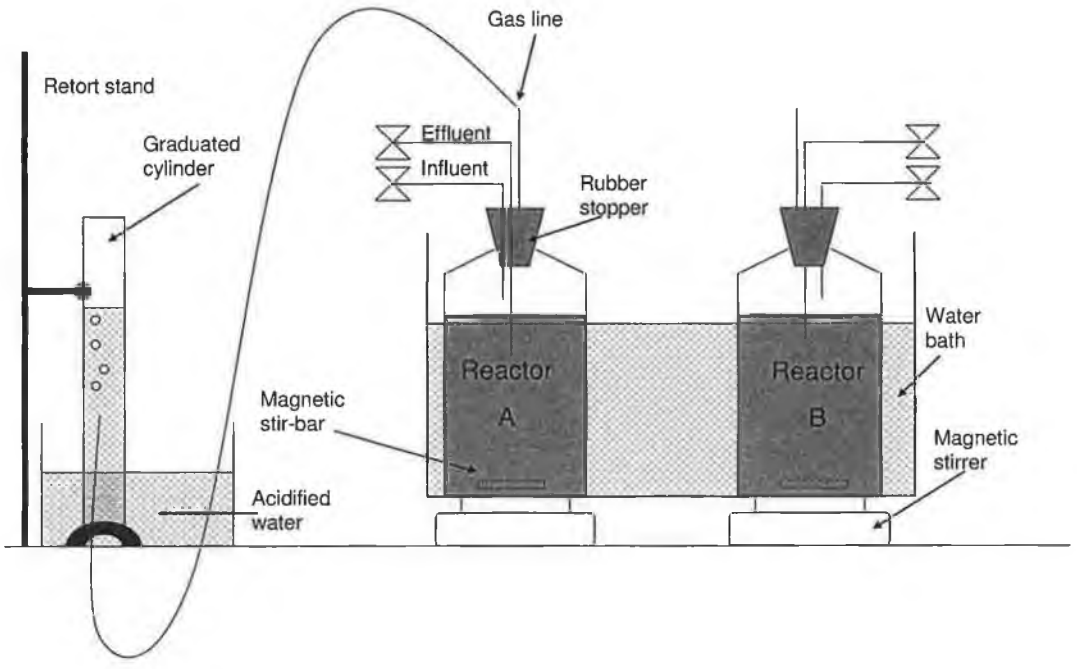


Figure 3.2 Schematic of basic anaerobic digestion units employed at the University of Melbourne.

3.3 Experimental Methods

3.3.1 Pilot-plant operation

Following an initial start-up phase, the ATAD pilot-plant was bucket-fed every 24 hours (semi-batch). Effluent sludge was first drawn away from the effluent valve, and then feed-sludge was added to the reactor via the inspection hatch. Feeding took approximately 1 hour, so the effective aeration time within the tank was 23 hours. The volume of sludge added and removed from the tank each day was measured via the level sensor. The reactor temperature was controlled by an automatic cooling system which circulated cool water within the tank wall. The cooling system was normally programmed

to begin cooling once the reactor contents reached 61.5 °C, and to switch off at 60 °C. These parameters could be changed as required.

The sludge fed to the pilot-plant was the same sludge that was fed to the full-scale ATAD plant at Killarney. This was a waste-activated sludge that resulted from the activated sludge works at Killarney WWTP. Before full-scale ATAD treatment at Killarney activated sludge is first gravity thickened in a picket fence thickener to between 2 and 3% total solids (TS). The thickened sludge is then conditioned, by the application of ZETAG 7867 (cationic polyacrylamide), at a concentration of approximately 3 g/Kg TS. The conditioned sludge is then further thickened to 5 - 6% TS by a belt filter press. This is necessary to increase the calorific content of the sludge for autothermal operation and for minimising footprint within the digestion operational ranges.

The thickened sludge is then stored in a storage tank, which is intermittently mixed. The sludge which was fed to the pilot-plant was taken from a sampling valve at the side of this storage tank. On taking the feed sludge, the first bucket was discarded to head of works because of the possibility of sludge settling to higher concentrations within the effluent pipe. As the sludge was well mixed within the tank, the feed sludge was considered to be representative of the storage tank contents.

3.3.2 Operation of anaerobic reactors

The anaerobic reactors at the University of Melbourne were fed on a semi-batch basis using peristaltic pumps to withdraw digested MAD sludge from the effluent line and to pump a WAS sludge (from Carrum WWTP) along the influent line. The temperature of the reactor contents was maintained at 37 $^{\circ}$ C by a circulatory heater in the water bath. The pH of the reactors was measured daily and was controlled by the addition of bicarbonate solution if it dropped below 6. Gas was collected using two water traps. The water in the water trap was acidified to pH 3 by the addition of dilute HCl to prevent the absorbance of CO_2. The volume of gas produced by the reactors was calculated from the displacement of water in the water trap. The water traps were purged of gas daily. Gas was sampled from the gas-line and analysed by gas chromatography for CO_2 and CH_4 composition.

3.3.3 Sludge solids concentration measurement

3.3.3.1 Total Solids

Total solids were measured according to Standard Methods (APHA *et al.*, 1995) and were presented as a percentage of sample weight (w/w %).

Three porcelain crucibles were dried in an oven at 100 $^{\circ}$ C for 24 hours. They were subsequently labelled and weighed on an *Adventurer* electronic balance. The balance was calibrated monthly using standard weights and all mass measurements were taken in

grams to an accuracy of 4 decimal places. 10-20ml of sludge was poured from the sampling vessel/storage container to each crucible. In cases where sludge had been allowed to settle, the sample was thoroughly mixed (by inverting and shaking the sampling vessel). In the case of more viscous sludges (for example sludges in excess of 5% TS) the sludge sample was homogenised using a standard *Kenwood* food blender. Blending thick sludge also served to improve flow properties. Once sludge samples were added to the crucibles, the weights of the crucibles containing the samples were taken. The crucibles were then transferred to a drying oven at 103 °C. The samples were dried for a minimum of 24 hours. The dry samples were then transferred to a dessicator and allowed to cool. Finally, the total solids content of sludge samples was calculated (as w/w %) according to the following equation:

$$\frac{(A-B)}{(C-B)}\times 100 \qquad (3.1)$$

Where A is the weight of the crucible and contents after drying at 103 °C, B is the empty crucible weight and C is the combined weight of the crucible and contents before drying.

3.3.3.2 Volatile solids

Volatile solids content was used as the principal representation of the organic/biomass content of sludge in this research.

The residue from the dry solids measurement was ignited to constant weight at 550 ± 50 °C for one hour in a muffle furnace. Following ignition, the remaining solids represented the total fixed (inorganic) solids, while the weight loss on ignition represented the total volatile solids. The total volatile solids contents of the wet samples were calculated as (w/w %) according to the following equation:

$$\frac{(A-D)}{(A-B)} \times 100 \qquad (3.2)$$

Where D is the weight of the crucible and contents after ignition.

3.3.4 Chemical oxygen demand (COD)

Chemical oxygen demand was also used as an indirect measure of the organic content of the sludges. Due to the thickened nature of many of the secondary sewage sludges studied in this research, COD was selected as a more accurate alternative to the Biochemical Oxygen Demand (BOD) test, which may have been compromised by the scale of the dilutions required to bring samples within range.

3.3.4.1 Total COD

Total COD was a measure of the combined COD of the solid and the solution-phases of sludge samples. Total COD was determined using the reactor digestion method (APHA *et*

al., 1995). A HACH (DR 2000) spectrophotometer was used in conjunction with pre-packaged COD vials. This instrument was calibrated using a blank vial containing only the reagents before further measurements were taken. Due to the high organic content of many of the sludges studied, medium or low range COD vials were not suitable for analysis (particularly in the case of the highly thickened feed sludge). Therefore, high range COD vials (0 - 15,000 mg/L) were used. Samples for total COD analysis were homogenised using a blender for 2 minutes. They were subsequently diluted to bring them within range of the instrument, usually by a factor of 5 - 7. All samples were measured in at least duplicate, and the results were presented in milligrams per litre (mg/L).

3.3.4.2 Soluble COD

The soluble COD of the solution-phase of sludge samples was measured. To remove any suspended material from samples for soluble COD analysis, the samples were centrifuged for 50 minutes at 13,000 rpm in a *Rotofix Hettich* Microfuge, followed by filtration through 1.5 μm Milipore filters.

3.3.5 Protein content of solution-phase

Soluble and colloidal protein analysis was conducted on samples according to the Hartree (1971) modification of the Lowry (1951) colorimetric assay for proteins using bovine serum albumin (BSA) as standard. The principle of the assay is that, under alkaline

conditions, the divalent copper ion forms a complex with peptide bonds in which it is reduced to a monovalent ion. Monovalent copper ions and the radical groups of tyrosine, tryptophan, and cysteine react with *Folin-Ciocalteau's* reagent to produce an unstable product that becomes reduced to molybdenum/tungsten blue.

Samples for analysis were first centrifuged in a *Rotofix Hettich* Microfuge at 13,000 rpm for 40 minutes and then passed through a 1.5 μm Milipore syringe filter. Filtrate samples were refrigerated within 2 hours of sampling. In most cases, this assay was performed within 24 hours of sampling to minimise biological effects. Alternatively, samples were frozen for later analysis.

The following reagents were prepared for the analysis

(a) Reagent A

2 g of analytical grade potassium sodium tartrate was weighed out on a Mettler balance and placed in a 1 L volumetric flask. 100 g of analytical grade sodium carbonate was subsequently weighed and added to the flask. This was dissolved in 50 mL of 1M sodium hydroxide solution and then diluted to a volume of 1 L with distilled water. The solution was transferred to a plastic container, labelled, and stored away from sunlight. This solution could be kept for several months.

(b) Reagent B

2 g of analytical grade potassium sodium tartrate was weighed out on a Mettler electronic balance and transferred to a 100 ml volumetric flask. 1 g of copper sulphate (pentahydrate) was subsequently weighed and added to this. 10 mL of sodium hydroxide solution was then added and the mixture and made up to 100 mL with distilled water. The solution was transferred to a plastic container, labelled and stored away from sunlight. This solution could be kept for several months.

(c) Reagent C

2 mL of *Folin-Ciocalteau's* reagent was diluted to 30 mL with distilled water. This solution was prepared on the day of analysis and never stored.

(d) Buffer solution

A buffer solution was prepared. This consisted of 0.15 M NaCl.

(e) BSA solution

A solution of analytical grade BSA (Sigma) was made up at a concentration of 500 mg/L in buffer solution. This solution was then frozen in aliquots to ensure conditions remain constant for analysis conducted at different dates.

For each sample the following procedure was carried out.

1. 1 mL of sample was added to a test tube.
2. 0.9 mL of Solution A was added to the test-tube using a micro-pipette.
3. The test tube was placed in a water bath at 50 °C for ten minutes, then allowed cool for 20 minutes to room temperature (20 °C).
4. 0.1 mL of Solution B was added, and allowed stand at room temperature for at least 10 minutes.
5. 3 mL of Solution C was added and mixed immediately.
6. The test tube was once again heated to 50 °C in a water bath.
7. Following cooling, absorbance was read at 650 nm (in 1 cm cuvettes) using a spectrophotometer.

A standard curve was prepared using several BSA samples (prepared in buffer solution) of known concentration and the concentration of protein in the unknowns was read off this standard curve at an absorbance of 650 nm.

3.3.6 Polysaccharide content of solution-phase

The basic principle of the Dubois *et al.* (1956) colorimetric determination of simple sugars in solution, is that simple sugars, oligosaccharides, polysaccharides and their derivatives, including the methyl ethers with free or potentially free reducing groups give an orange-yellow colour when treated with phenol and concentrated sulphuric acid. Samples for polysaccharide determination were prepared in the same manner as those for protein determination. The following reagents were used:

a) Analytical grade sulphuric acid,

b) Phenol, 5% w/w (stable for many months) which was prepared by adding 95 g of distilled water to 5 g of analytical grade phenol solution.

c) Distilled water (blank)

d) Glucose solution of known concentration (200 mg/L) as standard

For each sample the following procedure was carried out:

1. 1ml of sample or standard was placed into Pyrex test-tube.
2. 1ml of phenol solution was added to the test-tube and mixed rapidly.
3. 5ml of sulphuric acid was added slowly without mixing and this solution was left to stand for 10 minutes before mixing.
4. Following mixing the solution was left for a further 10-20 minutes.

5. Using a spectrometer, the samples were read at 490 nm for hexoses and 480 nm for pentoses and uronic acids. In this assay the colour is stable for several hours so readings did not have to be taken at once.

A standard curve (Glucose vs. Absorbance at 480 nm) was prepared, and the concentration of polysaccharide (mg/L) in the unknowns was read from this curve.

3.3.7 Total organic carbon (TOC)

Total organic carbon (TOC) was measured on sludge filtrate using a *Schimadzu* TOC analyser which used a catalytically-aided platinum 680 °C combustion technique for sample oxidation coupled with nondispersive infrared (NDIR) spectrometry for detection of carbon. TOC was calculated by subtracting the inorganic carbon value from the total carbon value.

3.3.8 DNA in solution-phase

The total DNA content of the solution-phase of sludge was measured using a florescence detection kit which was obtained from *Sigma-Aldrich* according to the method of Labarca and Paigen (1980). The fluorescent dye, Bisbenzimide H 33258 (*Hoechst 33258*) was used. This dye binds primarily to adenine-thymine (AT) sequences in the minor groove of double-stranded DNA (dsDNA), and is specific for quantitation of nanogram amounts of DNA (10 ng/ml to 10 mg/ml). Calf-thymus DNA was used as the standard. Samples of

filtrate were prepared in the same manner as those for protein and polysaccharide analysis. Analysis was conducted using a *Varian Cary Eclipse* fluorimeter using multi-well plates.

3.3.9 Particle size analysis

Particle size analysis was conducted on sludge samples using the *LS130 Coulter Counter*. The *Coulter Counter* uses the principle of electrical sensing zone method to obtain a particle size distribution (PSD) for a solid/liquid suspension and has been widely used to determine PSD values for sewage sludge (Andreadakis, 1993; Chu and Lee, 2001; Houghton *et al.*, 2002). However, the high shear found within the Coulter Counter is likely to have a destructive effect on sludge flocs (Jarvis *et al.*, 2005) and other methods of particle sizing such as the light scattering techniques employed by such instruments as the Malvern Mastersizer are more favourable (Houghton *et al.*, 2002).

3.3.11 Capillary suction time (CST) analysis

An analogue *Model 304M* CST device (*Triton Electronics*) was used to give an indication of sludge filterability in flocculation experiments. The assembled CST device consisted of a rectangular sheet of *Whatman no. 17* filter paper placed upon a rectangular piece of Perspex, embedded in which, were two electrodes, located at positions D_1 and D_2. A hollow stainless steel tube of 18mm diameter was centred on the filter paper and filled with sludge. The capillary suction of the filter paper drew filtrate from the sample in a

circular waterfront. A timing device attached to the electrodes was activated when the wetting front passed the electrode at position D_1 and stopped when the wetting front passed the electrode at position D_2. The time in which it took the wetting front to pass from D_1 to D_2 was taken as the capillary suction time.

Because of reported large variabilities in results obtained from the CST test (Johnson *et al.*, 2000) particularly for suspensions with low solids content, such as typically exhibited by sewage sludges, CST was always conducted in at least triplicate.

3.3.12 Preparation of flocculated sludges and determination of optimum polymer dose (OPD)

In this research, the optimum polymer dose was derived by a series of initial cup-tests in which a polymer solution was transferred from one plastic cup to a secondary cup containing sludge, and vice-versa, until a floc formed. The quality of this floc was then recorded. Once an indicative concentration was shown to form a floc, several capillary suction time (CST) tests were conducted at polymer concentrations in the neighbourhood of this concentration and the polymer dose which resulted in the lowest CST was taken to be the optimum polymer dose (OPD).

For reproducibility of results, all tests were conducted using the same batch of ZETAG 7867 polymer at Killarney, and the same batch of ZETAG 7587 at Melbourne. Studies have shown that polymer aging can have an effect on the performance of polymer (Owen

et al. 2002). For this reason, age effects were minimised by conducting all tests using an initial stock solution which was prepared at 0.4% concentration 24 hours before experimentation.

Manufacturer's instructions recommend the preparation of polymer solution at a concentration ranging from 0.1 - 1%. However, even at 0.4% the polymer performance was poor in treating the ATAD sludges. This was characterised by the formation of exceptionally large and poorly-defined floc. Hence, the stock solution was further diluted to 0.2% before conducting experiments. This was found to be a suitable concentration for testing. The polymer was prepared by adding the stock solution to distilled water being stirred at 600rpm by a magnetic stirrer.

The final criteria which were selected for optimum polymer dose determination were:

1. The preparation of a 0.4% stock solution 24 hours before testing while mixing at 600rpm.
2. Dilution of this solution to 0.2% 1 hour before testing while mixing at 600 rpm.
3. Transfer of the polymer solution via syringe to the sludge sample being mixed at 200 rpm in a glass beaker (using a magnetic stirrer).
4. 2 minutes of flocculation time followed by 2 inversions before the sludge CST is measured.

3.4 Biosludge Characterisation Protocol

3.4.1 Introduction

As outlined in the literature review, a protocol for the determination of dewatering parameters of sewage sludge in terms of the compressive-rheology theory of Buscall and White (1987) has recently been developed at the University of Melbourne. For a given sludge sample, the protocol combines truncated pressure-filtration data with batch settling data to obtain dewatering parameters over a range of solids concentrations from the gel-point (batch settling) to high solids (pressure filtration). Mathematical algorithms and curve fitting procedures are then used to characterise the sludge in terms of the following dewatering parameters: a hindered settling function, $R(\phi)$, compressive yield stress, $P_y(\phi)$ and diffusivity, $D(\phi)$.

This section outlines the laboratory methods which were used to obtain the dewatering parameters; these being batch settling, density measurements and pressure filtration. The biosludge characterisation protocol is then introduced, describing how the data obtained from the different laboratory characterisation techniques were integrated to give dewatering parameters over a wide range of solids concentrations. Finally, centrifugation techniques are described which were used to obtain dewatering parameters in an intermediate solids range which was not covered by batch settling and pressure filtration.

3.4.2 Density analysis

The solids concentration for sludges was measured as solids mass as a percentage of the total mass (wt %) by gravimetric techniques. This unit of measurement was unsuitable for use in filtration characterisation, as it is the solids volume fraction, ϕ, that influences the filtration rate. ϕ was therefore calculated from the solids mass (wt %) using ρ_s (density of solid fraction) and ρ_f (density of liquid fraction) according to:

$$\phi = \frac{\rho_f wt\%}{\rho_s(1 - wt\%) + \rho_f wt\%} \tag{3.3}$$

ρ_f was assumed to be 1000 kg/m3. If ρ_s was not known, it was measured using a density bottle (a bottle with an accurately known volume). The weight of the bottle when dry, full of water, and full of sludge of a known mass fraction (from oven drying) gave the mass, and therefore volume, of water in the sludge. Since the volume of the bottle was known, the solids density could be calculated. Small errors in solids measurement can cause large errors in density values since the sludge concentration was usually no more than 1 - 2% TS. To offset these errors, sludge was concentrated by centrifugation to as high a concentration as was possible without affecting its flow properties to such an extent that it would be too difficult to get the sludge into the narrow neck of the density bottle.

3.4.3 Transient batch settling

In a transient batch settling test, the settling rate of the supernatant-suspension interface is tracked as a function of time. In this research, transient batch settling tests produced data which was used to calculate $R(\phi)$ data for concentrations $\phi_0 < \phi < \phi_g$ as outlined by Usher (2002). This is typical of the range of solids concentrations found in thickeners. However, this data is also useful for calculating functional forms in filtration analysis.

In transient batch settling analysis, a graduated cylinder was filled with the sludge suspension. A cylinder of 500 ml or greater volume was used to avoid wall effects which can interfere with settling. It was often necessary to dilute the sludge by several factors, as the low density and highly networked nature of sewage sludge was such that it didn't always settle at its initial solid concentration. The metabolic activity of micro-organisms present in the sludge sometimes produced gaseous by-products which caused flotation effects which also impacted settling at longer times. Following the addition of the sludge to the cylinder, the height of the supernatant-suspension interface was measured as a function of time (h vs. t) until no further settling occured over a 24 hour period or sludge floatation occured. A settling curve, which tracked the supernatant-suspension interface was recorded from the settling test. Figure 3.3 shows transient batch settling test results for a flocculated ATAD sludge. The height was normalised by dividing the height of the supernatant/solid interface (h) by the initial height (h_0).

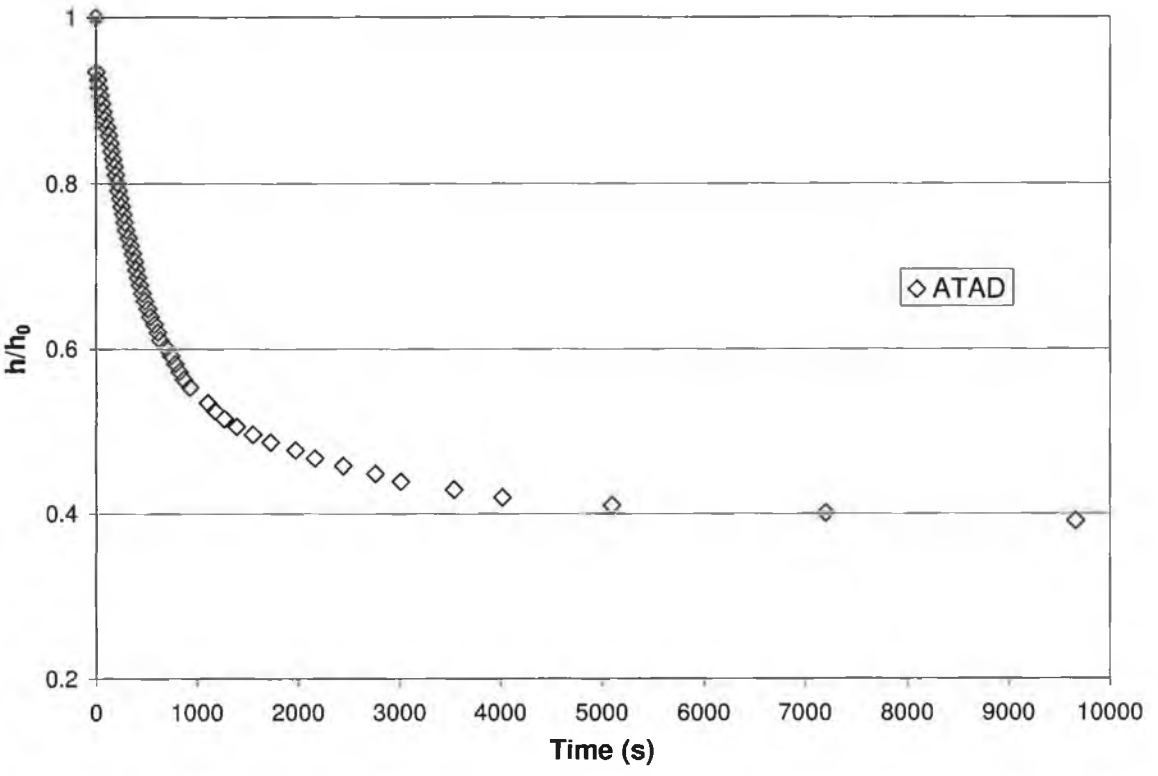


Figure 3.3 Normalised height (h/h_0) versus time (s) data from an ATAD batch settling test.

The hindered settling function, $R(\phi)$ for $\phi_0<\phi<\phi_g$, was then calculated using the suspension's initial solids volume fraction, ϕ_0, initial suspension height, h_0, initial solids settling rate, u, the solid-liquid density difference, $\Delta\rho$. High solids $Py(\phi)$ and $R(\phi)$ data were also required from high pressure filtration tests to perform the analysis. These inputs were used in a computer program BSAMS (Batch Settling Analysis Method Software) (de Kretser and Usher, 2004) which produced EXCEL spread-sheets with detailed functional forms for $P_y(\phi)$ and $R(\phi)$.

3.4.4 Equilibrium batch settling

Equilibrium batch settling provides the only simple technique available for determining the gel point, ϕ_g, and the compressive yield stress, $P_y(\phi)$, at solids concentrations near ϕ_g. ϕ_g provided useful information regarding the structure of flocs and the nature of interparticle interactions in the system. In addition, it is an important modelling and fitting parameter.

For accurate results, several equilibrium batch settling tests were performed simultaneously. In these tests either the initial suspension height, h_0, was kept constant and solids concentrations were varied, or the initial suspension concentration, ϕ_0 was kept constant and initial heights were varied (Usher, 2002). However, in situations where sample was limited, a single-test was performed. The test was performed as follows:

- A sludge sample of known initial solids concentration was added to a measuring cylinder (>500ml).
- The concentration of the sample was such that the equilibrium bed height was predicted to be greater than 25mm.
- The initial suspension height, h_0, was recorded
- The sample was allowed to settle until an equilibrium bed height was attained (i.e. no further settling had occurred within 24 hours)
- The final suspension height, h_f, was recorded.
- Estimates of the gel point, ϕ_g, and/or $P_y(\phi)$ values at a low ϕ were then calculated as outlined below.

The gel-point was estimated from the equilibrium batch settling of a single-cylinder test according to the following equation:

$$\phi_g \approx \phi_{av} \frac{\phi_0 h_0}{h_f} \tag{3.4}$$

In the case of multiple equilibrium batch settling tests, ϕ_g was calculated as the average of the estimates for each of the n cylinders:

$$\phi_g \approx \frac{\sum_{i=1}^{n} \phi_{av,i}}{n} \tag{3.5}$$

$P_y(\phi)$ data can also be determined from equilibrium batch settling data according to the method outlined by Usher (2002).

3.4.5 Pressure filtration

To fully characterise the filtration properties of sludge, several single pressure filtration tests over a range of pressures were performed. The pressures employed typically ranged from 5kPa to 300kPa. At the University of Melbourne a piston-driven filtration rig described by Usher *et al.* (2001) was used. A specially commissioned air-driven filtration rig was employed at Killarney WWTP. The filtration rigs which were used are shown in Figure 3.4.

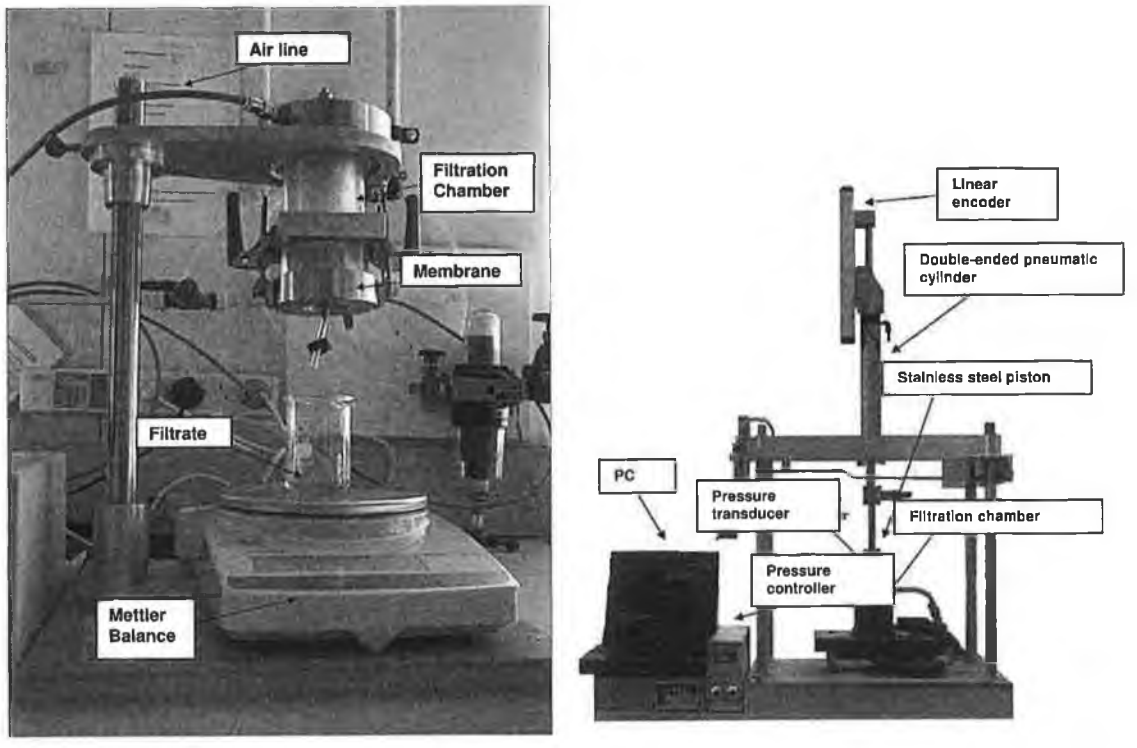


Figure 3.4 Air-driven filtration rig (left) and piston-driven filtration rig (right)

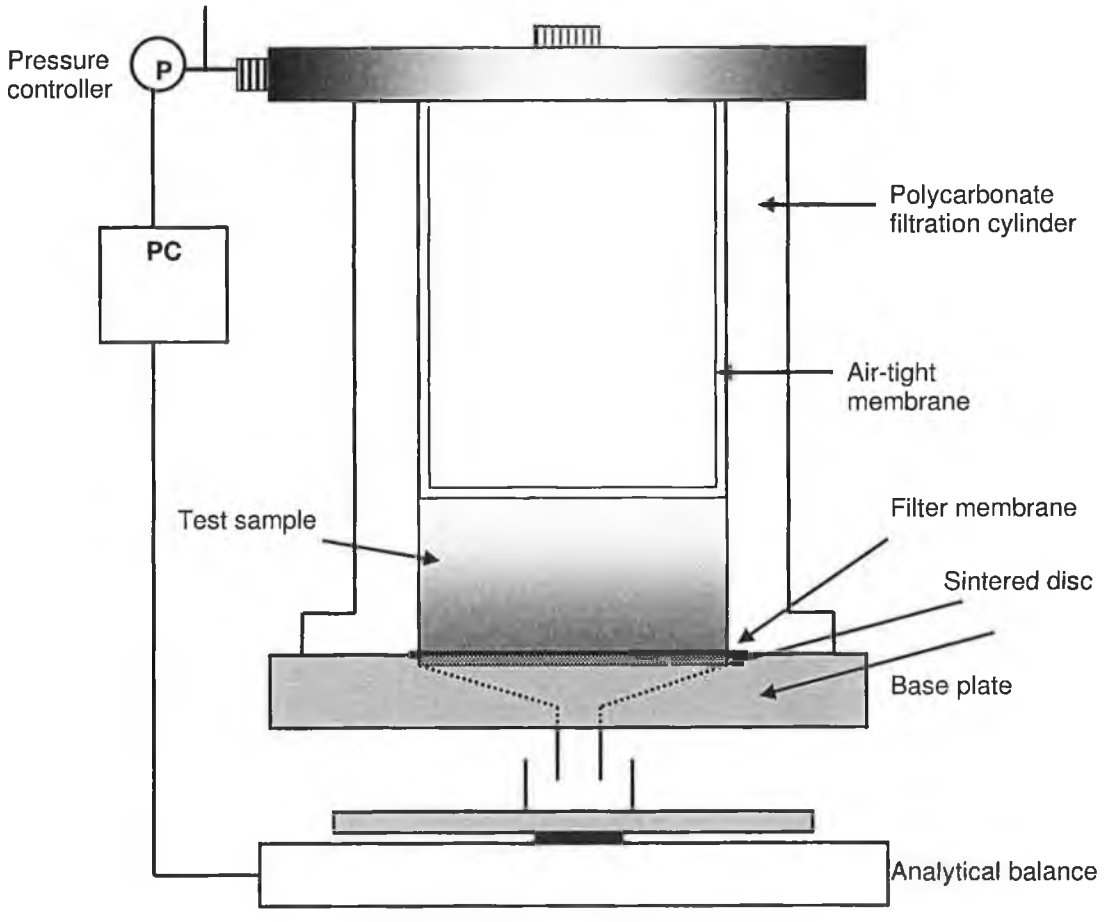


Figure 3.5 Schematic of air-driven filtration-rig

For the piston-driven rig, a linear encoder recorded the height of the suspension versus time. In the case of the air-driven filtration rig the mass of filtrate expelled was logged against time by a laptop which was connected to a Mettler balance. From this data, the height of the sludge suspension was calculated by performing the following mass balance:

$$\Delta h = \frac{m_{liq}}{\rho_l A_{cyl}} \qquad (3.6)$$

Where m_{liq} is the mass of filtrate expelled, ρ_l is the density of the filtrate, Δh is the change in height of the sludge suspension and A_{cyl} is the cross sectional area of the filtration chamber.

The height of the sludge suspension was then calculated according to:

$$h = h_0 - \Delta h \tag{3.7}$$

Where the final height of the sludge suspension is determined from the final displacement, Δh_f, according to the equation, $h_f = h_0 - \Delta h_f$. The h vs. t data were then converted into ϕ vs. t data according to either of the following equations:

$$\phi = h_0 \frac{\phi_o}{h} \tag{3.8}$$

$$\phi = h_f \frac{\phi_\infty}{h} \tag{3.9}$$

Where ϕ_0 is the initial solids concentration (before filtration), ϕ_f is the final solids concentration (following filtration), h_0 is the initial suspension height and h_f is the final suspension height. Equation 3.9 was preferable as there were fewer errors associated with it. Sources of errors associated with equation 3.8 included the loss of filtrate before the filtration run began, evaporation during the filtration test, difficulty in manually

measuring h_0 due to displacement of suspension by the measuring instrument, and inaccurate values for ϕ_0 which was often difficult to measure accurately for highly flocculated solutions.

For each filtration run, using the air-driven filtration rig, the following procedure was followed: A 0.65 μm *Milipore* membrane was placed over a sintered disk at the base of the filtration chamber. 30-50 ml of sludge of known solids concentration was then carefully added to the airtight chamber and the initial height (h_0) was measured. Once assembled, pressure was supplied to this chamber using compressed air. A Bronkhurst pressure-controller regulated the pressure within the filtration chamber. In air-driven filtration, an airtight membrane was required to separate the filter-cake from the compressed air. This was to minimize drying and to prevent air-breakthrough compromising the integrity of the filter cake. During filtration tests, particularly near the end of tests, this residual air can sometimes break through the filter-cake, desaturating the cake and potentially compromising the results.

To minimise the occurrence of air-breakthrough, care was taken to remove as much of the air remaining between the membrane and the wall of the filtration chamber prior to filtration testing. Also, a plastic disc, of a diameter slightly smaller than the interior diameter of the filtration chamber was placed on top of the sludge sample before each filtration test. This prevented desaturation of the filter-cake during air-breakthrough events.

The use of the membrane reduced the occurrence of such air-breakthrough events, but particularly in cases where the final cake height was small, air-breakthrough sometimes still occurred. This was due to residual air remaining between the membrane and the wall of the filtration cylinder. Figure 3.6 is an example of such an air-breakthrough event.

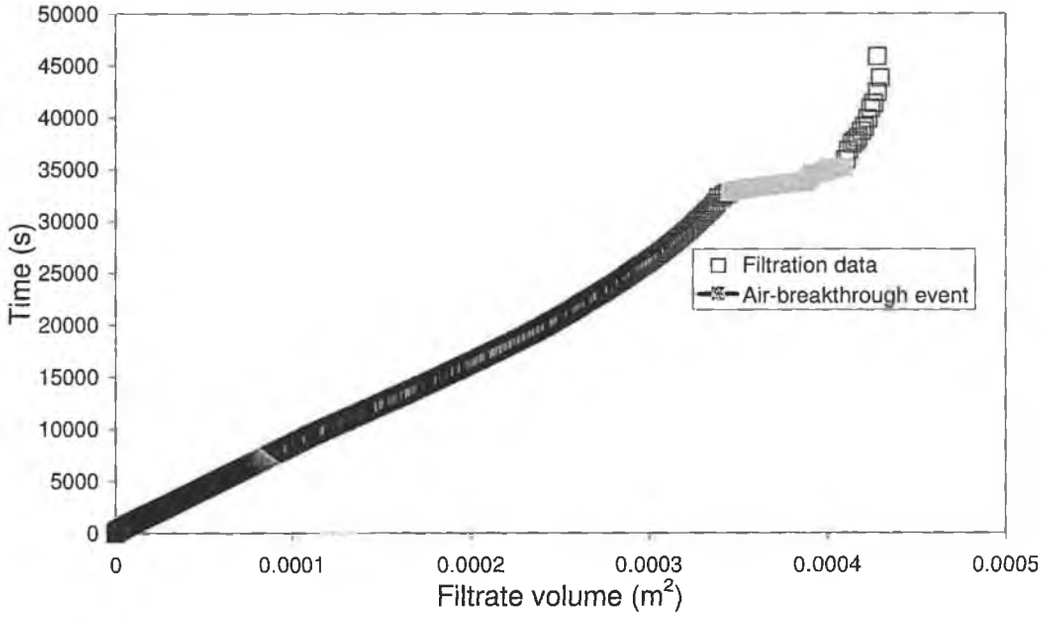


Figure 3.6 An example of an air-breakthrough event for a Luggage Point sample in a 100 kPa pressure-filtration test

The pressure in the filtration rig was controlled using a *Bronkhurst* pressure controller. LABVIEW software, integrated with the rig, calculated the height of the suspension automatically according to equation 3.6, and this could subsequently be checked against the manually measured final height following each filtration run. The following parameters were measured manually and were necessary inputs for the filtration software: initial solids volume fraction, initial suspension height, and suspension density.

3.4.6 Calculation of dewatering parameters from combined batch settling/pressure filtration

Figure 3.7 gives a complete overview of the analytical and experimental methods which were used to calculate $R(\phi)$, $P_y(\phi)$ and $D(\phi)$ across from low ϕ to high ϕ as part of this research.

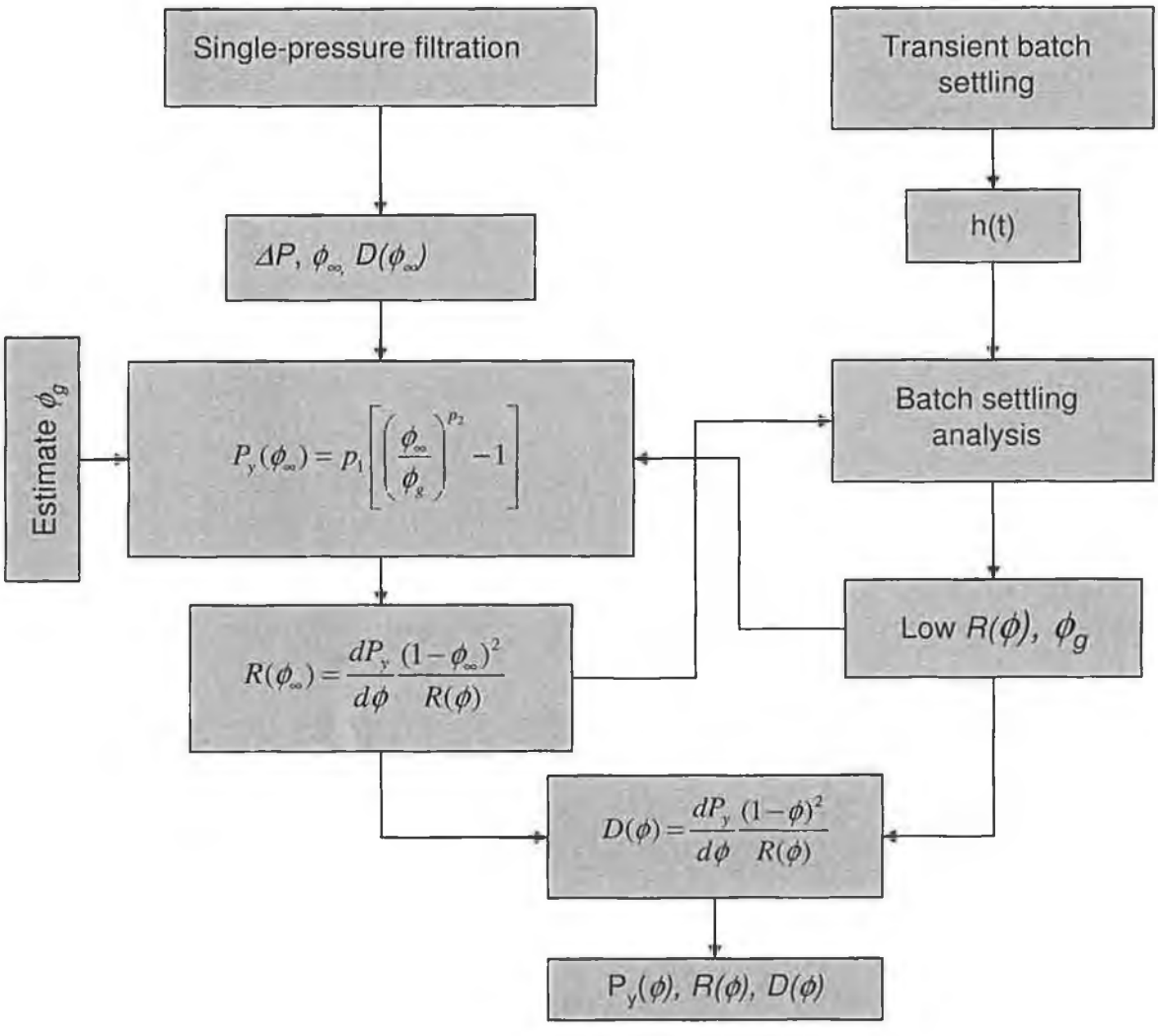


Figure 3.7 Overview of biosludge characterisation protocol analysis methods

As noted in Chapter 2, sewage sludges are exceptionally difficult to characterise in terms of $P_y(\phi)$ and $R(\phi)$ according to traditional methods. For inorganic sludges $P_y(\phi)$ is simply calculated from the filtration end-point in a pressure filtration test, however, for sewage sludges long compression times prevent an end-point from satisfactorily being determined. Additionally, in pressure-filtration tests of inorganic sludges, $R(\phi)$ is calculated from the inverse of the slope of the linear (cake formation) portion of a plot of t vs. V^2, where t is time and V is the specific volume of filtrate. The inverse of this slope is termed β^2. According to the following equation, the slope of a plot of β^2 versus ΔP is used to calculate $R(\phi)$.

$$R(\phi) \equiv \left(\frac{\lambda}{V_p}\right) r(\phi_\infty) = \frac{2}{\frac{d\beta^2}{d\Delta P}} \left(\frac{1}{\phi_0} - \frac{1}{\phi_\infty}\right)(1-\phi_\infty)^2 \qquad (3.10)$$

Where ϕ_∞ is the equilibrium volume fraction at ΔP, ϕ_0 is the initial solids concentration of the filtration test, V_p is the volume of a suspension particle and λ is the Stokes drag coefficient for a single particle in an infinite medium ($=6\pi a_p \eta$ for spherical particles, a_p is the radius of a particle and η is the fluid viscosity). However, for sewage sludges this linear region is too short, or non-existent, thus preventing accurate calculation of $R(\phi)$. Hence, an alternative method was required. A logarithmic function was fitted to truncated filtration data to predict an end-point, and ϕ_∞ and $D(\phi)$ were calculated (Usher 2002; Stickland, 2005). This method is outlined below.

During pressure filtration, it has been shown that filtration time varies logarithmically (to first order) with filtrate volume during cake compression (Landman *et al.*, 1997; Stickland, 2005; Usher, 2002):

$$t = E_1 - E_2 \ln(V_\infty - V) \tag{3.11}$$

Where

$$E_1 = \frac{h_0^2 \phi_0^2}{D(\phi_\infty)\phi_\infty^2}\left[T_C + \frac{4}{\pi^2}\ln\left(\frac{2A_0\phi_0 h_0}{\pi}\right)\right] \tag{3.12}$$

V_∞ is the equilibrium filtrate volume, h_0 is the initial suspension height, ϕ_0 is the initial solids volume fraction, ϕ_∞ is the equilibrium solids volume fraction, T_C is the dimensionless time when cake compression begins, $D(\phi_\infty)$ is the diffusivity at ϕ_∞, and A_0 is a constant, arising from the solution. Equation 3.11 is rearranged in terms of the average volume fraction, $<\phi>$, to give:

$$t = E_3 - E_2 \ln\left(\frac{1}{\langle\phi\rangle} - \frac{1}{\phi_\infty}\right) \tag{3.13}$$

Where

$$E_2 = \frac{4h_0^2\phi_0^2}{\pi^2 D(\phi_\infty)\phi_\infty^2} \tag{3.14}$$

and

$$E_3 = E_1 - \frac{4h_0^2\phi_0^2 \ln(\phi_0 h_0)}{\pi^2 D(\phi_\infty)\phi_\infty^2} \tag{3.15}$$

Thus, a logarithmic fit to the last m points of the compression data was used to give material parameter information since E_2 contains an expression for $D(\phi_\infty)$. A computational curve-fitting procedure developed by Stickland (2005) was used to randomly generate two hundred sets of m and ϕ_∞ from a range of possible values and to subsequently find the set that gave the minimum fitting error. The range was then reduced by 50% and the process was repeated until the values obtained were stable.

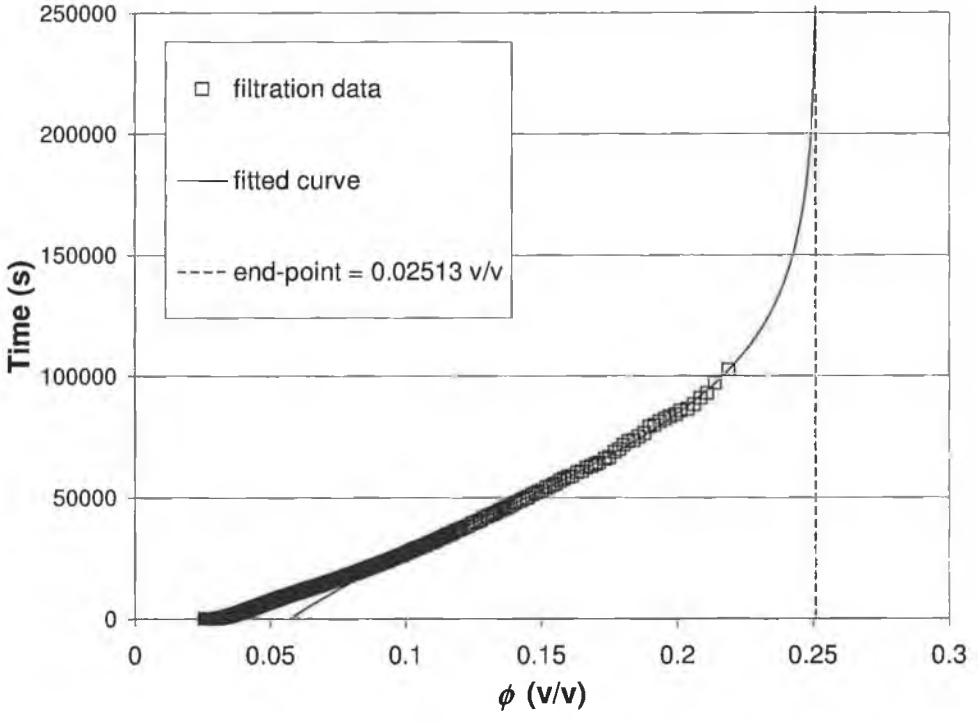


Figure 3.8 Log-fitting of filtration data

The log fitting procedure gave ϕ_∞ and $D(\phi_\infty)$ values for each pressure, which gave $P_y(\phi)$ since $\Delta P = P_y(\phi_\infty)$. $P_y(\phi)$ values were obtained at several different filtration pressures and a power law functional form (Equation 3.16) was fitted to the data:

$$P_y(\phi_\infty) = p_1\left[\left(\frac{\phi_\infty}{\phi_g}\right)^{p_2} - 1\right] \tag{3.16}$$

ϕ_g was estimated by ϕ_0 and the subsequent fit was used to calculate $R(\phi)$ according to:

$$R(\phi) = \frac{dP_y}{d\phi}\frac{(1-\phi)^2}{D(\phi_\infty)} \tag{3.17}$$

A functional form of the diffusivity of the sludge $D(\phi)$ could then be calculated from the functional forms of $P_y(\phi)$ and $R(\phi)$ according to the following equation.

$$D\phi = \frac{dP_y(\phi)}{d(\phi)}\frac{(1-\phi)^2}{R(\phi)} \tag{3.18}$$

3.4.7 Determination of dewatering parameters from centrifugation tests

Figure 3.9 shows a typical $P_y(\phi)$ versus ϕ functional form for an ATAD sludge which was obtained using the biosludge characterisation protocol described above. It is apparent from the data, that $P_y(\phi)$ data was not defined for a large range of solids concentrations which spanned an area of several orders of magnitude, from ϕ_g to higher ϕ values associated with pressure filtration. The curve-fit in this area was extrapolated from the high pressure filtration data to the gel-point. Equilibrium and transient centrifugation tests

could be used provide data points within this region. These methods can also provide settling profiles for sludge samples which will not readily settle in batch settling tests. This data can also be used in the calculation of medium range $R(\phi)$ values. Equilibrium and transient centrifugation techniques are described below.

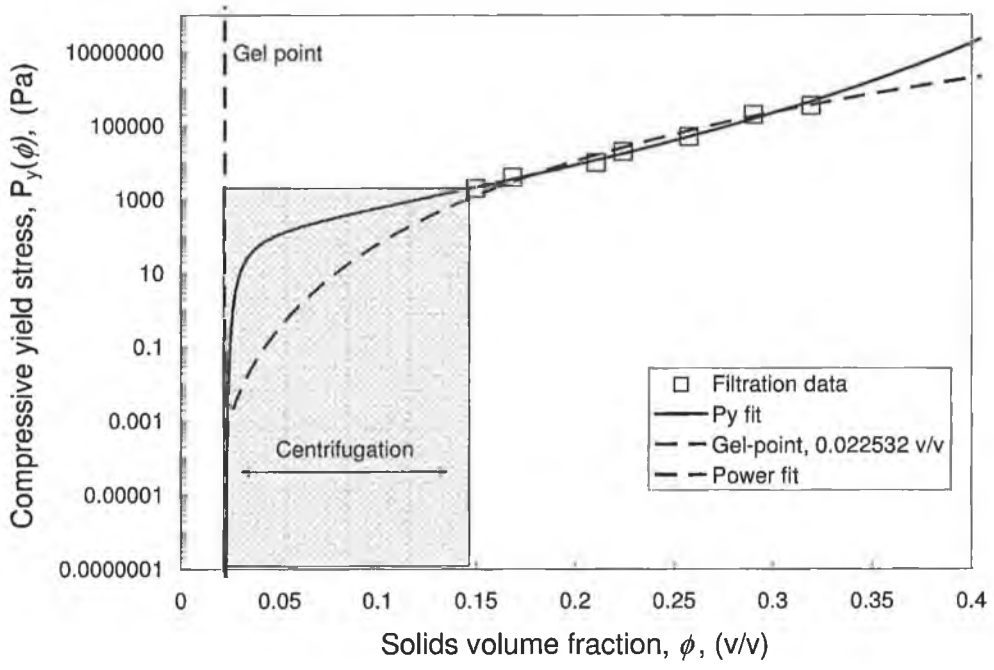


Figure 3.9 A $P_y(\phi)$ functional form obtained from batch settling and filtration analysis of a sewage sludge. The shaded area denotes the area from which data can be obtained from centrifugation

3.4.7.1 Equilibrium centrifugation

$P_y(\phi)$ data was obtained at intermediate solids concentrations by centrifugation to equilibrium solids, ϕ_∞ at a specific pressure, followed by a scrape test to determine a solids distribution profile for the resulting cake. Similar to the batch settling methods, both transient and equilibrium techniques were employed depending on the type of data

which was required. Green, (1997) described in detail a multiple speed equilibrium height technique, and a concentration profile technique, for obtaining $P_y(\phi)$ data from suspensions. In this research the concentration profile technique (scrape test) was employed to obtain $P_y(\phi)$ data points in an intermediate region that was not experimentally defined by batch settling tests and/or the lowest pressures applicable in pressure filtration. The method is described below:

A *Rotofix 32 Hettich* Centrifuge with a maximum speed of 4000rpm was used at Killarney WWTP for analysis. Round-bottom, 50ml translucent polycarbonate tubes were used to hold samples. Epoxy was added to these tubes and allowed to harden to provide a flat-bottom which was required for equal distribution of sample weight during centrifugation. At the University of Melbourne, a temperature-controlled *Jouan* centrifuge was used. This allowed centrifugation to be performed at 5 °C, which minimised microbial activity in the samples during settling. The scrape test procedure is detailed below:

1. The total height of the centrifuge tube and the height of the base were measured, h_t and h_b.
2. The centrifuge tube with a flat bottom was filled 90-95% full with a suspension of known concentration ϕ_0.
3. The initial suspension height was measured h_0.
4. The tube was centrifuged at constant speed S and centrifugal acceleration, g.

5. The average height of the interface between sediment and supernatant was measured regularly (five minute intervals were used at first but these were increased accordingly as settling slowed) until settling stopped and equilibrium had been reached (i.e. no further settling within 24 hours).
6. Equilibrium sediment height was then measured, h_f.
7. After h_f was attained the supernatant was poured from the top of the centrifuge tube.
8. A modified spatula with an adjustable crocodile clip was used for sectioning the sample at set intervals.
9. The sectioning depth of the spatula (h_d), was recorded and the top layer of sediment was carefully removed by scraping and transferred to a crucible of known weight for measurement of total solids by weight loss.
10. This was repeated in increments to the bottom of the centrifuge tube, ensuring that at least 1mm sections were taken at each step (for accuracy).
11. All samples were transferred to oven for solids determination.

A solids concentration profile was then be plotted against height. From this $P_y(\phi)$ was determined using an analytical spreadsheet. The equations for calculating $P_y(\phi)$ from the sectioning test were obtained from Green (1997).

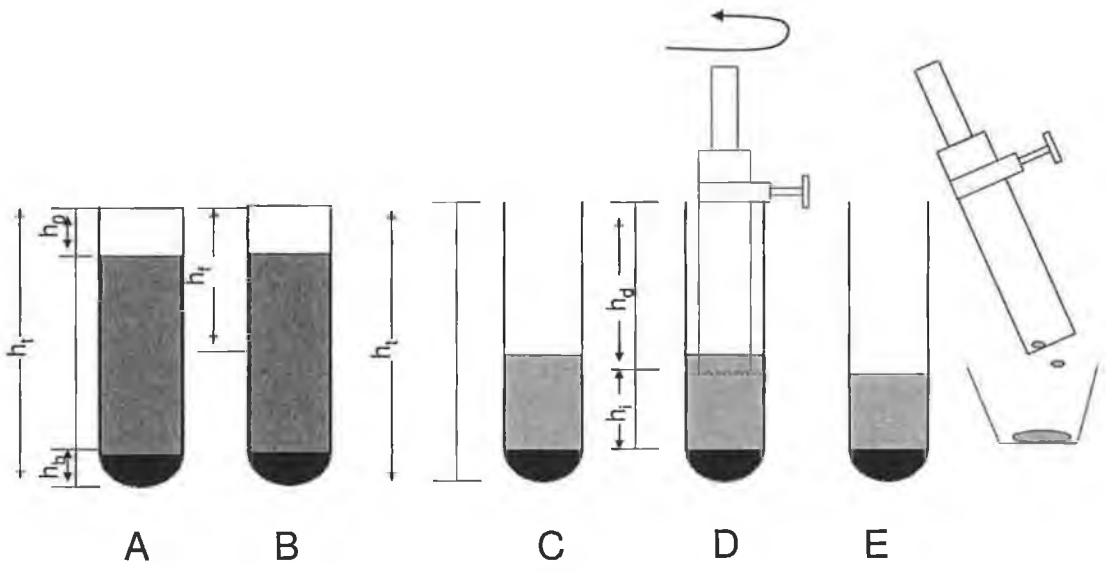


Figure 3.10 Scrape test procedure to determine the concentration profile of a suspension in a centrifuge tube; A) suspension at initial concentration, B) suspension at equilibrium, C) supernatant is poured off, D) sectioning depth of spatula is set, E) layer of sediment is scraped off and transferred to weighing tin.

3.4.7.2 Transient Centrifugation analysis

There was sometimes difficulty in settling sewage sludges in batch settling tests under the influence of gravity only. Hence, transient *h* versus *t* profiles from centrifugal settling tests proved more useful in comparing the settling characteristics of these sludges. Two methods of settling analysis were employed. The first method employed the same centrifuges used in the equilibrium settling method. The centrifuge was stopped at intervals and the sediment-supernatant interface was measured. Initially, stoppages of 5 minutes were used. This allowed sufficient time for the centrifuge to reach the set speed. When the measured change in the sediment-supernatant interface was less than 0.5 mm during a 5 minute interval the settling period was increased to 10 minutes, and so forth, until no settling was recorded within a 24 hour time period.

Height (h) data was then normalised to a dimensionless height, *h(-)*, using the following equation:

$$h(-) = \frac{h}{h_0} \tag{3.19}$$

A drawback of the transient centrifugation method was an uneven distribution of the sediment-supernatant interface, which was probably due to the acceleration and deceleration of the centrifuge. Therefore, a continuous on-line measurement without such interruptions is a preferable alternative. This can be achieved by use of LUMiFuge® 110 brand centrifuge.

3.4.7.3 LUMiFuge® 110

The LUMiFuge® 110 is a 'dispersion analyser' and was able to measure the settling behaviour of suspensions online. The instrument had a built-in light source located above the sample and a CCD sensor below. Therefore, the instrument was able to measure the transmission through the tube (at all positions along the radius of the tube) with increasing time. A transmission profile was obtained from the instrument (% transmission along the radius of the sample tube). These transmission profiles were then transformed into a *h* vs. *t* profile. This was done using SEPVIEW software, by selecting a certain transmission % (called a trigger %). This was deemed to be the point where the settling interface was situated. A 10% transmission was appropriate as the trigger.

CHAPTER 4: Pilot-Plant digestion dynamics

4.1 Introduction

One of the principal aims of the research was to relate digestion conditions to the dewatering properties of ATAD sludge. To achieve this, a 500 litre ATAD pilot-plant was commissioned at Killarney WWTP to produce ATAD sludges under controlled conditions. This pilot-plant was a unique piece of equipment of bespoke design. The performance of the pilot-plant was analysed using a number of parameters. These were chemical oxygen demand (COD) (soluble and total), temperature, pH, total solids (TS) and volatile solids (VS). This Chapter presents the digestion data and evaluates the performance of the ATAD pilot-plant.

4.2 Batch Trials

4.2.1 Introduction

The pilot-plant configuration and operational details are described in Chapter 3 (Materials and Methods). Initially, two batch digestions (Trial 1 and Trial 2) were conducted to firstly determine, whether the pilot-plant could attain thermophilic temperatures, and secondly, to evaluate the reproducibility and stability of conditions within the reactor.

4.2.2 Feedstock composition

The feedstock used in the retention time trials was a mixture of waste-activated sludge (WAS) which originated on-site at Killarney WWTP and a small amount of imported septic-tank discharge. The feedstock at Killarney was unique as it consisted of a blend of three different types of secondary sludge. Fine-bubble diffuse-aeration, surface aeration and oxidation ditches are all utilised as activated-sludge treatment processes at the plant. The surface aeration and fine-bubble diffuse-aeration tanks are in operation throughout the year, the oxidation ditches are brought on-line during the summer months, which is when the peak hydraulic load to the plant is experienced. Ferric chloride is added prior to aeration for phosphate removal.

In routine operation at the plant waste sludge from the activated-sludge processes is sent to a picket-fence thickener where it was thickened to approximately 1 - 2% solids (w/w). The waste sludge is then further thickened to 5.5 – 6% in a belt-filter press. Zetag 7867 is used as a conditioning agent and applied at 3 – 4g /kg TS. In this study, thickened WAS was used as the feedstock for the digestion trials.

In Figure 4.1, the percentage (w/w) total solids (TS) are presented as a function of time (hr) for both of the retention time trials. In Trial 1 the starting TS was 5.93% (w/w). In Trial 2 the starting TS was 6% (w/w). The pilot-plant temperature (°C) is presented against time (hr).

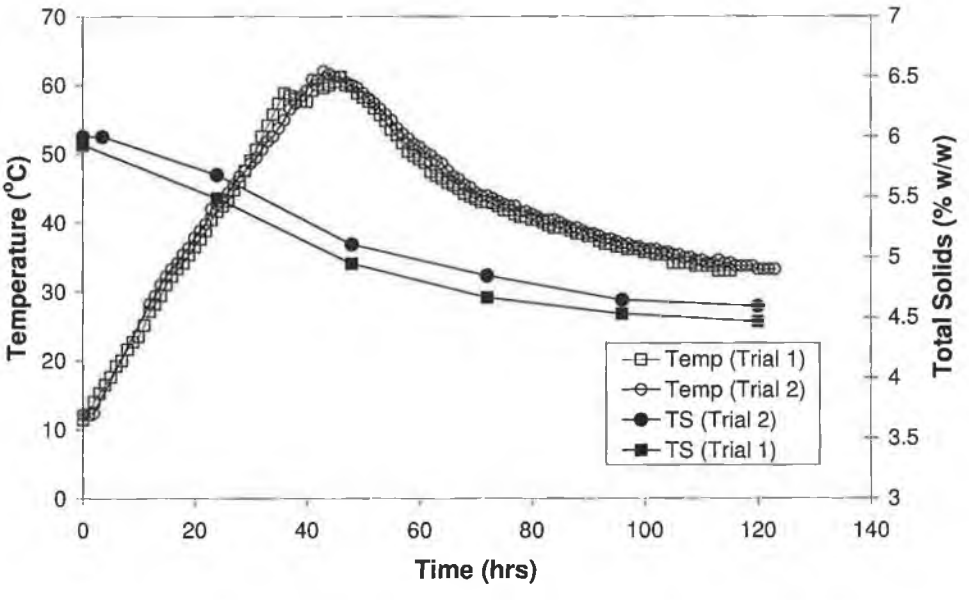


Figure 4.1 Total solids (% w/w) and temperature (°C) versus time (hrs) within the pilot-plant reactor during batch digestions (Trial 1 and Trial 2).

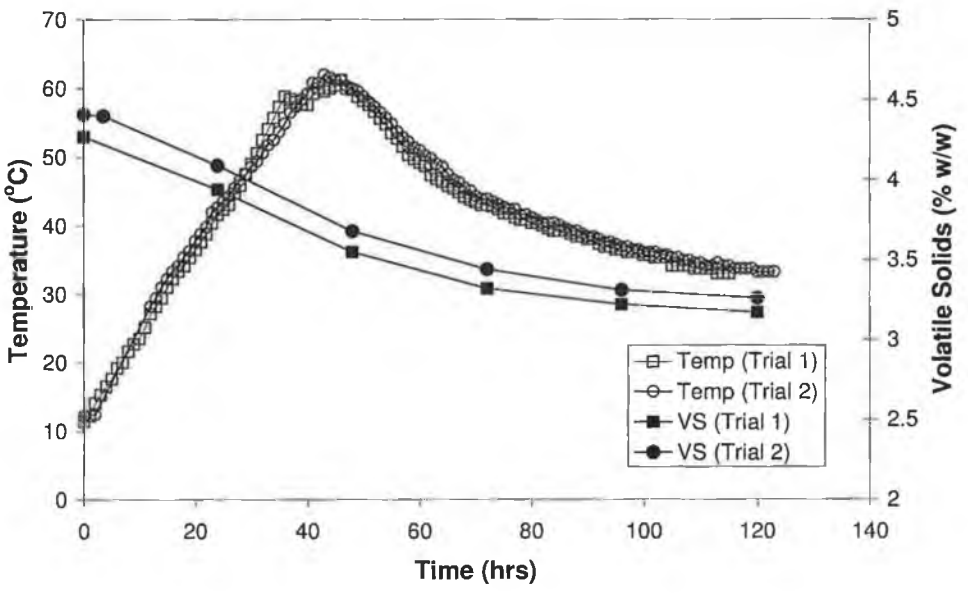


Figure 4.2 Volatile solids (% w/w) and temperature (°C) versus time (hrs) within the pilot-plant reactor during batch digestions (Trial 1 and Trial 2).

In Figure 4.2 the percentage (w/w) volatile solids (VS) are presented as a function of time within the pilot-plant for the two trials. In Trial 1 the starting VS was 4.27% (w/w) and in Trial 2 it was 4.41% (w/w).

4.2.3 Temperature

In Trial 1 the initial temperature of the feed sludge was 11.4 °C. In Trial 2 the baseline temperature of the feed sludge was 12.2 °C. As the baseline temperature of the feed-sludge differed by less than 1 °C between the batch digestion trials, and the starting solids concentration were also similar, the trials allowed for an examination of the relationship between solids removal and temperature evolution. During the batch digestion trials the pilot-plant's automatic cooling system was programmed to operate once the temperature

of the plant contents reached 61 °C, and stop operating once the temperature dropped below 60 °C.

Temperature increased in the pilot-plant at a similar rate during each batch trial (Figure 4.1). During Trial 1 the temperature increased at an average rate of 1.31 °C/hr during the first 36 hours of digestion, and during Trial 2, the temperature increased at an average rate of 1.25 °C/hr over the same period. It is possible that the marginally lower solids concentration of the feed sludge for Trial 1 facilitated the slightly greater rate of temperature increase, due to the increased viscosity of the sludge facilitating improved heat transfer.

Temperatures in excess of 55 °C were achieved, and maintained for 20 hours in each Trial. This showed that the feedstock contained sufficient substrate to facilitate autothermal operation. The maximum temperature of 61 °C attained in both trials represented a maximum temperature differential of 49.6 °C between the feedstock and the pilot-plant contents for Trial 1, and 48.8 °C for Trial 2.

In both batch trials the temperature continued to decrease following activation of the cooling system, and did not recover to pre-cooling levels. This decrease in temperature occured at similar rates (Figure 4.1) for both trials. Following 120 hours of digestion, the temperature of the pilot-plant contents fell to 33 °C for Trial 1, and 33.7 °C for Trial 2.

A separate trial established that a moderate quantity of heat energy was imparted to the sludge from the mixing/aeration equipment. In this trial the pilot-plant was filled with water at 8 °C and following 24 hours of mixing and aeration the temperature of the water rose to 24 °C and stabilised at this temperature. The ambient temperature ranged from 8 - 14 °C during the trial.

4.2.4 Total and volatile solids removal

Total solids and volatile solids destruction rates coincided closely during the batch digestion trials. For Trial 1 the TS concentration of the feedstock was 5.93% (w/w) and for Trial 2 it was 6% (w/w). These values were close to the maximum solids concentrations of 6 - 7% recommended for the operation of ATAD reactors (Ponti *et al.*, 1995; Kelly, 2003). TS above 6% can cause significant impacts on the rheological properties of ATAD sludge, most notably resulting in reduced viscosity, which affects such parameters as mixing, heat transfer and oxygen transfer efficiency (Jewell and Kabrick, 1980).

In Trial 1, 65% of the total VS reduction occurred within the first 48 hours of digestion. Following this, sludge temperature dropped. It is probable that following an initial high rate of digestion, the rate then slowed, due to a reduction in metabolic activity. Over the following 48 hours, a further 30% of the total VS destruction occurred, and the temperature of the pilot-plant dropped to 37 °C.

In Trial 2, 63% of the total VS destruction occurred within the first 48 hours of digestion. As in Trial 1, the temperature of the pilot-plant began to decrease following 48 hours of digestion. Over the subsequent 48 hours of digestion, 37% of the total VS destruction occurred. The total VS reduction which occurred over the 5 day batch digestion trials was 25.7% for Trial 1 and 26% for Trial 2.

4.2.5 pH

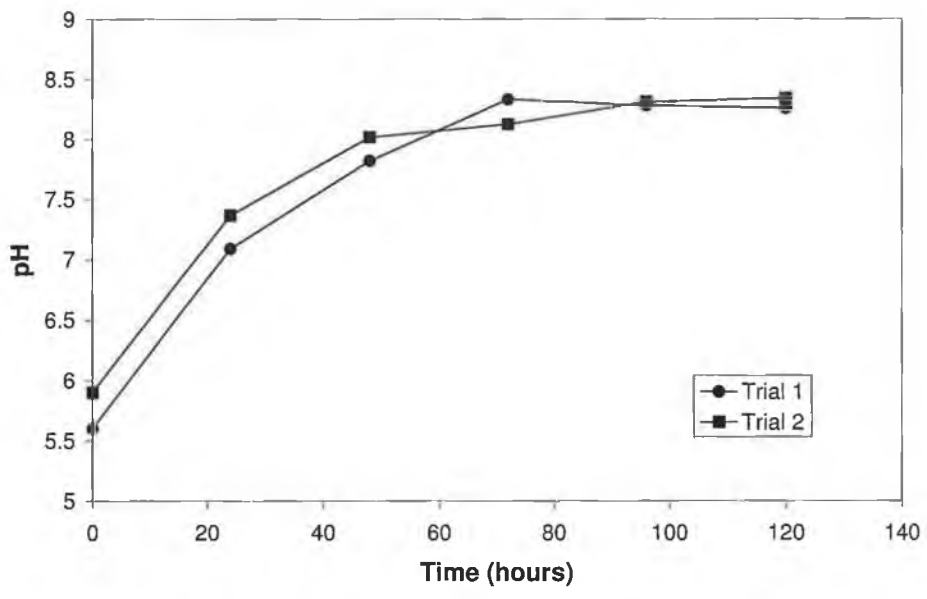


Figure 4.3 Changes in pH during batch digestion trials

Figure 4.3 shows pH values within the reactor during the batch digestion trials. pH values were similar in both trials. pH increased sharply over the first 60 hours and then stabilised above pH 8. It is reported in the literature that these are typical pH values for an ATAD system (Staton *et al.*, 2001). The high pH found in ATAD systems may be linked to the

hydrolytic release and subsequent acid-base transformation of reduced nitrogen (Staton *et al.*, 2001)

4.3 Semi-batch trials

4.3.1 Introduction

The ATAD pilot-plant was operated at two different HRTs; 7 day and 10 day. Reports varied in the literature about the most appropriate retention time/organic loading rate for an ATAD system; both of which are related parameters (Jewell and Kabrick, 1980; LaPara and Alleman, 1999). Short retention times can lead to excessive cooling (due to the large volumes of feed sludge at ambient temperature). This restricts the establishment of a successful thermophilic biomass. Alternatively, a retention time which is too long is likely to lead to substrate-limited conditions. This is because the organic loading rate is insufficient to facilitate the needs of the respiring biomass.

There is limited information in the literature regarding optimum process conditions for thermophilic reactors. LaPara *et al.* (1999) found that COD removals of 20,000 - 40,000mgl^{-1} were required, coupled with an oxygen transfer efficiency of 10 - 20%. Jewell and Kabrick (1980) postulated a simple equation for the extent of autoheating in ATAD systems

$$\Delta T = 2.4\Delta COD \qquad (2.1)$$

Where ΔT is the increase in temperature (°C) in the aerated sludge and ΔCOD is the COD (g/L) which is oxidised at hydraulic retention times of less than 8 days. It is also stated in the literature that an influent-solids concentration of between 4% and 7% serves as an appropriate rule of thumb, for the minimum and maximum starting solids concentrations for ATAD reactors treating activated sludge (LaPara and Alleman, 1999). The influent sludge to the pilot plant had a very high total COD (as high as 90,000 mg/L). Average COD values reported for ATAD in the literature ranging from 25,000 mg/L to 60,000 mg/L (Ponti *et al.*, 1995a; Scisson, 2003). On the basis of COD loading, the feed sludge was well in excess of the minimum COD of 25,000 mg l^{-1} which was specified by Ponti *et al.*, (1995a) as being required for 'autothermal' operation.

4.3.2 Start-up

Figure 4.4 gives an overview of the VS content of the influent and effluent, temperature and the TS content of the influent over the start-up for the pilot-plant

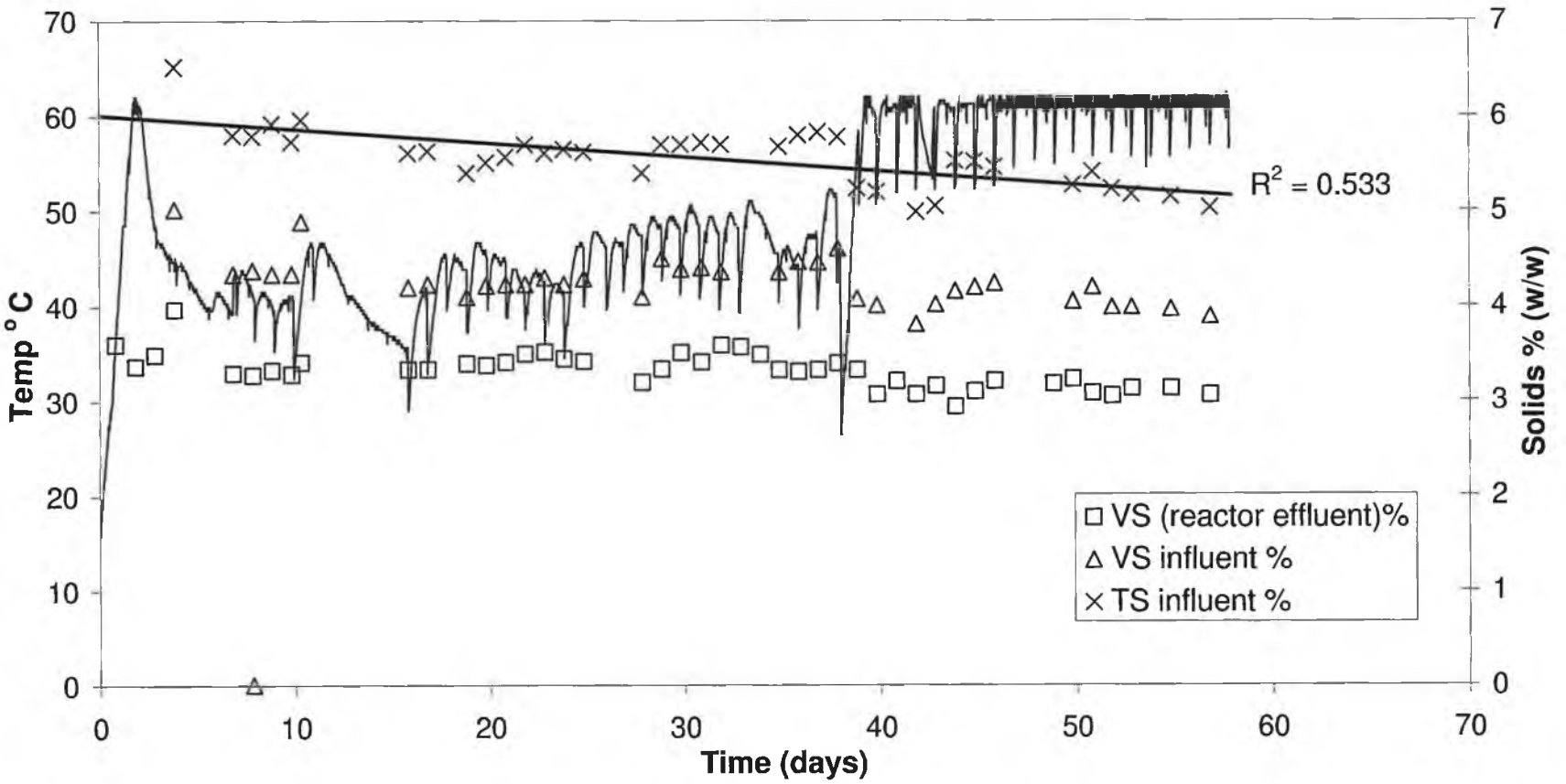


Figure 4.4 Volatile solids and total solids concentration (% w/w) in the influent of pilot plant and temperature (°C) over start-up trials

Following the batch trials, the pilot-plant was emptied and cleaned, then fed 500 L of thickened activated sludge at 5.6% (w/w) TS. The temperature of reactor contents quickly rose to 60 °C (within 36 hours) and then began to decline (Figure 4.4). After 48 hours, a 10 d HRT feeding regime was implemented (with approximately 50 L being wasted and fed each day). The level sensor was used to ensure that 500 L of sludge was maintained in the pilot-plant at all times. Evaporation was offset by the addition of water. While temperatures did not recover to thermophilic levels, the rate of cooling, which followed the initial peak in temperature, slowed down. It's concluded that operating on a 10 day HRT time provided an insufficient organic load for the attenuation of thermophilic temperatures.

The feeding regime was switched to a 7.1 day HRT on Day 15, with 70 L of sludge being fed/wasted daily. Over the following several days, the average temperature within the pilot-plant continued to drop, despite brief peaks in temperature following feeding. Following 10 days of operation, the pilot-plant was fed 160 L of sludge to increase the organic load in an effort to attain thermophilic temperatures. The temperature initially rose to 45 °C in the following 24 hours, and the 7.1 day HRT was reinstated, and despite the temperature recovering to 45 °C on the subsequent day, average temperatures declined to mesophilic levels.

From day 16, the plant was operated on a 5 day HRT (to increase the organic load) and the reactor showed signs of stabilisation at 48 ± 1 °C (the thermo-tolerant zone). The

pilot-plant was operated on a 5 day HRT for 25 days (5 retention times). The temperature approached the thermophilic zone by day 36 (50.6 °C). Throughout the trial various efforts were made to determine why thermophilic temperatures were not being attained and maintained. 2 additional boreholes were opened along the shaft of the aerator to facilitate the input of extra air, without any effect. These were then closed and the piping used to actively draw away effluent gases and condensate was removed to ascertain whether too much air was being drawn through the system and effectively cooling the reactor contents, this also had no effect.

From day 16 to day 36, the pilot-plant was achieved between 19 and 25% VS destruction. This is below the 38% recommended by the *Code of good practice for the use of biosolids in agriculture* (Fehily, Timoney & Co. 1999). As the full-scale plant at Killarney was achieving the 38% target, on a 7 day retention time, utilising the same feedstock, it was unclear why VS destruction levels were so low in the pilot-plant. These low substrate utilisation rates were the likely reason for temperatures failing to increase to thermophilic values. It is possible that the large volume changes (1/5 of the reactor volume) at already mesophilic temperatures cooled the reactor contents below a threshold value from which the thermophiles could recover and thrive.

4.3.3 Seeding of pilot-plant with thermophilic biomass

On day 40, 14 litres of sludge from Reactor 2B (of the full scale ATAD plant) were mixed with the influent to the pilot-plant in an effort to 'inoculate' it with a thermophilic biomass. Kelly and Mavinic (2003) stated that there is no need to inoculate an ATAD reactor in such a manner. However, in light of the difficulties in attaining thermophilic temperatures, it was an option which was worthy of investigation.

On Day 41 the reactor was emptied of 400 L of sludge, due to an operational issue with the vertical impeller. Following this, the reactor was filled once again to the operational level with fresh sludge at 5.6% (w/w) TS and the temperature within the pilot-plant had reached 60 ^{o}C by day 42. On this occasion, a 5 day HRT was implemented immediately upon attenuation of thermophilic temperatures. On the 5 day HRT, 100 L of sludge was fed to the plant daily. Thermophilic temperatures were maintained. It was not clear why implementation of the 5 day HRT was successful on this occasion and not on day 16. However, it is possible that once an initial false-peak of thermophilic temperatures was reached during which mesophilic and thermo-tolerant bacteria were likely to still exist in significant numbers, the reactor needed to be fed a significant volume of sludge at first to maintain these temperatures until the thermophiles dominated. On day 16, the 5 day HRT was implemented when temperatures were within the mesophilic zone (30 ^{o} C). It is likely that the thermophilic biomass took a while to properly establish itself, and such a thermo-tolerant transition phase between mesophilic temperatures and thermophilic temperatures has been reported in the literature (LaPara and Alleman, 1999).

Initially, during the start-up trials, it was thought that the implementation of a 10 day HRT may not have been a sufficient organic loading rate to meet initial energy requirements. However, data from later trials proved that thermophilic temperatures can be maintained at significantly lower organic loading rates than those initially implemented during the start-up period.

The inoculation of the pilot plant with sludge from Reactor 2B may also have been necessary to establish a stable thermophilic biomass, even though it was stated in the literature that such an inoculation is not required for ATAD processes (LaPara and Alleman, 1999). Significantly, the rheological nature of the influent sludge had also altered between day 1 and day 40 of the start-up period. A linear regression analysis of the total solids concentration of the influent sludge revealed a gradual drop in solids concentration over the time period in question (Figure 4.4). The decrease in solids concentration may have facilitated better mixing of the sludge and hence, improved aeration and substrate utilisation, despite the reduced organic loading. Following this initial start-up period, the pilot plant feeding regime was switched to a 7.1 day retention time in the first of the retention time trials.

4.4 7.1 day and 10 day retention time trials

4.4.1 Introduction

Retention time is an important parameter in any activated sludge process. Aerobic processes are typically run at shorter retention times than anaerobic processes, due to the

higher substrate utilisation rates which are found in aerobic systems, compared to anaerobic systems (Metcalf *et al.*, 2001). In the typical operation of ATAD systems, retention times are generally quite short (5 – 10 days), and are often required to be within the limits specified by legislation which may dictate mandatory minimum retention times, such as in Killarney (a mean retention time of at least 7 days) (Fehily, Timony & Co., 1999). The retention time employed in any sludge digestion system must also be longer than the growth rate of the slowest growing organism required for the process.

Retention time trials were also desirable as the pilot plant had not been commissioned previous to this research, and such trials were necessary to provide vital information regarding process stability, extent of nutrient removal, and the limits of operation. Varying retention time was also necessary to develop kinetic coefficients for the process, such as those described by Metcalf *et al.*, (2001). Also, much of the research focussed on ATAD dewatering has linked poor dewatering properties to solution biopolymers, which may be released during digestion. A study evaluating performance over multiple retention times may be able to draw some inferences regarding the rates of formation and removal of these compounds and the subsequent effects on dewatering.

It is desirable to run trials which evaluate retention time for at least a minimum of 2 steady-state periods (Metcalf *et al.*, 2001). A steady-state period was defined for the purpose of this research as any retention time subsequent to the initial passage of two retention times, i.e. a trial consisting of six retention times, would consist of four steady-state periods. The 2 HRTs which were considered at Killarney were 7.1 day and 10 day.

The 7.1 day HRT trial was run for 20 steady-state periods and the 10 day HRT was run for 6 steady-state periods.

4.4.2 7.1 day HRT

4.4.2.1 Total solids

Throughout the duration of the 7.1 d HRT trial, temperature within the reactor was maintained between 60 - 61.5 ^{o} C via cooling. However, temperature dropped daily into the thermo-tolerant zone immediately following feeding, due to the cooler temperature of the influent sludge

Average TS and VS destruction data were obtained from the difference between the average influent TS and VS values and the average effluent TS and VS values, following an acclimatisation period of 14 days digestion (two retention times). This allowed for the assumption of steady-state conditions. Figure 4.5 gives an overall breakdown of TS removal on a 7.1 d retention time and Figure 4.6 gives the overall breakdown of VS removal on a 7.1 d retention time.

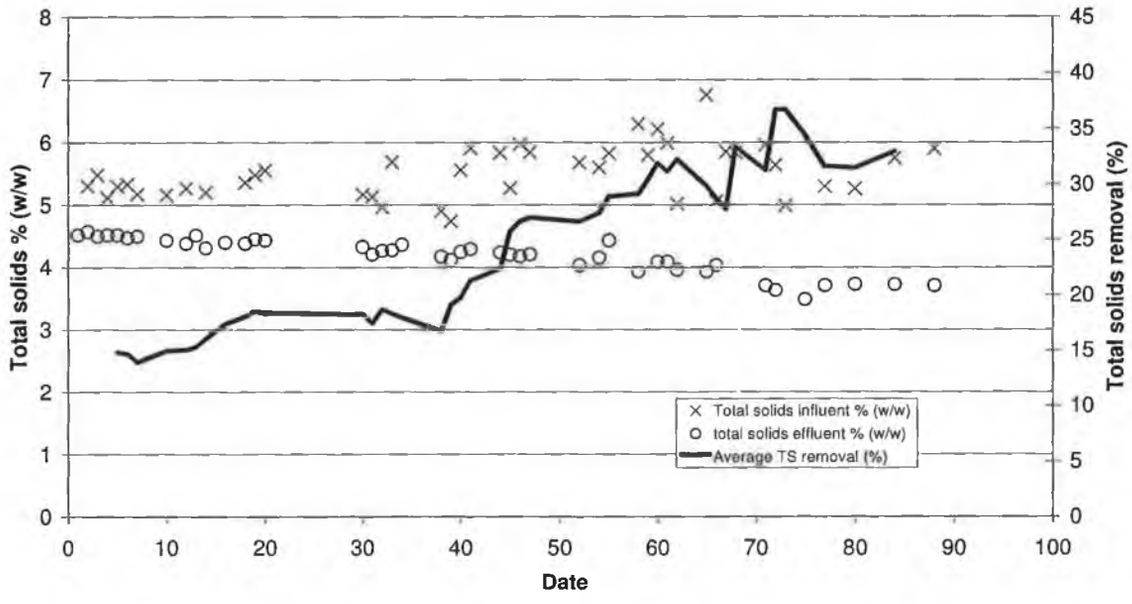


Figure 4.5 Total solids removal in ATAD pilot-plant (7.1 day HRT)

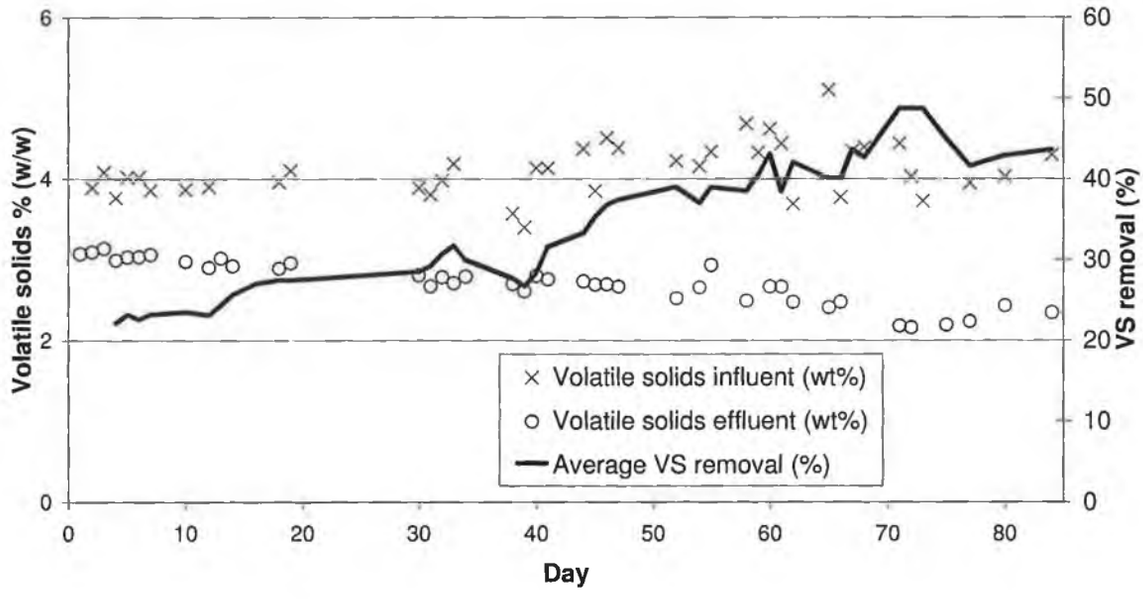


Figure 4.6 Volatile solids removal in the pilot-plant (10 day HRT)

A 3 point moving average was plotted against the secondary y-axis tracking average solids removal as a percentage. Over the 7.1 day retention time, the average TS content of the influent sludge fed to the pilot plant was 5.5% with wide variation (minimum TS of 4.74% and a maximum TS of 6.75%). The average TS content of the effluent was 4.19 % (minimum TS of 3.7% and a maximum of 4.57%). The average TS removal was 24% over the duration of the 7.1 d HRT, with a trend toward increasing efficiency, suggesting that the biomass never reached optimum steady-state conditions. The average influent VS expressed as a percentage influent TS was 74% and the average effluent VS expressed as a percentage of effluent TS was 65%.

4.4.2.2 Volatile solids

For VS destruction the data were as follows. The average VS content of the influent sludge was 4.11% (with maximum and minimum values of 5.1% and 3.4% respectively and the average VS content of the effluent sludge was 2.7% (with maximum and minimum values of 3.1% and 2.2% respectively) Overall the average VS destruction was 35% with a trend toward increasing efficiency. From Figure 4.7, it is apparent that the pilot plant did not stabilise until August 2004, in terms of TS removal. This stabilisation did not occur until the passage of at least 10 retention times at a 7.1 d HRT. All dewatering analysis was conducted following this period of time. It is likely that the passage of several retention times is required for real steady-state conditions to be achieved.

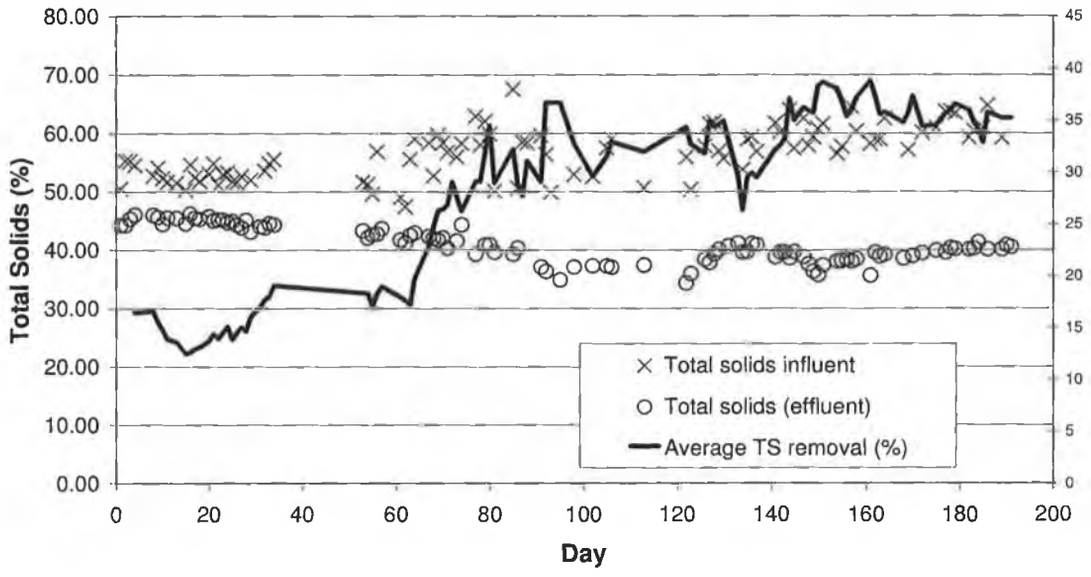


Figure 4.7 TS % (w/w) and average removal (%) in the pilot-plant over entire HRT trial period

4.4.2.3 Process stability

Influent to the pilot plant was somewhat inconsistent in terms of solids content. Due to the high volume that had to be fed the reactor each day (70 litres) it was not possible to maintain equal solids concentration, and, additionally, while the influent sludge could be diluted in instances where it was thicker than the desired constituency, a dilute influent sludge (below the desired consistency), which was more often the case, could not be thickened. However, these variations in the feed sludge solids concentrations to the pilot-plant simply represented normal annual fluctuations in the feed solids concentration at the

full-scale ATAD at Killarney, therefore, the pilot-plant retention time trials can be directly related to typical full-scale operation, where the same fluctuations occured.

Once thermophilic temperatures were established the system proved resilient to changes in organic loading rate, which was an issue due to high variability in the solids content of the influent sludge. The reactor contents recovered temperature quickly (<1.5 ^{o} C/hr) following feeding.

During the start-up period, pilot plant digestion performance was only assessed according to solids removal. A decision was taken to also measure COD values (both total and soluble) for the influent sludge and reactor effluent for the dewatering trials. Data relating to COD removal and solubilisation at several retention times coupled with the solids removal allows for theoretical kinetic models to be developed for the pilot plant at a later date in the manner of those described in Metcalf *et al.,* (2001).

4.4.3 10 day HRT

Following the 7.1 day retention time trial the pilot-plant was switched to a 10 d HRT feeding regime. Due to the difficulties associated with achieving thermophilic temperatures when first commissioning the pilot plant, the decision was taken not to fully empty the pilot plant before switching to the 10d HRT in order to retain a viable thermophilic biomass. Instead the feeding regime was switched to 50 litres of influent sludge/day from 70 litres/day. As with the 7.1 d retention time, average TS and VS

removal values were calculated following the duration of 2 HRTs (20 days) allowing for the assumption of steady state conditions.

Figure 4.8 and Figure 4.9 give the overall breakdown of solids removal on the 10 d HRT.

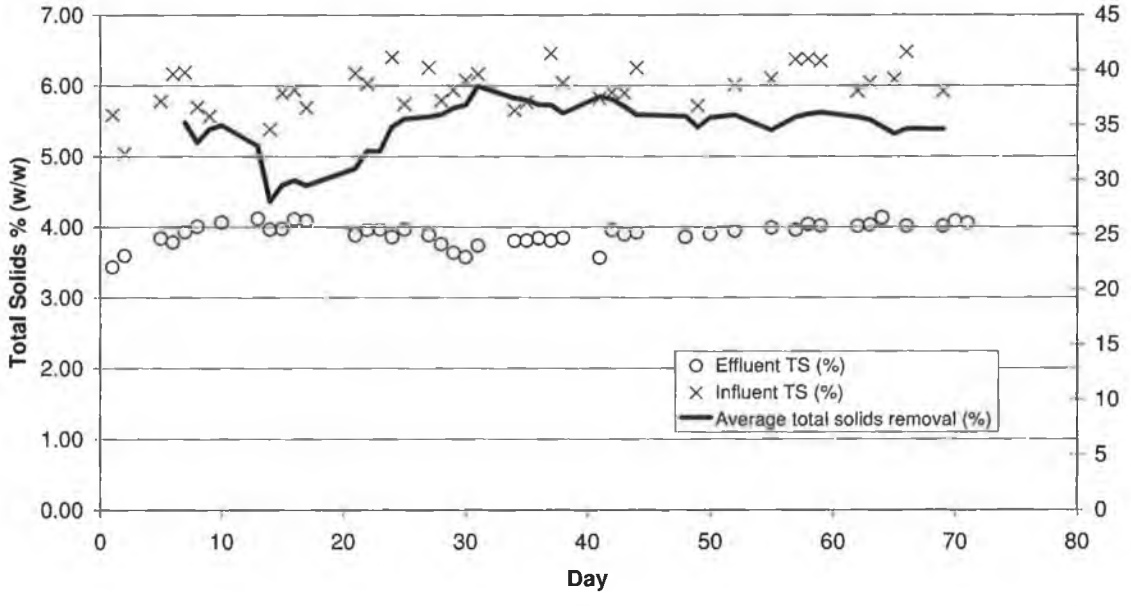


Figure 4.8 Total solids removal in the pilot-plant (10 day HRT)

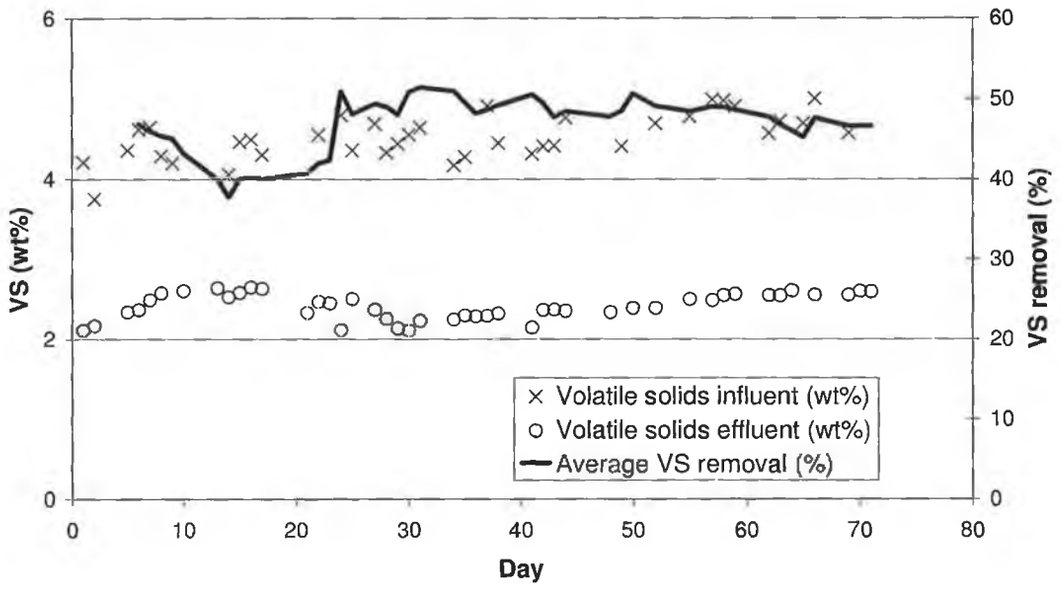


Figure 4.9 Volatile solids removal in the pilot-plant (10 day HRT)

There was a smaller deviation from the mean average solids concentration of the influent sludge over the period of the 10 d HRT trials than was the case during the 7.1 d trials. The average TS of the influent sludge was 5.96%, with a maximum value of 6.48%, and a minimum value of 5.65 %. The influent sludge had greater solids content on average the during the 10 d HRT trials, than during the 7.1 d HRT trials. The average TS of the effluent were 3.9%, with a maximum of 4.23% and a minimum of 3.56%. The average TS removal on the 10 d HRT expressed as a percentage was 34.62%.

The average VS of the influent on the 10 d HRT was 4.52% (with a maximum and minimum of 5% and 3.75% respectively). The average VS of the effluent on the 10 d HRT was 2.4% (with a maximum and minimum of 2.65% and 2.11% respectively). The

average VS removal on the 10 d HRT expressed as a percentage was 46.69%. The average influent VS expressed as a percentage influent TS was 80% and the average effluent VS expressed as a percentage of effluent TS was 68%.

In terms of solids removal, the pilot plant operated quite successfully on a 10 d HRT. Throughout the operation on the 10d HRT volatile solids removal exceeded the 38% recommended in the *Code of good practice for the use of biosolids in agriculture* (Fehily, Timoney & Co. 1998).

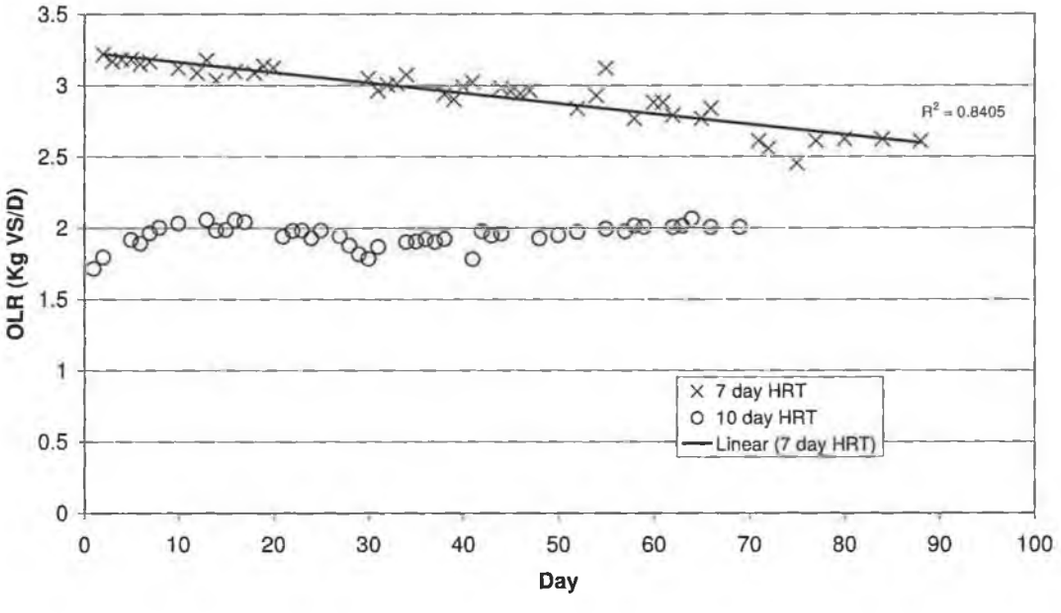


Figure 4.10 Organic loading rates (expressed in Kg VS/Day) on 7.1 day and 10 day HRTs in the pilot-plant

Figure 4.10 outlines the organic loading rates, expressed in kilograms of volatile solids per day for the two retention time trials. During the 7.1 day HRT trial the organic loading rates gradually decreased over the period of the trial. This could have been due to the experiments being conducted over the summer months. The volume of sludge treated at Killarney increases substantially during the summer months, and the increased throughput leads to a lower solids concentration in the feed as the thickening/dewatering equipment is put under increased pressure. The organic loading showed less fluctuation on the 10 day HRT trial, and this may also have led to more stable conditions within the pilot-plant and consequently improved solids removal.

Ponti *et al.*, (1995a), in a study investigating the use of ATAD to treat municipal wastewater, found that increased organic loading rates led to better overall solids destruction. For the ATAD pilot-plant the greatest organic loading rates were during the 7.1 day HRT, however, the best solids removal rates were on the 10 day HRT. Overall, the organic loading rate was more stable during the 10 day HRT and that system stability may have been the principal reason for the improved solids removal on the 10 d HRT.

4.5 COD removal and solubilisation in the ATAD pilot-plant

4.5.1 Introduction

For a detailed appraisal of digestion dynamics within the pilot plant, a more rigorous appraisal of parameters was required than solely measuring solids removal. Total COD and soluble COD were selected as appropriate parameters to measure the utilisation of

available oxidisable substrate, and the manner in which soluble material is released into solution. COD samples were taken twice weekly throughout the retention time trials.

4.5.2 Total COD removal on 7.1 day HRT

Figure 4.11 gives a breakdown of total COD removal on a 7.1d HRT.

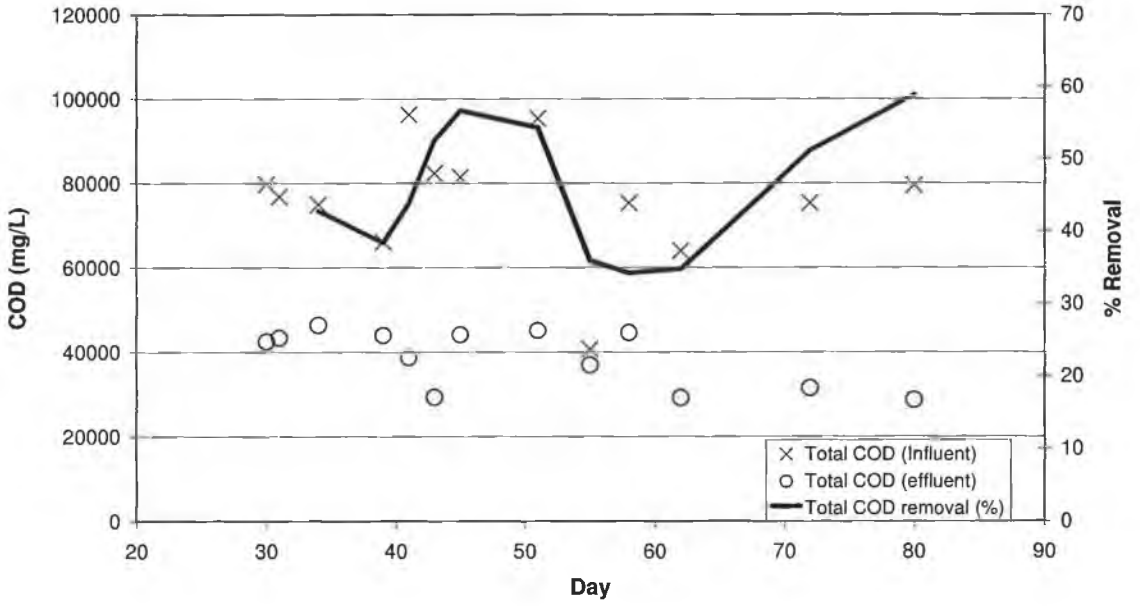


Figure 4.11 Total COD removal on 7.1 day HRT in ATAD pilot-plant

The total COD in the influent sludge in Killarney was exceptionally high (70,000 – 100,000 mg/L). The average COD removal (%) is expressed using a 3 point moving average. The high variability in the influent COD loading reflected the variability in the influent sludge solids concentration. Average total COD in the influent over for the duration of the 7.1 d HRT trial was 76,161 mg/L with maximum and minimum values of

96,231 mg/L and 40,587 mg/L respectively (further illustrating variability in influent nutrient content). The average total COD in the effluent was 38,575 mg/L, with maximum and minimum values of 46,334 mg/L and 28,623 mg/L respectively. The average total COD removal over the entire trial expressed as a percentage was 49.36%. Ponti *et al.*, (1995a) postulated that ATAD systems operate at optimum efficiency in terms of substrate utilisation at around 50% total COD removal.

4.5.3 Total COD removal on 10 day HRT

Figure 4.12 gives a breakdown of total COD removal on a 10 d HRT.

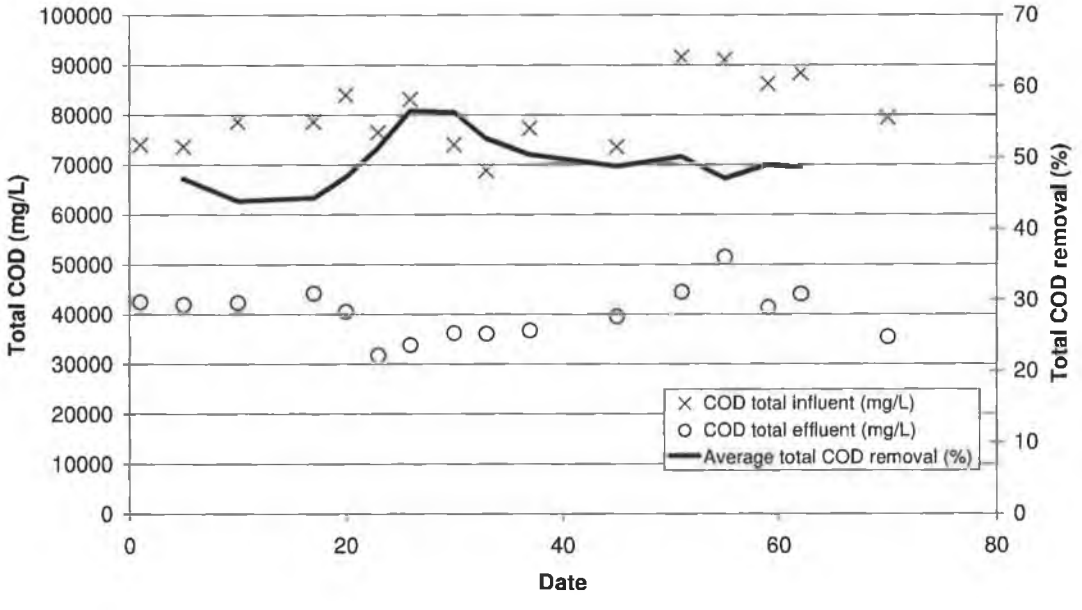


Figure 4.12 Total COD removal on 10 day HRT in ATAD pilot-plant

The COD removal results on the 10 day HRT showed nutrient removal rates were more stable than during the the 7.1 day HRT trial. This was due to more consistent influent solids content. Average total COD in the influent over the duration of the 10d HRT trial was 80,336 mg/L and the maximum and minimum values were 91,513 mg/L and 68,764 mg/L respectively. The average total COD in the effluent was 40,430 mg/L with maximum and minimum values of 51,451 mg/L and 31,701 mg/L respectively. The average total COD removal for the trial was 49.67%. The results show little difference between total COD removal between 7.1 and 10 d HRTs. This contrasted with TS and VS removal which were both higher on the 10 d HRT than the 7.1 d HRT. However, it must be noted that COD sampling and analysis was performed twice weekly, while solids sampling and analysis was performed daily. With the noted variation in influent solids concentration, it is likely therefore that the VS removal rates give the best indication of true nutrient removal rates at each HRT, however, the COD removal rates are worth regarding in their own right and show that COD removal was significant at each HRT.

4.5.5 Ratio of COD to volatile solids

The ratio of total COD to volatile solids within the pilot-plant was calculated for each retention time. While COD values (expressed as mg/L) were expected to fluctuate throughout the trials, the ratio of COD to volatile solids was expected to remain relatively stable. This was found to be the case. The ratio of COD to volatile solids was calculated by dividing COD values (mg/L) by the sludge volatile solids content (expressed as mg volatile solids/kg sludge) for each COD result. The results were then averaged. The ratio

was 1.56 on the 7.1 day HRT with a standard deviation of 0.211. The ratio was 1.69 on the 10 day HRT with a standard deviation of 0.184. Standard deviation analysis was performed using EXCEL. While VS were used as the primary representative of biodegradable material in this study, COD was also used, and the determination of a stable ratio between the influent COD and VS is a helpful tool in planning further digestion trials or calculating changes in plant load. The total COD values were expected to exceed VS (in terms of mg/L) and this was the case. COD is a measure of the total oxidisable compounds in the sludge, and thus COD values often overestimate the energy available for biological action (Metcalf *et al.*, 2001)

4.4.4 COD solubilisation within ATAD pilot-plant

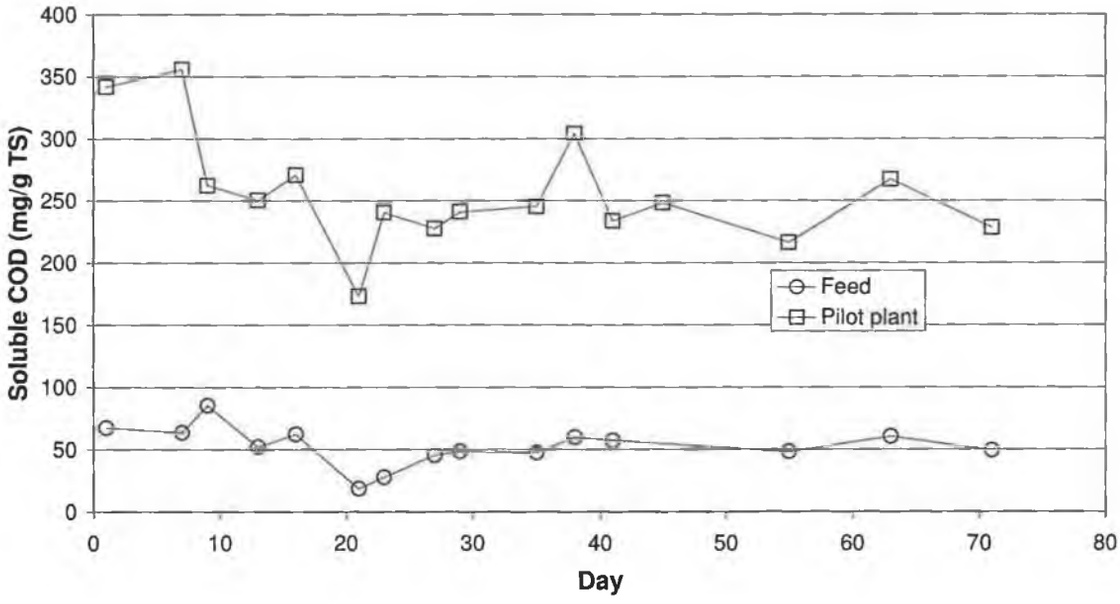


Figure 4.13 Soluble COD in the feed sludge and in the pilot-plant during the 7.1 day retention time trial. Soluble COD was normalised for solids and is expressed as milligrams soluble COD per gram total solids.

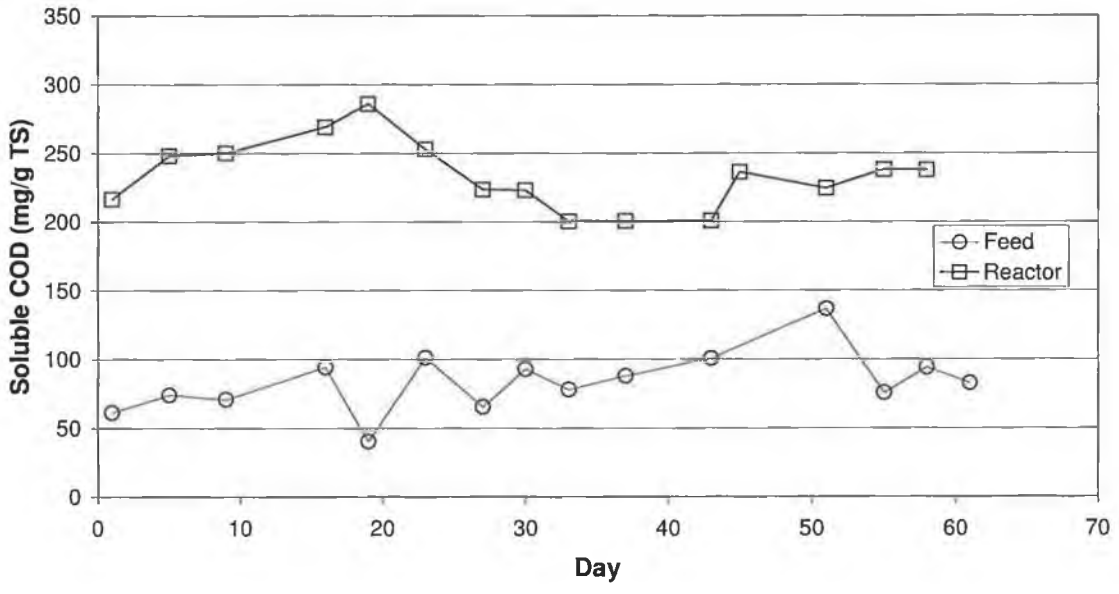


Figure 4.14 Soluble COD in the feed sludge and in the pilot-plant during the 10 day retention time trial. Soluble COD was normalised for solids and is expressed as milligrams soluble COD per gram total solids.

Solution COD was determined to be an important parameter to measure in this study. Solution COD gave an indication of the quantity of substances available for oxidation in solution; be these proteins, polysaccharides or otherwise. It was also an indicator of the accumulation of non-degradable by-products, which may hamper dewatering. Finally it quantified the oxygen demand/polluting potential of the filtrate.

One of the most marked differences that were noted between the influent sludge and the effluent sludge, at both retention times, was the large increase of soluble COD which

occurred during digestion within the pilot-plant. It is thought that at temperatures required for ATAD, large amounts of intracellular material are released into solution due to the lysis of mesophilic cells (Murthy *et al.*, 2000; Zhou *et al.*, 2002; Novak *et al.*, 2003; Zhou *et al.*, 2003). Lysis leads directly to an increase in soluble COD, some of which is available for re-assimilation into the thermophilic biomass. It is thought that the bulk of soluble COD is released into solution in a short period of time following feeding of an ATAD reactor due to an initial heat-shock effect, and hence the quantity of this material should reduce as a function of digestion time as it is re-assimilated into the thermophilic biomass. The results from the pilot-plant retention time studies suggested that more complicated processes were in fact occurring. While initially, following feeding, the bulk of soluble COD is attributable to temperature-lysis effects, increased retention time led to unchanging or increasing soluble COD, and a darkening of filtrate in the effluent sludge (Figure 4.15).

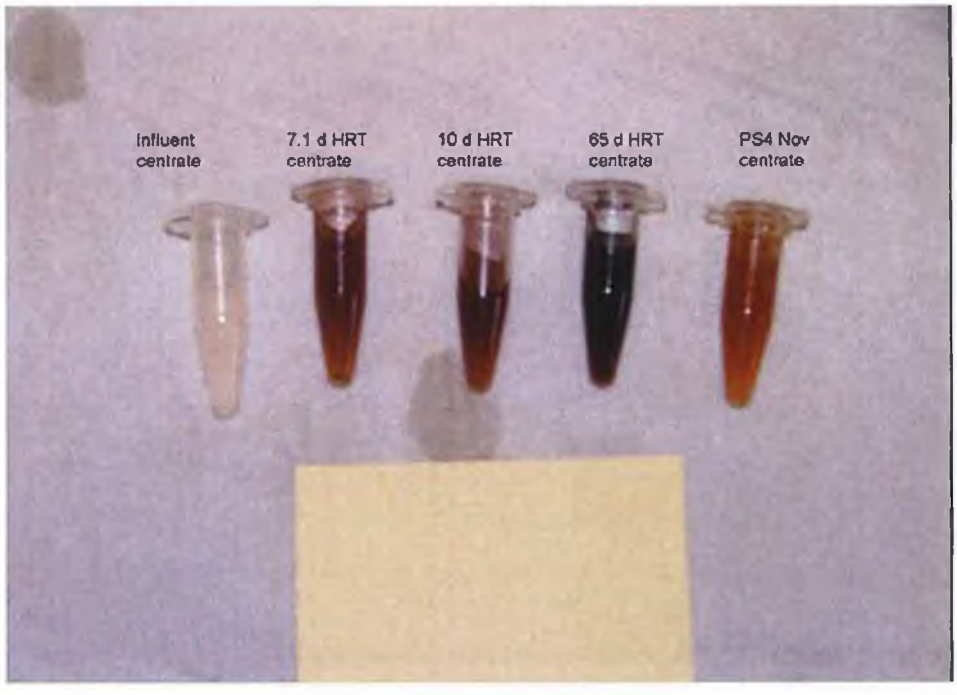


Figure 4.15 Sludge filtrate samples for soluble COD analysis

This suggested that concurrent with digestion, certain substances were being released into solution which were recalcitrant, and were not easily re-assimilated into the thermophilic biomass. This could be analogous to the behaviour observed in the aerobic digestion of sludges at mesophilic temperatures by Novak *et al.*, (2003), where it was observed that increased retention time led to increased colloidal material being released into solution, and subsequently poorer dewatering characteristics.

Many researchers have linked soluble COD (and in particular solution proteins and polysaccharides) to poor dewatering in ATAD sludge (Murthy *et al.*, 2000; Zhou *et al.*, 2003). The theory that such substances negatively affect dewatering is developed later in the thesis, with reference to the sludges studied at Killarney. It is thought that the recalcitrant substances mentioned above had a negative impact on sludge dewatering and this was directly related to increasing digestion time.

Figure 4.16 presents the average (%) total COD removal for three retention times. The 3rd retention time (65 d) represented a period following the 10 day retention time trial, during which the pilot plant was still operated. The pilot-plant was operated for a farther 55 days without feeding following the 10 day retention time trial to assess the total energy content of the sludge; and it is a reasonable assumption that for typical ATAD operation, virtually 100% of the possible COD removal had occurred following 65 days of digestion. Figure 4.16 illustrates that at a 7.1 day retention time 86% of the total COD removal (following

65 days) had already occurred. This suggests that increasing the retention time beyond 7 days for ATAD systems has little benefit in terms of COD removal.

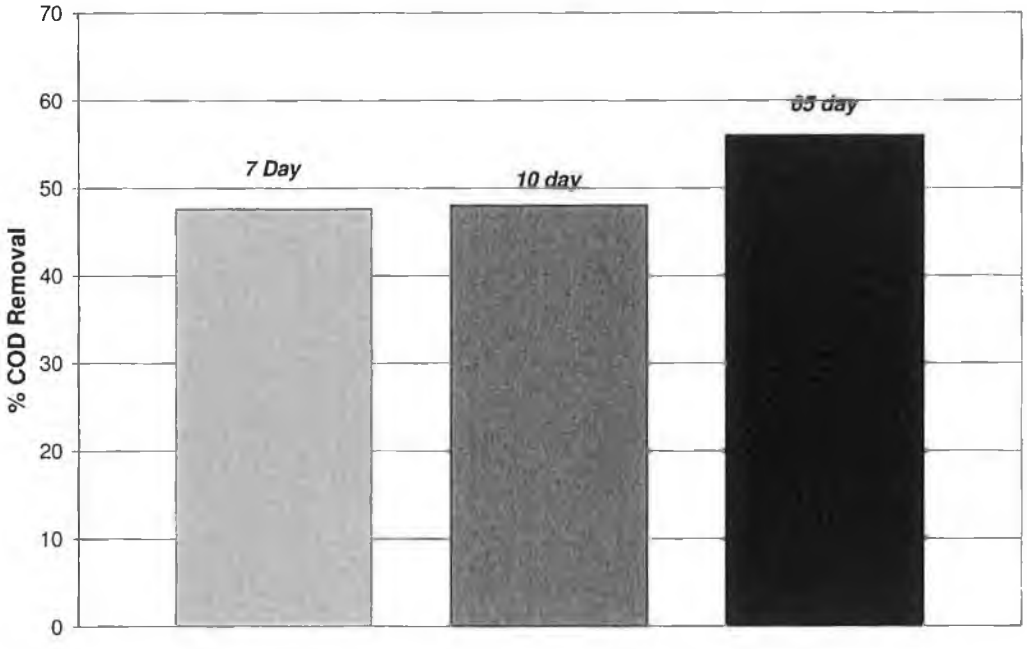


Figure 4.16 Average total COD removal (%) for specific retention times in the pilot plant.

The average soluble COD in the pilot-plant on a 7.1 d HRT was 256 mg/g TS (normalised for solids) this dropped slightly to 233 mg/g TS during for the 10 d HRT, however it increased significantly to 337 mg/g TS after 65 days digestion. If, as postulated by Zhou *et al.*, (2003) the soluble COD was available for re-assimilation into the biomass, then one would expect soluble COD to have decreased as retention time increased, reflecting the lengthened period that this material is available for re-assimilation. This was the case when comparing the 7.1 d HRT with the 10 d HRT,

however following 65 days digestion the significant increase in soluble COD was indicative of the accumulation of non-digestible soluble material in the pilot-plant.

The aerobic thermophiles in the pilot plant required some form of soluble substrate for survival, but as the quantity of COD(s) was shown to increased following 65 days of digestion, recalcitrant substances must instead have been released into solution as a product of cell lysis or as by-products of digestion. This must have happened at an equal or greater rate than digestible substances were being removed. These substances may have contributed to the increasingly dark filtrate at higher retention times (see Figure 4.15).

4.4.5 Full-scale soluble COD results

In the full-scale treatment plant at Killarney, there appeared to be a different dynamic in COD solubilisation. Figure 4.17 gives the average soluble COD content across one set of ATAD reactors (1A and 2A) and in the storage tanks following sampling.

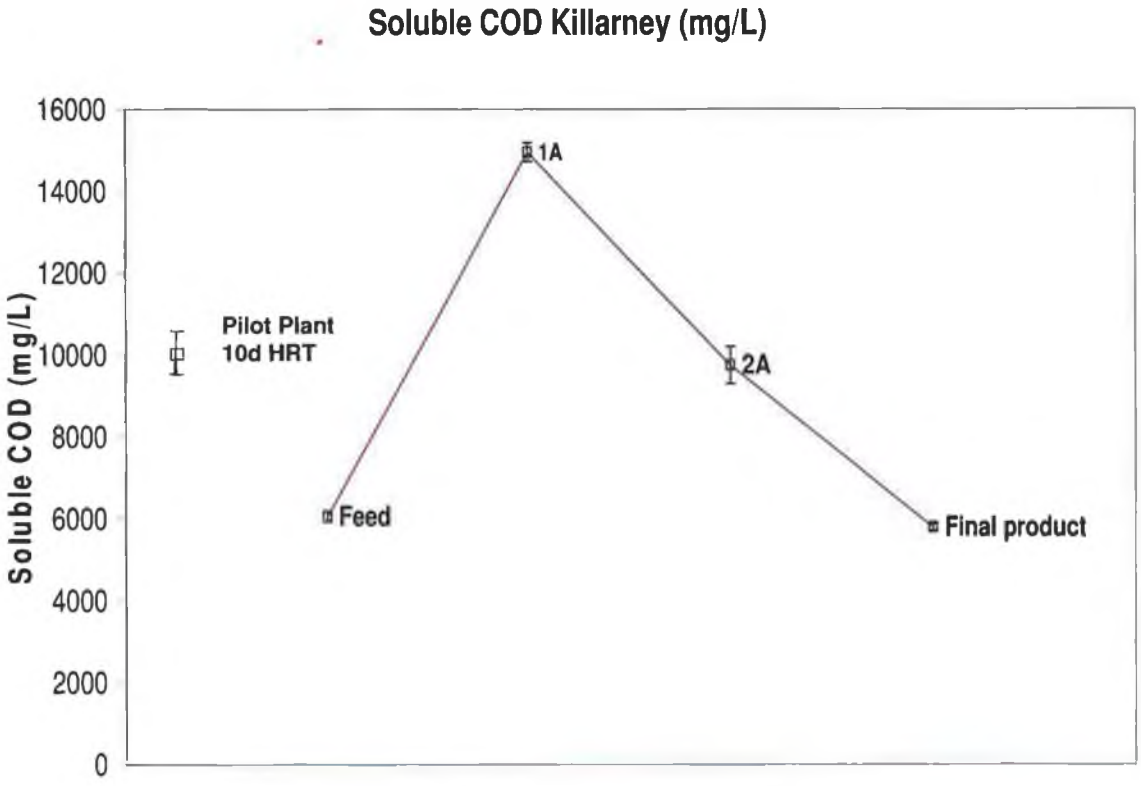


Figure 4.17 Soluble COD values for the ATAD reactors and storage tanks at Killarney WWTP

Soluble COD values for the influent sludge and the 10d HRT pilot plant sludge are included for comparison. The quantity of soluble COD, and by inference, the extent of lysis, was much more pronounced in Reactor 1A than in the pilot plant. Temperatures are lower in Reactor 1A (45 – 55°C) than in the pilot plant. If the most pronounced cause of lysis in ATAD systems is high temperature, then a less pronounced lysis effect would be expected in 1A than in the pilot-scale reactor where temperatures were higher (60°C). However, this was not found to occur (Figure 4.17). Therefore it is considered that the

higher soluble COD in Reactor 1A must have resulted from enzymatic lysis of substrate, the enzymes being produced by a more versatile biomass than that at 60 °C.

This finding concurred with work by Lapara, Konopka *et al.*, (2001) who believed that the hydrolysing and substrate utilising abilities of thermophilic biomass deteriorate as a function of increasing temperature. Due to the different conditions of temperature, biomass, and enzymatic activity found in Reactor 1A, in comparison to those found in the pilot-plant, the biomass that was fed into Reactor 2A, which was operated at true thermophilic temperatures, as was the pilot plant (58 – 65°C), had a different constitution to that which was fed to the pilot plant (influent sludge). So while Reactor 2A and the pilot plant were operated at similar temperatures, they were treating sludge which was constitutionally different.

Furthermore, while Reactor 1A had a higher soluble COD content than the pilot-plant sludge at three different retention times, the sludge supernatant from 1A, did not exhibit the same dark-brown coloration as the pilot plant supernatants, which suggested that the compounds responsible for the high soluble COD were unlike those found in the pilot plant sludge. It is possible that more diverse and active enzymes were present in Reactor 1A, and the by-products of digestion were therefore not as recalcitrant, and were more amenable to digestion than those produced in the pilot-plant, and this intermediate thermo-tolerant step improved overall soluble COD removal.

A recent study of thermophilic aerobic digestion (Li *et al.*, 2009), demonstrated that proteolytic activity in thermophilic digestion was optimal at 50 °C (analogous to 1A). They isolated a sludge-lysing bacterial strain (*Brevibacillus* sp.) from WAS, and inoculated sterilised and unsterilised sludge with this strain and conducted digestion experiments at 30, 40, 50 and 55 °C. They demonstrated that the species was capable of very high rates of proteolysis and solids degradation, and inoculation of sterilised sludge with the strain resulted in 32% TSS removal following 120 hours of digestion at 50 °C. However, when the temperature was increased to 55 °C (analogous to the pilot plant and 2A) the strain was inactivated and solids removal rates declined dramatically. It is very likely that strains such as *Brevibacillus* sp. exist in the WAS at Killarney and thrive in 1A, but the selective effect of thermophilic temperatures in 2A (and the pilot plant) reduces the viability of such strains.

In Reactor 2A there was a reduction in COD (Figure 4.16). This demonstrated that some of the substances released into the solution phase in Reactor 1A were available as substrate for the micro-organisms in Reactor 2A. Notably, the dark brown colour which characterised all three pilot plant sludges was also present in the supernatant from Reactor 2A, but to a lesser extent. Reactor 2A was operated within a similar temperature range to the pilot-plant (58 – 62 °C). Therefore the substance or substances responsible for the colour could be linked to a temperature regime in excess of 55 °C.

In summary the ATAD treatment works at Killarney was operating as a two-stage system. A set of two digesters was operated in sequence; the first digester in the set was

operated at thermotolerant temperatures (1A), while the second digester was operated at thermophilic temperatures (2A), with a retention time of approximately 3.5 d in each digester. Because the feed to Reactor 2A (which came from Reactor 1A) differed in temperature, enzyme activity and biomass than the feed to the pilot plant (which was WAS), the pilot plant was not directly comparable to the full-scale plant at Killarney.

Finally, in the sludge storage stage at Killarney there was a farther notable decrease (38%) in soluble COD. The retention time of sludge in the post-process storage tanks at Killarney was calculated to be between 14 and 28 days, depending on the frequency of removal of sludge for land spreading (which was dependent on weather conditions). The decrease in soluble COD corresponded with an average decrease of 15% in TS in the sludge storage tanks. This had large implications for dewatering, which are examined in Chapter 5.

4.6 Conclusions

A 500 litre ATAD pilot plant was commissioned at Killarney WWTP to examine the development of thermophilic conditions at two key HRTs (7 day and 10 day) and the effect of these process conditions on sludge dewatering. The performance of the pilot-plant was assessed in terms of the following parameters; COD removal, COD solubilisation, pH, temperature, total solids removal, and volatile solids removal.

Batch trials established that the pilot-plant was capable of attaining temperatures of 60 ^{o} C with a feed sludge concentration of 5.9 – 6% (w/w) within 36 hours of feeding.

Achieving thermophilic temperatures proved difficult during a prolonged start-up period for the ATAD pilot-plant. Thermophilic temperatures were achieved and maintained first on a 5 day retention time and then on a 7.1 day HRT following seeding of the pilot-plant with sludge from the full-scale ATAD reactors operating at Killarney WWTP.

The pilot-plant achieved average TS removal of 24% and VS removal of 35% on a 7.1 d HRT, and average TS removal of 35% and VS removal of 47% on a 10 d HRT. Operation proved more stable on the 10 day HRT than on the 7.1 d HRT. This may have been due to less fluctuation in the organic loading rate over the period of the 10 d HRT trials.

COD removal was very similar over the two retention time trials. This was interesting as VS removal rates were greatest on the 10 day HRT. For instance, while COD removal averaged at 49% on the 7.1 day HRT, VS removal was only at 35%. And while COD removal averaged at 50% on the 10 day HRT, VS removal was at 46.69%. This could have been due to the frequency at which COD measurements were taken (twice a week) meaning that the results did not reflect the true average COD content within the process.

CHAPTER FIVE: Dewatering characterisation of Anaerobic and ATAD sludges

5.1 Introduction

This Chapter outlines the characterisation of anaerobically-digested and ATAD-digested sewage sludges. These materials have non-traditional filtration characteristics, and all exhibited high compressibility coupled with low permeability. This makes their characterisation by traditional methods difficult. The biosludge characterisation protocol, which was outlined in Chapter 3, was used to overcome the difficulties associated with the characterisation of such non-traditional sludges.

The Chapter is divided into five sections. Section 5.2 describes the characterisation of two mesophilic anaerobic digested (MAD) sludges at the University of Melbourne in 2003. Section 5.3 examines the dewatering properties of several sludges which were sampled at Killarney WWTP. These sludges originated from several different sources and included activated sludge, ATAD sludge from the pilot-plant operated on 7 and 10 day HRTs, ATAD sludge from the full-scale treatment plant, and ATAD from the product storage tanks.

Section 5.4 outlines the dewatering properties of ATAD sludges which were sampled form three treatment plants in continental Europe. These treatment plants differed

significantly from Killarney WWTP in the configurations of their ATAD set-up as they did not employ a pre-ATAD conditioning/thickening step, and the influent sludge to their ATAD reactors was a mixture of primary and secondary sludge. Hence the influent sludge to these reactors was of a lower solids concentration, as compared to Killarney which employs a pre-ATAD conditioning step on an influent consisting solely of secondary sludge.

In addition to the extraction of sludge dewatering parameters, solution colloids were also measured quantitatively for all of the sludges which were studied. These substances were measured as COD, polysaccharides and proteins. The relationship between these parameters and dewatering properties such as the optimum polymer dose are examined in section 5.5.

5.2 Characterisation of anaerobic sludges

5.2.1 Introduction

An air-driven filtration rig, described in Section 3.4.5, was commissioned at The University of Melbourne for the characterisation of two MAD sludges. These sludges originated from Luggage Point WWTP in Queensland, Australia, and Mt. Martha WWTP in Victoria, Australia. The Mt. Martha sludge was characterised in an unconditioned state only, while the Luggage Point sludge was characterised in an unconditioned state and following conditioning with polyelectrolyte at a concentration of 9g/kg TS. This was to

determine whether flocculation resulted in changes in the material characteristics which were detectable in the high pressure regime by the pressure filtration tests.

5.2.2 Sludge properties

Sludge samples were placed in refrigeration conditions (5 ^{o} C) immediately upon being received at the lab. Using the air-driven filtration rig, a series of high pressure filtration tests were conducted on the sludges at pressures ranging from 5kPa to 300kPa. During each filtration test the transient suspension height was calculated from the transient mass/volume of filtrate (which accumulated in a receptacle upon the analytical balance). On completion of the filtration test, transient suspension height versus time data was subsequently converted to average suspension volume fraction versus time data according to equation 3.9.

In pressure-filtration tests, sewage sludge rarely, if ever, compresses to equilibrium (Kapur *et al.*, 2002; Stickland, 2005). Therefore, the dewatering characteristics were extracted from single-pressure filtration tests by fitting of a logarithmic function to the compression stage of experimental data (see Section 3.4.6). Figure 5.1 gives an example of the log-fitting technique on a Luggage Point sample at 100kPa.

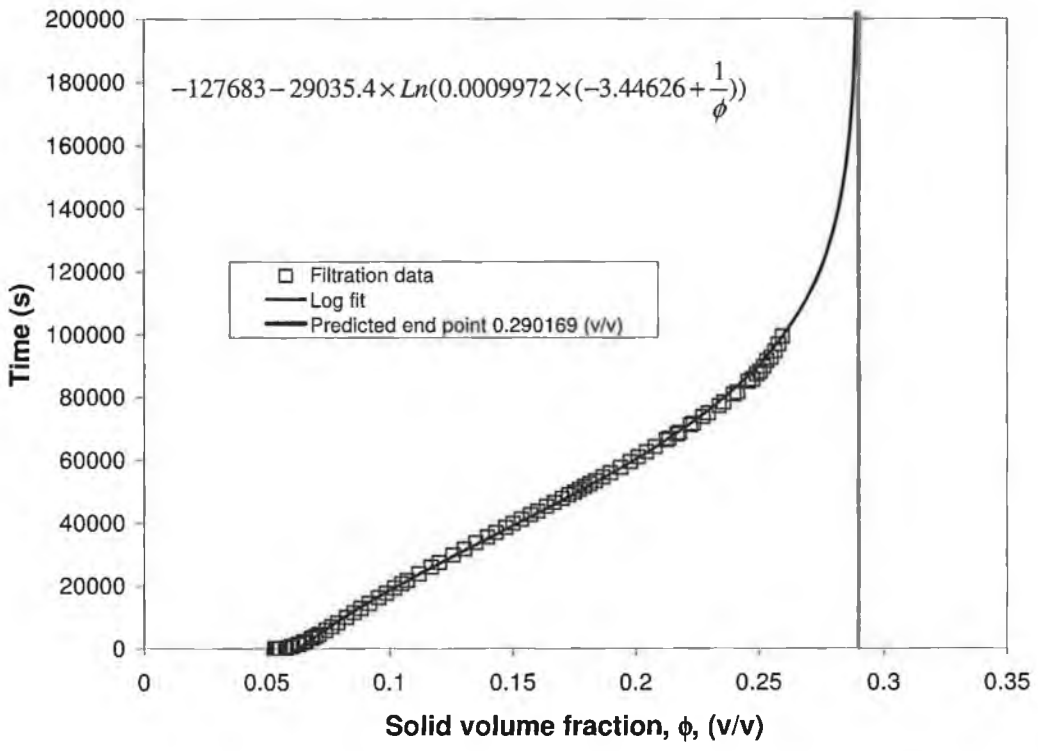


Figure 5.1 Log-fitting of an end-point to filtration data obtained from a pressure-filtration test on Luggage Point sludge at 100kPa.

The log-fitting method gave $P_y(\phi)$ and $D(\phi)$ values for each filtration test. A functional form, such as that described in equation 3.16 was then fitted to the $P_y(\phi)$ data. ϕ_g was estimated as ϕ_0 and $R(\phi)$ was then calculated according to equation 3.17. Batch settling analysis was then used to calculate low $R(\phi)$ data and ϕ_g. If this value of ϕ_g was significantly different from the previous estimate of ϕ_g, it was then used to recalculate the high $R(\phi)$ data and the batch settling analysis was repeated until ϕ_g was stable (usually only one or two iterations were necessary). A functional form could then be calculated for $D(\phi)$ using the functional forms of $P_y(\phi)$ and $R(\phi)$ according to equation 3.18.

The material characteristics of the sludges are presented in Table 5.1, 5.2 and 5.3. The solid volume fraction was calculated according to Equation 3.3, following the experimental determination of the density of the solid fraction of the sludge. This was calculated as 1100kg/m^3 for both sludges.

Table 5.1 Luggage Point MAD material characteristics (unflocculated samples)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
5	0.142829	0.146188	6.12×10^{-10}	1.68×10^{14}		
10	0.16805	0.173477	2.56×10^{-10}	6.80×10^{14}		
50	0.217731	0.2302	1.83×10^{-10}	2.19×10^{15}		
100	0.260907	0.290169	1.65×10^{-10}	4.59×10^{15}	0.02773	0.0235
200	0.268091	0.350774	1.40×10^{-10}	8.70×10^{15}		
300	0.334655	0.367376	1.15×10^{-10}	1.18×10^{16}		

Table 5.2 Luggage point MAD material characteristics (flocculated at 9g/Kg TS using ZETAG 7578)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
10	0.18206	2.86×10^{-10}	5.12×10^{14}	0.0234	0.01319
20	0.212052	1.48×10^{-10}	1.42×10^{15}		
50	0.245236	1.65×10^{-10}	1.78×10^{15}		
100	0.336803	8.15×10^{-11}	6.96×10^{15}		
200	0.342947	1.12×10^{-10}	5.19×10^{15}		
300	0.433178	7.33×10^{-1}	1.17×10^{16}		

Table 5.3 Mt. Martha MAD material characteristics (unflocculated samples)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
10	0.117324	0.131138	1.91×10^{-10}	4.93×10^{14}	0.0268	0.024
50	0.219991	0.244148	8.31×10^{-11}	7.36×10^{15}		
150	0.271123	0.308963	8.27×10^{-11}	1.40×10^{16}		
200	0.199178	0.311697	6.16×10^{-11}	1.92×10^{16}		
300	0.233446	0.352965	6.21×10^{-11}	2.58×10^{16}		

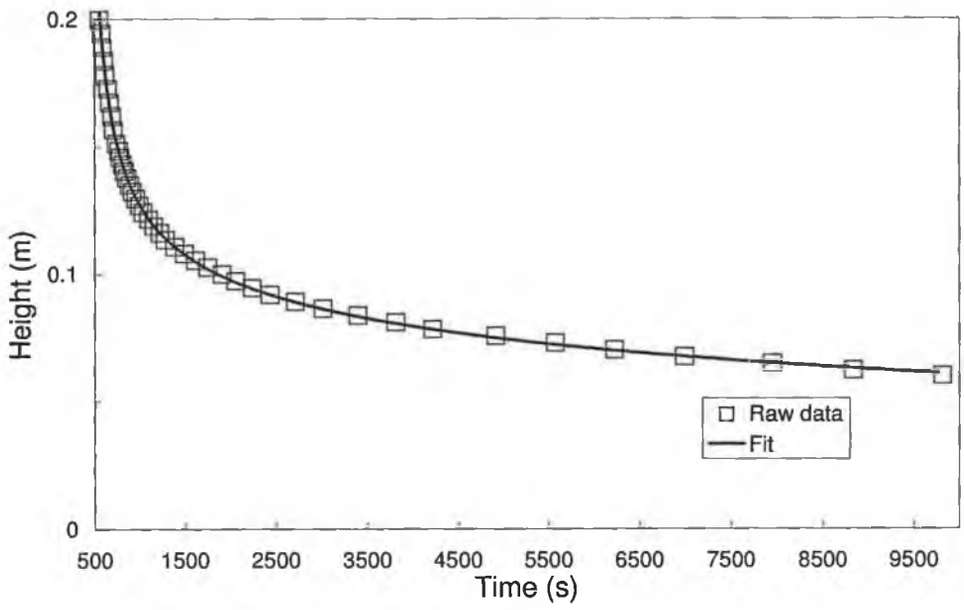


Figure 5.2 Transient batch settling data (height versus time) for Mt. Martha sample ($\phi_0 = 0.0033$).

5.2.3 Compressive yield stress, $P_y(\phi)$

The $Py(\phi)$ data for all three sludges described a material which compressed to high volume fractions at high pressures. Furthermore, the calculated gel-points were very low (Table 5.1, 5.2 and 5.3). A low gel-point is indicative of a network structure capable of supporting loads at low solids volume fraction. These two factors when taken together are consistent with gel-like materials. High molecular weight biopolymers such as extracellular polymeric substances (EPS) found within sewage sludges possibly contribute to such a networked, compressible structure.

$Py(\phi)$ data obtained from filtration testing were plotted against ϕ for all of the sludges on semi-logarithmic coordinates in Figure 5.3.

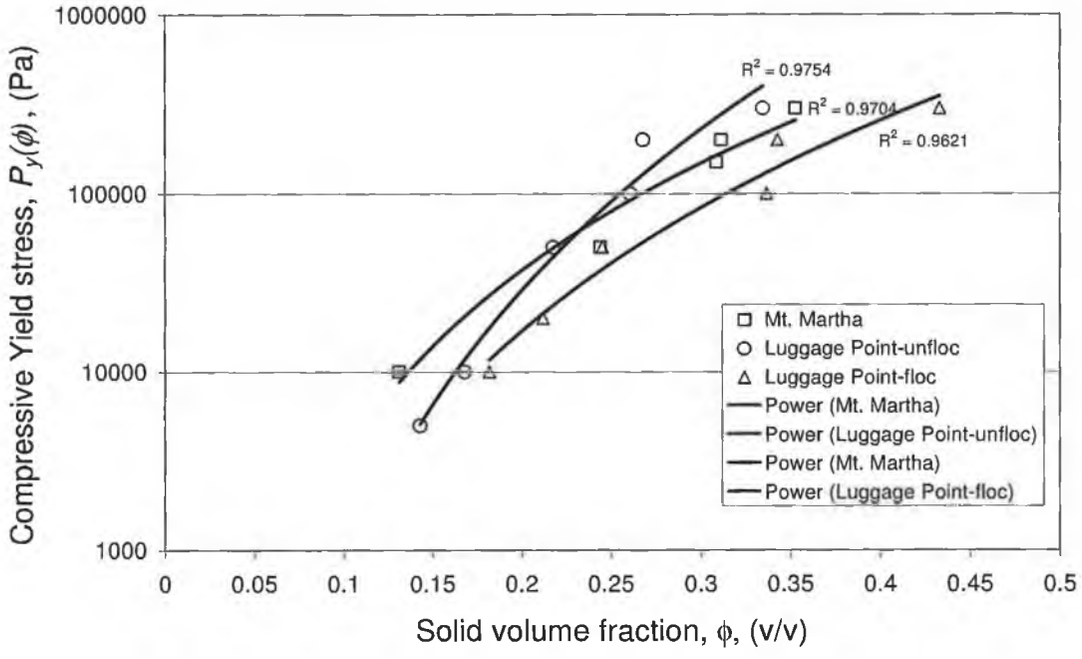


Figure 5.3 $P_y(\phi)$ plotted against solids concentration ϕ from pressure-filtration tests of Australian MAD sludges showing power-law behaviour.

Using the in-built curve-fitting function in EXCEL power-law functional forms were fitted to the data. It is evident that a power-law relationship existed for $P_y(\phi)$ vs. ϕ in each of the cases. However, this simple relationship did not hold at lower ϕ, and more complex functional forms were required to describe $P_y(\phi)$ at concentrations approaching ϕ_g. A computer programme (BSAMS), which was developed at The University of Melbourne by deKretser and Usher, was therefore used to apply more rigorous curve-fitting equations to the $P_y(\phi)$ data. This fitting procedure is semi-empirical and two user-defined inputs ϕ_{cp} and b_1 were manipulated to get the best fit.

Figure 5.4 shows the $P_y(\phi)$ values for the unflocculated Luggage Point sample. Three curve-fits were used to describe the data and the fitting parameters are given in table 5.4. The fitting parameters for the Py 1 and Py 2 curve-fits were generated by the B-SAMS computer programme.

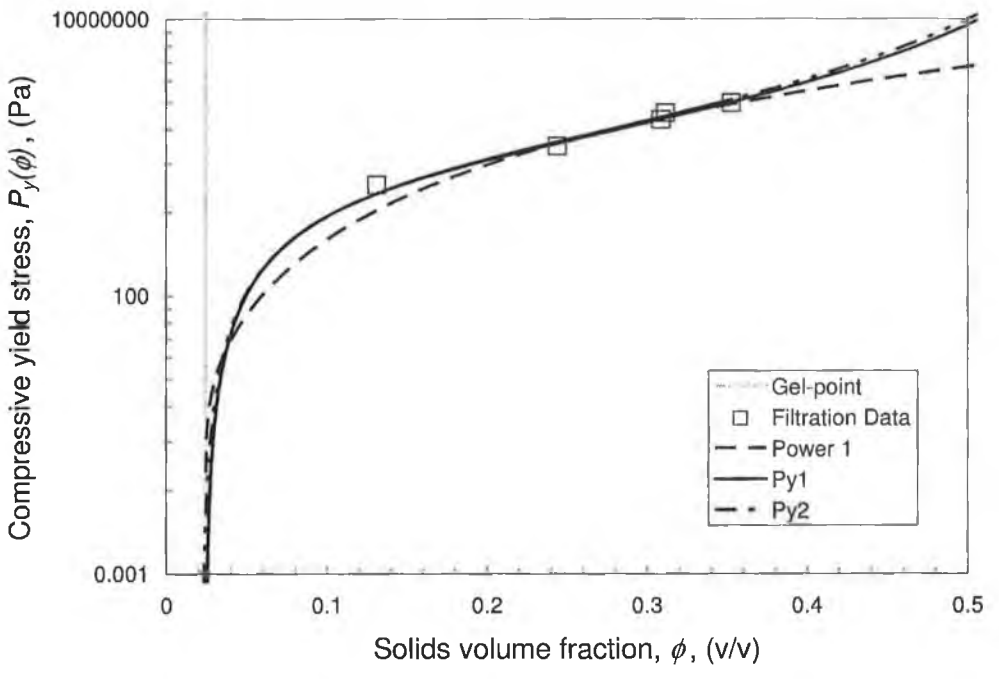


Figure 5.4 $P_y(\phi)$ as a function of ϕ for unflocculated Luggage Point MAD sample. Curve-fits were created by the BSAMS software and the fitting parameters are given in Table 5.4

Table 5.4 Curve-fitting parameters for $P_y(\phi)$ curve-fits of unflocculated Luggage Point $P_y(\phi)$ data

Curve-fit	*Fitting equation*	*Fitting Parameters*
Power 1	$1.90136(-1+1.56016\times10^{7}\phi^{4.45861})$	$\phi_{g1} = 0.02436,\ \phi_{g2} = 0.0221$
Py 1	$\left(a_1\frac{(\phi_{cp}-\phi)(b_1+\phi-\phi_{g1})}{(\phi-\phi_{g1})}\right)^{-k_1}$	$a_1 = 0.106,\ a_2 = 0.1155$ $b_1 = 0.1,\ b_2 = 0.1$ $k_1 = 3.876,\ k_2 = 4.013$
Py 2	$\left(a_2\frac{(\phi_{cp}-\phi)(b_2+\phi-\phi_{g2})}{(\phi-\phi_{g2})}\right)^{-k_2}$	$\phi_{cp} = 0.63$

The curves created by the BSAMS programme described the data well. $P_y(\phi)$ increased steeply above the gel-point as a function of solids concentration. Figure 5.5 gives the $P_y(\phi)$ data and curve-fits for the Mt. Martha sample. The fitting parameters are listed in Table 5.5. The curve-fits fitted the data well and a similar functional form to the Luggage Point sample was evident. Both sludges were unflocculated MAD samples and the data suggested that, independent of the originating treatment plant, such MAD sludges may exhibit similar compressive behaviour.

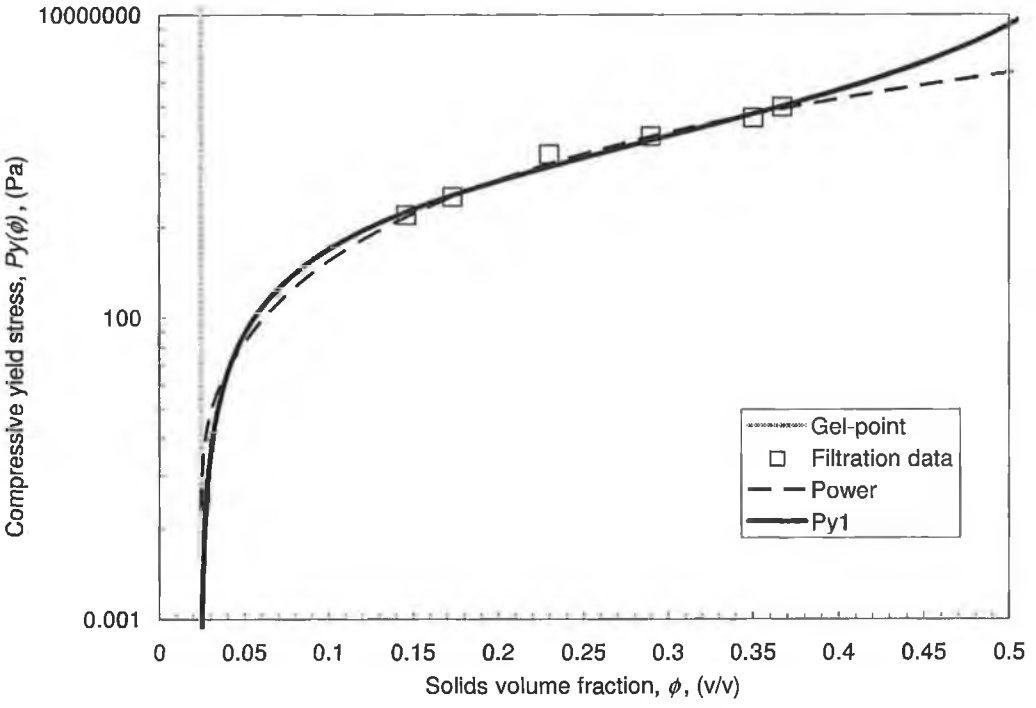


Figure 5.5 $P_y(\phi)$ as a function of ϕ for unflocculated Mt. Martha MAD sample. Curve-fits were created by the BSAMS software and the fitting parameters are given in table 5.5

Table 5.5 Curve-fitting parameters for $P_y(\phi)$ curve-fits of unflocculated Mt. Martha $P_y(\phi)$ data

Curve-fit	*Fitting equation*	*Fitting Parameters*
Power 1	$1.63433(-1+1.472878\times10^{7}\phi^{4.44819})$	$\phi_{g1} = 0.024464$ $a_1 = 0.040071$
Py 1	$\left(a_1\frac{(\phi_{cp}-\phi)(b_1+\phi-\phi_{g1})}{(\phi-\phi_{g1})}\right)^{-k_1}$	$b_1 = 0.3$, $k_1 = 3.125985$, $\phi_{cp} = 0.6$

Figure 5.6 shows the $Py(\phi)$ pressure-filtration data and curve-fits for the Luggage Point flocculated sample. The curve-fitting parameters are given in Table 5.6. The sample was flocculated with ZETAG 7587 cationic polyelectrolyte which was applied at a concentration of 9g/Kg TS. Also included were $P_y(\phi)$ data points near the gel-point which were calculated from batch settling tests. The power-law curve fit describes the data well. Figure 5.7 shows the $P_y(\phi)$ curve-fits at low solids concentrations near the gel-point, and it is apparent that the power-law fit does not match the data as well as the more rigorous BSAMS fit, which is more appropriate for describing the data in this region.

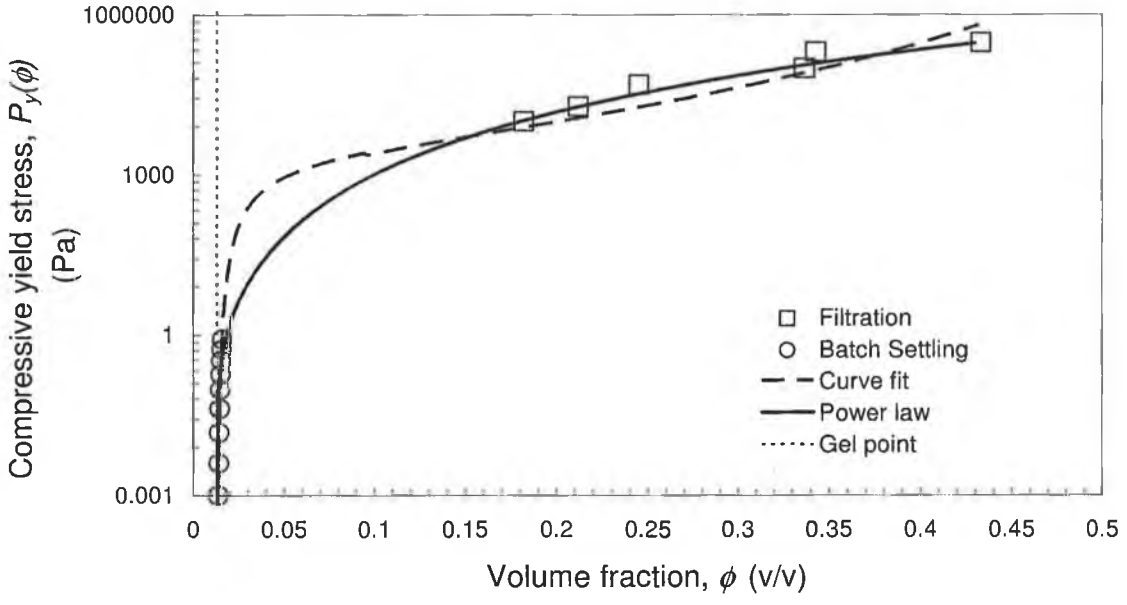


Figure 5.6 $P_y(\phi)$ as a function of ϕ for the flocculated Luggage Point MAD sample. Curve-fits were created by the BSAMS software and the fitting parameters are given in Table 5.6.

Table 5.6 Curve-fitting parameters for $P_y(\phi)$ curve-fits of flocculated Luggage Point $P_y(\phi)$ data

Curve-fit	*Fitting equation*	*Fitting Parameters*
Power 1 Py 1	$0.381996495301(-1+20080776.42527\times\phi^{3.88496357861})$ $\left(a_1\frac{(\phi_{cp}-\phi)(b_1+\phi-\phi_{g1})}{(\phi-\phi_{g1})}\right)^{-k_1}$	$\phi_{g1}=0.024464,$ $a_1=0.040071$ $b_1=0.3$ $k_1=3.12598$ $\phi_{cp}=0.6$

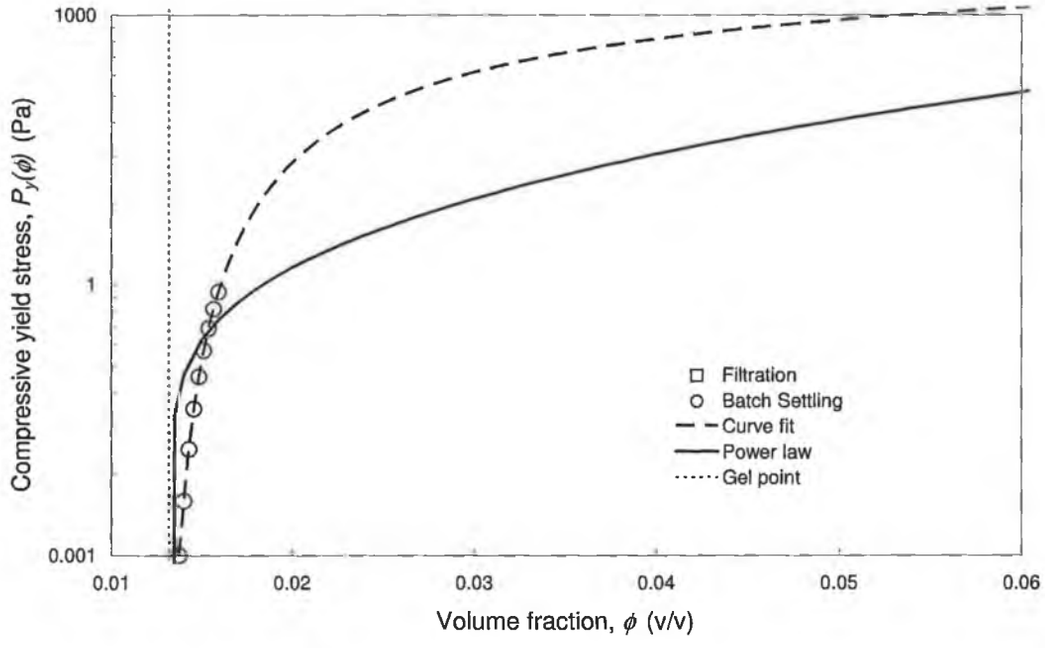


Figure 5.7 $P_y(\phi)$ as a function of ϕ for the flocculated Luggage Point MAD sample, showing $P_y(\phi)$ fits at low solids concentration. Curve-fits were created by the BSAMS software and the fitting parameters are given in Table 5.7.

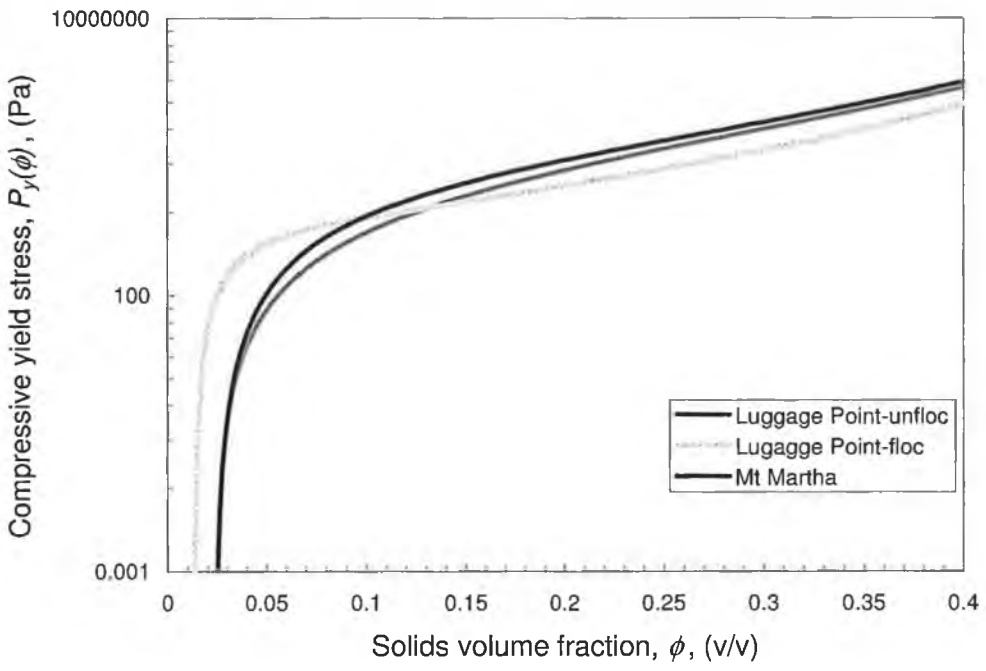


Figure 5.8 *Py(ϕ)* functional forms for Luggage Point (unflocculated and flocculated) and Mt. Martha MAD samples.

Figure 5.8 compares the BSAMS functional forms for the three sludge samples. The flocculated Luggage Point sample was the most compressible of the three. The greater compressibility of the flocculated sludge is possibly linked to charge neutralisation. Keiding *et al.* (2001) showed that the charged surface of sludge particles induce a cloud of counter ions in the saturating water in the filter cake, creating an osmotic counter-pressure to filtration (as the filtrate leaving the sludge cake will have the same concentration of ions as the saturating water in the filter cake). Charge neutralisation brought about by cationic flocculants reduces this effect allowing the sludge to compress to higher solids concentrations, an example of this may be the behaviour which is occurring in Figure 5.8. Overall the three sludges exhibited good compressibility characteristics at high pressures, reaching 0.3 solids (v/v) at pressures above 300kPa.

For biological sludges, such as the samples examined, it has been noted that, under compression, a 'threshold pressure' exists, beyond which sludge network structure collapses markedly, leading to the term 'super-compactable sludge', which has been noted by researchers such as Wu *et al.* (2001). This was apparent for each of the three MAD samples, as $P_y(\phi)$ dropped steeply approaching the gel-point, suggesting a very weak network exists at low solids concentrations. This network compresses dramatically above a certain threshold pressure. Due to this, a simple relationship between sludge compression and applied pressure cannot easily be formulated, and modelling the compressive yield stress across from ϕ_g to ϕ_∞ for high pressures is difficult if sufficient experimental data is not available across the full range of solids concentrations. However, the rigorous curve-fits provided by the BSAMS software fitted the data well for the three sludges once the empirical fitting parameters had been optimised.

Figures 5.4 to 5.6 also showed that pressure-filtration and batch settling were unable to provide compressive yield stress data in an intermediate solids regime. This is the area in which an inflection of the curve occurred. The behaviour in this intermediate region is likely to dictate the speed of many solid/liquid separation processes. Techniques described by Green (1997) are able to extract compressibility data in this region allowing a more detailed curve-fit to be applied. In Chapters 6 and 7, a centrifugation technique described by Green (1997) is used to describe this region for a number of sludges.

5.2.4 Hindered Settling Function, $R(\phi)$

The hindered settling function is a material property which characterises the permeability of the sludge. The hindered settling function is inversely related to a Darcian permeability, so a higher $R(\phi)$ represents a material which is more permeable. Figures 5.9, 5.10 and 5.11 present the high volume fraction $R(\phi)$ data obtained for the Luggage Point and the Mt. Martha sludges. Figure 5.12 compares the $R(\phi)$ functional forms for the three sludges. The data is presented on semi-logarithmic co-ordinates and $R(\phi)$ is expressed as Pa. It must be noted that what appear as small differences in $R(\phi)$ on semi-logarithmic co-ordinates can have a large effects on sludge dewatering. $R(\phi)$ data for solids concentrations lower than the gel-point was obtained from batch settling tests and is also included in each of the figures.

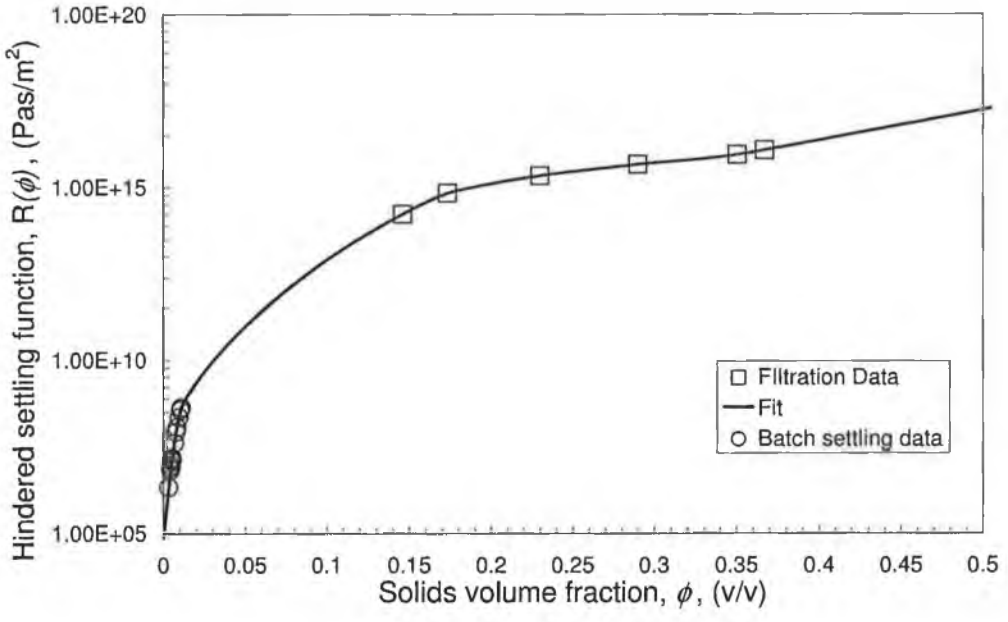


Figure 5.9 $R(\phi)$ versus ϕ data for unflocculated Luggage Point sample. Data calculated from pressure-filtration and batch settling tests.

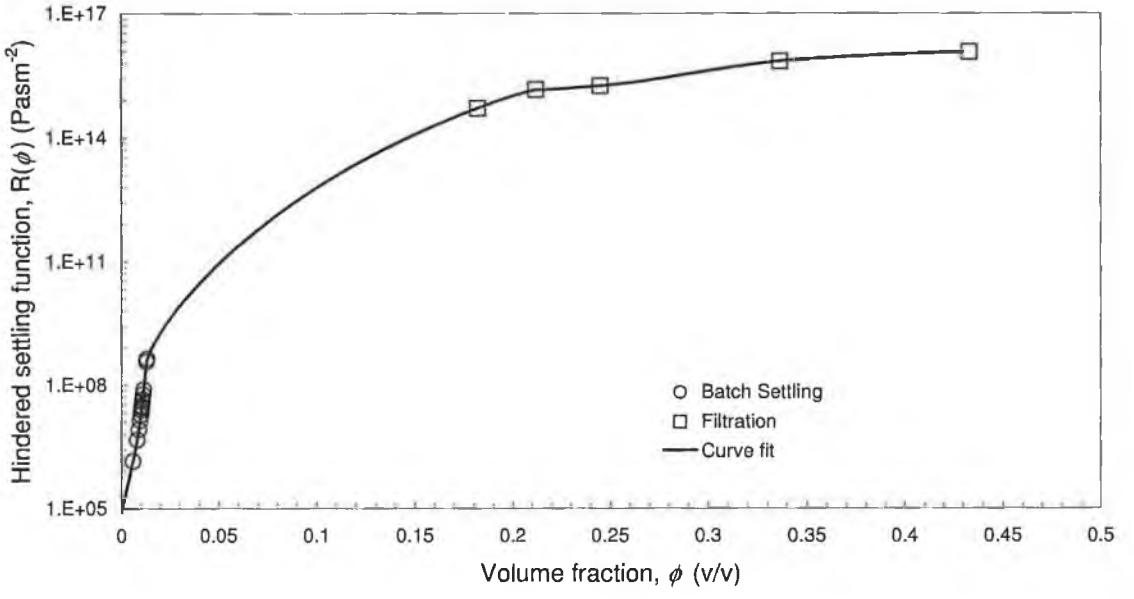


Figure 5.10 *R(ϕ)* versus ϕ data for flocculated (9g/Kg TS) Luggage Point sample. Data calculated from pressure-filtration and batch settling tests.

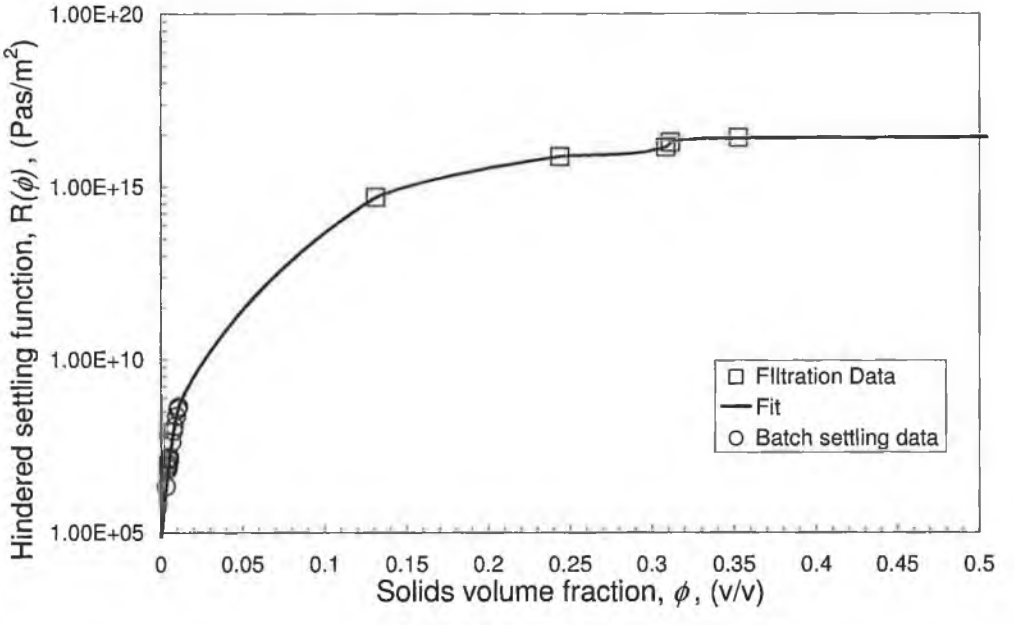


Figure 5.11 *R(ϕ)* versus ϕ data for unflocculated Mt. Martha sample. Data calculated from pressure-filtration and batch settling tests.

For each of the samples $R(\phi)$ increased steeply as a function of solids concentration. These increases covered several orders of magnitude. The implication of this is that the samples analysed became exceptionally impermeable at low solids concentrations, with the Mt. Martha sample exhibiting $R(\phi)$ values in excess of 1×10^{15} Pas/m^2 at concentrations above 0.15 v/v. To put the impermeability of these sludges into context, typical $R(\phi)$ values for a red mud suspension, measured by Usher (2002) across a similar solids concentration, 0.1 – 0.3 v/v, ranged from 1×10^{10} Pas/m^2 to 1×10^{11} Pas/m^2.

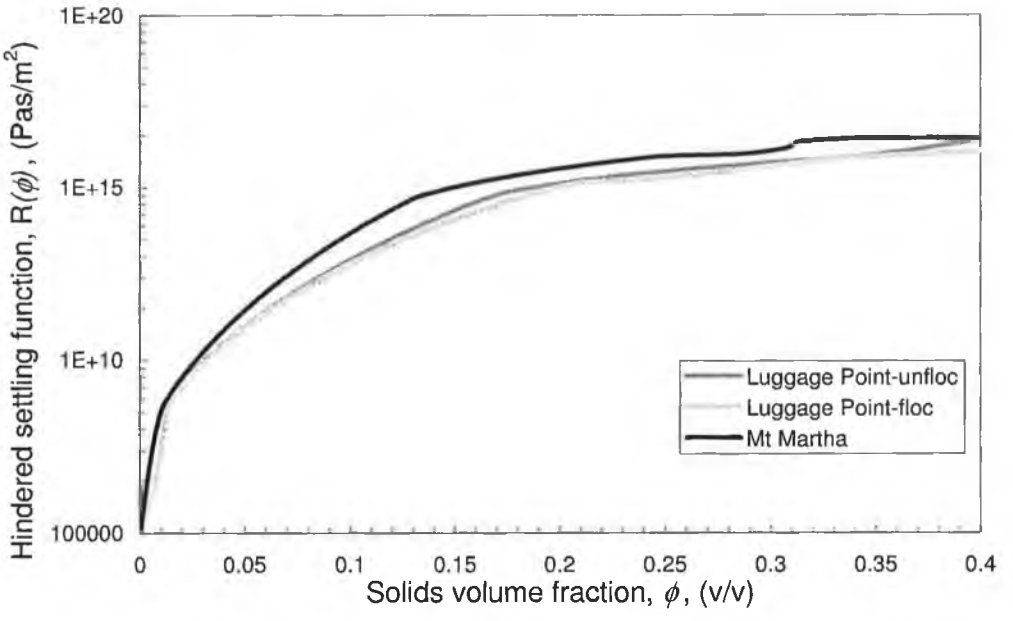


Figure 5.12 $R(\phi)$ functional forms for Luggage Point (unflocculated and flocculated) and Mt. Martha MAD samples.

Figure 5.12 gives the $R(\phi)$ functional forms for the three samples. The data shows that the Luggage Point sample which was flocculated was slightly more permeable. However, the difference between the unflocculated and flocculated samples is minor compared to the difference between the permeability of the Luggage Point samples and the sample

obtained from Mt. Martha WWTP. The Mt. Martha sample shows a much lower permeability than the two Luggage Point samples.

Many authors have noted that permeability is the controlling factor in sewage sludge dewatering (Wu *et al.*, 2001; Kapur *et al.*, 2002), and these results suggested that the final obtainable solids achievable by unit operations such as filter-presses and centrifuges may, on the face of it, appear to be dictated by the sludges ultimate compressibility but are in fact dictated by the permeability. Sewage sludges require an exceptionally long time to reach end-points in compression, and it may be the case that, on-site, an operator may assume that a sludge has compressed to equilibrium, when it is still compressing.

As was the case with the $P_y(\phi)$ data, there is a region in the $R(\phi)$ curves which is not described by the experimental techniques described. This region falls between the batch settling data and the high pressure data and spans over 5 orders of magnitude for the three sludges. The data points obtained from batch settling, for the flocculated Luggage Point sample in particular (Figure 5.10) suggested a different trend in $R(\phi)$, with a steeper rise than that described by the curve-fit outputted from the BSAMS software. As with compressive yield stress data, a number of techniques have been described which allow the experimental determination of $R(\phi)$ in this region. These include gravity permeation (Aziz, 2004) and transient centrifugal analysis techniques (Green, 1997).

Hindered settling data resulting from batch settling of sewage sludges should be treated with caution. The solid phase of the sludges studied had a density which is quite close to

water (1100 kg/m^3). Denitrification, a side effect of which is the production of bubbles of insoluble N_2, and other anaerobic microbial activity can have an effect on sludge settling. Indeed, in all cases where settling was performed on anaerobic sludges, if left long enough, a proportion of the sludge eventually floated to the top of the settling cylinder, due to gases produced by microbial activity, and it must be assumed that, even before the floatation occurs, these gases have an effect on the sludge settling rate.

5.2.5 Diffusivity, $D(\phi)$

Diffusivity values obtained for the three sludges are shown in Figure 5.13.

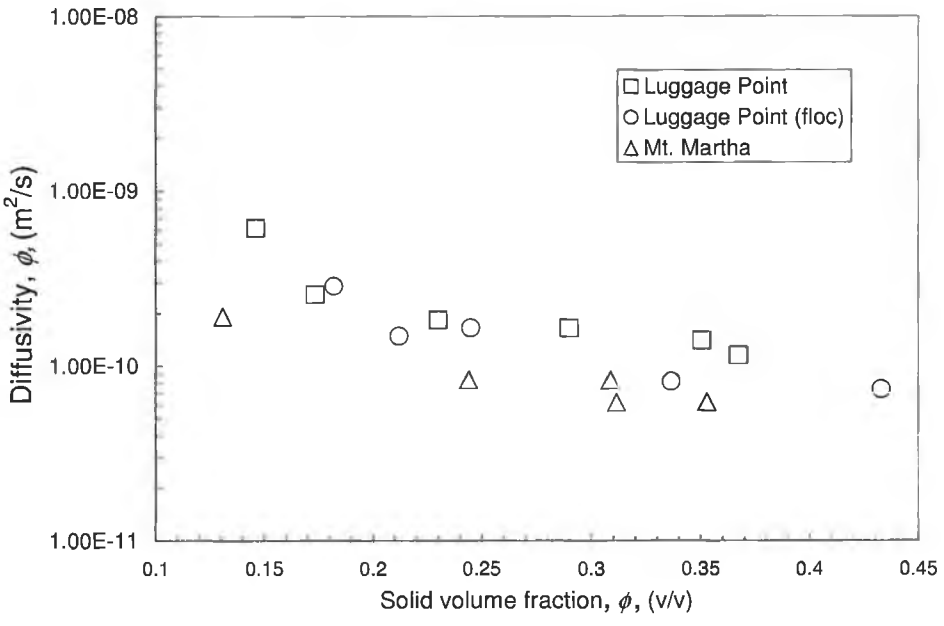


Figure 5.13 Diffusivity, $D(\phi)$, as a function of ϕ for flocculated Luggage Point, unflocculated Luggage Point and unflocculated Mt. Martha sludge. Data obtained from log-fitting of end-points to pressure-filtration data.

At high solids concentrations, inorganic suspensions (such as zirconia) exhibit increasing $D(\phi)$ with increasing solids concentration (Usher, 2002). However, as outlined in Chapter 2, non-traditional materials such as sewage sludges exhibit exceptionally low diffusivities at high ϕ, with a peak in the $D(\phi)$ curve occurring at very low ϕ. This is indicative of very compressible materials. Stickland (2005) explained the theoretical reason for this behaviour. ϕ increases as a function of filtration. Typically $R(\phi)$ also increases as filtration proceeds. Simultaneously, the rate of change in the increasing $P_y(\phi)$ decreases. As the rate of change in $R(\phi)$ is greater than the rate of change in $P_y(\phi)$, for solids concentrations above ϕ_g, in materials that have deformable, rearrangeable structures that contain high molecular weight and cross-linked biomolecules, such as sewage sludges (Stickland, 2005). $D(\phi)$ decreases with ϕ for solids concentrations above the gel-point. From Figure 5.13, it is evident that the Mt. Martha and the Luggage Point sludges all exhibited decreasing $D(\phi)$ values as a function of increasing ϕ, at high solids concentrations.

A $D(\phi)$ functional form was plotted using MATHEMATICA for the unflocculated Luggage Point samples (Figure 5.14).

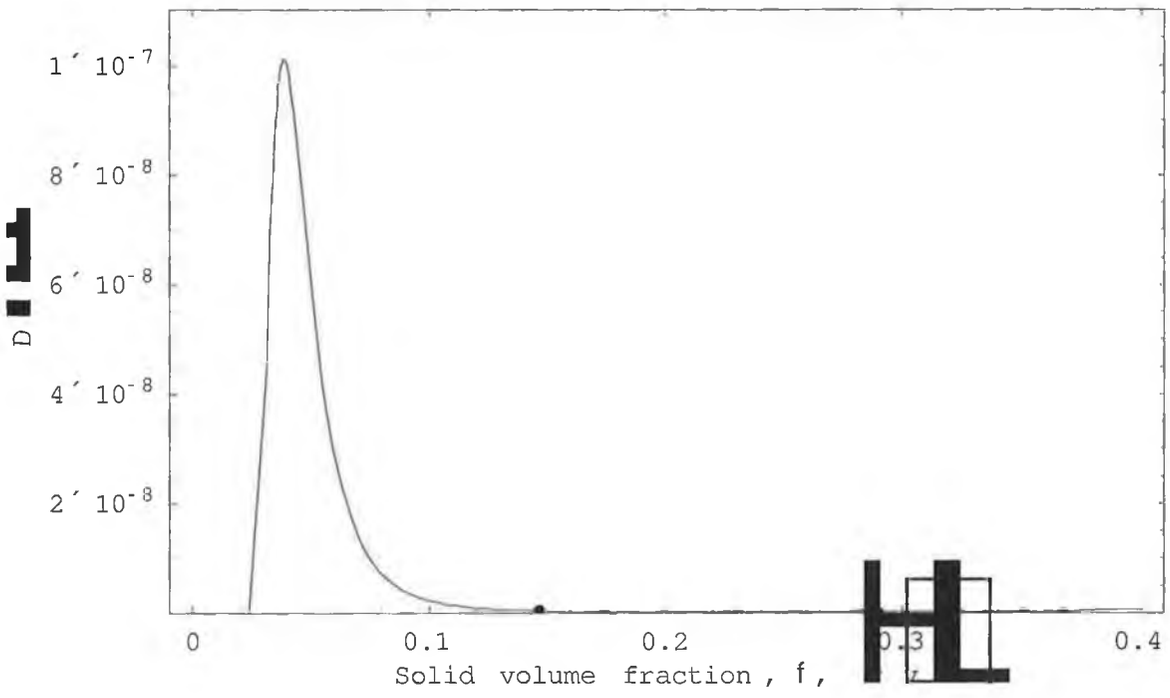


Figure 5.14 $D(\phi)$ functional form for unflocculated Luggage Point samples.

The functional form was calculated for ϕ according to equation 3.17 using the P_y1 functional form obtained for $P_y(\phi)$ (Table 5.4) and the $R(\phi)$ functional form from the BSAMS analysis. The functional curve shows a maximum near the gel-point and is then monotonically decreasing. Materials exhibiting such characteristics in $D(\phi)$, typically show short cake-formation times and long-cake compression times in filtration, as is the case for biosludges (Stickland, 2005).

5.2.5 Conclusions

- At The University of Melbourne an air-driven filtration rig was commissioned and used to characterise three MAD samples (originating from Luggage Point and Mt Martha WWTPs) according to the biosludge characterisation protocol. All three sludges exhibited very low permeability (orders of magnitude lower than that of inorganic sludges) as characterised by $R(\phi)$ and exceptionally high compressibility as characterised by $P_y(\phi)$.

- The method was able to detect differences in dewatering properties between the Mt. Martha and the Luggage Point sludges which were more marked than differences between the flocculated and unflocculated Luggage Point sludges. This suggested that sludges resulting from the same type of digestion regime (in this case MAD) can differ quite significantly in dewatering properties.

5.3 Characterisation of sludges at Killarney WWTP

5.3.1 Introduction

The 500 L ATAD pilot plant was operated at two separate HRTs to relate this parameter to dewatering properties and secondly to relate this parameter to materials which have been shown by other researchers to affect ATAD dewatering (Murthy *et al.*, 2000; Zhou *et al.*, 2003). The materials investigated were colloidal and soluble materials which are released into solution during digestion, these being proteins, polysaccharides and soluble

COD. Also characterised were sludges resulting from the full-scale ATAD works at Killarney ATAD plant, from both reactors, 1A and 2A, which operate at different average temperatures and from the product storage tanks where the sludge is stored for different amounts of time.

The application of the compressive rheology theory of Buscall and White (1987) to sewage sludges was discussed in detail in Chapter 2. The theory has been proven to successfully characterise many inorganic sludges in terms of compressibility, permeability, and diffusivity in an unparalleled manner (Harbour *et al.*, 2001; Usher, 2002). The parameters described have subsequently been used to successfully predict inorganic sludge behaviour in a number of dewatering unit operations (Stickland, 2005). However, sewage sludge is difficult to describe in terms of this theory, due to inordinately long compression regimes. A unique sewage sludge characterisation protocol has been devised to overcome these issues (described in Chapter 3) and one of the main aims of the research is to determine the sensitivity of sewage sludge characterisation, by using the Buscall and White (1987) approach. This entailed evaluating whether the method can firstly, distinguish between sewage sludges produced by different digestion regimes (ATAD, MAD and WAS) and secondly, whether it could be used to determine the effects of conditioning chemicals within the regime. Results outlined below go some way towards an evaluation of the method, and some limitations are outlined at the end of the section.

5.3.2 Sludge properties

Sludge samples were placed in refrigeration conditions (5 ^{o} C) immediately upon being received at the lab. Using the air-driven filtration rig, a series of high pressure filtration tests were conducted on the sludges at pressures ranging from 2kPa to 300kPa. During each filtration test the transient suspension height was calculated from the transient mass/volume of filtrate (which accumulated in a receptacle upon the analytical balance). On completion of the filtration test, transient suspension height versus time data was subsequently converted to average suspension volume fraction versus time data according to equation 3.9. The material characteristics of the sludges are given in Tables 5.7 – 5.10. The calculated solids densities of the sludges were 1100kg/m^3 for the feed sludge and 1300kg/m^3 for all of the ATAD sludges. The density of the liquid fraction was assumed to be 1000kg/m^3 for all sludges.

Table 5.7 Killarney waste activated sludge (WAS) material characteristics (flocculated at 3g/Kg TS using ZETAG 7867)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
5	0.085494	0.0886044	2.29×10^{-9}	3.90×10^{13}		
10	0.110705	0.111758	1.64×10^{-9}	1.43×10^{14}		
50	0.15535	0.16889	7.51×10^{-10}	1.68×10^{15}		
100	0.16095	0.185565	5.73×10^{-10}	3.19×10^{15}	0.045	0.0201
300	0.193471	0.22982	3.99×10^{-10}	1.05×10^{16}		

Table 5.8 Killarney PS4a ATAD post-storage sludge (flocculated at 33g/Kg TS using ZETAG 7867)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
10	0.100152	0.102487	1.08×10^{-9}	2.07×10^{13}		
50	0.155382	0.164541	6.61×10^{-10}	5.12×10^{14}		
100	0.229824	0.235157	3.24×10^{-10}	7.58×10^{15}		
200	0.238723	0.244969	2.86×10^{-10}	1.07×10^{16}	0.0211	0.0256
250	0.200195	0.249673	2.66×10^{-10}	1.28×10^{16}		
300	0.260587	0.269272	2.37×10^{-10}	2.14×10^{16}		
450	0.250155	0.271318	2.29×10^{-10}	2.41×10^{16}		

Table 5.9 Killarney PS4b ATAD post-storage sludge (flocculated at 25g/Kg TS using ZETAG 7867)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
2	0.14995	0.14995	8.33×10^{-10}	5.39×10^{13}		
4	0.167388	0.168603	5.24×10^{-10}	1.75×10^{14}		
10	0.208071	0.210615	4.51×10^{-10}	7.79×10^{14}		
20	0.222543	0.224268	4.23×10^{-10}	1.21×10^{15}	0.0275	0.0225
50	0.252468	0.257511	3.27×10^{-10}	3.50×10^{15}		
200	0.183497	0.290279	2.59×10^{-10}	8.79×10^{15}		
350	0.268563	0.319246	2.10×10^{-10}	1.85×10^{16}		

Table 5.10 Killarney PS2 ATAD post-storage sludge (flocculated at 24g/Kg TS using ZETAG 7867)

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
4	0.126469	0.126469	5.92×10^{-10}	1.98×10^{13}		
10	0.194319	0.1987	4.03×10^{-10}	3.31×10^{14}		
50	0.286072	0.28827	3.84×10^{-10}	2.33×10^{15}		
100	0.30055	0.309476	2.92×10^{-10}	4.35×10^{15}	0.045	0.0201
200	0.22306	0.320284	2.03×10^{-10}	7.38×10^{15}		
300	0.34001	0.354773	1.96×10^{-10}	1.24×10^{16}		
400	0.250333	0.369152	1.16×10^{-10}	2.52×10^{16}		

Feed was the activated sludge which was fed to the full-scale ATAD works and pilot plant at Killarney. 1A and 2A were sludges directly sampled from the full-scale ATAD reactors at Killarney WWTP. These two reactors were operated in series, with thermotolerant temperatures present in 1A, and true thermophilic conditions present in 2A. Following digestion in reactor 2A, sludge was pumped to large product storage tanks at Killarney where it is often kept for several weeks before being spread on the land. PS4 and PS2 were product storage tanks at Killarney. PS4 was sampled at two different dates PS4a and PS4b. Samples PP7, PP10 were the pilot plant sludges, the numbers delineate the HRT in days. G1, G2 and G3 were sludges sampled from European ATAD plants. G1 was sampled from S.I.A.S Ueberseyen WWTP in Luxembourg. G2 was sampled from Herbrechtingen WWTP, Germany. And G3 was sampled from Scwharmstedt WWTP, Germany.

The fitting parameters used for the $Py(\phi)$ functional forms are given for sludges in Table 5.11

Table 5.11 Fitting parameters for the $Py(\phi)$ functional forms of sludges sampled at Killarney

	ϕ_{c1}	B_1	A_1	k_1	ϕ_{cp}
Feed	0.020195	0.01	0.613105	9.048291	0.63
PS4a	0.02563	0.01	0.541318	7.908861	0.63
PS4b	0.022532	0.002	1.085962	12.063969	0.63
PS2	0.022872	0.05	0.100777	3.530962	0.6
G1	0.024868	0.01	0.497067	6.487429	0.63
G2	0.040512	0.05	0.254775	4.99772	0.63
G3	0.023987	0.01	0.497079	6.883701	0.63

The OPD for each of the sludges was calculated according to the method detailed in Section 3.3.12 and the values are given in Table 5.12.

Table 5.12 Optimum polymer dose (OPD) for sludges studied at Killarney, OPD expressed in g/Kg TS, the average CST (s) at the OPD is also presented.

ID	*Feed*	*1A*	*2A*	*PS4a*	*PS4b*	*PS2*	*PP7*	*PP10*	*G1*	*G2*	*G3*
OPD	4	83	78	33	25	24	89	Failed	20	17	7
CST	9	65	60	19	16	20	62	n/a	14	16	20

The OPD (as calculated from CST tests) varied quite significantly for ATAD sludge which originated from different sources, and as such it was difficult to distinguish a trend in OPD for ATAD sludge in general. For instance, the OPD for G3 was 7g/Kg TS, while the OPD for 1A was 83g/Kg TS. The pilot plant sludge had an OPD of 89 g/Kg TS on a 7

day HRT, and an optimum polymer dose could not be determined for the pilot plant sludge on a 10 day HRT, so poor were the sludge properties. Notably, the OPD for the sludge which resulted from the full-scale reactors (1A and 2A) at Killarney was significantly higher than that which resulted from the product storage tanks (PS4 and PS2). Even when an OPD was determined for sludges 1A, 2A and PP7, the average CST at the OPD for each of these sludges remained over 60 seconds. This is in excess of the CST value of <20s defined by Agarwal (2007) as necessary for satisfactory dewatering. Overall, it was evident that post-process storage reduced the OPD at Killarney, and that the ATAD sludges which resulted from European ATAD plants had lower OPD than the sludges sampled at Killarney.

Recent work by Agarwal *et al.,* (2005) suggested that for some ATAD sludges the presence of positively charged biocolloidal material in the solution-phase may hinder the effectiveness of using positively charged polyelectrolyte to condition ATAD sludge, and a two-stage conditioning regime, with cationic additives followed by anionic additives was recommended. It was possible that this is the case for sludges 1A, 2A and PP7. As the minimum achievable CST was quite high at the optimum polymer dose (>60s) there was a possibility that cationic polyelectrolyte alone was unable to condition the sludge to an acceptable state of flocculation for successful dewatering, due to the presence of positively charged colloidal species interfering with flocculation. Further tests on colloidal species in the solution phase of the sludge would be required to determine this.

Due to the poor settlebality and exceptionally long filtration times exhibited by the pilot-plant sludges, efforts to characterise their dewatering properties in terms of batch settling and high pressure filtration proved ineffective. In face of the difficulties in characterising the sludge which originated in the pilot plant, the experimental plan was changed, and more in-depth dewatering characterisation was instead conducted on the final product sludge at Killarney. A significant reduction in the OPD following storage of ATAD sludge at Killarney is shown in table 5.7. The average OPD fell from 78g/kg TS in Reactor 2A to as low as 24g/kg after storage (PS2).

5.3.5 Compressive yield stress, $P_y(\phi)$

This section presents the compressive yield stress results for the sludges which were sampled at Killarney. $Py(\phi)$ functional forms were described according to the following equation.

$$\left(a_1 \frac{(\phi_{cp} - \phi)(b_1 + \phi - \phi_{g1})}{(\phi - \phi_{g1})} \right)^{-k_1}$$

The fitting parameters for each of the curve-fits are given in Table 5.14. Simple power-law functional forms did not fit the data well and are not shown.

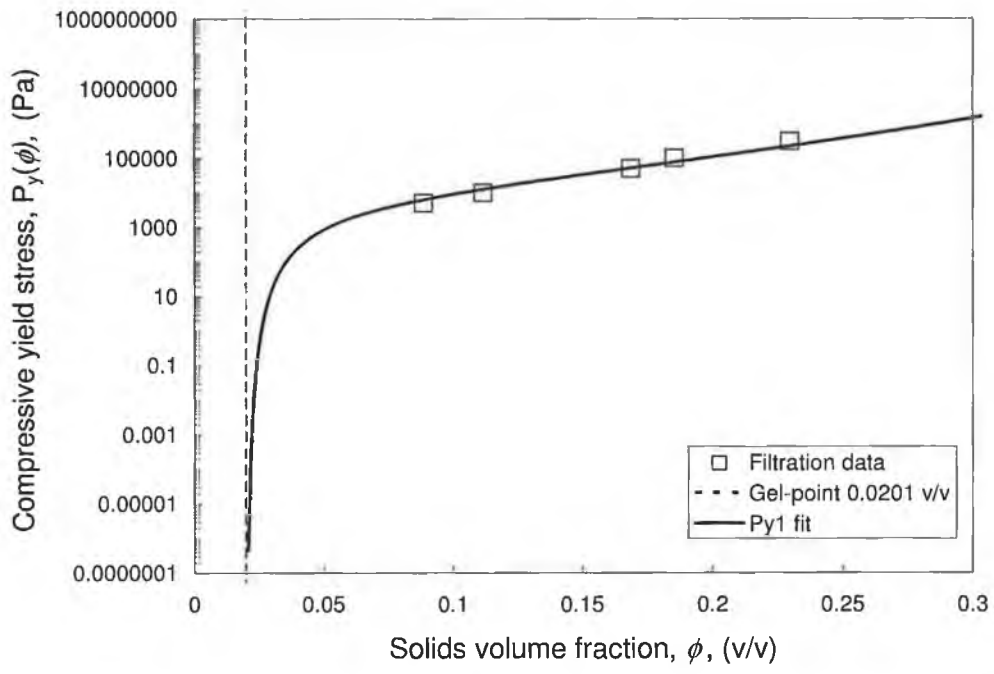


Figure 5.15 $P_y(\phi)$ as a function of ϕ for the feed sludge (AS) at Killarney. The sludge was conditioned using ZETAG 7867 at a concentration of 4g/kg TS.

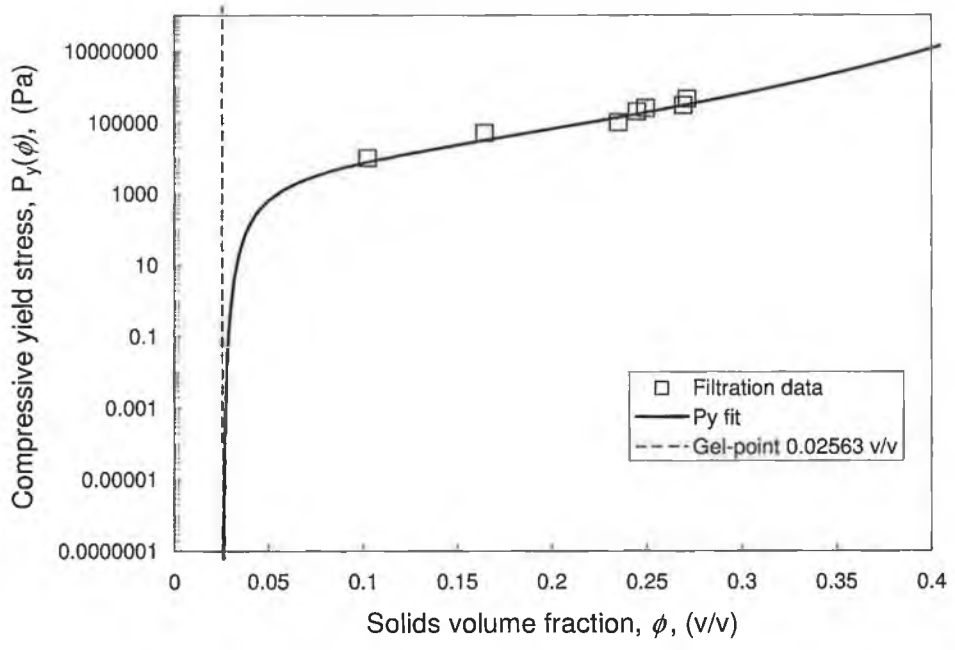


Figure 5.16 $P_y(\phi)$ as a function of ϕ for PS4a (post-storage ATAD) at Killarney. The sludge was conditioned using ZETAG 7867 at a concentration of 33g/kg TS.

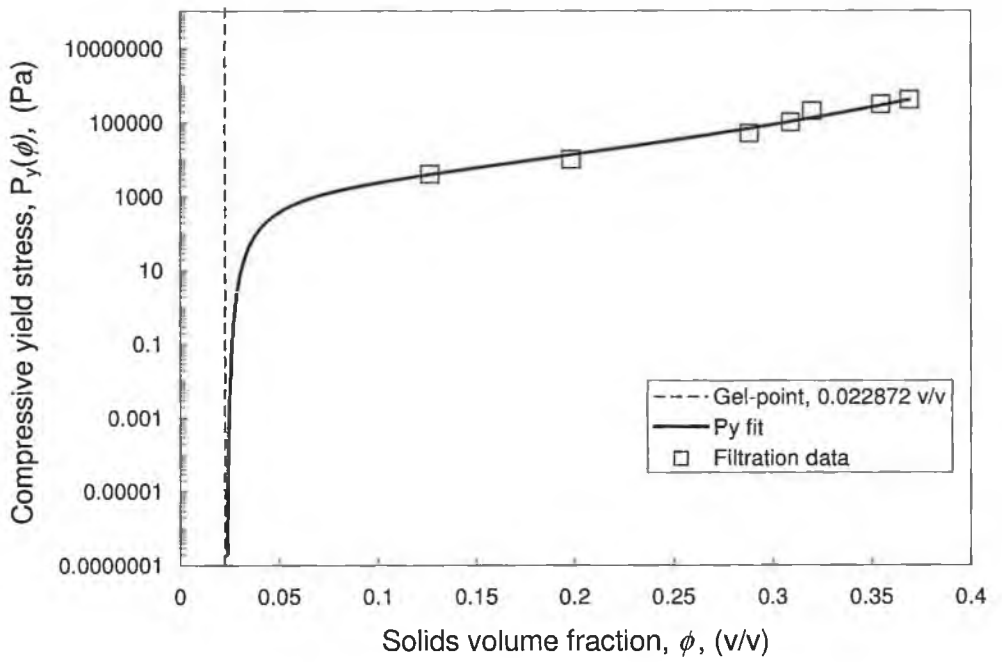


Figure 5.17 $P_y(\phi)$ as a function of ϕ for PS4b (post-storage ATAD) at Killarney. The sludge was conditioned using ZETAG 7867 at a concentration of 25g/kg TS.

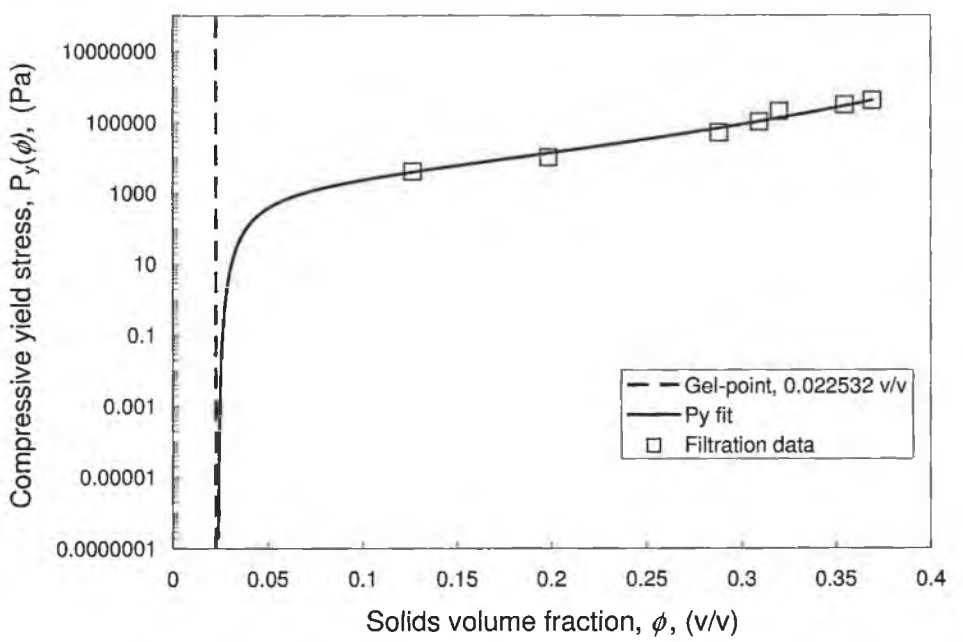


Figure 5.18 $P_y(\phi)$ as a function of ϕ for PS2 (post-storage ATAD) at Killarney. The sludge was conditioned using ZETAG 7867 at a concentration of 24g/kg TS.

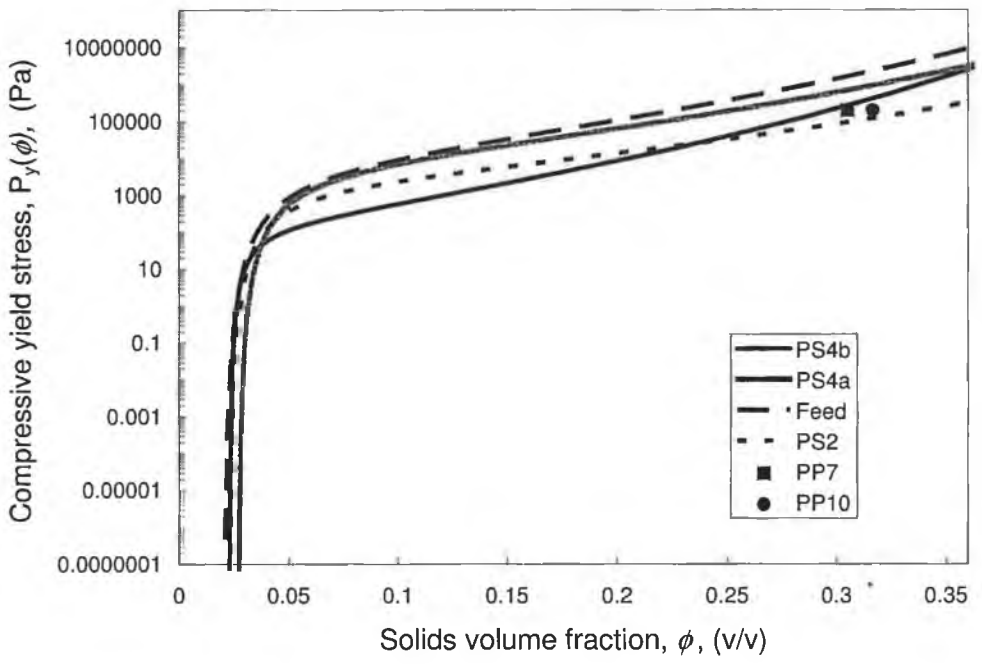


Figure 5.19 *Py(ϕ)* functional forms for Feed, PS4a, PS4b and PS2.

$P_y(\phi)$ was plotted as pascals (Pa) against specific solids concentrations ϕ (v/v) for each of the sludges (Figure 5.15 – Figure 5.19). Data from truncated filtration tests were used to estimate ϕ_∞ data points using the logarithmic curve-fitting technique described in Section 3.4.6. Gel-points were calculated from batch-settling tests. *Py(ϕ)* functional forms described the data obtained from filtration tests for the four sludges (Figures 5.15 - 5.19).

Figure 5.15 gives the $P_y(\phi)$ for the feed sludge at Killarney. The feed sludge was the least compressible of the four sludges characterised (Figure 5.19). The feed sludge is an activated sludge resulting from a combination of surface aeration and diffuse aeration processes at Killarney WWTP. It has been noted in the literature that activated sludge consists of discrete flocs which consist of an EPS matrix in which individual bacterial

cells are suspended. This EPS matrix has been described as 'highly hydrated' (Jin, 2003), and is also negatively charged due to the ionisation of anionic functional groups on the EPS surface, such as the carboxyl group (Liu and Fang, 2002). Keiding *et al.* (2001) suggested that osmotic pressure between the activated sludge filter cake and the filtrate provides a counter-pressure to filtration, due to negatively charged functional groups on the EPS and associated counter-ions. It is possible that these factors may result in activated sludge having good filtration characteristics at low ϕ but being ultimately less compressible than digested sludge at higher ϕ. ATAD digestion degrades the EPS matrix resulting in lower particle sizes than that of activated sludge. Additionally, this destruction of the floc structure may make such digested sludges more compressible. Increased levels of soluble and colloidal biopolymer material in the solution phase of digested sludge are thought to be indicative of erosion and digestion of the EPS matrix, and have been found to correlate positively with OPD by researchers (Novak *et al.*, 2003). Overall, the $P_y(\phi)$ data showed that the digested sludges were more compressible than the activated sludge.

The product storage sludges (PS4a, PS4b and PS2) were more compressible than the feed sludge at Killarney. PS4a (Figure 5.16 and Figure 5.19) was the least compressible of the three product storage sludges, and also had the highest OPD (Table 5.7). PS4a was sampled from a product-storage tank at Killarney after one week's storage time, PS4b was sampled from the same product-storage tank three weeks subsequent to this, and no fresh sludge was added to the tank during this period. This was to assess whether prolonged storage impacted on ATAD dewatering properties. PS2 was also stored for 4

weeks before sampling, though it was sampled from a different product storage tank to PS4a and PS4b. The sludges had similar gel-points, however, the feed sludge had the highest gel-point. Of the post-storage sludges PS4a had the highest gel-point.

Overall, the sludges which had been stored for four weeks (PS4b and PS2) were more compressible than PS4a. There was a marked improvement in compressibility for PS4b over PS4a, particularly at low pressures (Figure 5.19). Furthermore the improvement in compressibility corresponded with a drop in the OPD from 33g/kg TS to 25g/kg TS.

Only two points are shown in Figure 5.19 for the pilot-plant sludges. Though filtration times were inordinately long for these sludges, they compressed to very similar solids concentrations to the product storage sludges.

5.3.6 Hindered settling function, $R(\phi)$

The hindered settling function results are presented in Figure 5.20 – 5.23, and Figure 5.24 compares the $R(\phi)$ functional forms for the three sludges.

The feed sludge was the most impermeable of the three sludges studied. It was expected that this sludge would exhibit good permeability when compared to the ATAD sludges, due to the highly developed floc structure found in activated sludges. However, the opposite was found to be the case. The higher gel-point determined for the activated sludge was indicative of a readily settleable sludge.

Overall, the data showed that, concurrent with the improvement in compressibility, there was an improvement in permeability for the sludge which was stored for four weeks. PS4b and PS2 show very similar $R(\phi)$ profiles, and also had very similar OPD (25 g/kg TS and 24 g/kg TS respectively). There was an improvement of approximately an order of magnitude when PS4a is compared to PS4b. $R(\phi)$ data points were not calculated for PP7 and PP10, as the calculation of $R(\phi)$ required batch-settling data. Batch settling data were not obtainable for these sludges as the filtrate was very turbid, and a transient solid-liquid interface could not be determined. In addition, following flocculation by the addition of polymer, the sludges did not settle even at solids concentrations as low as 0.005 (v/v).

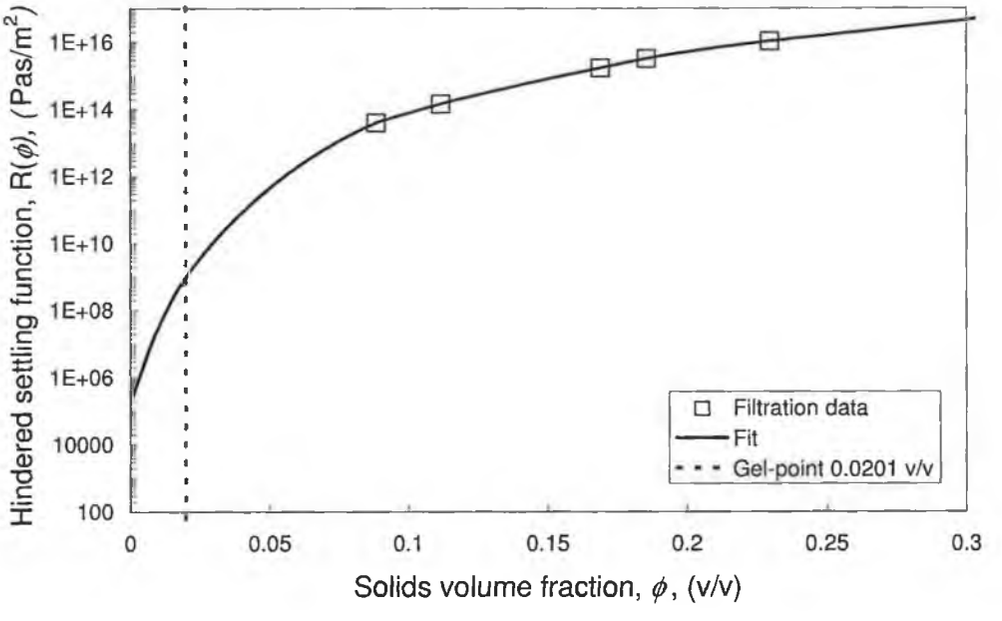


Figure 5.20 $R(\phi)$ versus ϕ data for feed sludge at Killarney, flocculated at 4g/kg TS using ZETAG 7869. Data calculated from pressure-filtration and batch settling tests.

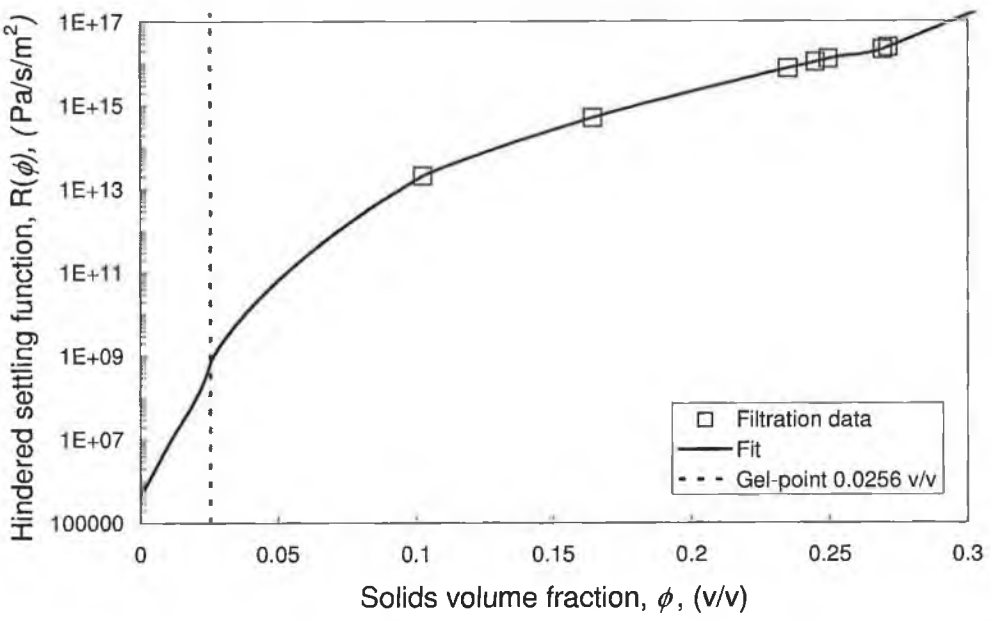


Figure 5.21 $R(\phi)$ versus ϕ data for PS4a (post-process ATAD) flocculated at 33g/kg TS using ZETAG 7869. Data calculated from pressure-filtration and batch settling tests.

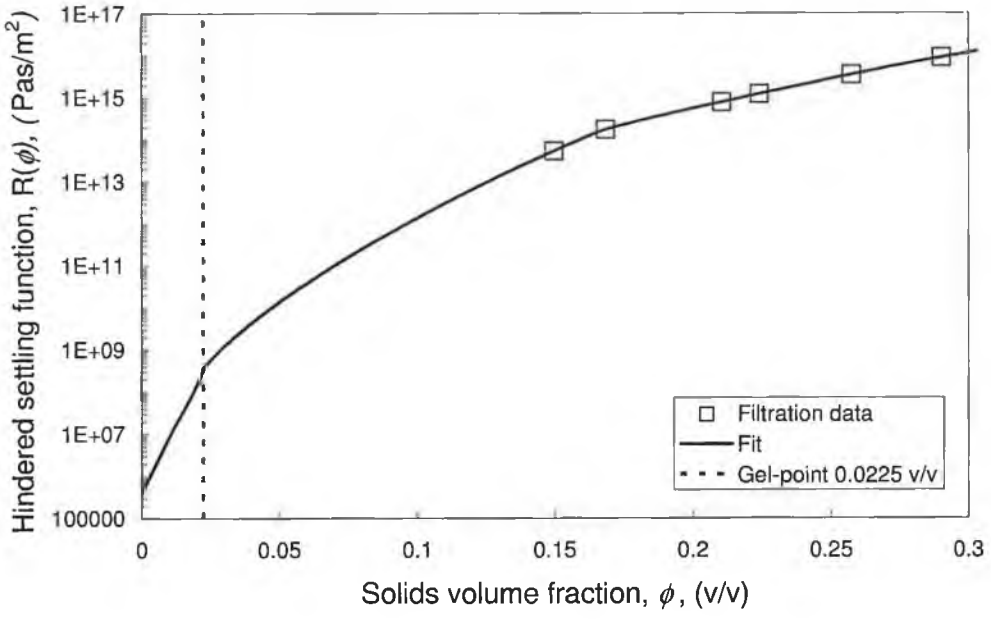


Figure 5.22 $R(\phi)$ versus ϕ data for PS4b (post-process ATAD) flocculated at 25g/kg TS using ZETAG 7869. Data calculated from pressure-filtration and batch settling tests.

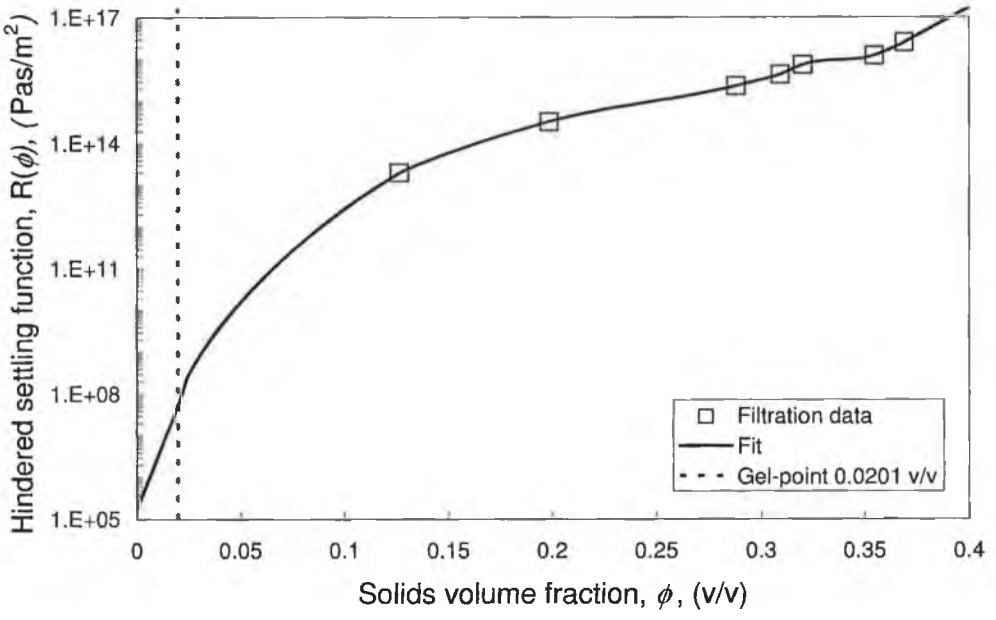


Figure 5.23 $R(\phi)$ versus ϕ data for PS2 (post-process ATAD) flocculated at 24g/kg TS using ZETAG 7869. Data calculated from pressure-filtration and batch settling tests.

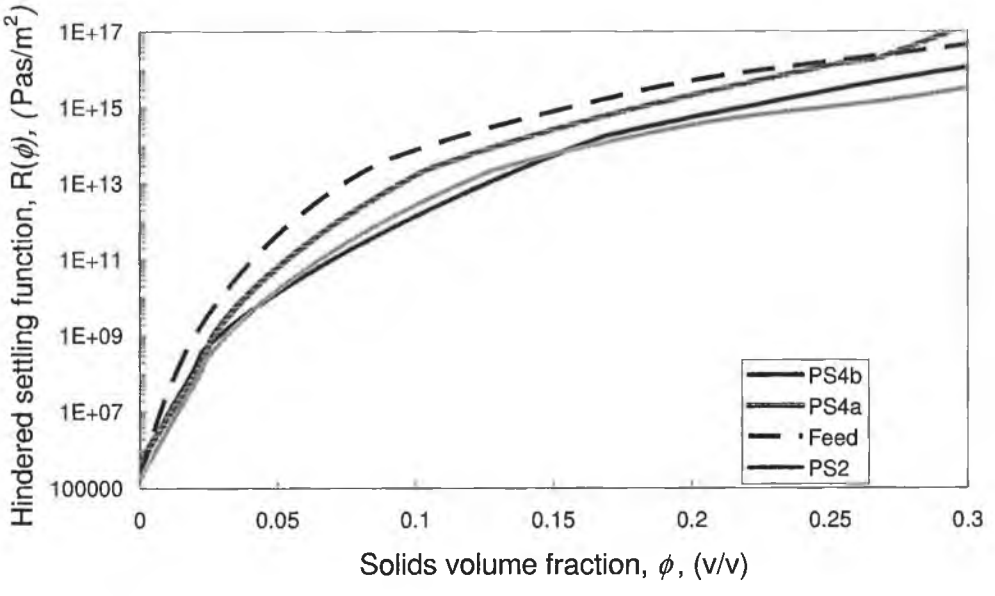


Figure 5.24 $R(\phi)$ functional forms for Feed, PS4a, PS4b and PS2 at Killarney.

5.3.7 Diffusivity, $D(\phi)$

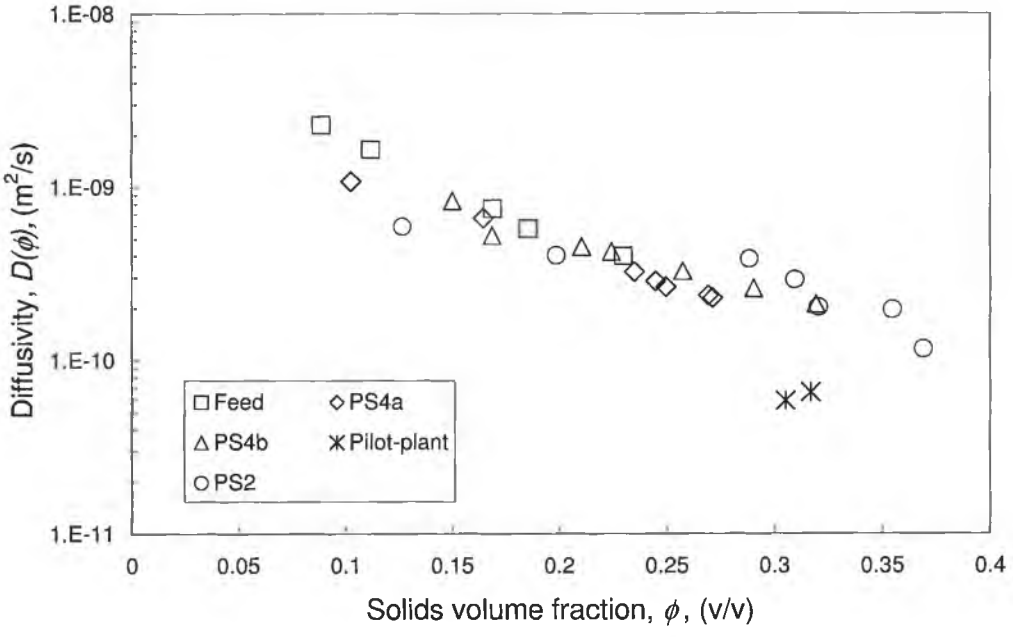


Figure 5.25 $D(\phi)$ versus ϕ data for Feed, PS4a, PS4b and PS2 at Killarney

There is a marked similarity for the $D(\phi)$ values obtained for the sludges at Killarney. A declining trend is evident for the four sludges, with only the pilot-plant sludges showing notably lower diffusivity values, which is indicative of materials with poor dewatering properties.

5.3.7 Conclusions

- The biosludge characterisation protocol was used to characterise several sludges at Killarney WWTP in terms of $Py(\phi)$, $R(\phi)$ and $D(\phi)$. These sludges were an activated-sludge, the pilot-plant ATAD sludges (a limited characterisation) and

three post-storage ATAD sludges. The activated sludge was shown to be incompressible and impermeable at high solids concentrations associated with pressure filtration and this may have been due to the highly hydrophilic and gel-like floc structure found in activated sludges.

- The pilot-plant sludges were difficult to characterise using the biosludge characterisation protocol due to exceptionally long filtration times, undefined OPD, and poor settling characteristics (negating the conduction of batch settling tests).

- Post-storage ATAD sludges were characterised using the biosludge characterisation protocol and these were shown to have dewatering properties which were analogous to mesophilic-anaerobically digested sludges. The duration of storage time was shown to correlate with improved dewatering properties.

- It is proposed that ATAD operators who wish to improve ATAD sludge dewatering store sludges in mesophilic conditions for as long as possible before dewatering unit operations.

5.4 Characterisation of Continental European ATAD sludges

5.4.1 Introduction

This section examines the dewatering properties of three sludges sampled from operating ATAD plants in Luxembourg and Germany. There were a number of significant

differences in the operational parameters employed at these plants in comparison to Killarney. All of the plants were fed a mixture of primary and secondary sludge. This is in contrast to the ATAD at Killarney which is fed on secondary sludge alone. Secondly, pre-ATAD conditioning is not employed at the European plants, and as a consequence of this, the concentration of the feed sludges fed to these reactors is lower than that fed to the reactors at Killarney. It is probable that an ATAD reactor fed solely on secondary sludge at concentrations below 4% TS would be unable to reach thermophilic temperatures (Jewell and Kabrick, 1980). However, due to the typically higher calorific content of primary sludge, the blend of primary and secondary sludge fed the reactors in Germany and Luxembourg has sufficient calorific content to attain thermophilic temperatures without the need to thicken the sludge to as high a solids concentration as at Killarney. The density of the solid fraction of the three sludges was calculated to be approximately 1300g/L and the density of the liquid fraction was assumed to be 1000g/L.

G1 was sourced from S.I.A.S. Uebersyren, Luxembourg. This ATAD plant was the biggest ATAD in Europe until 2003. It was designed for a 35000 p.e. The sludge fed to the reactors at S.I.A.S. Uebersyren consisted of a mixture of primary and secondary municipal sludge, with volatile solids (VS) representing approximately 76% of the TS. During the winter months (when the sludge was sampled) the sludge treated by the plant contains a large amount of de-icing fluids from a nearby international airport. WAS fed to the ATAD reactors at S.I.A.S is gravity thickened without the addition of cationic polymers or other conditioning agents. The ATAD operated at 55 ^{o}C and a retention time of 6 days.

G2 was sourced from Herbrechtingen WWTP in Germany. Like S.I.A.S Uebersyren the feed sludge at Herbrechtingen consisted of a mixture of primary and waste-activated sludge, which is fed to the ATAD reactors at a concentration of approximately 2.4 – 3% TS following gravity thickening. Volatile solids represented 65% of the total solids for G2. The retention time in the ATAD reactors at Herbrechtingen was 7 days.

G3 was sourced from Schwarmstedt WWTP in Germany. The feed sludge fed to the ATAD reactors at Schwarmstedt consisted of 80% primary sludge, with the remaining 20% being secondary municipal sludge. Volatile solids represented 70% of the total solids for G3. The feed sludge was thickened to approximately 3% TS before being fed to the ATAD reactors at Schwarmstedt. The retention time was 6.4 days.

The OPD values for the sludges are shown in Table 5.11, and their material characteristics are given in Table 5.13, 5.14 and 5.15. Once conditioned to their OPD, each of the sludges was readily settleable in batch settling tests. Each of the sludges had a lower OPD than those sampled at Killarney ATAD. This may be due to the absence of a pre-conditioning step, which may interfere with subsequent conditioning due to residual polymer possibly interfering with conditioning. It may also have been due to the presence of primary sludge in the feed.

Table 5.13 Material characteristics G1, S.I.A.S Ueberseyen WWTP, Luxembourg

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
4	0.124399	0.128052	4.04×10^{-10}	3.56×10^{14}		
10	0.178367	0.186322	1.89×10^{-10}	1.73×10^{15}		
50	0.23211	0.244665	1.74×10^{-10}	3.24×10^{15}		
100	0.265243	0.268998	1.67×10^{-10}	4.03×10^{15}	0.0193	0.0220
200	0.211896	0.319397	2.14×10^{-10}	4.23×10^{15}		
300	0.261571	0.374779	5.85×10^{-11}	1.96×10^{16}		

Table 5.14 Material characteristics G2, Herbrechtingen WWTP, Germany.

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
10	0.1461	0.15356	2.46×10^{-10}	2.69×10^{14}		
50	0.2608	0.27254	1.31×10^{-10}	5.42×10^{15}		
100	0.2806	0.28624	1.05×10^{-10}	8.18×10^{15}		
200	0.2726	0.34593	8.61×10^{-11}	2.03×10^{16}	0.0114	0.0405
300	0.2268	0.34680	7.75×10^{-11}	2.27×10^{16}		

Table 5.15 Material characteristics, G3, Scwharmstedt WWTP, Germany.

$P_y(\phi_\infty)$ (kPa)	ϕ_∞ (v/v) meas	ϕ_∞ (v/v) pred	$D(\phi_\infty)$ (m^2/s)	$R(\phi)$ ($Pa\ s/m^2$)	ϕ_0	ϕ_g
5	0.101103	0.101754	2.48×10^{-9}	3.89×10^{13}		
10	0.203324	0.207214	1.45×10^{-9}	3.15×10^{14}		
50	0.224664	0.228494	1.26×10^{-9}	4.42×10^{14}		
100	0.253638	0.255056	1.39×10^{-9}	5.00×10^{14}	0.0145	0.027

200	0.332034	0.345793	8.04×10^{-10}	1.45×10^{15}		
300	0.30206	0.321741	8.87×10^{-10}	1.53×10^{15}		

5.4.2 Compressive yield stress, $P_y(\phi)$

The $P_y(\phi)$ data for G1, G2 and G3 are shown in Figures 5.26 – 5.28, and the $P_y(\phi)$ functional forms are given in Figure 5.29. The $P_y(\phi)$ profiles of the European ATAD sludges were roughly consistent with those of other biosludges studied (the Melbourne MAD sludges and the Killarney ATAD sludges), insofar as they all exhibited a rapid increase in $P_y(\phi)$ near the gel-point. G2 was the most compressible of the three sludges. It had an exceptionally high gel-point (0.0405 v/v), and compressed to higher ϕ at all pressures. G1 and G3 had similar gel-points and $P_y(\phi)$ profiles.

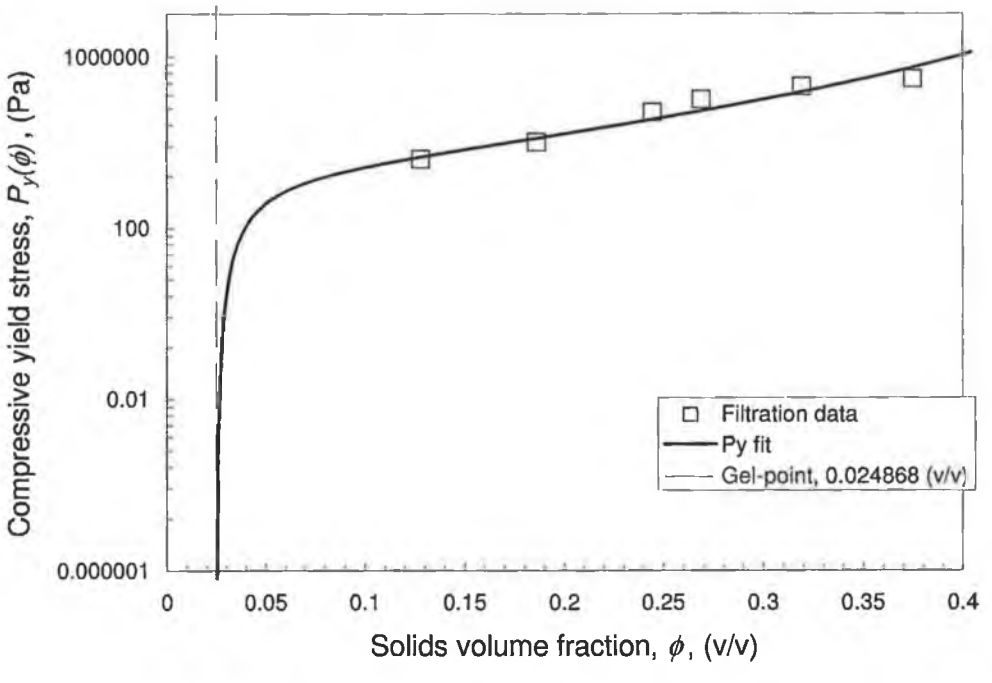


Figure 5.26 $P_y(\phi)$ versus ϕ data for G1 (ATAD) flocculated at 20g/kg TS using ZETAG 7867. Data calculated from pressure-filtration and batch settling tests.

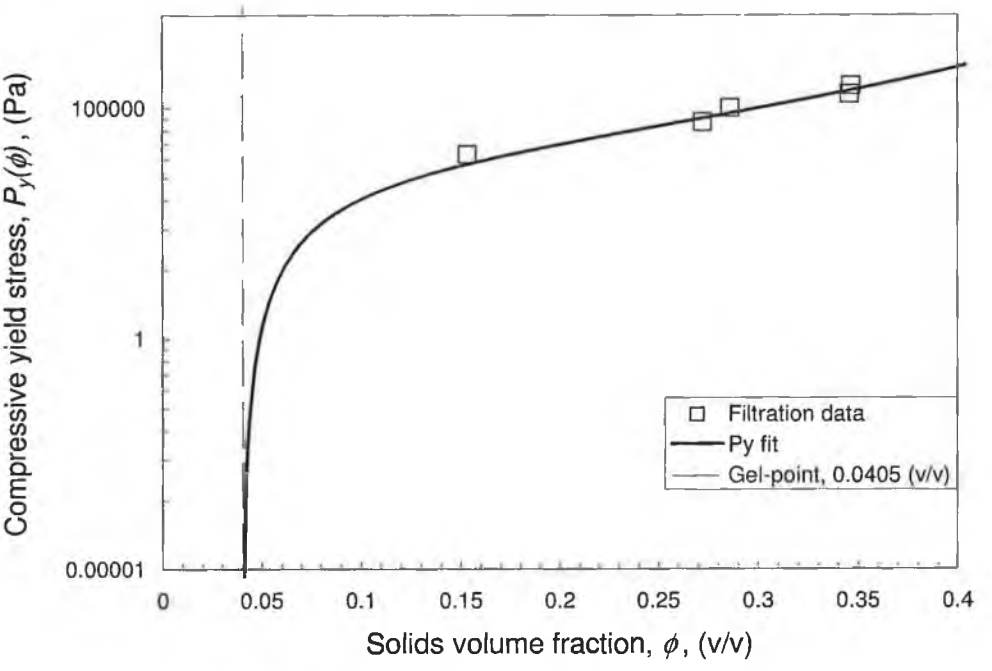


Figure 5.27 $P_y(\phi)$ versus ϕ data for G2 (ATAD) flocculated at 17g/kg TS using ZETAG 7867. Data calculated from pressure-filtration and batch settling tests.

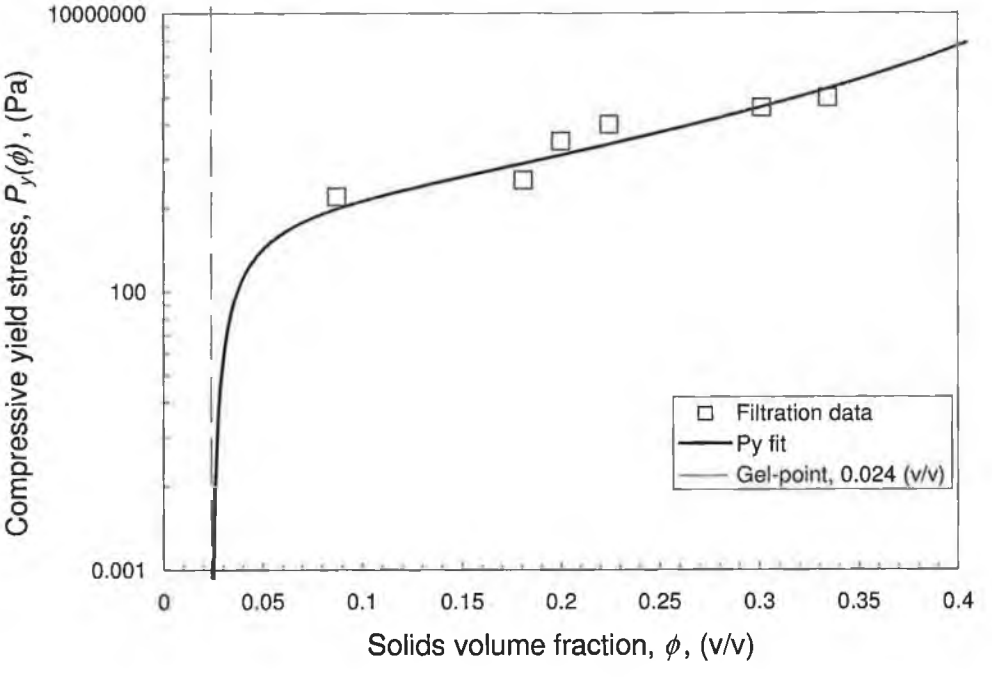


Figure 5.28 $P_y(\phi)$ versus ϕ data for G3 (ATAD) flocculated at 3g/kg TS using ZETAG 7867. Data calculated from pressure-filtration and batch settling tests.

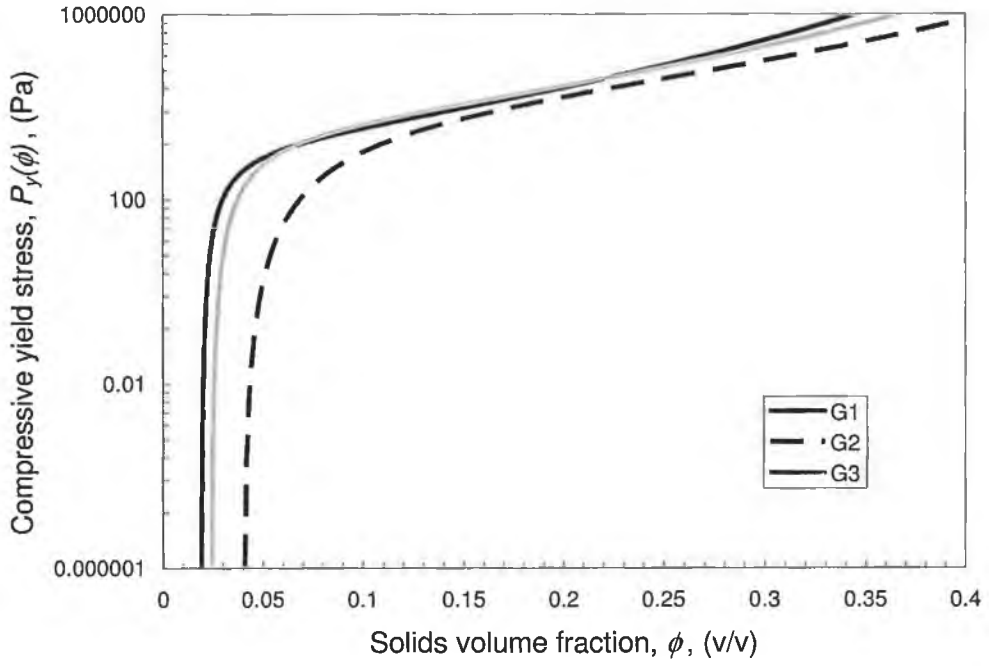


Figure 5.29 $P_y(\phi)$ functional forms for European ATAD sludges, G1, G2 and G3.

5.4.3 Hindered settling function, $R(\phi)$

The $R(\phi)$ data for G1, G2 and G3 are presented in Figures 5.30 – 5.32 and the $R(\phi)$ functional forms are presented in Figure 5.33.

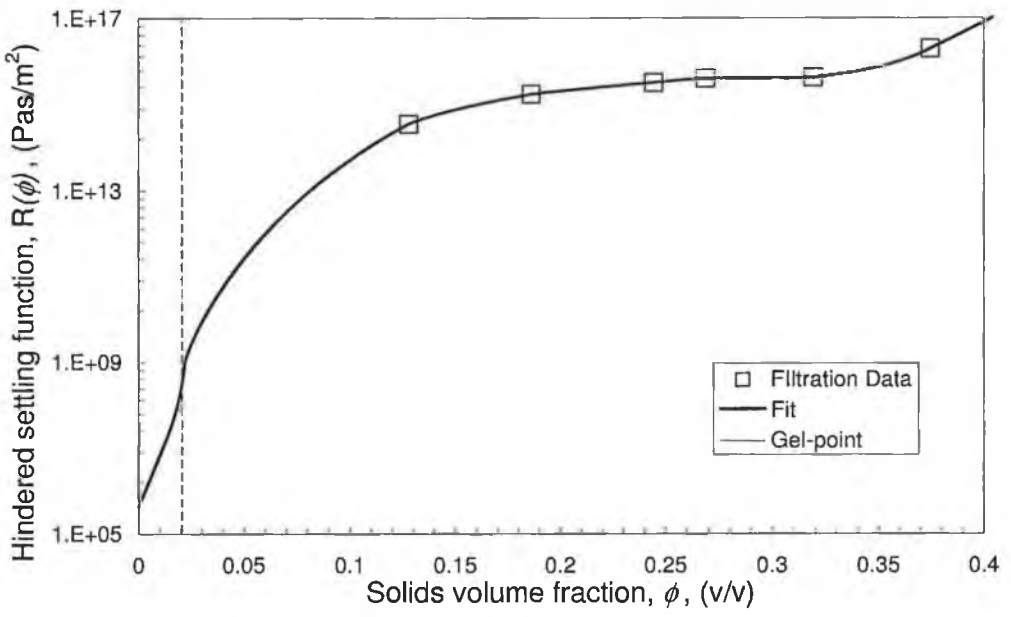


Figure 5.30 $R(\phi)$ versus ϕ data for G1 (ATAD) flocculated at 20g/kg TS using ZETAG 7867. Data calculated from pressure-filtration and batch settling tests.

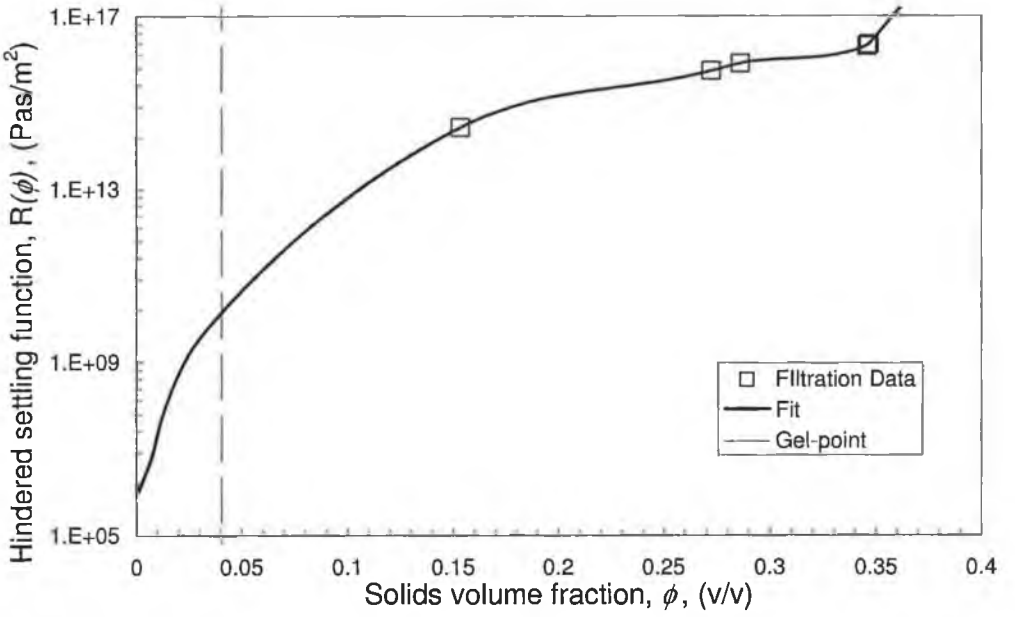


Figure 5.31 $R(\phi)$ versus ϕ data for G2 (ATAD) flocculated at 17g/kg TS using ZETAG 7867. Data calculated from pressure-filtration and batch settling tests.

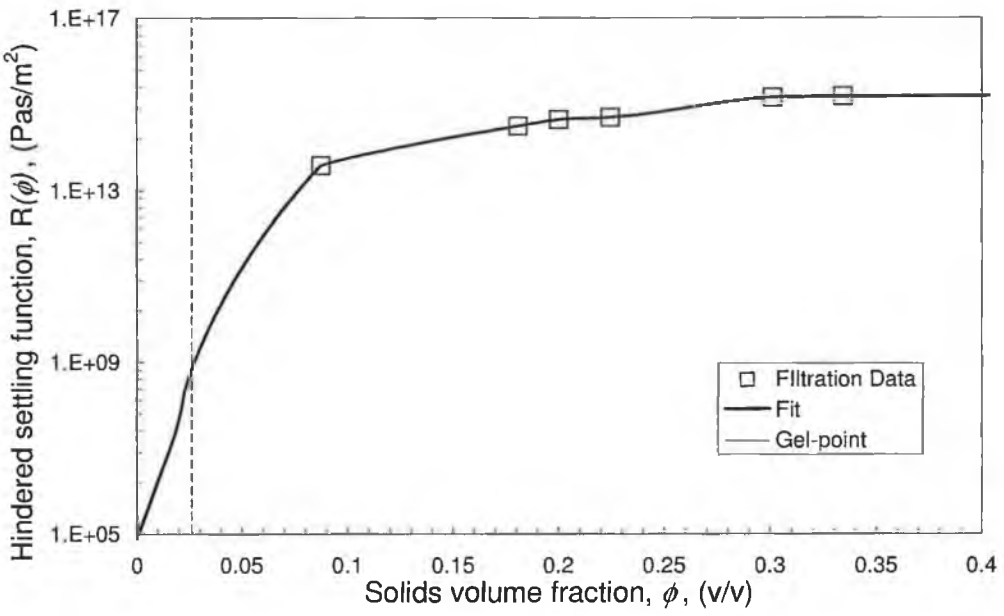


Figure 5.32 $R(\phi)$ versus ϕ data for G3 (ATAD) flocculated at 3g/kg TS using ZETAG 7867. Data calculated from pressure-filtration and batch settling tests.

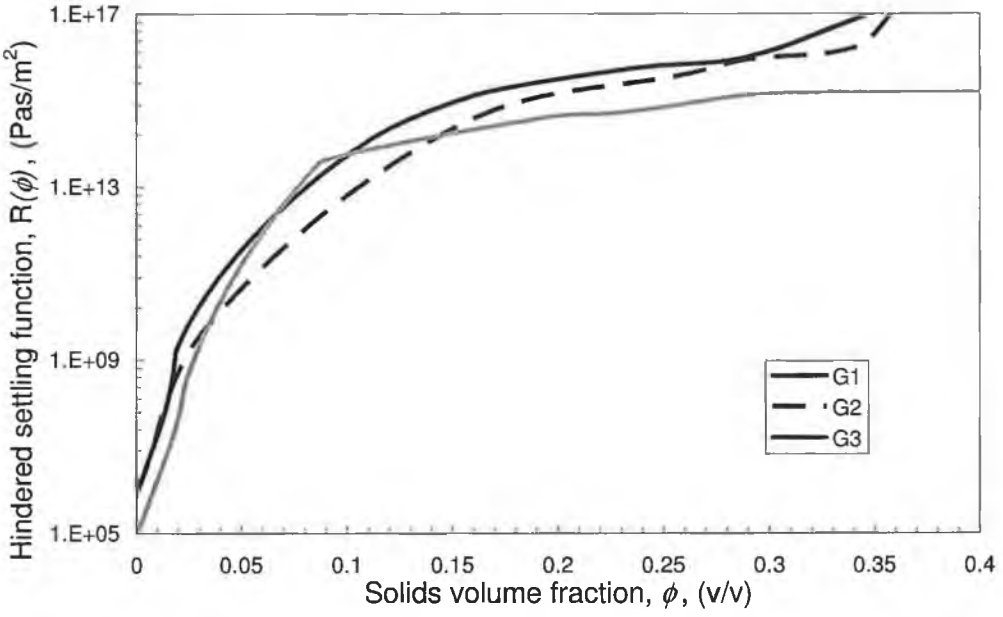


Figure 5.33 $R(\phi)$ functional forms for G1, G2, and G3

Figure 5.33 shows that, at low ϕ, G3 was the most permeable of the three sludges. At intermediate ϕ, 0.05 – 0.15 v/v, G2 was the most permeable, and, at higher ϕ, G3 was the most permeable. Overall G3 was the most permeable of the three. It is notable that G3 was the sludge which had the highest proportion of primary sludge in the feed sludge (approximately 80%). It has been noted by other authors (Zhou *et al.,* 2002) that the proportion of primary sludge in the feed to an ATAD reactor may be an important governing factor of the overall dewaterability as measured by CST. Zhou *et al.* (2002) described an experiment in which the ATAD was used to treat secondary sludge, mixed secondary and primary sludge, and primary sludge. They found that increasing the ratio of primary to secondary sludge in the feed to the ATAD reactor improved the subsequent sludge dewatering properties in terms of CST (which is an indication of permeability). The $R(\phi)$ results for G3, which had the highest proportion of primary sludge as a constituent of feedstock of the sludges that were studied, show that, overall this sludge had the best permeability. This may be due to the high content of primary sludge fed to the reactor at Schwarmstedt WWTP.

5.4.4 Diffusivity, $D(\phi)$

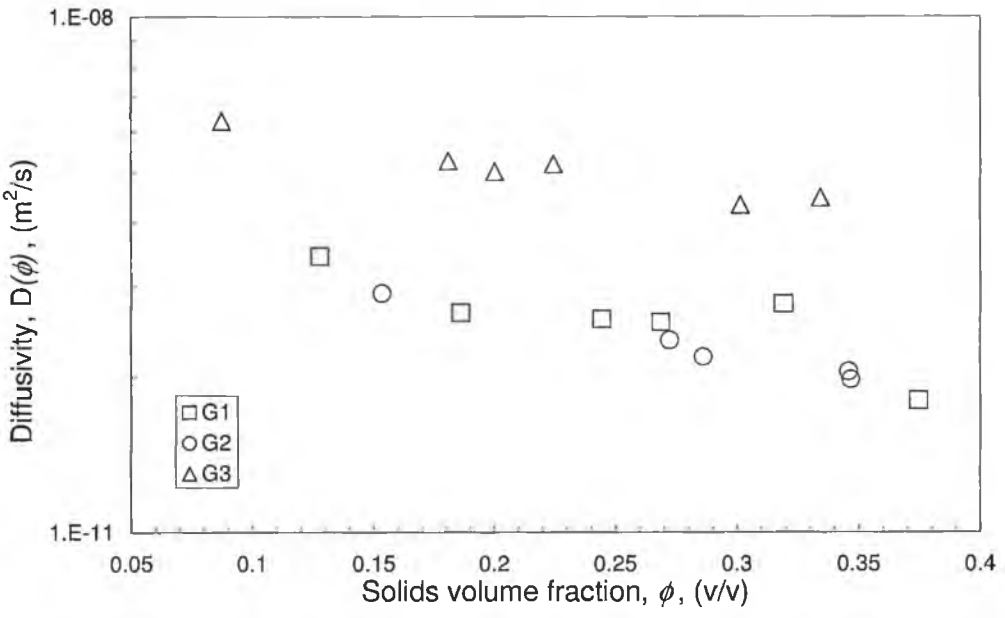


Figure 5.34 $D(\phi)$ values (from pressure filtration tests) for G1, G2 and G3

The $D(\phi)$ data are shown in Figure 5.34. Similar trends in $D(\phi)$ were evident for G1 and G2. Additionally, the data shows that G3 had the highest $D(\phi)$ values for each filtration test. This showed that G3 was the most readily dewaterable of the three sludges.

5.4.5 Conclusions

- Three sludges resulting from ATAD plants in Germany and Luxembourg were characterised using the biosludge characterisation protocol. The ATAD plants from which these sludges were sampled from differentiated from Killarney ATAD plant as they did not use a pre-ATAD conditioning step and were fed a mixture of primary and secondary sludge. The sludges exhibited $Py(\phi)$ profiles consistent with other MAD and ATAD sludges characterised at Melbourne. G2 was the most compressible of the sludges studied.

- G3 exhibited the lowest $R(\phi)$ values of the three sludges. G3 had the highest proportion of primary sludge in its feedstock, and larger particle sizes associated with primary sludges may have resulted in the low $R(\phi)$ values.

- G3 also exhibited the highest $D(\phi)$ values, making it the most readily dewaterable of the three sludges, and it also had significantly better dewatering properties to all other wastewater treatment sludges characterised as part of this work.

5.5 Physico-chemical properties and relationship to dewatering properties

5.5.1 Introduction

In this section the physico-chemical properties of the sludges studied are related to dewatering properties (in particular the optimum polymer dose). The substances which were focussed on were solution biopolymers, primarily proteins and polysaccharides which are released into solution during digestion. This is a direct result of floc erosion and cell-lysis. Several authors have related these materials to poor sludge dewatering properties (Murthy, 1998; Murthy *et al.,* 2000; Novak *et al.,* 2003; Zhou *et al.,*2003).

Table 5.16 Physico-chemical properties and solution biopolymer contituents of sludges studied at Killarney (mean results with standard deviations are reported).

Sludge source	*CODt (mg/L)*	*CODs (mg/L)*	*Solution protein (mg/L)*	*Solution polysaccharide (mg/L)*	*pH*	*CST (s)*
FEED	82021±1043	3010±42	467±13	363±0	6.11	9
1A	53803±882	14500±743	5654±129	2145±102	7.61	65
2A	46800±544	9800±1026	3323±272	2164±88	8.48	60
PP7	44038±1355	8940±1073	3051±261	2873±257	8.43	62
PP10	33779±343	9531±263	3933±135	2279±293	8.51	n/a
PS4a	38400±416	8327±308	4173±276	1334±16	8.28	19
PS4b	37833±807	5787±82	2351±313	993±77	7.57	16
PS2	36500±550	5490±102	2589±174	1091±103	7.77	20
G1	34458±1559	2054±61	1695±91	944±0	8.44	14
G2	15187±1158	2309±155	848±47	454±22	7.42	16
G3	37205±4608	11854±77	4480±332	2199±333	5.55	20

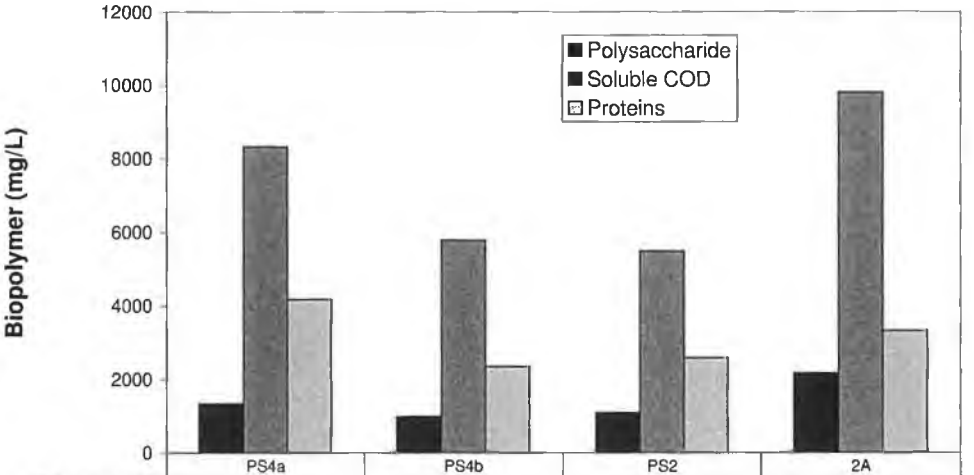
5.5.2 Solution proteins

Zhou *et al.* (2002) found that ATAD digestion resulted in as much as 10 times the volume of proteins being released into solution during digestion as was the case for mesophilic digestion. They found that protease treatment of the filtrate resulted in an improvement in ATAD dewaterability, as measured by CST. This suggested that solution proteins had a negative effect on ATAD dewatering properties. Table 5.16 shows that there were very high levels of proteins present in the solution phase of the ATAD sludges sampled at Killarney. The pilot-plant sludges (PP7 and PP10) and the full-scale ATAD reactors (1A and 2A) had solution protein concentrations in excess of 3000 mg/L. 1A had

a solution protein concentration of 5654 mg/L. The scale of these concentrations can be seen relative to that of the feed-sludge at Killarney which had a solution protein concentration of 467 mg/L. This shows that the volume of proteins which are released into solution as a result of ATAD digestion in both the pilot-plant and the full-scale plant at Killarney was roughly in accordance with the ten-fold increase described by Zhou *et al.* (2002).

The high concentration of solution proteins was associated with high soluble COD, with protein obviously being a significant contributing factor to the soluble COD total. The values also corresponded roughly to those reported by Murthy (1998), who, in a study examining the benefits of mesophilic aeration on subsequent ATAD dewatering, reported solution protein concentrations of 2080 mg/L in an ATAD reactor at College Station, Texas and 3420 mg/L in an ATAD reactor at Princeton, Indiana. At both of these treatment plants the concentration of solution protein was shown to increase as a function of digestion time. The proportion of solution protein in the pilot-plant filtrate increased as a function of digestion time from 3051 mg/L on a 7 d HRT to 3933 mg/L on a 10 d HRT. However, it must also be noted at Killarney, that the proportion of protein in the liquid phase in the full-scale treatment works was shown to be less in Reactor 2A (the second in series) than 1A (the first in series). This could be explained by the different dynamic in the full-scale works than in the pilot-plant. Different temperatures of operation were found in 1A to 2A while in the pilot-plant the concentration was maintained at 60 ^{o}C.

Murthy (1998) also reported a reduction in solution biopolymers in the post-ATAD holding tanks at Princeton and College Station which corresponded with a significant reduction in CST. At Killarney, a similar trend is evident. The holding tanks in which ATAD sludge had been stored for four weeks, PS4b and PS2, had lower levels of solution proteins than the sludge sampled from reactors 1A and 2A. Solution protein concentrations of 2351 mg/L and 2589 mg/L were found in samples PS4b and PS2 respectively. This corresponded with a decrease in OPD from 83g/Kg TS in 1A, 78g/Kg TS in 2A to 25 g/Kg TS in PS4b and 24g/Kg TS in PS4a.



	PS4a	PS4b	PS2	2A
Polysaccharide	1334	993	1091	2164
Soluble COD	8327	5787	5490	9800
Proteins	4173	2351	2589	3323

Figure 5.35 Solution biopolymers (mg/L) for post-storage ATAD sludges at Killarney

Figure 5.35 compares the solution proteins, solution polysaccharides and solution COD for the three post-storage sludges studied at Killarney. Also included are average values for 2A (which represents the feed to the post-storage tanks). Lower concentrations of protein for the sludges which were stored for four weeks were evident. This corresponded with lower levels of soluble COD and lower levels of solution polysaccharides, though the decrease in protein was more notable than that of polysaccharides, which suggested that the residual polysaccharides may be more recalcitrant.

The European ATAD sludges, G1 and G2, exhibited lower concentrations of solution protein than the ATAD sludges sampled at Killarney (Table 5.15). However, G3 had an exceptionally high concentration of solution protein (4480 mg/L). This was also reflected in the high soluble COD value for G3 (11854 mg/L). This was remarkable insofar as G3 exhibited a relatively low OPD (Table 5.7) and excellent permeability as measured by $R(\phi)$ (Figure 5.33). G3 was an outlier in many respects. For the other sludges studied, solution biopolymers correlated with the optimum polymer dose. However this was not the case for G3. There were some notable other differences between G3 and other ATAD sludges studied. G3 had the lowest pH of all of the ATAD sludges studied (pH 5.55), this figure is exceptionally low for ATAD sludges which usually exhibit slightly basic conditions due to the high levels of ammonia stripping within ATAD reactors. G3 also had the highest proportion of primary sludge in the feed to the ATAD reactor from which it was sampled. Zhou *et al.* (2001) found that ATAD sludges which resulted from a feedstock consisting of a high proportion of primary sludge had better dewatering properties than those with a feed sludge consisting of secondary sludge. In addition, Zhou

et al., (2001) found that ATAD sludges resulting from a feedstock consisting of a high proportion of primary sludge did not exhibit a clear correlation between solution biopolymers and optimum polymer dose. G3 may be an example of this, or may even have been a primary sludge incorrectly mislabelled as an ATAD at source in Germany. Because of this G3 is not considered in the following sections which correlate OPD and biopolymers.

Figure 5.36 plots the optimum polymer dose against solution protein concentration for all of the sludges sampled at Killarney.

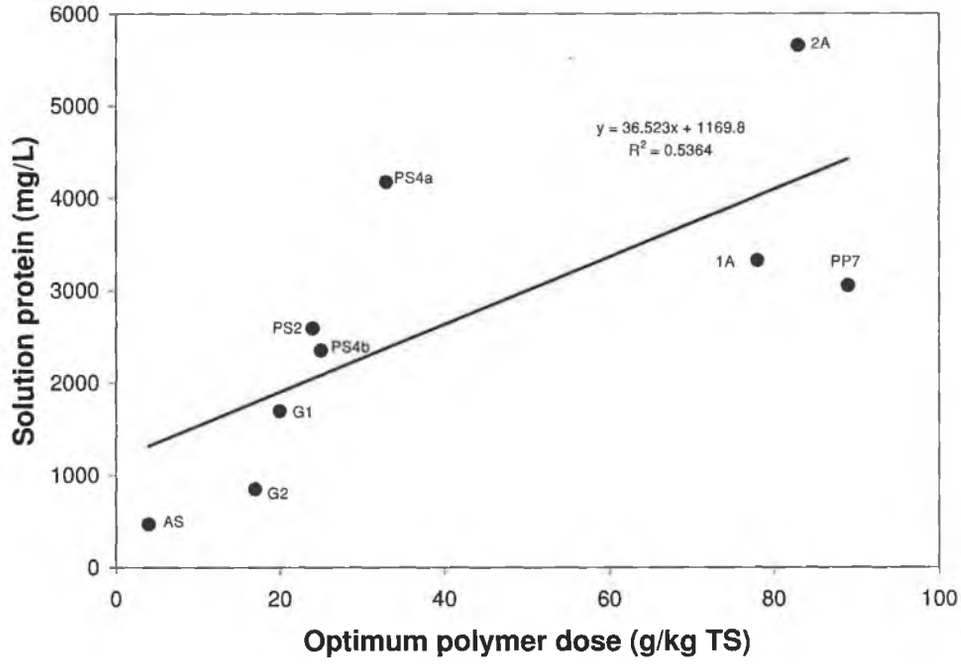


Figure 5.36 Relationship between solution-phase proteins and optimum polymer dose for sludges at Killarney

There was a weak correlation between solution proteins and the OPD ($R^2 = 0.5364$).

5.5.3 Solution polysaccharides

Solution polysaccharide was shown to increase as a function of ATAD digestion for the sludges studied at Killarney. The concentration of solution polysaccharides in the feed sludge at Killarney was 363 mg/L. In reactor 1A the concentration had risen to 2154 mg/L and was relatively similar in reactor 2A (2164 mg/L). This was in contrast to solution protein and soluble COD, both of which were relatively lower in reactor 2A to reactor 1A. This suggested that the solution polysaccharides may be more resistant to degredation during the ATAD process at Killarney. Novak *et al.* (2003) found that, for sludges digested mesophilically under anaerobic and aerobic conditions, the OPD corresponded directly to the volume of biopolymer released into solution. They also noted that, in the case of aerobic digestion, the released polysaccharides were more recalcitrant than the released proteins. Similarly, while the solution polysaccharide levels for PS4a (which had been stored for one week) were lower (1334 mg/L) than those found in 1A and 2A, the decrease in residual solution polysaccharide between PS4a and the sludges which had been stored for four weeks (PS4b and PS2) was not as notable as the decrease in protein and soluble COD.

Solution polysaccharides decreased in the pilot-plant from 2873 mg/L on a 7 day retention time to 2279 mg/L on a 10 day retention time. This was in contrast to solution proteins which showed a relative increase when the retention time was switched from 7 to 10 days. This finding was in contrast to Murthy (1998) who found that, at Princeton and College Station ATAD plants, both solution protein and polysaccharide increased as a function of retention time.

In Figure 5.37 the relationship between solution polysaccharide and OPD is shown for the Killarney and European ATAD sludges. There was a much stronger correlation (R^2 = 0.9394) between solution polysaccharides and the OPD, than there was between solution proteins and OPD. This would suggest that the polysaccharide fraction in the solution-phase was the biggest contributor to the polymer demand.

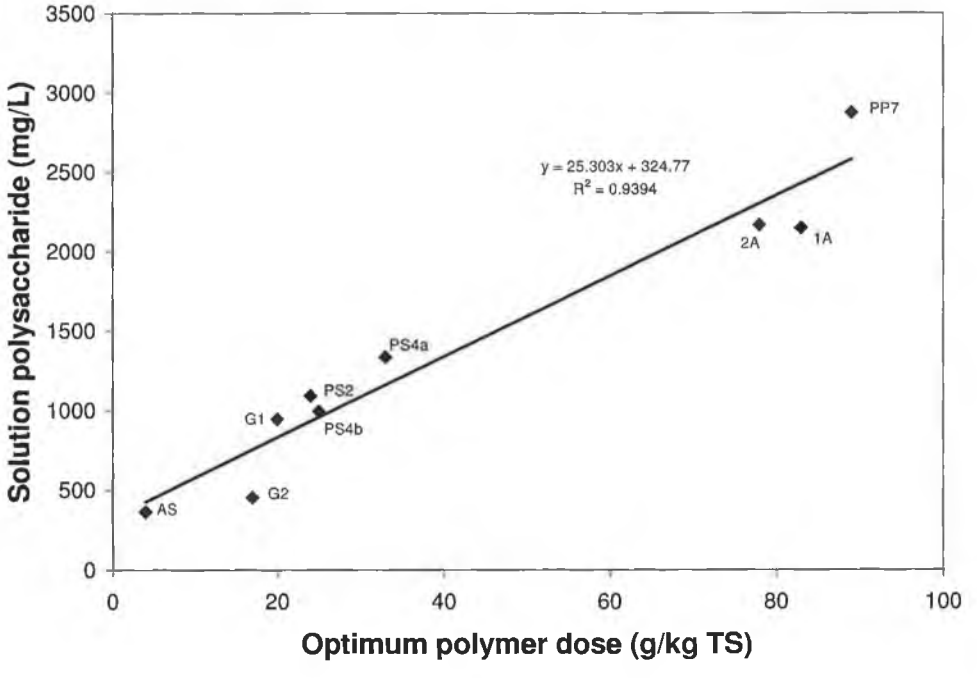


Figure 5.37 Relationship between solution-phase polysaccharides and optimum polymer dose for sludges at Killarney

5.5.4 Soluble COD

Soluble COD encompasses all of the organic materials within the solution phases of the sludge. This also includes other materials such as humic substances, which may also affect sludge dewatering. In Figure 5.38, the relationship between soluble COD and the

OPD is plotted. There was a correlation between soluble COD and the OPD (R^2 = 0.7306).

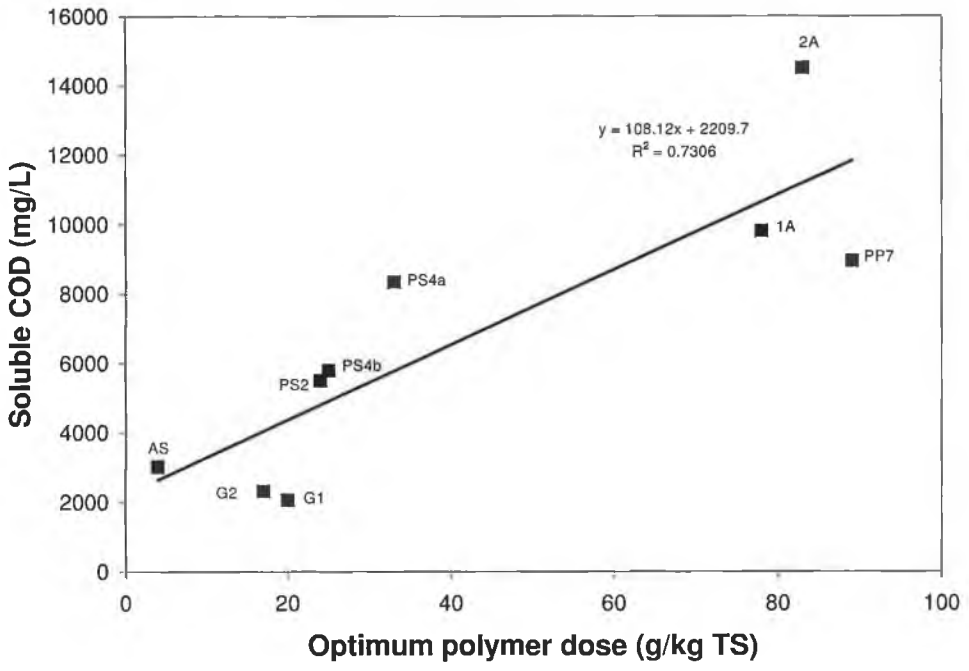


Figure 5.38 Relationship between soluble COD and optimum polymer dose for sludges at Killarney

5.5.6 Conclusions

- The ATAD sludges which were studied all had an exceptionally high soluble COD content in relation to activated sludge.

- Solution proteins and polysaccharides accounted for a large proportion of the soluble COD.

- Soluble COD, solution proteins and solution polysaccharides all showed some correlation to the OPD, with the highest correlation found between solution polysaccharides and the OPD.

- ATAD sludge which had been stored for four weeks had lower concentrations of solution proteins and polysaccharides than sludge which had been stored for one week, this also corresponded with lower pH values, lower OPD, and improved dewatering properties as measured by CST, $P_y(\phi)$, $R(\phi)$ and $D(\phi)$

CHAPTER SIX: Centrifugation methods for dewatering analysis of sludges

6.1 Introduction

In Chapter 5, the biosludge characterisation protocol was used to determine dewatering properties of sewage sludges using a combination of batch settling tests and pressure-filtration. The biosludge characterisation protocol described sludge dewatering properties at high ϕ (obtained from pressure-filtration tests) and lower ϕ (obtained from batch-settling analysis). However, for most sludge, there existed between these two regions an area of intermediate ϕ for which the sludge dewatering properties were not described. Data therefore needed to be extrapolated across this region which spanned several orders of magnitude for $P_y(\phi)$ and $R(\phi)$; both of which parameters showed a rapid non-linear increase at intermediate ϕ for the majority of the sewage sludges which were examined.

In this Chapter, the application of centrifugation techniques (described in Section 3.4.7) to various sludges is described. These methods were used to derive experimental dewatering data for sludges at solids concentrations which are not described by batch-settling and pressure filtration. Low-speed centrifugation (1000 - 4000 rpm) was used to obtain transient sludge settling data.

$P_y(\phi)$ data was obtained from a 'scrape-test' which was performed on centrifuged suspensions once they had settled to equilibrium height. The scrape-test was based upon the method described by Green (1997) and is described in Section 3.4.7. For each data-set obtained from the scrape-tests, a discrete solution based upon a trapezoidal rule was used to determine $P_y(\phi)$ values.

A LUMiFuge®110 'dispersion analyser' was also used to obtain transient settling data for some of the sludges. The LUMiFuge®110 is a centrifuge which can measure the settling behaviour of samples whilst online. The specifics of the LUMiFuge®110 are given in Table 6.1.

Table 6.1 Operational parameters of the LUMiFuge®110 'dispersion analyser' centrifuge

Speed range	Total measurement time	Sampling rate	Temperature range
300-3000rpm (12-1200*g*)	8 minutes – 42 hours	1 second – 600 seconds	4 – 45 °C

The output from the instrument was a transmission profile (% transmission along the length of the sample tube). The transmission profiles were then transformed into height versus time profiles by selecting a certain transmission % (known as a trigger %) which was deemed to be the point at which the suspension interface is located. For the sludges examined here, 10% transmission was used as the trigger %.

Section 6.2 describes the application of the transient centrifugal analysis and the scrape test to MAD sludges. The techniques were used to determine the effect of polyelectrolyte on MAD dewatering properties. A WAS sludge was also characterised, and subsequently compared to a WAS sludge which was modified using freeze-thaw conditioning.

Section 6.3 discusses experiments which were conducted to determine whether significant changes occurred in the composition and quantity of biopolymeric materials in the solution-phase of sludge during refrigerated storage (5 ^{o}C). The following substances were measured in the solution phase: DNA, polysaccharides, proteins, and total organic carbon (TOC). Changes in sludge dewatering properties during storage were also measured. Finally, particle size analysis was conducted on several sludge samples. A Coulter Counter was used to describe the size distribution of sludge flocs.

Section 6.4 describes investigations into the dewatering properties of MAD sludge which had been modified enzymatically. Lab-scale anaerobic digesters were commissioned to produce MAD sludge in a controlled environment. Enzyme solutions were then applied to the sludges which were produced during anaerobic digestion. The enzymes which were used were protease, glucosidase and cellulase. Following enzyme addition, the Hartree (1972) modification of the Lowry assay (Lowry *et al.*, 1951) and the Dubois assay (Dubois *et al.,* 1956) were used to measure changes in the quality and composition of solution proteins and polysaccharides respectively. Dewatering properties were measured as transient settling behaviour during low-speed centrifugation, and $P_y(\phi)$ values were obtained from equilibrium centrifugation scrape-tests.

6.2 Dewatering characterisation of sludges using centrifugation methods

6.2.1 Introduction

The centrifugation method was used to characterise a MAD sludge which had been sampled from Carrum WWTP in Melbourne Australia. An assumed solids density of 1100kg/m^3 was used for the analysis. The MAD sludge had a ϕ_0 of 0.0173 and a pH of 7.08.

For settling analysis at 1000rpm, h versus t data was normalised using the following relationship, normalised height $h(-) = h/h_0$. This allowed direct comparison between samples with different h_0. The height differences were due to the creation of a flat interior base in each centrifuge tube (created by the addition of epoxy resin). This varied from tube to tube, and because of the necessity of weight equalisation of the tubes before centrifugation (to avoid damage to the centrifuge rotor), the initial sediment heights often differed.

For each scrape-test a mass conservation check was used to compare the value of $h_0\phi_0$ with the cumulative sum of $h_i\phi_i$ values for each scrape-test section. The $P_y(\phi)$ values were rejected if the value for the cumulative mass balance fell outside a tolerance of ±20%. In some cases there were notable discrepancies between the value of $h_0\phi_0$ and $\sum h_i\phi_i$ (for the

scrape-test sections). There were several possible causes of such discrepancies. These may have included residual sludge from a previous scrape (of lower solids concentration) diluting subsequent scraped layers, and height measurement errors. To minimise errors, care was taken during scrapes to ensure that residual sludge did not remain in the test-tube from previous scraped layers. This was done by removing as much sludge as possible from the tube with a spatula, and by wiping the inside of the tube with tissue before the subsequent scrape was taken. The height of the suspension interface often varied from the mean height across the suspension horizontal plane. To counter this, a suitable number of point values were measured around the centrifuge-tube perimeter to derive an accurate mean height. The suspension interface was therefore measured at four points, each separated by 90°. For all of the sludges reported, the mass-check error was less than the tolerance limit of ±20%.

6.2.2 Centrifugal characterisation of flocculated and unflocculated MAD samples

The centrifugation techniques were used to determine differences between flocculated and unflocculated MAD samples in terms of permeability (settling) and $P_y(\phi)$, (scrape test). The sludges examined were sampled from Carrum WWTP in Melbourne Australia. This treatment plant is known as 'The Eastern Treatment Plant' and treats approximately 43% of Melbourne's wastewater. The plant employs diffuse aeration in the activated sludge stage, and the secondary sludge is treated by anaerobic digestion.

ZETAG 7187 was used as the conditioning polyelectrolyte flocculant. It was made up from a powder, and was prepared and applied in the manner described in Section 3.3.12.

The settling properties of the unflocculated and flocculated samples were determined in duplicate, and showed excellent agreement in each case (Figure 6.1). The flocculated samples showed better settling properties than the unflocculated samples.

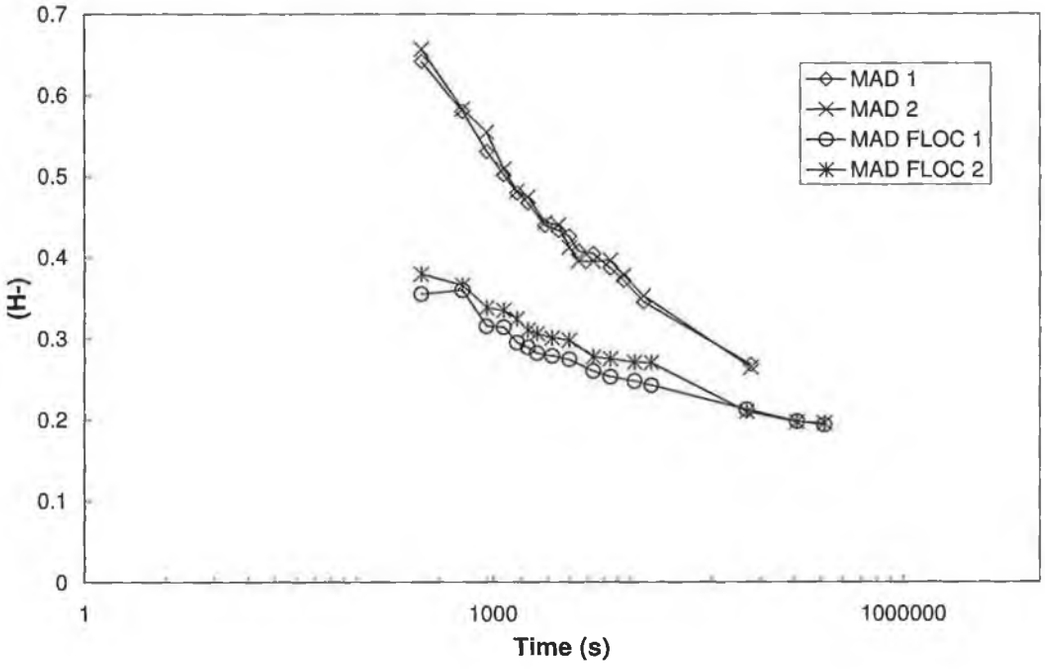


Figure 6.1 Transient centrifugal settling data (1000 rpm) for unflocculated Carrum MAD sludge and MAD flocculated at 9g/Kg DS (ZETAG 7187). The data is plotted on semi-logarithmic co-ordinates.

The $P_y(\phi)$ profiles which were determined for the samples are shown in Figure 6.2. There is little difference between the $P_y(\phi)$ profiles for the flocculated and unflocculated samples. Johnson *et al.* (1997) found that, for an alum based sludge, the addition of polyelectrolyte to enhance dewatering improved the rate of dewatering (permeability) but did not affect the ultimate compressibility as measured by $P_y(\phi)$. This may also have occured for the Carrum MAD sludge. The addition of polyelectrolyte enhanced the rate

of dewatering as evidenced by the faster rate of settling in the settling test (Figure 6.1), however, the ultimate compressibility of the sludge was similar, as evidenced by the $P_y(\phi)$ data (Figure 6.2).

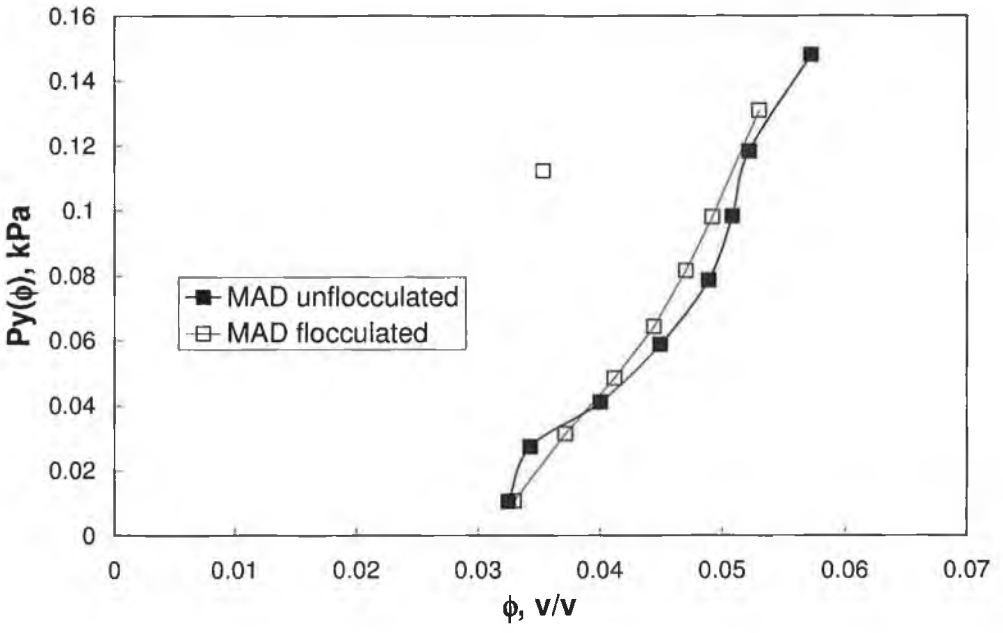


Figure 6.2 $P_y(\phi)$ versus ϕ for unflocculated Carrum MAD sludge and MAD sludge flocculated at 9g/kg DS using ZETAG 7187.

6.2.2 WAS modified by freeze-thaw conditioning.

Freeze-thaw conditioning is a physical conditioning process. Physical conditioning processes are very rarely used in full-scale Biosolids dewatering operations. Dentel (2001) noted that such processes are either not as successful, or economical as alternative chemical conditioning methods.

Freezing rate has been cited as a critical scale-up parameter for the freeze-thaw processes. While freeze-thaw conditioning is uneconomical if freezing is to be accomplished with refrigeration equipment, 'natural' freeze-thaw application in cooler climatic zones is used on a scattered basis (Dentel, 2001). Despite its limited full-scale application to sewage sludges, freeze-thaw conditioning has been extensively studied (Sanin *et al.*, 1994;; Martel, 2000; Örmeci and Vesilind, 2001; Lai *et al.*, 2004; Tao *et al.*, 2006). It is likely that it has been investigated so extensively because of its simplicity as a process, its effectiveness in improving dewatering properties, and the low-costs involved in its investigation.

Freeze-thaw conditioning was shown to improve WAS dewatering properties by several authors (Vesilind *et al.,* 1991; Lee and Hsu, 1994; Örmeci and Vesilind, 2001). A number of mechanisms are thought to contribute to this. The freeze-thaw process transforms the sludge floc structurally into a more compact form (Vesilind *et al.,* 1991), and it is also thought to reduce the content of 'bound water' in the sludge through a process known as 'gross floc migration' (Lee and Hsu, 1994). Gross floc migration is the mechanism, during freezing, by which sludge flocs are pushed away from the moving ice-front, becoming, during the process, more concentrated and dehydrated. If the freezing rate is too high some of the flocs can become trapped within the ice-crystal, preventing gross floc migration. Hence, freezing rate is believed to influence the effectiveness of freeze-thaw conditioning, and slow freezing rates are thought to be preferable to fast freezing rates (Chu *et al.*, 1999).

The temperature employed in freeze-thaw conditioning experiments varied in the literature: -10 °C (Lai *et al.,* 2004), -17 °C (Chu *et al.*, 1999; Jean *et al.,* 2001), -18 °C (Martel, 2000), -20 °C and -40 °C (Lai *et al.,* 2004). Lai *et al.* (2004) proposed that -20 °C is the optimum temperature for the process, as at temperatures higher than this freezing of the sludge may be incomplete, and at lower temperatures gross floc migration may be hindered. Lai *et al.,* (2004) also found that dewaterability of freeze-thaw sludge was optimal when the sludge was thawed out at room temperature. Thawing at higher temperatures was thought to negatively impact dewatering properties due to cracking of the frozen sludge which may break down the aggregated flocs into smaller pieces.

In this study, a 1 litre WAS sample from Carrum WWTP was frozen at -20 °C for 24 hours in a commercial freezer and then thawed for a further 24 hours at room temperature (23 °C). The initial solids concentration of the WAS was 0.033 v/v, with an assumed solids density of 1100 kg/m^3, and following freeze-thaw conditioning the solids concentration was measured as 0.032 v/v. This showed that the freeze-thaw process had little or no effect on the overall solids concentration of the sludge. The pH of the sludge was measured as 6.81 before freeze-thaw conditioning, and 6.77 following freeze-thaw conditioning.

Batch settling analysis was conducted on the unconditioned WAS and the freeze-thaw WAS (FT-WAS). FT-WAS for batch settling analysis was diluted to a solids concentration of 0.01 v/v. The transient batch settling curves for the conditioned and unconditioned sludges are shown in Figure 6.3. The sludges had different ϕ_0, and because

of this the settling rates (Figure 6.3) cannot be directly compared, as settling rate is dependent on solids concentration (Usher, 2005).

ϕ_g was determined from batch settling tests for the FT-WAS and WAS and was 0.0256 and 0.015 (v/v) respectively. Freeze-thaw conditioning therefore increased ϕ_g. The increase in ϕ_g was likely due to the formation of a more compact and readily settleable floc structure through the 'gross floc migration' process. The FT-WAS had a visibly more granular and compact floc structure than the WAS sludge.

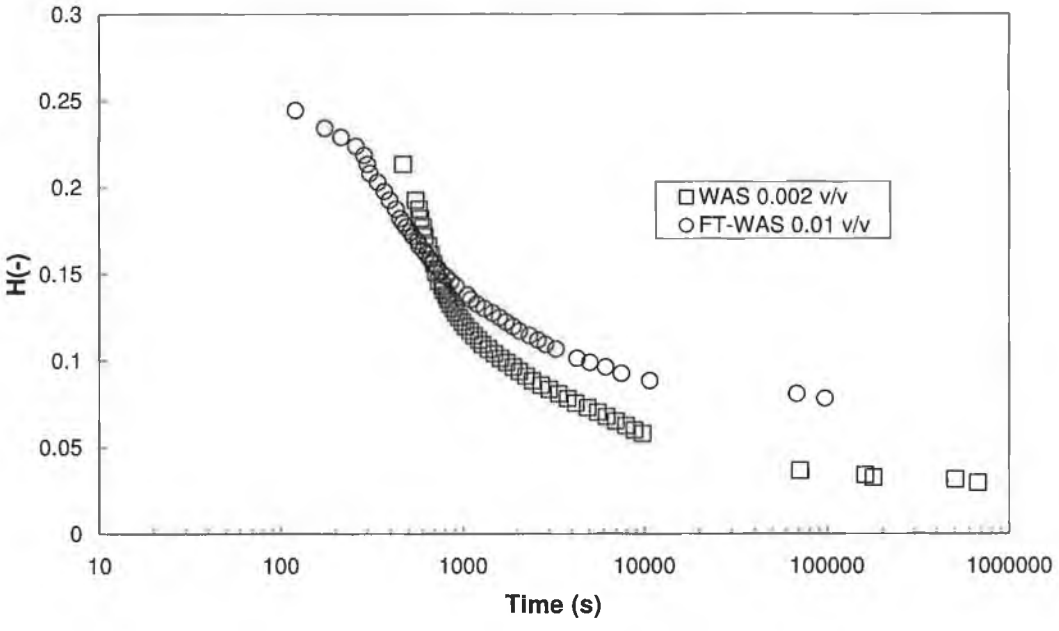


Figure 6.3 Transient batch settling data for FT-WAS and untreated WAS from Carrum WWTP. Data shown on semi-logarithmic co-ordinates.

Figure 6.4 shows the transient centrifugal settling data for the FT-WAS and the untreated WAS at 1000rpm. There is a marked difference in settling behaviour for the two sludges.

The FT-WAS had almost settled to equilibrium at the first time of measurement (300 seconds). In contrast, the untreated WAS samples were still settling at the termination point of the test.

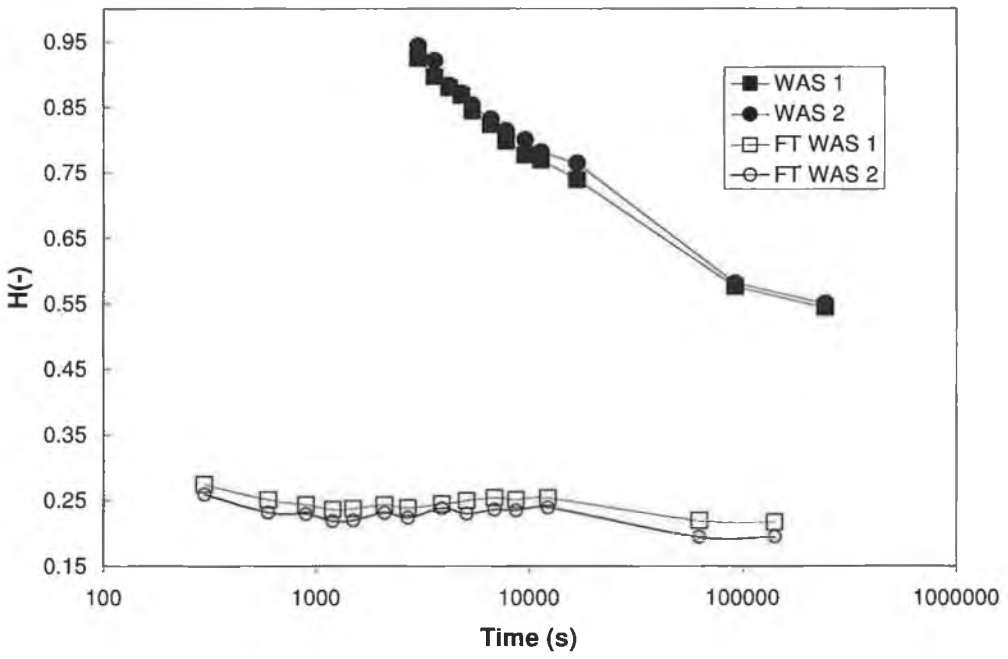


Figure 6.4 Settling data at 1000rpm for unconditioned Carrum WAS sludge (WAS 1 and WAS 2) and freeze-thaw conditioned WAS (F-T WAS 1 and FT WAS 2)

In Figure 6.5 $P_y(\phi)$ (kPa) is plotted against ϕ (v/v) for the untreated WAS and the FT-WAS. The data were obtained from equilibrium scrape-tests following settling at 1000 rpm and are presented in duplicate. Freeze-thaw conditioning caused a significant increase in compressibility.

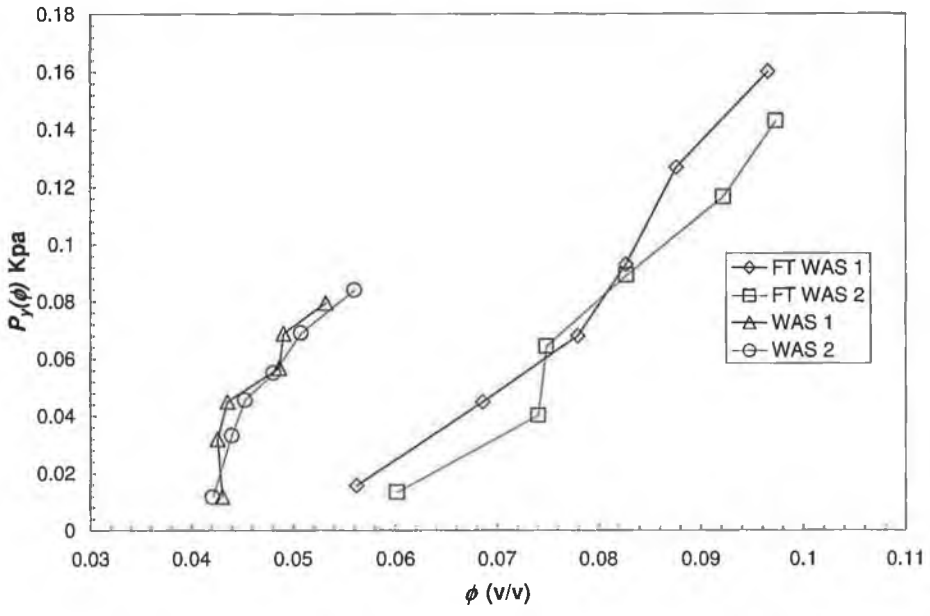


Figure 6.5 $P_y(\phi)$ (kPa) plotted against ϕ (v/v) for unconditioned Carrum WAS sludge (WAS 1 and WAS 2) and freeze-thaw conditioned WAS (F-T WAS 1 and FT WAS 2).

Lean *et al.* (2001), in a study of the effect of freeze-thaw conditioning on the dewatering properties of a WAS sludge, reported a decrease in CST from an original value of 43.7 seconds to 31.5 seconds following 24 hours of freezing. This represented an improvement in sludge permeability at low solids concentrations. They also conducted 24 hour gravitational settling tests, and reported a dimensionless h_f/h_0 value (where h_f was what they referred to as the 'equilibrium suspension height' and h_0 was the initial sediment height before settling). Freeze-thaw conditioning resulted in a dramatically lower h_f/h_0 value for the conditioned sludge than for the unconditioned sludge (0.97 as opposed to 0.07). This indicated a large improvement in compressibility, assuming that the starting solids concentrations of the conditioned and unconditioned samples were similar.

While the results obtained from the centrifugation and batch settling tests conducted on the Carrum WAS cannot be directly compared to those presented in the paper by Lean *et al.* (2001), very similar trends are evident. The settling data (Figure 6.5) showed a similarly large improvement in permeability for freeze-thaw conditioned sludge, and the increase in the gel-point from 0.015 to 0.0256, combined with the large decrease of $P_y(\phi)$ as a function of ϕ following conditioning (Figure 6.5), demonstrated a corresponding large improvement in compressibility.

A pressure filtration test was also conducted at 50kPa for the FT-WAS and is included in Figure 6.6, which is a composite of the complete set of $P_y(\phi)$ data.

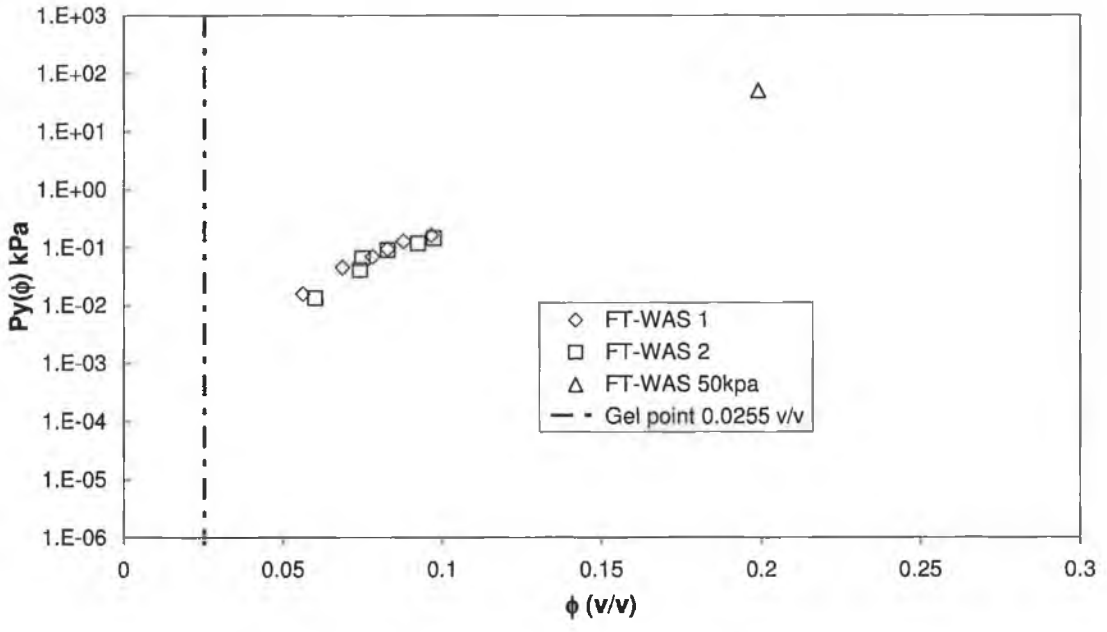


Figure 6.6 Composite of $P_y(\phi)$ versus ϕ data for Carrum FT-WAS. Data obtained from batch settling, centrifugation at 1000 rpm and pressure filtration at 50kPa.

6.2.3 Conclusions

- Low-speed centrifugation dewatering analysis was successfully used to characterise unconditioned and conditioned MAD sludge in terms of permeability and compressibility. The method provided dewatering data in a region not described by pressure-filtration and batch settling tests alone. The data showed that conditioning MAD sludge with cationic polyelectrolyte improved the sludge permeability but had little effect on the sludge compressibility

- Freeze-thaw conditioning was used to condition a WAS sludge which was then characterised using a combination of centrifugation, batch settling and pressure filtration. The freeze-thaw process was shown to improve the WAS dewatering properties in terms of both permeability and compressibility. The improvements were similar to those reported in the literature, and were possibly caused by a process known as 'gross floc migration'.

6.3 Changes in biopolymeric composition of liquid-phase of sludge during storage

6.3.1 Introduction

It has been postulated by researchers that poor dewatering properties of MAD sludge (Novak *et al.,* 2003) and ATAD sludge (Zhou *et al.*, 2002) are linked to high levels of biopolymers in solution. Results presented in Chapter 5 showed positive correlations between the quantities of solution COD, proteins and polysaccharides with the OPD for several sewage sludges. Changes in the quantity of these substances in solution may also be indicative of microbial activity, which still occurs at low temperatures, although at slow rates. For example, a study of deep lake sediments (Nozhevnikova *et al.*, 1997) showed that methanogenisis occurred at all temperatures between 2 and 70 °C, with an exponential relationship between temperature and the volume of methane produced between 2 and 30 °C.

It was reported by deKretser *et al.* (2005) that the dewatering properties of a MAD sludge changed during storage. The change was evident as an improvement in settling characteristics which occurred between day 2 and day 4 of storage (in refrigerated conditions) when centrifuged at 1000rpm. Published work has remarked on biological activity and subsequent changes in sludge properties during storage (O'Kelly, 2005). In view of this, the improvements in settling behaviour reported by deKretser *et al.* (2005)

may have been linked to a time-dependent decrease of colloidal species in the solution phase of MAD.

To determine the effects of storage on the composition and quantity of sludge biopolymers, a time-dependent experiment was devised in which a sample of MAD sludge was stored at 5 °C for several days (Trial 1). This experiment was repeated with fresh MAD at a later date (Trial 2). The following parameters were chosen for investigation: protein, polysaccharide, total organic carbon (TOC) and DNA in solution. In addition, sludge dewatering properties were determined, in terms of $P_y(\phi)$, OPD and transient centrifugal settling analysis.

MAD sludge was sampled from Carrum WWTP (Victoria, Australia). The TS of the samples were 1.4% (Trial 1) and 1.63% (Trial 2). The density of the solid phase of the sludges was assumed to be 1100 kg/m^3. This gave ϕ of 0.0127 v/v for Trial 1 and ϕ of 0.0148 v/v for Trial 2. The sludge pH was 7.21 for Trial 1 and 7.08 (Trial 2). Changes in pH were negligible over the duration of the trials and are not reported. All samples for biopolymer analysis were centrifuged in a Microfuge at 13,000 rpm for 40 minutes and subsequently filtered through 0.45μm milipore filters and frozen immediately for subsequent proteins and polysaccharides analysis, which was conducted on all samples contemporaneously. This ensured constant and stable assay conditions for the analysis.

6.3.1 Solution proteins, polysaccharides and DNA

Protein concentration was measured using the Hartree (1973) modification of the Lowry colorimetric assay (Lowry *et al.*, 1951). Bovine serum albumin (BSA) was used as the protein standard. A standard curve obtained for absorbance at 650nm for known concentrations of BSA solution is presented in Appendix I. Solution polysaccharide was measured using the Dubois phenol-sulphuric acid method (Dubois *et al.*, 1956). A standard curve for absorbance at 480nm for glucose of known concentration is given in Appendix II.

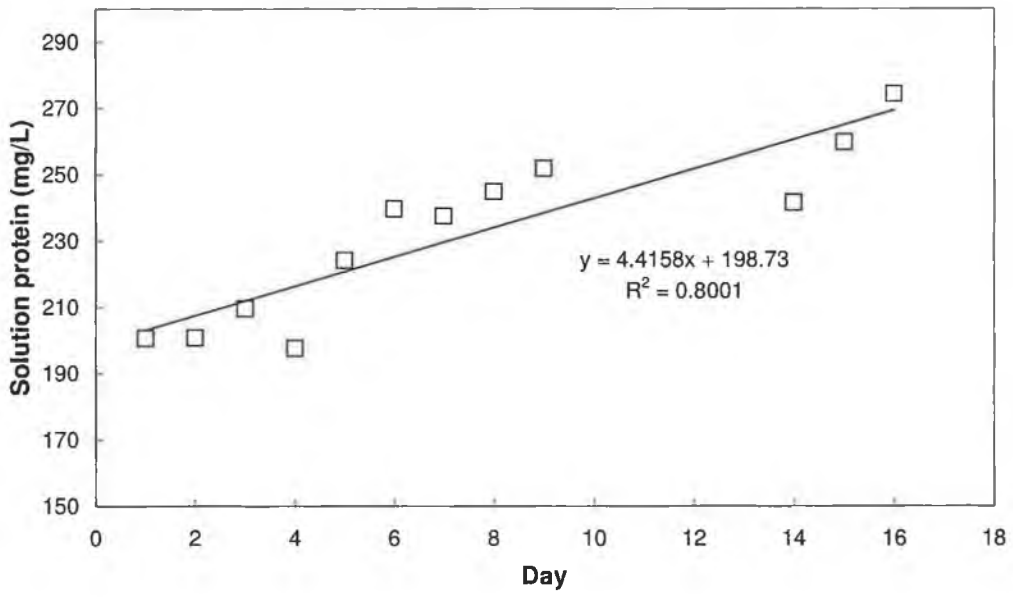


Figure 6.7 Trial 1: Concentration of protein (mg/L) in the solution phase of Carrum MAD sludge sample stored at 5 °C.

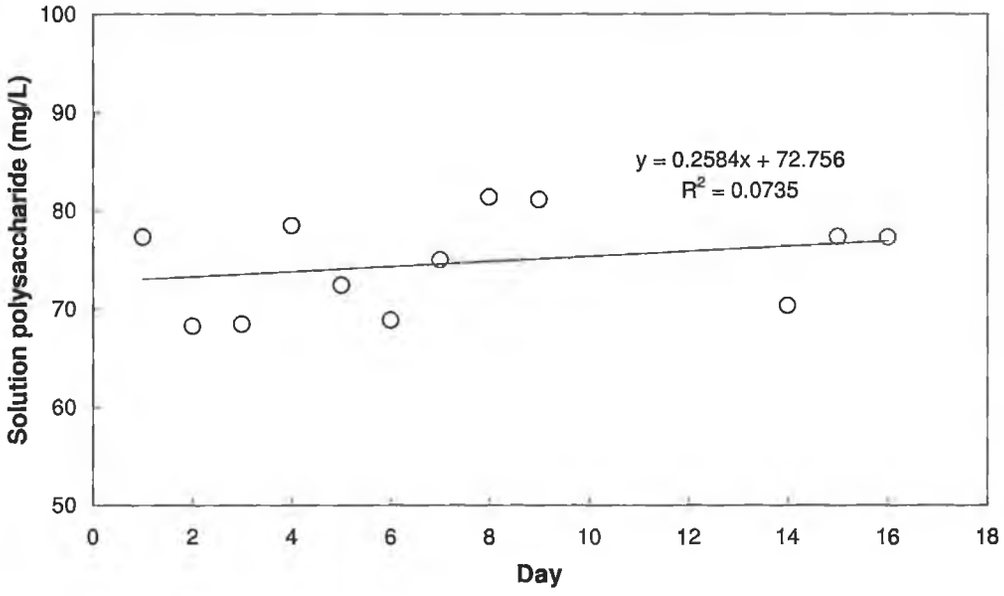


Figure 6.8 Trial 1: Concentration of polysaccharide (mg/L) in the solution phase of Carrum MAD sludge sample stored at 5 °C.

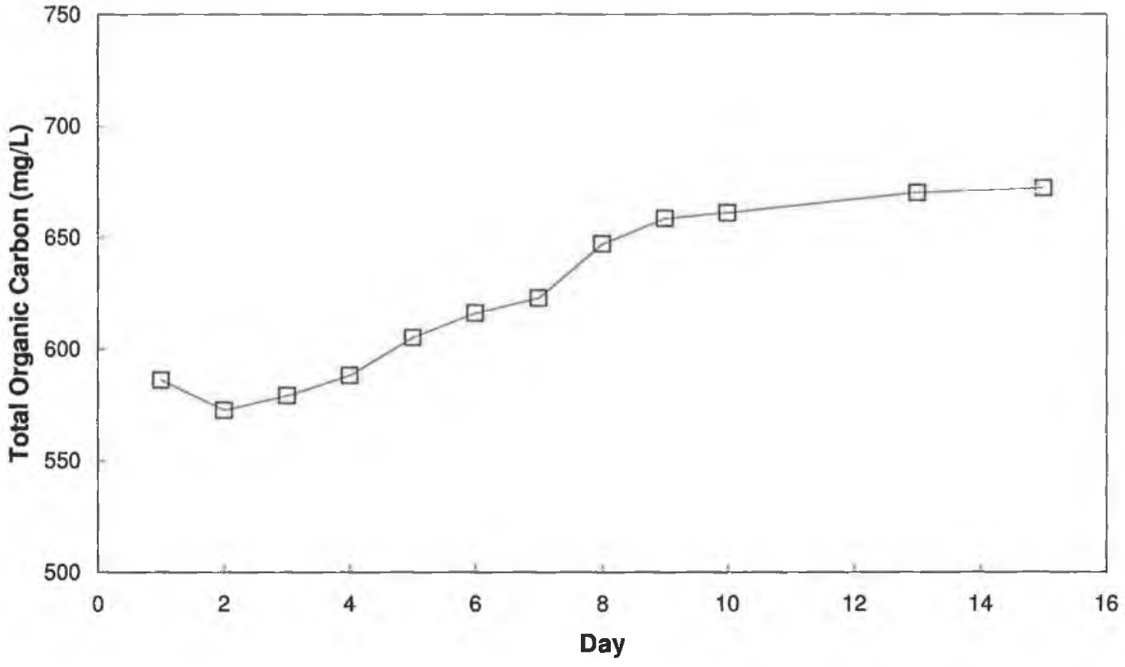


Figure 6.9 Trial 1: Concentration of total organic carbon in solution phase of Carrum MAD sludge stored at 5 °C.

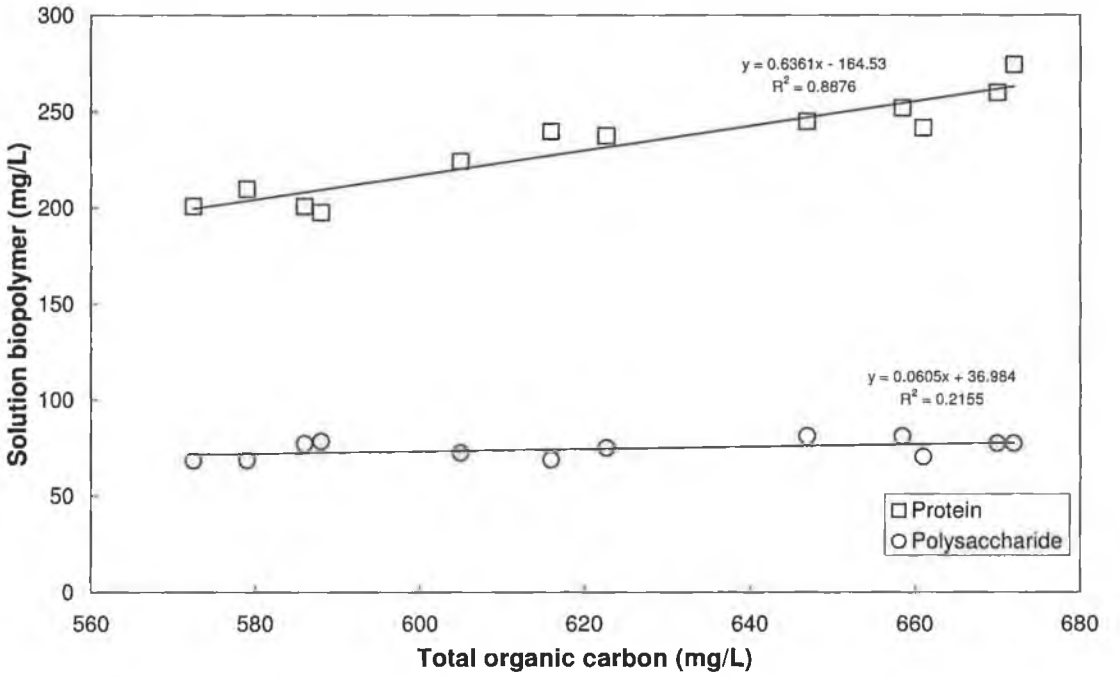


Figure 6.10 Trial 1: Relationship between proteins (mg/L) and polysaccharide (mg/L) to total organic carbon (TOC) in the solution phase of Carrum MAD sludge samples stored at 5 °C.

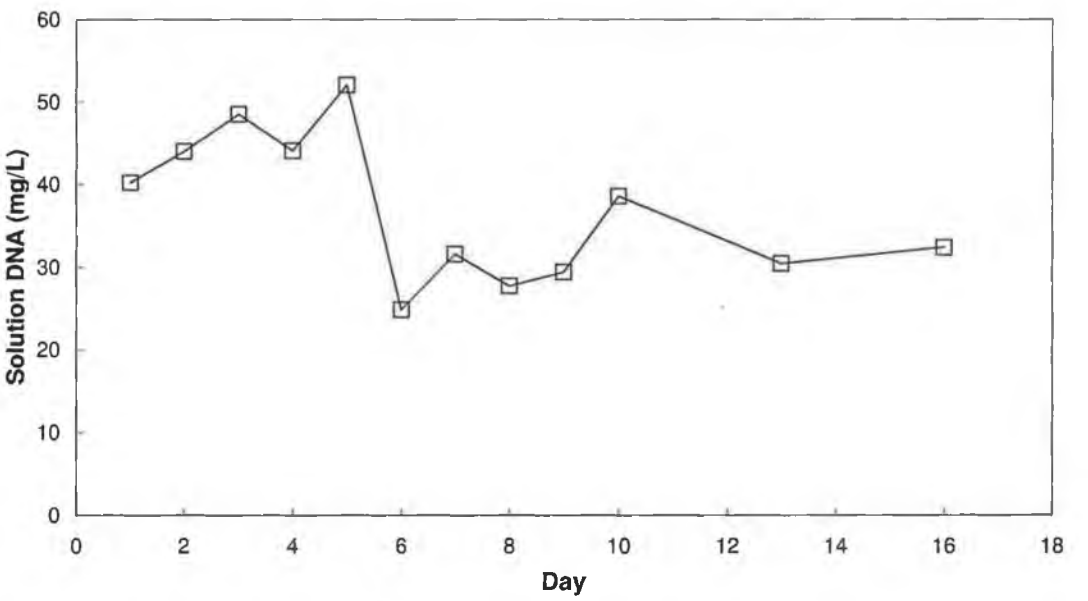


Figure 6.11 DNA (mg/L) in solution phase of MAD sludge stored at 5°C during trial 1.

The concentration of solution proteins is plotted as a function of time for Trial 1 in Figure 6.7. There was a linear increase in solution proteins, whereas polysaccharides showed little increase in concentration (Figure 6.8). Novak *et al.* (2003) noted that, during anaerobic digestion, the release of colloidal proteins is greater than that of polysaccharides. They proposed that two types of mechanisms are involved in the binding of biopolymers within floc. One type is associated with divalent cations and the second type is associated with iron. The type associated with iron degrades under anaerobic conditions, releasing proteins into solution (Novak *et al.,* 2003). The data presented in Figure 6.7 suggests that something similar may have occurred during Trial 1. While the rates of release of protein were not as great as those reported by Novak *et al.* (2003), similar mechanisms could still have been responsible for the release of protein, perhaps as a result of metabolic activity of psycrophilic bacteria, which remain active at the temperature of storage, 5 °C (Nozhevnikova *et al.*, 1997).

Total organic carbon (TOC) increased in solution in Trial 1 (Figure 6.9). This was expected, as the increase in biopolymers (which contain carbon) should directly contribute to such an increase. Figure 6.10 shows the relationship between solution proteins, solution polysaccharides and the TOC in solution during Trial 1. The increase in proteins clearly correlated with the increase in solution TOC (R^2 = 0.8876) while the polysaccharides showed poor correlation (R^2 = 0.2155). Therefore, the most significant contributor to the increase in TOC was protein.

Solution DNA was also measured during Trial 1 (Figure 6.13). Increased solution DNA is a possible indicator of cell lysis during storage. DNA was measured using the Bisbenzimide H33258 flourimetric assay described in Section 3.3.8. Calf thymus DNA was used as standard. Excitation was at 360nm and emissions were recorded at 460nm. The concentration of DNA in solution increased at first then decreased markedly after day 5. It has been noted by Bura *et al.* (1998) that DNA does not survive well in storage and degenerates rapidly even at -20°C. Their research showed that storage of extracted EPS samples at -20 °C from a WAS, resulted in a 60% decrease in detectable DNA after 1 month.

The DNA data does not exhibit the same stable trends as the protein and polysaccharide data. This may be due to deterioration in the quality of, or reduction in the quantity of detectable DNA following storage. Therefore, the lability of DNA prevented firm conclusions to be drawn regarding its concentration in the soluble phase, and solution DNA was not measured during Trial 2.

During Trial 2 a similar trend of increasing solution protein was evident. A more definite linear relationship was shown (R^2=0.885), than for Trial 1 (Figure 6.12). The concentration of solution proteins increased from 170mg/L to 239mg/L (an increase of 40%) over a period of six days. Solution polysaccharide concentrations varied little during Trial 2 (Figure 6.13). As significant time dependent changes occurred in the concentration of sludge proteins during storage at 5 °C for both trials, further

investigations were conducted to establish whether there were corresponding changes in dewatering properties.

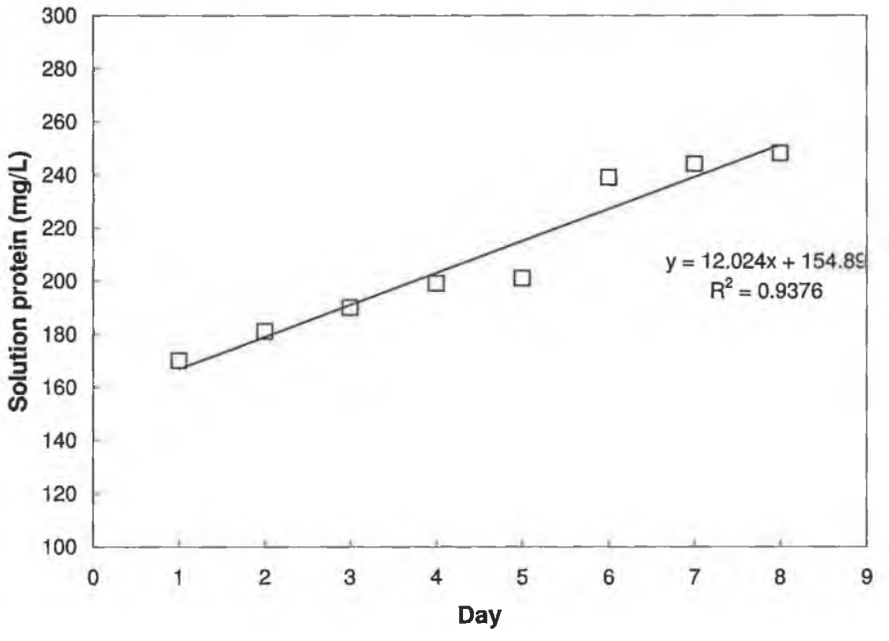


Figure 6.12 Trial 2: Concentration of protein (mg/L) in the solution phase of Carrum MAD sludge sample stored at 5 °C.

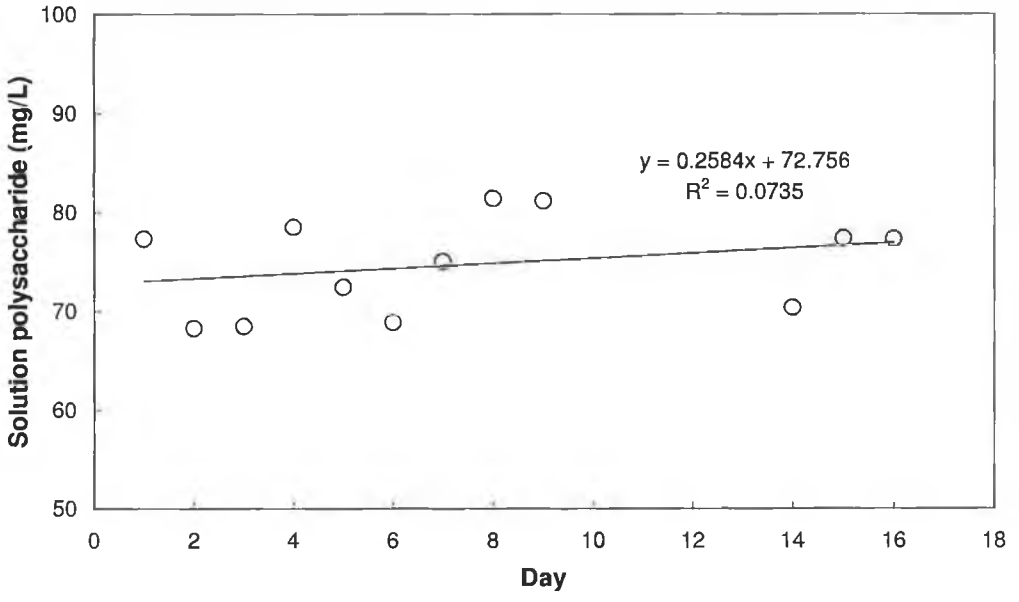


Figure 6.13 Trial 2: Concentration of polysaccharide (mg/L) in the solution phase of Carrum MAD sludge sample stored at 5 °C.

6.3.2 Dewatering properties

6.3.2.1 Trial 1

Table 6.2 gives the OPD values for the sludge during Trial 1 and Trial 2. The OPD was measured using the method outlined in Section 3.3.12. ZETAG 7187 cationic polyelectrolyte was used as the conditioning agent. Little change was observed in the OPD. The mean CST (s) at the OPD was also measured. Similarly, the CST remained relatively stable, though the CST values were slightly higher during Trial 2. This was surprising, as Novak *et al.* (2003) established that the concentration of solution biopolymer was a significant contributing factor to the polymer demand for sewage sludges. Solution biopolymer was also shown to correlate with polymer demand for the ATAD sludges studied in Chapter 5.

Table 6.2 Optimum polymer dose (g/kg DS) and CST (s) at the OPD, for Carrum MAD sludge during Trial 1

DAY	*OPD (g/Kg DS)*	*CST (s)*
1	9	35
3	9	38
5	10	38.5
10	9	35
15	9	41
Trial 2		
1	9	44
5	10	48
10	10	41
15	10	52

Settling tests were performed on the stored samples from Carrum during Trial 1 to determine whether there were time-dependent changes in settling behaviour. The data is presented in Figure 6.14. There were no significant changes in settling behaviour during the trial. A LUMIFUGE was also used for settling analysis over a period of 34 days for trial 1. The LUMIFUGE data has the advantage of being continuous online sediment solid-liquid interface measurement, which omits the errors associated with the movement of the solid-liquid interface during centrifuge braking and restarts, such as that associated with the traditional method, in which samples have to be removed from the centrifuge at set time-intervals in order to measure the height of the solid-liquid interface. The LUMIFUGE data is presented in Figure 6.15. Little change occurred in settleability, with

only the sludge from day 37 showing any noticeable improvement in settling behaviour compared to the other samples. However, this may have been due to solids removal having occurred over the prolonged storage time.

The time-dependent change in settling behaviour of the MAD sludge as described by deKretser *et al.* (2005) was not reproduced during these trials; those changes may have been due to a conformational or charge-distribution changes in flocs that are not linked to the distribution of biopolymers in solution.

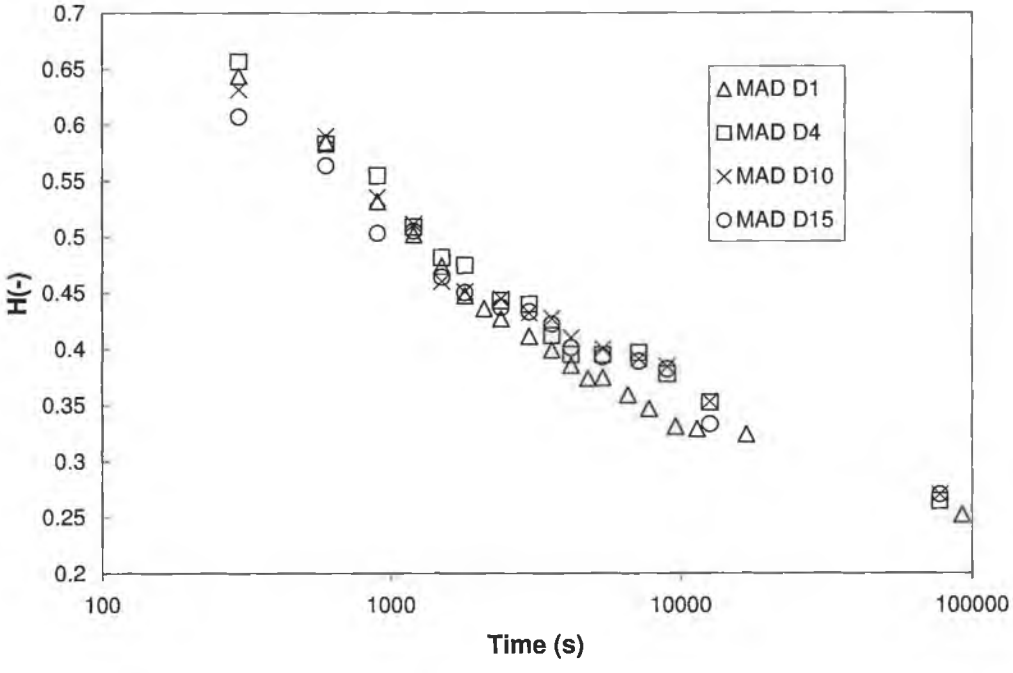


Figure 6.14 Normalised height *(h-)* vs *t* settling data for Carrum MAD sludge during trial 1 (days 1, 4, 10 and 15) at 1000rpm.

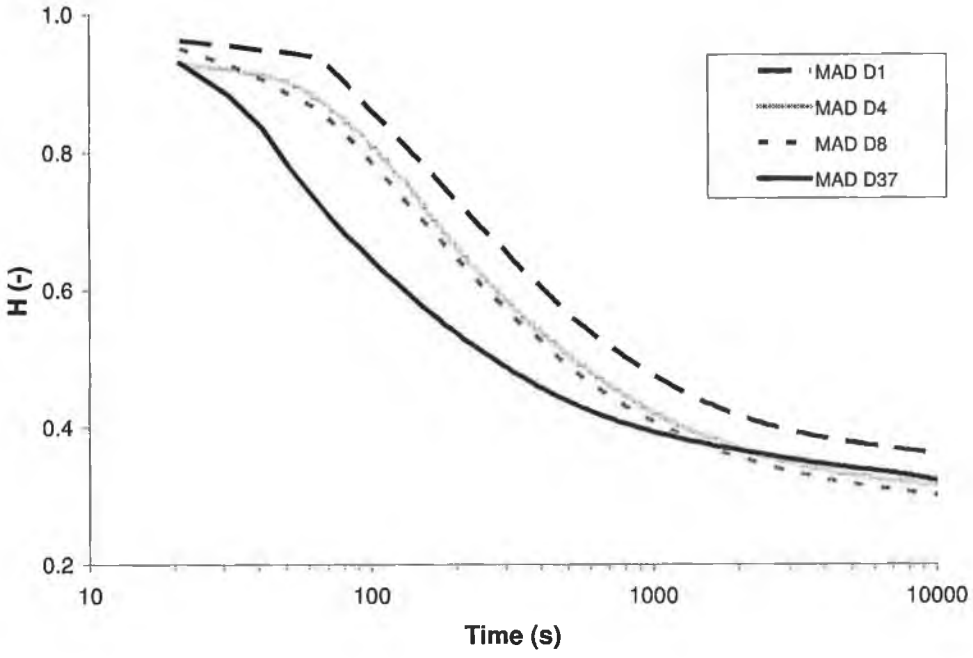


Figure 6.15 Lumifuge normalised height (h-) vs t settling data for Carrum MAD

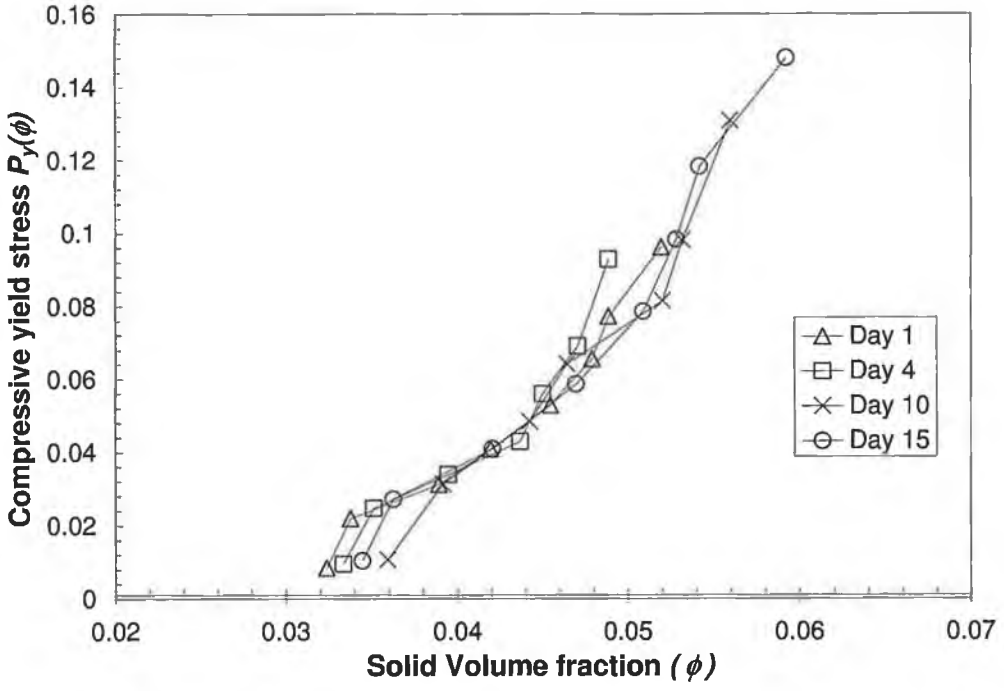


Figure 6.16 $P_y(\phi)$ vs ϕ for Carrum MAD sludge as a function of time (days)

$P_y(\phi)$ remained similar during Trial 1 (Figure 6.16). There was little change in the compressibility of the sludge between day 1 and day 15 of the trial.

6.3.2.2 Trial 2

Centrifugal settling tests were only conducted on day and day 15 for Trial 2 (Figure 6.17). The sample from day 1 settled slightly better than the sample from day 15, however, the difference is negligible. No scrape-tests were conducted on samples from Trial 2.

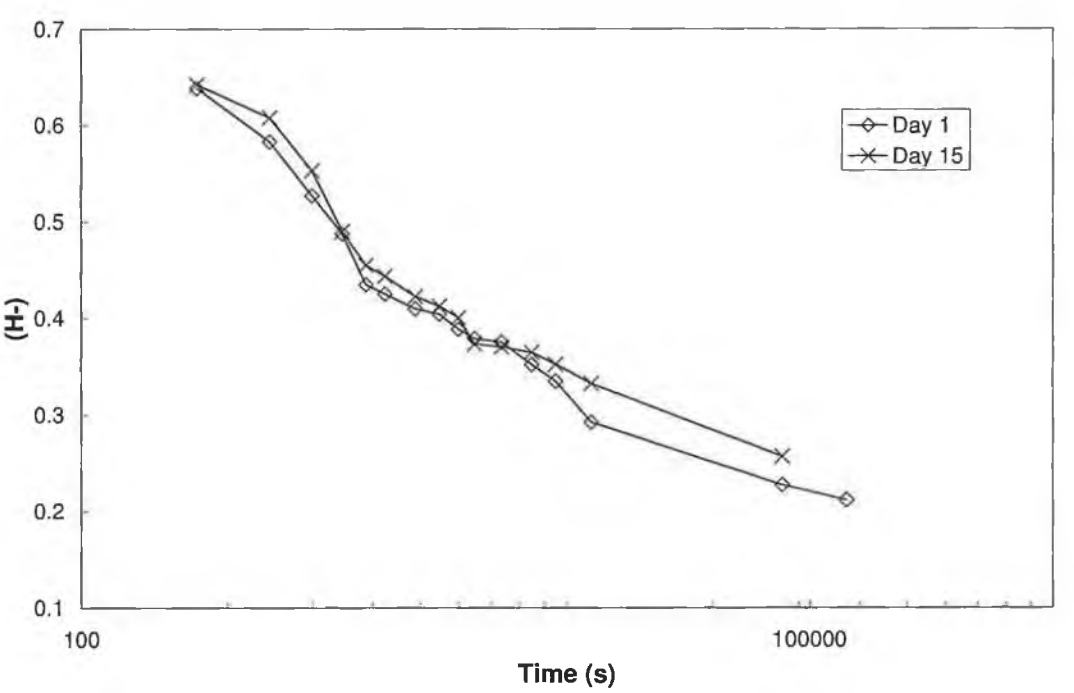


Figure 6.17 Normalised height *(h-)* vs *t* settling data for Carrum MAD sludge during trial 2 (days 1 and 15) at 1000rpm.

6.3.2.3 Conclusions

Overall, no real change in MAD sludge dewatering properties occurred during storage at 5 °C, however, the quantity of TOC and proteins in the solution phase increased markedly during each trial. It was expected that an increase in such negatively charged biopolymers would have increased the OPD of the sludge samples. This did not occur. It is possible that the quantity of solution proteins provided a negligible amount of negatively charged surface area to bind with polyelectrolyte in comparison to the floc surface area and floc EPS.

6.3.3 Particle size distribution

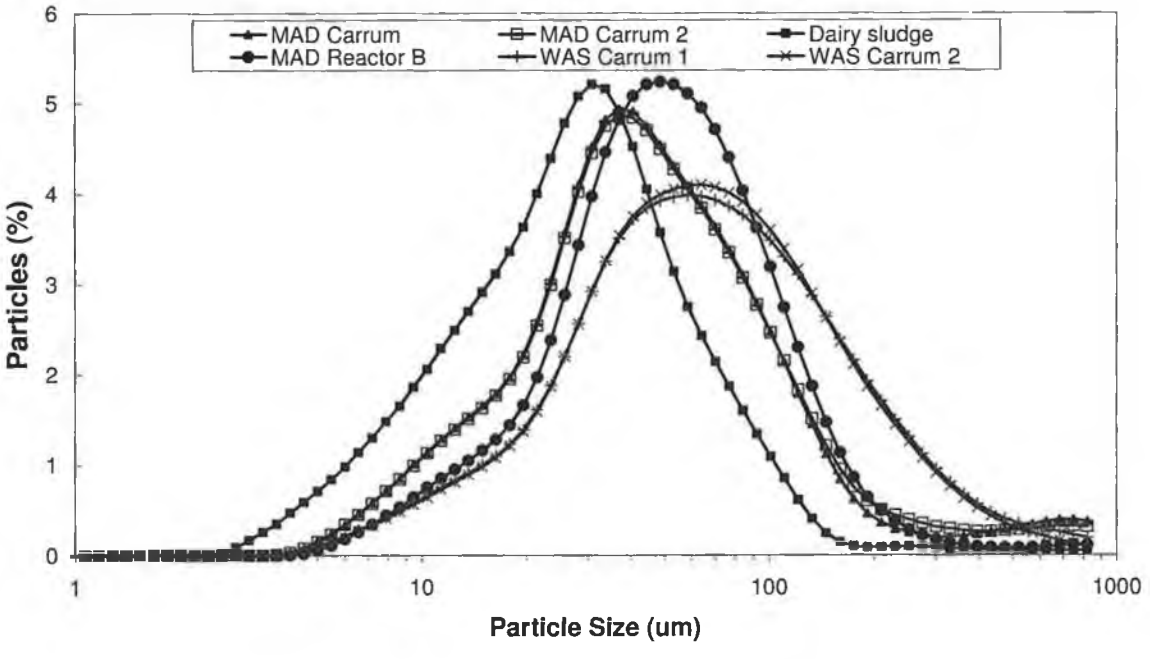


Figure 6.18 Particle size distribution curves (μm) for Carrum WAS and MAD sludges, laboratory generated MAD, and dairy sludge.

Particle size distribution curves were generated (Figure 6.18) for three types of sludge, WAS, MAD and Dairy Sludge using a Coulter Counter. The sludge samples which were used were MAD sludge from Carrum, WAS from Carrum, MAD generated in the lab in batch anaerobic digestion of Carrum WAS and dairy sludge from New Zealand. The distribution curves show that the WAS had the widest distribution of floc sizes, with the curve peaking between 60 and 80μm. The MAD sludges had on average smaller particle sizes than the WAS. MAD sludge produced in bench-top anaerobic digesters in the lab had a peak in particle size distribution curve at a lower size than the MAD sludge from Carrum WWTP. This was likely due to the presence of higher shear rates in the full-scale digesters at Carrum. A New Zealand dairy sludge was included for comparison, and had the lowest average particle size of all the sludges.

6.3.4 Conclusions

- Despite an improvement in dewatering properties being noted in a previous study, no real improvement in the dewatering properties of MAD sludge was found following prolonged storage in refrigerated conditions. This suggested that sludge could be stored for several days for dewatering analysis using the biosludge characterisation protocol without notable change in the sludge dewatering properties.

- The concentration of protein and TOC were shown to increase significantly in the solution phase of a MAD sludge during refrigerated storage. The ratio of TOC to protein remained stable, which showed that the primary contribution to the

increase in solution TOC was proteins being released into solution, most likely from degeneration of floc structure.

- The concentration of polysaccharide in solution remained relatively stable over the same period, and the concentration of solution DNA decreased.

- Particle size analysis of sludge samples using a COULTER COUNTER showed MAD sludge to have a lower particle size on average than WAS, with MAD from Carrum WWTP having lower average particle size than MAD from bench-top anaerobic digestion. This is likely to have been due to higher shear rates found in the full-scale digesters.

6.4 An examination of the effects of enzyme addition on MAD dewatering properties

6.4.1 Introduction

Hydrolysis is regarded as the rate limiting step in anaerobic sludge digestion (Metcalf and Eddy, 2001). Several studies have investigated the enhancement of microbial enzymatic activity by the addition of commercial enzymes (Whiteley et al, 2003; Watson et al, 2004). Enzyme addition has been extensively studied as a means of enhancing hydrolysis and solids destruction during sludge digestion (Maunoir *et al.*, 1990; Barjenbruch and Kopplow 2003; Mshandete *et al.*, 2005). Hydrolytic enzymes break down polymeric substances like proteins, polysaccharides, lipids, and additionally can cause a release of macromolecules, e.g., humic substances, that are non-specifically bound to the mentioned substrates (Wawrzynczyk et al., 2007).

The impacts of enzymatic modifications on the dewatering properties of sewage sludges have not been widely reported (Ayol, 2005a; 2005b). The work which has been conducted in the area suggested that enzymatic pre-treatments improve dewatering properties of sludge. Ayol (2005a) found that the addition of a commercial enzyme product (consisting of lipases, proteases and cellulases) to MAD sludge at 37 ^{o}C resulted in improved dewatering properties in terms of CST, solid contents of final product, filtrate turbidity and suspended solid measurements.

Numerous studies have suggested if the ECP components of sewage sludge are reduced the dewaterability may be improved. In this study the effects of adding enzymes to degrade the ECP components were investigated through the measurement of:

- protein and polysaccharides concentrations in solution;
- changes in solids content of the sludges
- the changes in the sludge settling ability and compressibility.

Enzymatic pre-treatments are a promising potential addition to the wastewater sludge treatment process and hence, a careful evaluation of the effects of their addition on subsequent sludge dewatering is necessary.

6.4.2 Bench-scale anaerobic digester operation

In August 2005 two 5 l bench-scale MAD reactors were commissioned at Melbourne University: RA and RB. Each reactor had a working capacity of 4 l, and was maintained at 37 ^{o}C in a water bath. A schematic of the reactor design is given in Figure 3.2. Mixing was provided by egg-shaped magnetic stir-bars. The magnetic stir-bars were unable to mix sludge with a solids content greater than 2.5% TS.

The reactors were fed a WAS sludge which was sampled from Carrum WWTP (with an average solids content of 1.84% w/w). Table 6.3 gives the characteristics of the Carrum WAS which was used as the feed sludge for these trials.

Table 6.3 Characteristics of feed sludge used in bench-scale MAD reactors

	Total solids (% w/w)	*Volatile solids (% w/w)*	*pH*
Minimum	0.78	0.64	6.21
Maximum	2.45	1.97	6.48
Mean (±SD)	1.84±0.503	1.53±0.4135	

The reactors were operated on a 16d HRT, with 250ml of effluent wasted from each reactor every day. Figures 6.19 and 6.20 give the TS and VS in the influent and effluent of RA and RB. Solids data is presented only from day 29 onward. Unfortunately, during the first few weeks of operation, poor mixing and inefficient sampling dictated that the solids results obtained prior to day 29 were not representative of the true conditions within the reactors, and have thus been disregarded.

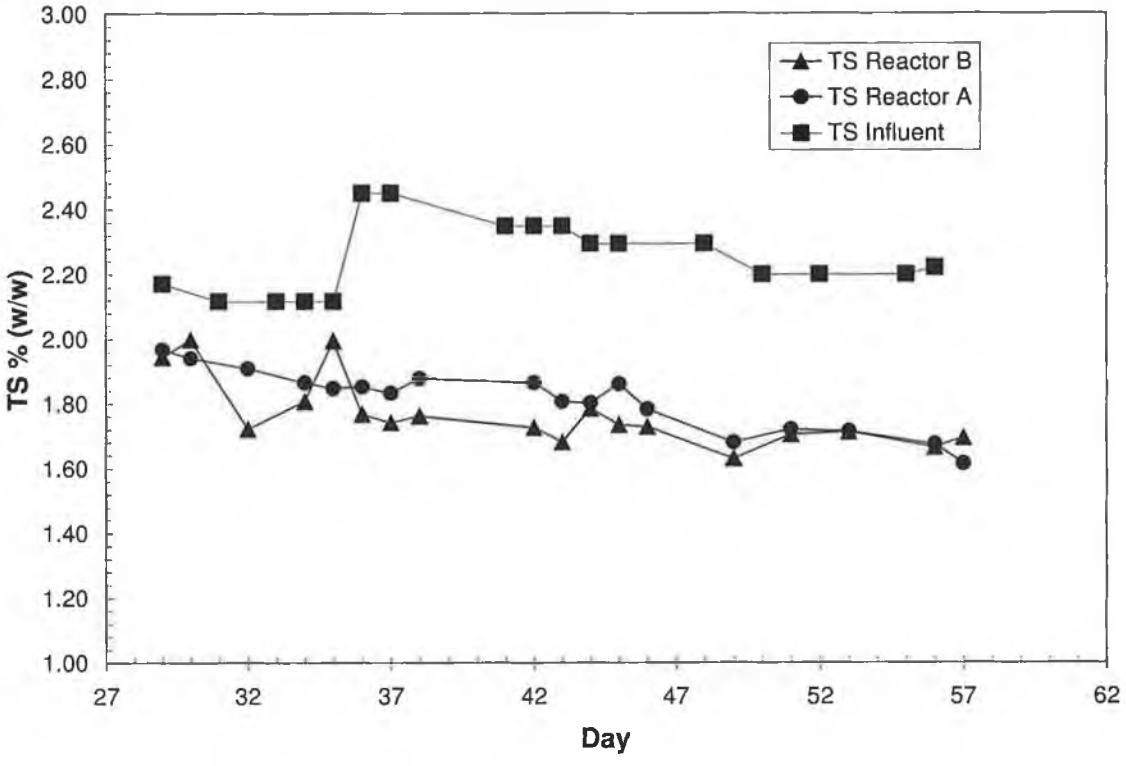


Figure 6.19 TS (%w/w) of influent to reactors, and of reactor A and reactor B during steady-state MAD digestion.

For stable operation on a 16d HRT, approximately 25% and 24% TS removal was being achieved in RA and RB respectively. The VS removal was 35% and 36% for RA and RB respectively. The average VS of the influent sludge expressed as a percentage of TS was 82%, and for RA and RB was 72% and 73% respectively. These figures show that once stable operation was achieved within the reactors, that solids removal rates were more or less identical in RA and RB.

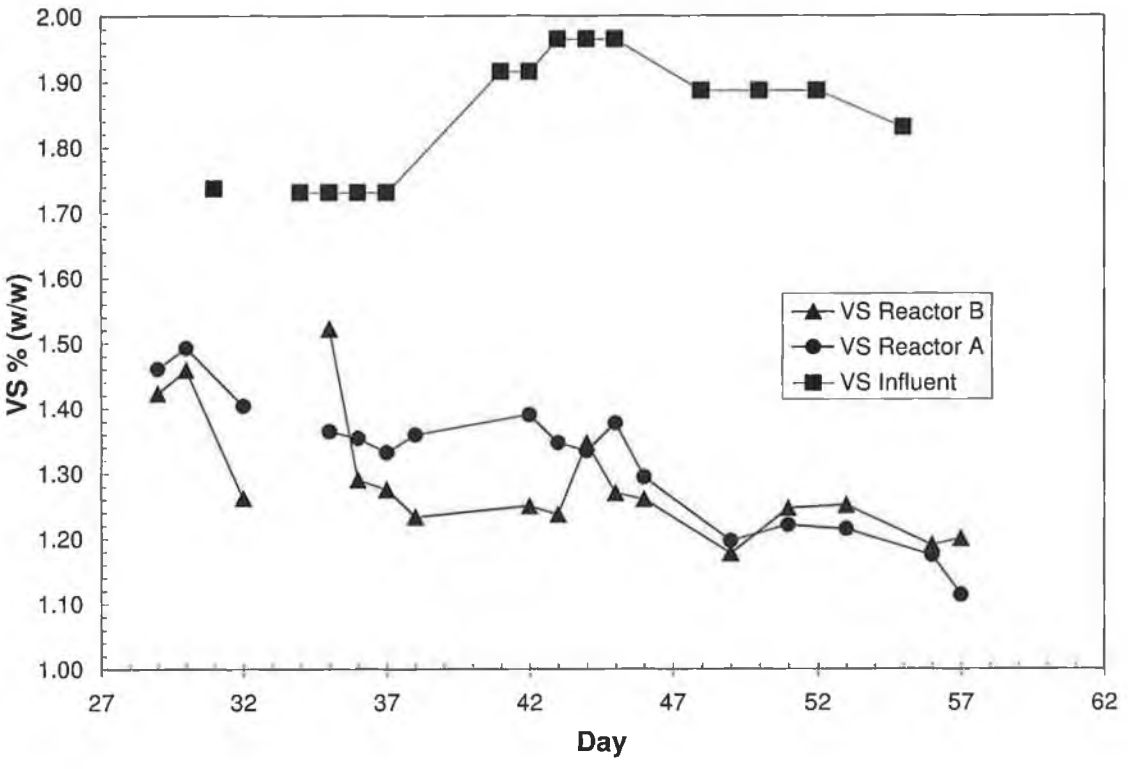


Figure 6.20 VS (%w/w) of influent to reactors, and of reactor A and reactor B during steady-state MAD digestion.

Figure 6.21 gives the daily biogas production for the two reactors. During stable operating conditions, RA and RB were producing on average 702 ±22 ml and 709 ±18 ml biogas per day. These figures were low, as the feed sludge was of low strength (average 1.53% VS w/w), and the HRT (16 d) was high. The mean volume of CH_4 in the biogas was 55% for both reactors (Figure 6.22). Metcalf and Eddy (2001) state that biogas from anaerobic digestion contains on average 65-70% CH_4 by volume. It is not known why the volumetric yield of CH_4 in this study was lower than the average described by Metcalf and Eddy (2001).

Because the total organic loading rate of both reactors was known (in terms of VS), and the total quantity of VS destroyed within each reactor was also known, the CH_4 yield per gram VS destroyed could be calculated for RA and RB. This was based upon the weekly biogas production and the $\%CH_4$ in the biogas. For the final four weeks of operation, RA produced 385 ml CH_4/ g VS destroyed, and RB 324 ml CH_4/ g VS destroyed. These values are lower than the typical values of 750-1200 ml described by Metcalf and Eddy (2001).

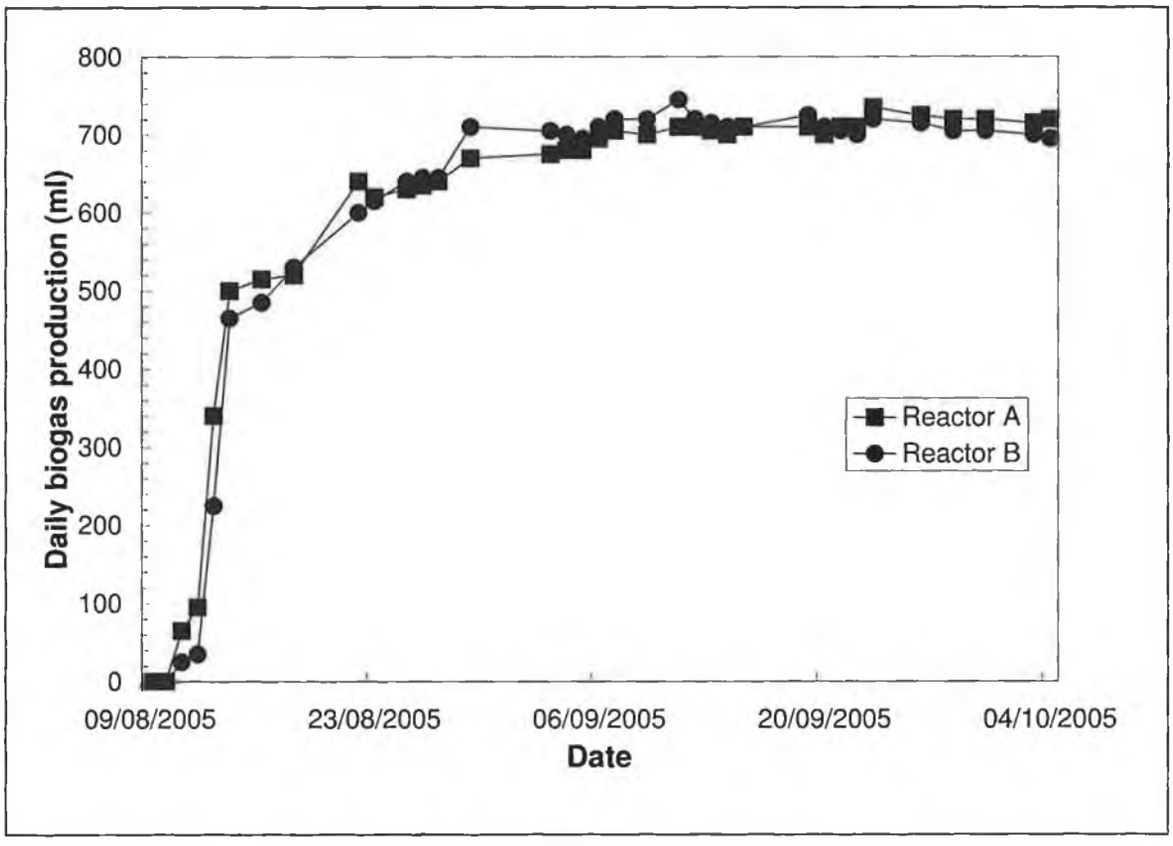


Figure 6.21 Daily biogas production (ml) for RA and RB

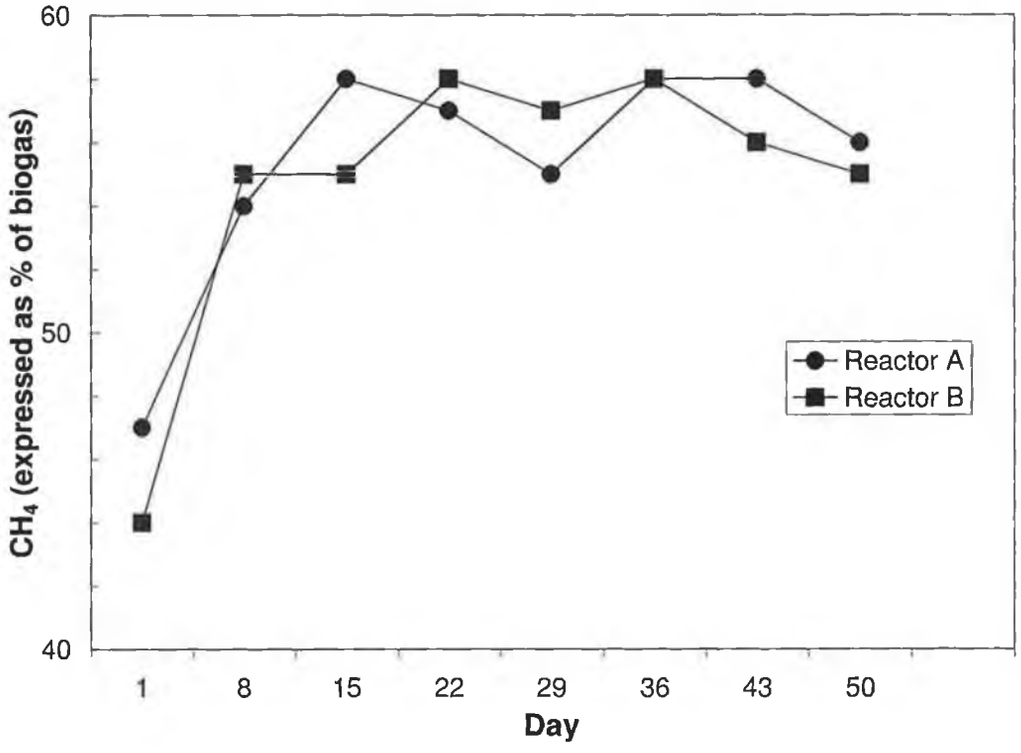


Figure 6.22 Weekly CH_4 values in biogas of Reactor A and Reactor B (CH_4 expressed as % (v/v) of biogas).

Figure 6.23 shows pH values for the reactor effluent over the period of their operation. Similar to the solid and CH_4 data, both reactors show similar pH profiles, and this indicates that stable operating conditions were achieved in each. Optimum pH for successful operation of anaerobic reactors is around neutral, which is the range that was maintained in each reactor following an initial start-up period, before the pH stabilised. At pH below 6.8 methanogenic activity is inhibited (Metcalf and Eddy, 2001).

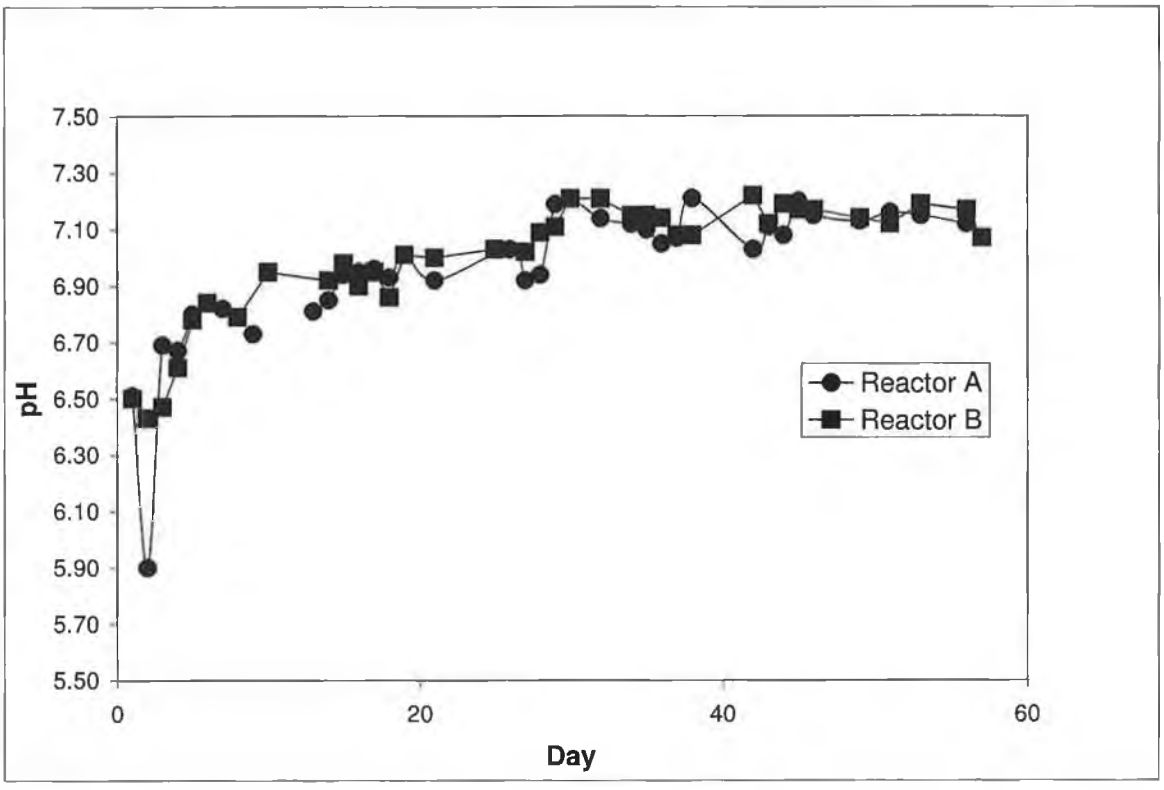


Figure 6.23 pH of Reactor A and B

6.4.3 Enzyme addition experiments

6.4.3.1 Introduction

The following enzymes were used: protease from *bacillus* sp., protease from *aspergillus sp*, cellulase, and glucosidase. Details of the enzymes are given in Section 3.2.1. The concentrations of enzyme applied were based upon those utilised by Ayol (2005) which ranged between 0 – 100mg/L. The enzymes were selected on the basis that the biopolymers that interfere most with sludge dewatering properties are proteins and

polysaccharides (Novak *et al.,* 2003; Ayol, 2005a; Ayol, 2005b). Enzyme activity has been shown to decline during both anaerobic and aerobic digestion. During aerobic digestion glucosidase activity was shown to decline to almost zero following ten days of digestion. This may result in the increased levels of solution polysaccharide reportedly found in aerobic digesters. During anaerobic digestion enzyme activity for both protein and polysaccharide degradation has been shown to decline (Novak *et al.*, 2003; Ayol, 2005). Supplementation of enzymes to the anaerobic digestion process is therefore a method by which the degradation of solution biopolymers may be enhanced, improving sludge dewatering properties.

6.4.3.2 *Experimental outline*

Initially, it was planned to spike concentrations of selected enzyme solutions into RB and measure changes in dewatering properties against RA (which was to act as the control reactor). However, as the reactors were operating on a 16 d HRT, this would have entailed at least 16 days in between each enzyme addition, and also the possibility of the enzymes causing a toxic shock to the micro-organisms within RB, causing the reactor to fail. It was instead decided to conduct three controlled trials using sludge sampled from RA. Both digesters were operated as normal throughout the trials. The concentrations of enzyme used in each trial are given in Table 6.4. In Trial 1, 3 different concentrations of protease were added to the sludge. In Trial 2 cellulase and glucosidase were added to the sludge, and in Trial 3 a mixture of cellulase, glucosidase and protease was investigated. In each trial a control was also added in which no enzymes were added.

For each trial, 500ml of sludge was sampled, which was in turn subdivided into four 100 ml samples for enzyme addition. 2.5ml of enzyme solution was added to each sample. The samples were placed in Schott bottles and incubated for 24 hours in a water bath at mesophilic temperature (37 °C). Following 24 hours incubation, the enzymatically modified sludges were investigated in terms of transient centrifugal settling properties (an indication of permeability), $P_y(\phi)$, solution proteins, solution polysaccharides and solids content (TS and VS). The results of the trials are presented in the Tables and Figures below.

Table 6.4 Enzyme doses for experimental trials

	Enzyme added	***Concentration***
Trial 1	Protease	10 mg/L
	Protease	30 mg/L
	Protease	100 mg /L
Trial 2	Glucosidase	0.1% w/v, (1.875 ml)
	Cellulase	30 mg/L
	Mix – glucosidase, cellulase, protease	0.1% w/v (0.625 ml), 30 mg/L, 30mg/L
Trial 3	Protease	200 mg/L
	Cellulase	100 mg/L
	Mix – glucosidase, cellulase, protease	20 mg/L,100 mg/L, 100 mg/L

Table 6.5 Sludge solids content (before and after enzyme addition)

	Sample	*TS% (w/w)*	*VS% (w/w)*	*VS (% of TS)*	*TS reduction (%)*
Trial 1	Control	1.798	1.332	73.72	-
	Protease 10 mg/L	1.763	1.286	72.56	1.924
	Protease 30 mg/L	1.742	1.253	71.62	3.138
	Protease 100 mg/L	1.692	1.233	72.54	5.880
Trial 2	Control	1.723	1.246	72.33	-
	Glucosidase 0.1% w/v,	1.703	1.244	73.02	1.158
	Cellulase 30 mg/L	1.746	1.249	71.55	-1.357
	Mix - protease 30 mg/L, cellulase 30 mg/L, glucosidase 0.1% w/v	1.720	1.247	72.49	0.190
Trial 3	Control	1.558	1.147	73.60	-
	Protease 200 mg/L	1.506	1.087	72.15	3.354
	Cellulase 100 mg/L	1.552	1.115	71.85	0.379
	Mix – protease 100mg/L, cellulose 100 mg/L, glucosidase 20 mg/L	1.472	1.051	71.43	5.528

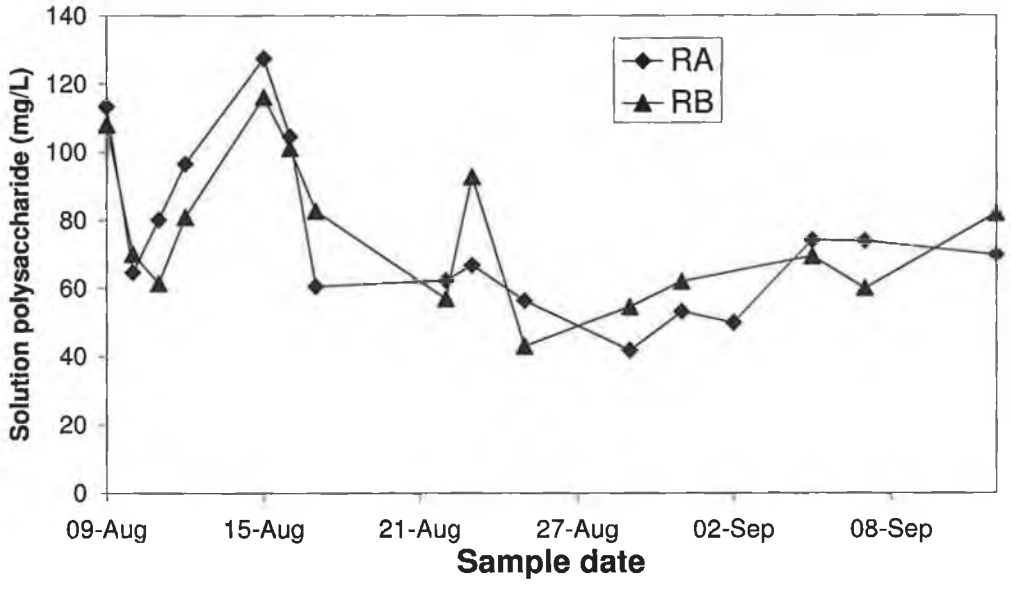


Figure 6.24 Solution polysaccharide in RA and RB

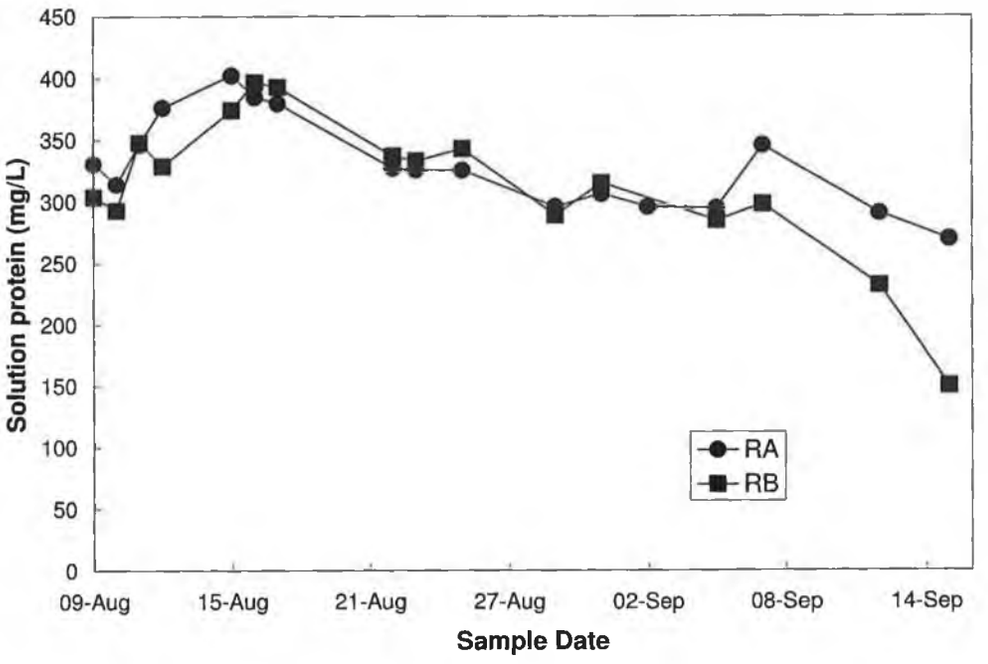


Figure 6.25 Solution proteins in RA and RB

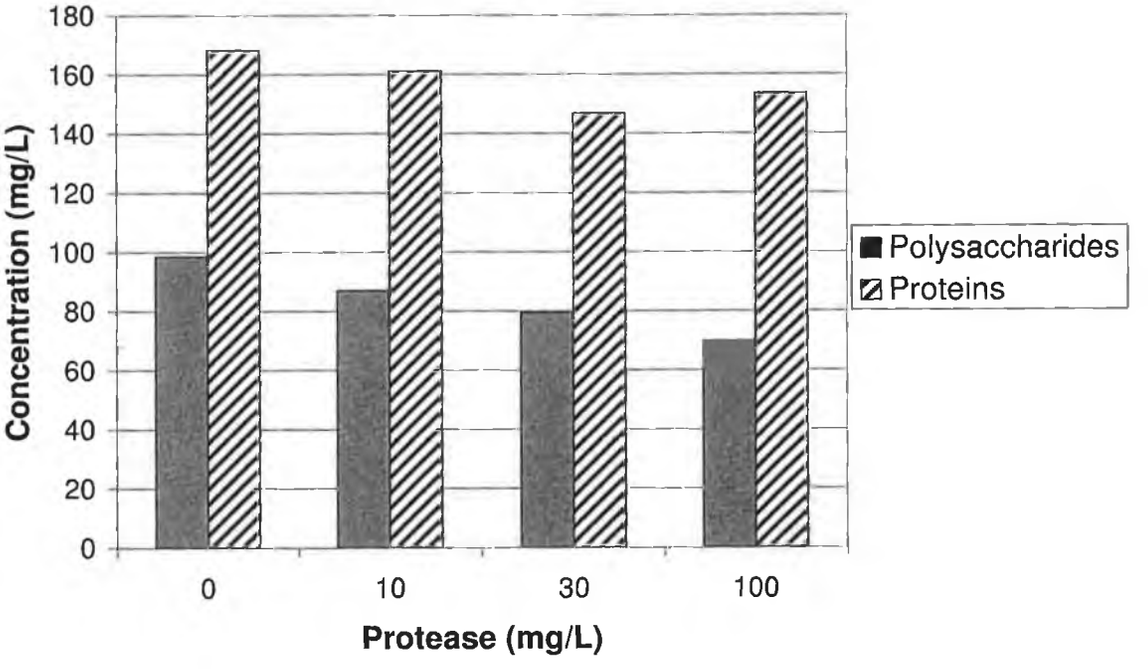


Figure 6.26 Solution biopolymers remaining after addition of enzymes in Trial 1.

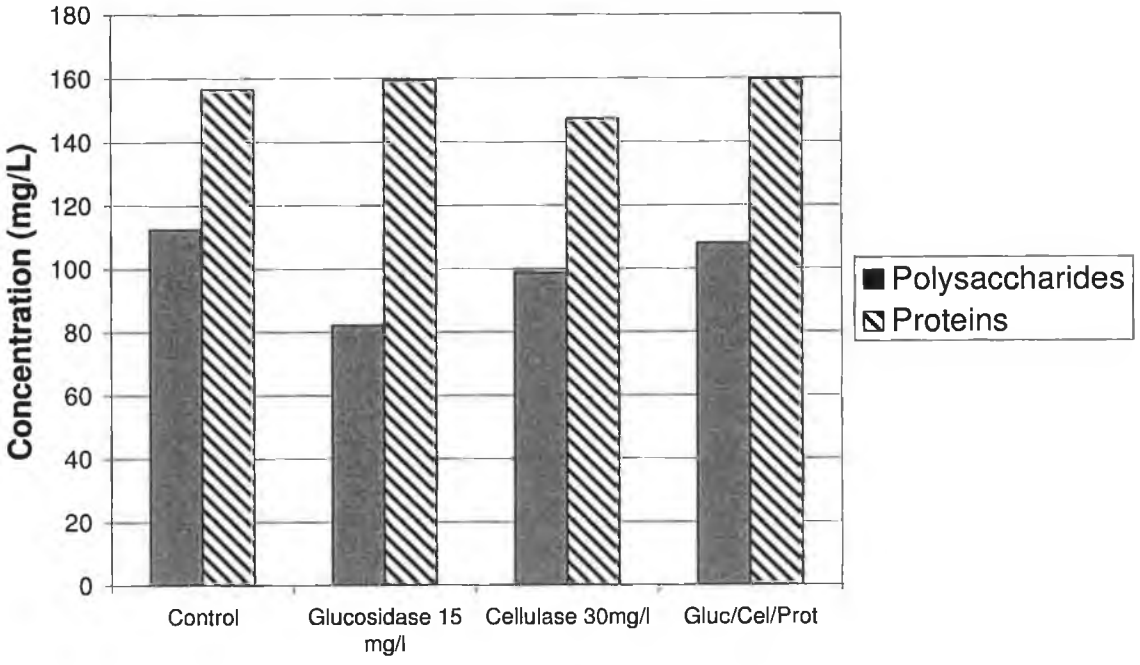


Figure 6.27 Solution biopolymers remaining after addition of enzymes in Trial 2

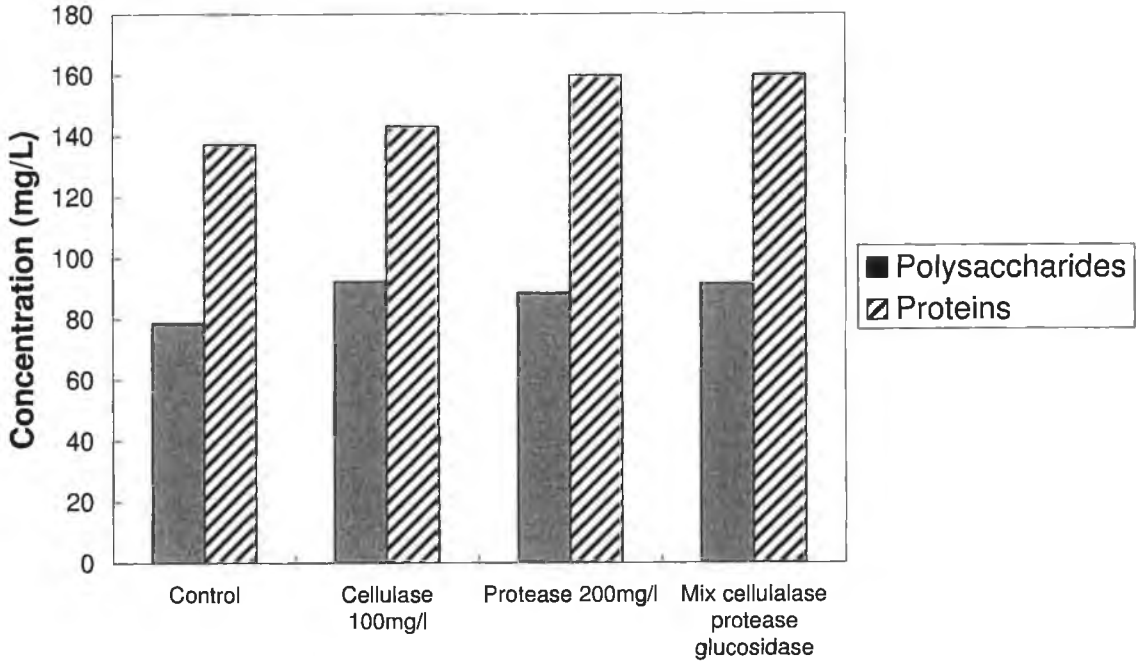


Figure 6.28 Solution biopolymers remaining after addition of enzymes in Trial 3

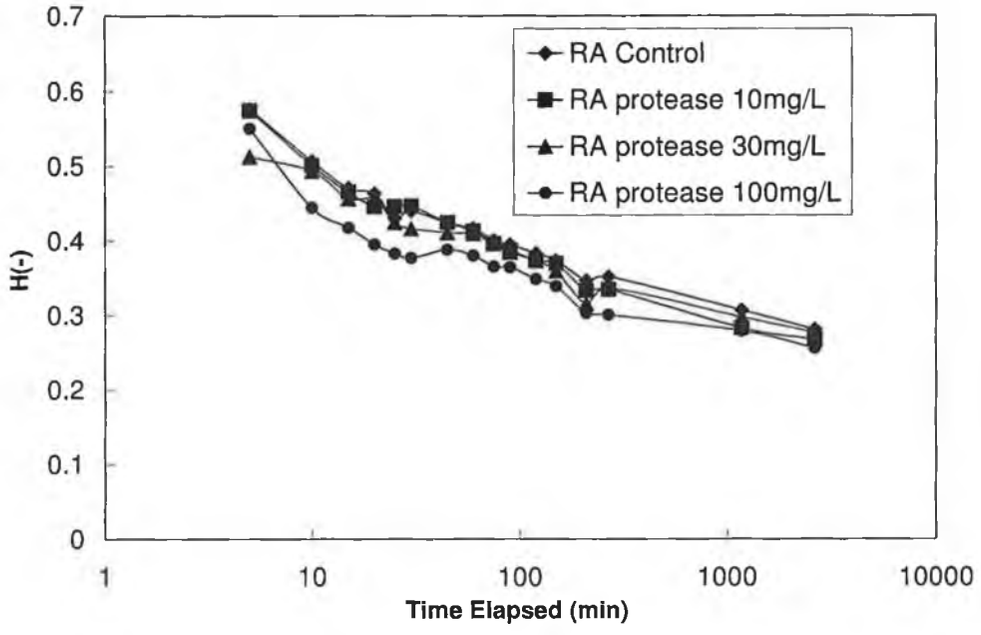


Figure 6.29 Transient centrifugal settling data (1000 rpm) after addition of enzymes to sludge (Trial 1)

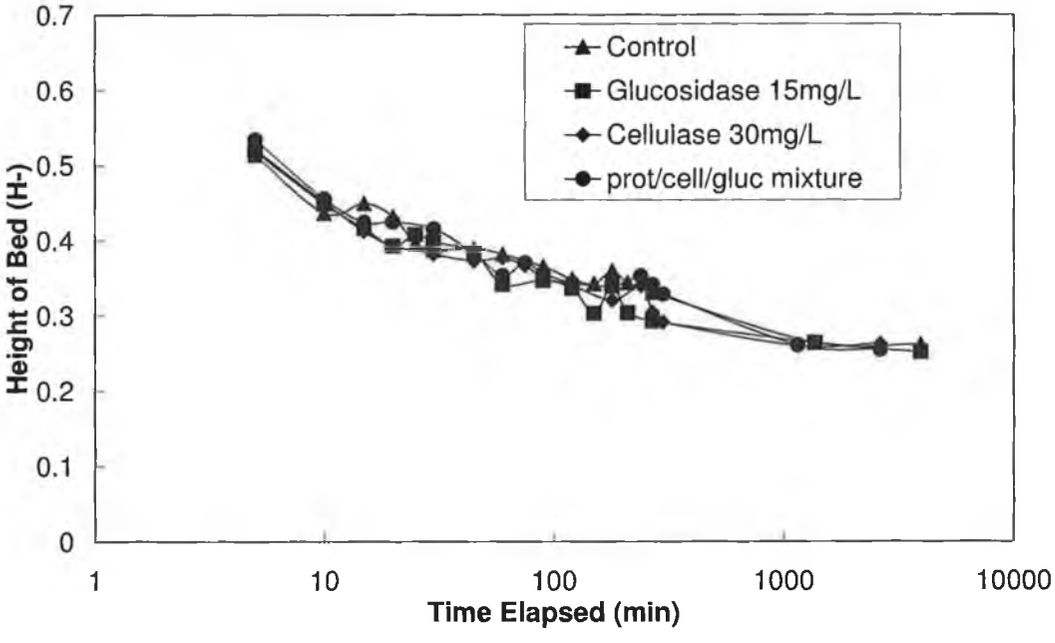


Figure 6.30 Transient centrifugal settling data (1000 rpm) after addition of enzymes to sludge (Trial 2)

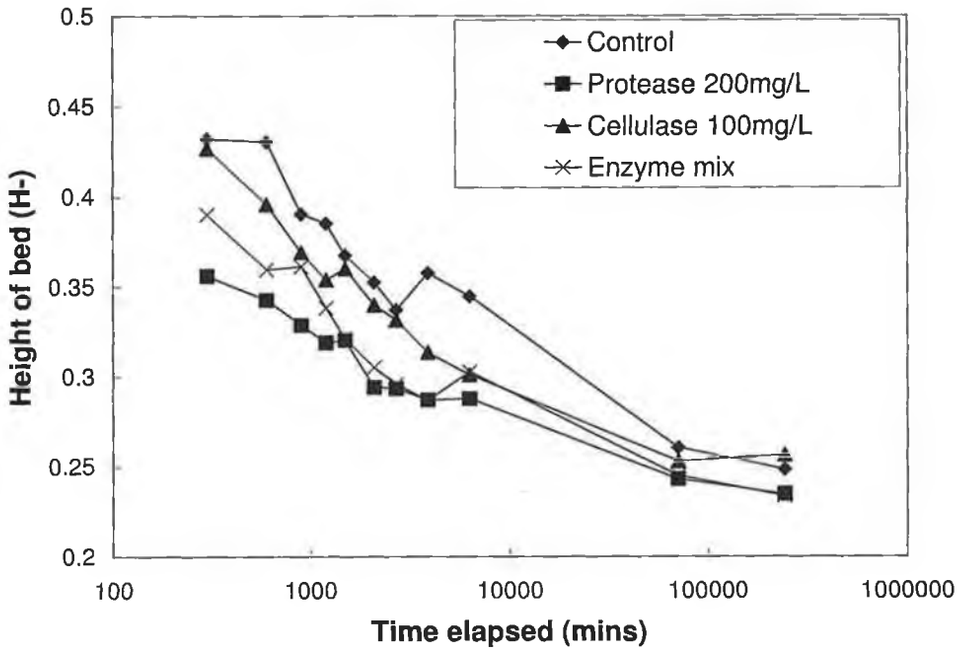


Figure 6.31 Transient centrifugal settling data (1000 rpm) after addition of enzymes to sludge (Trial 3)

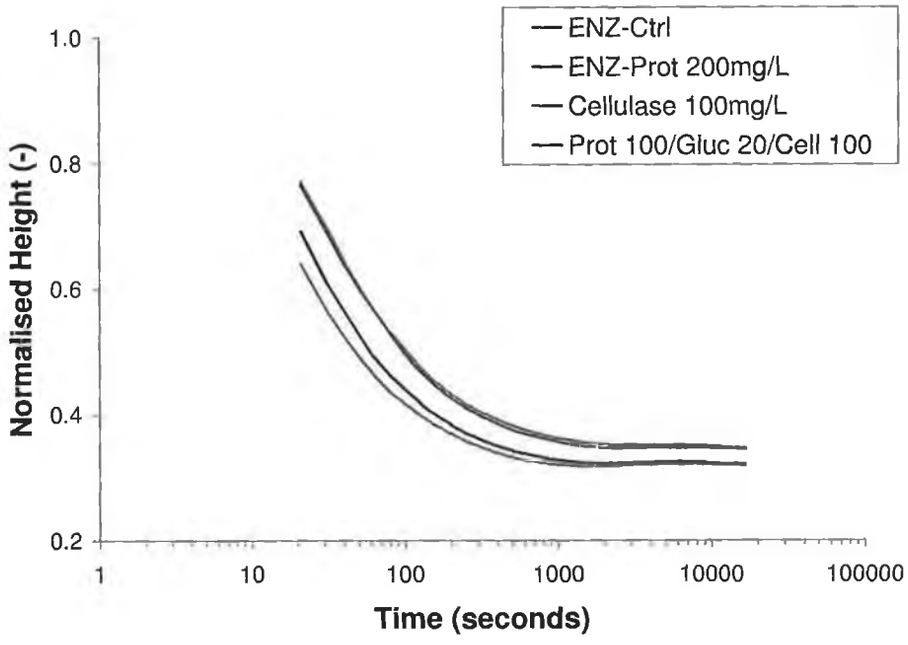


Figure 6.32 Transient centrifugal settling data (1000 rpm) after addition of enzymes to sludge (Trial 3), data obtained from LUMIFUGE.

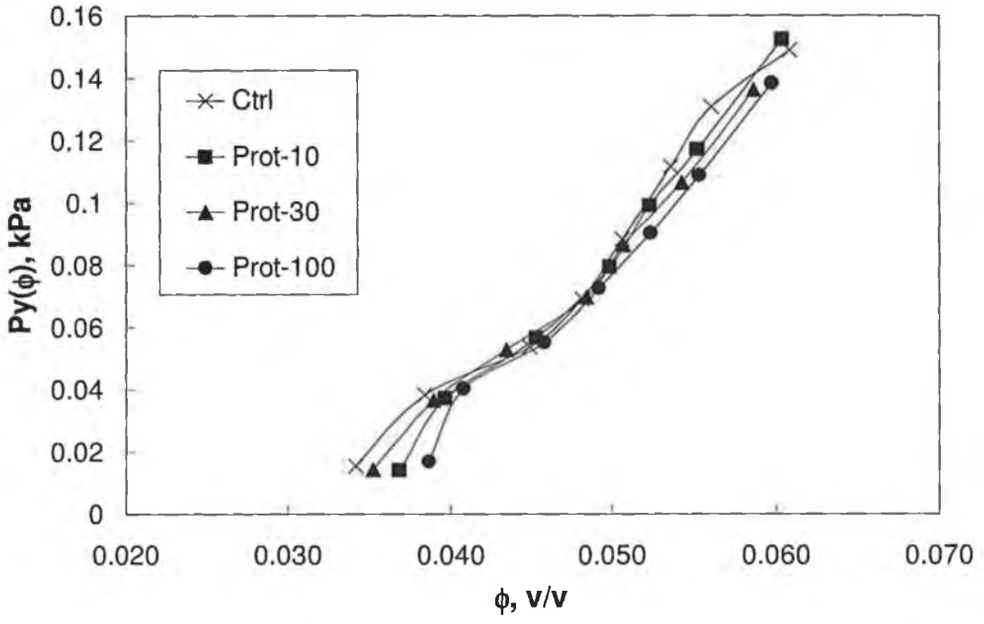


Figure 6.33 $P_y(\phi)$ vs ϕ determined from centrifugal scrape tests after addition of enzymes to sludge (Trial 1).

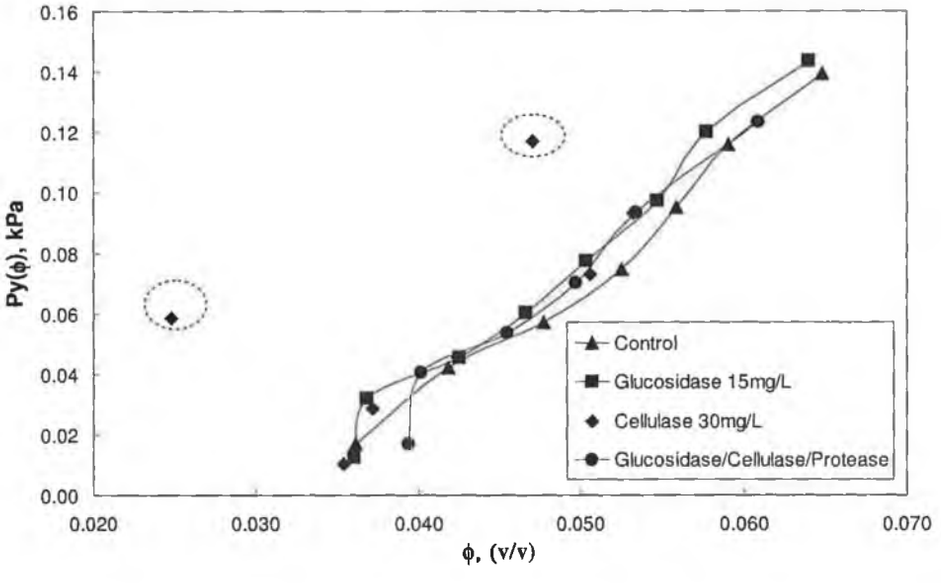


Figure 6.34 $P_y(\phi)$ vs ϕ determined from centrifugal scrape tests after addition of enzymes to sludge (Trial 2).

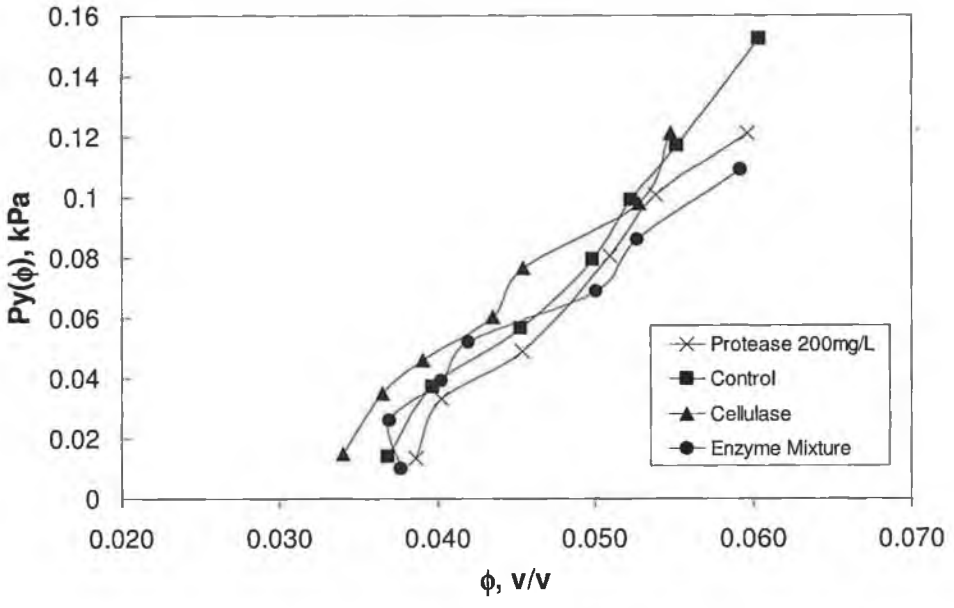


Figure 6.35 $P_y(\phi)$ vs ϕ determined from centrifugal scrape tests after addition of enzymes to sludge (Trial 3).

6.4.3.2 Discussion

During the trials the concentration of solution proteins and polysaccharides was monitored in RA and RB (Figures 6.24 and 6.25). The quantities of both solution proteins and polysaccharides were comparable in each digester. It can be concluded that process conditions were similar for RA and RB. This is reinforced by the solid, gas, and pH data (Figures 6.19 – 6.23). The quantity of solution protein was in excess of polysaccharide in both digesters. The average protein: polysaccharide ratio in RA was 4.4, while it was 5.5 for RB. This is in keeping with Novak *et al.* (2003) who reported that during batch digestion experiments the quantity of solution proteins in an anaerobic system was 3-5 times greater than that of solution polysaccharide.

The addition of the enzymes did not greatly alter the properties of the sludge, with the 3 Trials producing only minor changes in solids destruction, solution biopolymers, settling rates and compressibility. Ayol (2005a) observed a reduction of over 50% in solution protein levels by applying a commercial enzyme mixture (100 mg/L) to sludge. The product consisted of a mixture of protease, lipidase, anaerobic bacteria, *Aspergillus oryzae* and an enzyme complex mixture (other hydrolytic enzymes). The concentrations of the individual constituents of this mixture were not reported in the paper. In contrast, the enzymes which were used in this research were of known constituency, concentration and of high purity. It is possible that due to the wider range of enzymes in the mixture reported by Ayol (2005a) some component or components of the mixture had a more significant impact on sludge dewatering than others. Notably, the enzyme mixture utilised by Ayol (2005a) contained lipidase, which was not used in the experiments reported here.

In this study, the addition of protease at 30mg/L resulted in a 13% reduction in solution protein, while the addition of 100 mg/L of protease resulted in an 8% reduction in solution protein (Figure 6.26). Increased levels of solution proteins and polysaccharides were detected after the addition of glucosidase and the 3-enzyme mixture (Figure 6.27 and Figure 6.28). The enzymes added had limited effect on the concentration of, and may have contributed to, the level of biopolymer being detected, either directly or by eroding extracellular polymers from sludge flocs. The addition of protease at 30 mg/L resulted in the greatest reduction in solution biopolymer (%).

Slightly improved settling rates corresponded with the addition of protease at 100mg/L (Figure 6.29) but there was no discernable effect on $P_y(\phi)$ (Figure 6.33). This may indicate that solution protein plays a more important role than polysaccharides in sludge dewatering properties. None of the enzyme additions had a discernable effect on $P_y(\phi)$. Figure 6.32 shows the Lumifuge data for Trial 3. As the Lumifuge allows for continual online settling analysis the settling curves are smoother, and variations in the curve shape, associated with the braking of the centrifuge at the time of measurement, are not present. The data shows that cellulase addition had negligible effect on the settling properties, however, the addition of protease at a concentration of 200 mg/L and a mixture of protease, cellulase and glucosidase, did improve settling properties in relation to the control sample.

Overall, little discernable change to sludge dewatering properties was achieved by the addition of selected enzymes, with only protease (in isolation) slightly improving sludge settling. No appreciable change occurred in $P_y(\phi)$ for any enzyme addition. In future work it may be more beneficial to use a more broad-ranging enzyme mixture such as that reported by Ayol (2005), with subsequent tests to isolate the components of such a mixture which may improve sludge dewatering properties.

As proteins have been shown to play a significant role in the physical properties of MAD sludge, further work should focus particularly on the addition of protease to sludges, perhaps in larger doses than those reported here. Lectins are also thought to be important

in bioflocculation (Higgins and Novak, 1997), therefore investigating the effects of enzyme addition on lectin in flocs may also be a beneficial for further characterization of enzymatically modified sludges. Also, as enzyme addition alone does not seem to have a major impact on sludge properties, further studies could focus on enzyme pre-treatment to reduce the amount of flocculant required to condition the sludge.

6.4.3.3 Conclusions

- Similar process conditions were achieved in each of two bench-scale anaerobic digesters (working volume 4 L), with 35 – 36% VS removal and production of biogas with a CH_4 content of approximately 55% on a 16 d HRT.

- The quantity of solution polysaccharide was similar in each digester, with a protein:polysaccharide ratio ranging between 4 and 5.5.

- Protease, glucosidase, cellulase were added in varied concentrations to samples of anaerobic sludge which were incubated for 24 hours at mesophilic temperatures.

- Little change in sludge dewatering properties in terms of settling and compressibility occurred after the addition of enzymes, with only the addition of protease and a mixture of all three enzymes slightly improving settleability.

CHAPTER SEVEN: Characterisation of batch-digestion and stored ATAD sludges by centrifugation and pressure-filtration

7.1 Introduction

In this Chapter, further investigations into ATAD dewatering are described. The centrifugation techniques used to characterise MAD sludge in Chapter 6 were used in conjunction with batch settling tests and pressure-filtration to characterise pilot-plant ATAD, and ATAD resulting from the product storage tanks at Killarney WWTP. Principally the work focussed on dewatering properties of sludge resulting from two batch digestions within the pilot-plant. These were conducted using two types of feedstock; a low strength WAS which had not been thickened, and a high strength WAS which had been thickened in a belt-filter press following polyelectrolyte conditioning.

For the investigation of post-storage ATAD sludge, centrifugation scrape tests were also conducted at 2000rpm and 4000rpm (in addition to 1000rpm) to increase the range of the $P_y(\phi)$ data sets. Ferric sulphate and ZETAG 7867 polyelectrolyte were investigated as conditioning agents for post-storage ATAD sludge.

7.2 Dewatering properties as a function of digestion time

7.2.1 Introduction

Batch digestions were necessary to isolate the changes in sludge dewatering properties during ATAD digestion. The retention time trials outlined in Chapter 4 and 5 described ATAD dewatering properties at steady-state conditions at 7d and 10d retention times. The temperature of operation was always within the thermophilic region during these trials. The principle aim of batch digestion was to assess incremental changes in sludge dewatering properties as a function of digestion time and temperature. The use of centrifugation allowed for multiple samples to be characterised simultaneously. This overcame the long time periods required for pressure-filtration characterisation. Two batch digestions were conducted.

7.2.2 Trial 1

During Trial 1, a WAS sludge was used as the pilot-plant feedstock. This WAS had been thickened to 4.95% (w/w) using the belt-filter press, and conditioned with ZETAG 7869 at 3g/kg DS. During the trial, the temperature of the pilot-plant peaked at 60 ^{o}C between day 3 and day 4 of digestion; true thermophilic conditions. TS decreased from 4.95% to 4% between day 1 and day 6 of the trial. VS decreased from 3.86% (w/w) to 2.72% (w/w) between day 1 and day 6 of the trial, a 29.5% reduction in VS.

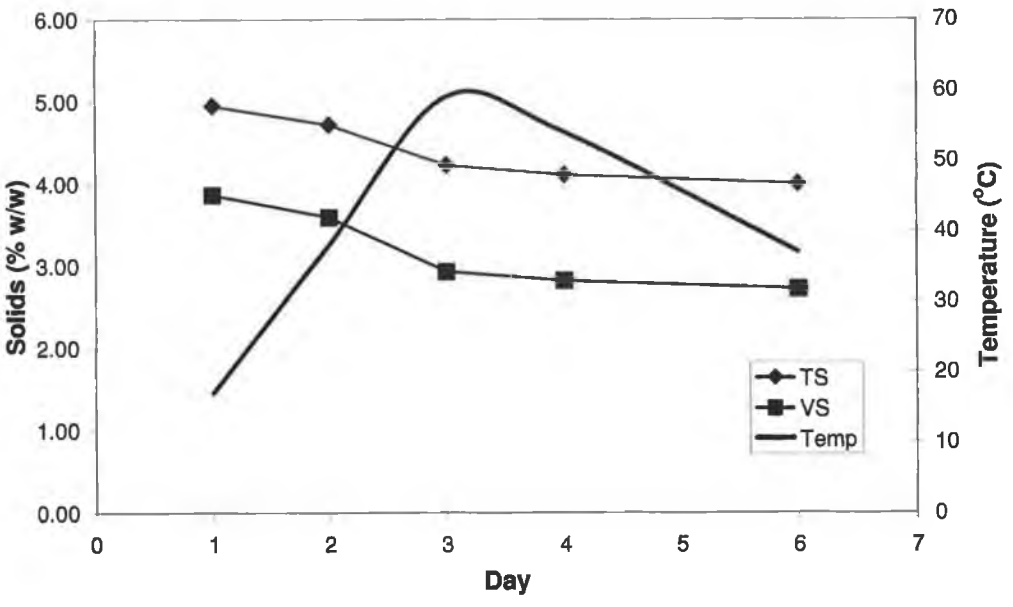


Figure 7.1 Solids (% v/v) and temperature within the pilot-plant during batch digestion (Trial 1)

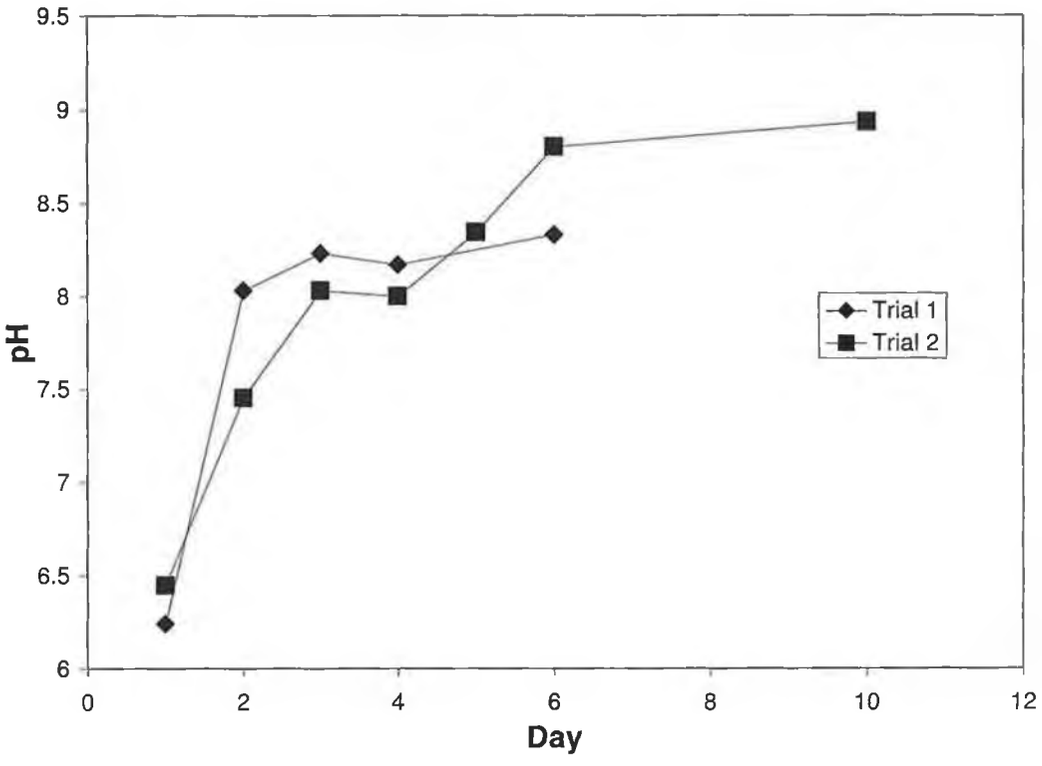


Figure 7.2 pH of pilot-plant sludge during batch digestions (Trial 1 and Trial 2)

A large quantity of solution biopolymer was released into solution during Trial 1. The soluble COD of the sludge increased from 754 mg/L at the start of the Trial to 3988 mg/L following 4 days of digestion. There was a corresponding increase in solution protein and polysaccharide (Figure 7.3). This was reflected by an increase in the OPD (Table 7.1), which correlated very strongly with the quantities of biopolymers in the solution phase of the sludge (Figure 7.4). The initial large increase in soluble COD, during the first 3 days of the trial, was likely to have resulted from endogenous respiration, and to some extent, it may have resulted from heat-shock effects due to high temperatures. During endogenous respiration cell lysis results in intracellular organic material being released into solution. Following 4 days of digestion the OPD was 22 g/kg DS. This is similar to

the post-storage ATADs, but much lower than that obtained for the pilot-plant during the retention time trials reported in Chapter 5.

Table 7.1 Optimum polymer dose values for pilot-plant sludge (trial 1 and 2)

TRIAL 1						
Day	**1**	**2**	**3**	**4**	**5**	**10**
OPD (g/Kg TS)	5	5	9	10	11	10
TRIAL 2						
Day	**1**	**2**	**3**	**4**	**6**	
OPD (g/Kg TS)	4	6	18	22	20	

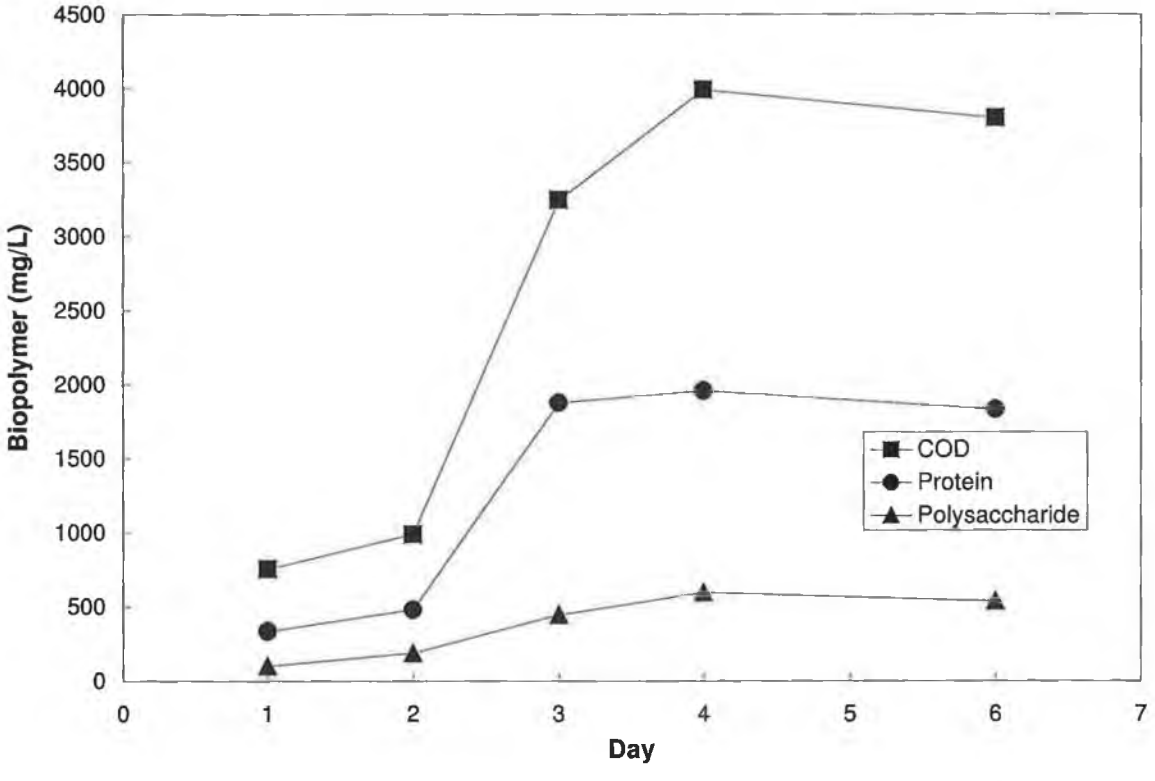


Figure 7.3 Solution COD, protein, and polysaccharide within the pilot-plant during batch digestion (Trial 1)

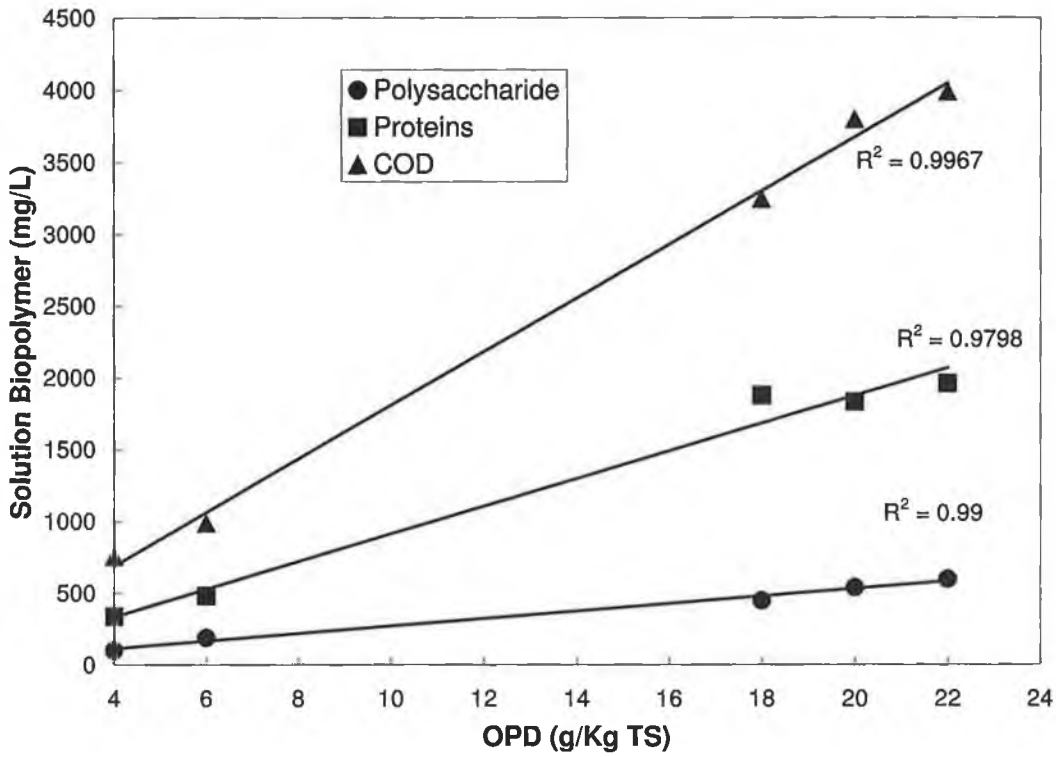


Figure 7.4 Solution COD, protein, and polysaccharide plotted against the optimum polymer dose (OPD) for pilot-plant sludge (Trial 1)

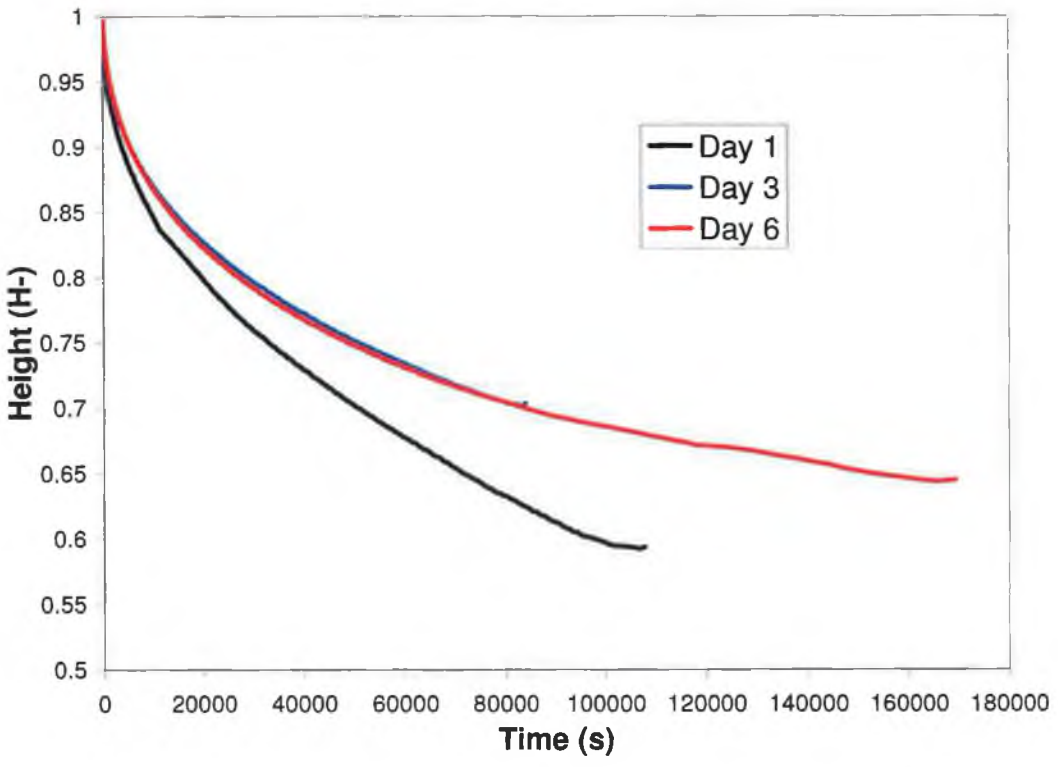


Figure 7.5 Dimensionless suspension height (H-) as a function of time for pressure-filtration testing at 200 kPa during Trial 2.

Centrifugation settling tests were not conducted on the sludge obtained from the pilot-plant during trial 1. Three separate pressure-filtration tests were conducted on the trial sludge at an applied pressure of 200 kPa using the air-driven filtration rig. These were conducted on Day 1, 3 and 6 of digestion. Figure 7.5 shows the dimensionless height of the suspension (h/h_0) during each filtration test. The suspension height was calculated according to Equation 3.6. The change in suspension height is directly proportional to the rate at which filtrate is expressed through the filter membrane during filtration. Longer filtration times represent poorer dewatering properties. There was a significant increase in

filtration time, between Day 1 and Day 3 of digestion, while the filtration times for Day 3 and Day 6 were similar.

Zhou *et al.* (2002) found that ATAD sludge dewatering properties deteriorated significantly over a short period of time during a batch digestion trial conducted at 60 °C. The principal deterioration occurred within the first 24 hours of digestion. Following several more days of digestion they found that dewatering properties, as measured by the CST test, then improved slightly or remained similar. During Trial 1, the increase in filtration time occurred between Day 1 and Day 3 of digestion and filtration times were similar for Day 3 and Day 6, this may be representative of similar mechanisms occurring as were reported by Zhou *et al.* (2002). Overall, during Trial 1 there was a significant deterioration in dewatering properties in the first 3 days of digestion. This corresponded to an increase in biopolymeric material into solution which correlated strongly with the OPD.

7.2.3 Trial 2

The second batch digestion was conducted on using a WAS sludge of low solids (2.54% w/w) concentration as the feedstock (Figure 7.6), and was conducted over a longer time period (11 days). The WAS feedstock was sampled from the picket-fence thickener. This feedstock differed significantly from that used in Trial 1, and the retention time trials reported in Chapter 5, insofar as the sludge had not been conditioned using polyelectrolyte, or thickened by belt-filter press. These steps are usually necessary to

increase the solids concentration of the sludge for ATAD digestion. Because of this, the calorific content of the sludge was probably not high enough to attain thermophilic temperatures within the pilot-plant (Figure 7.6).

The DS of the sludge decreased from 2.54% on day 1 to 1.85% by day 10, with a corresponding decrease in VS from 1.86% to 1.24% (a 33.33% reduction in VS). The highest temperature attained during the trial was 42.5 °C on day 3 of digestion. The OPD increased to a maximum of 11 kg/tDS following 10 days of digestion (50% of the OPD following 6 days of digestion in Trial 1).

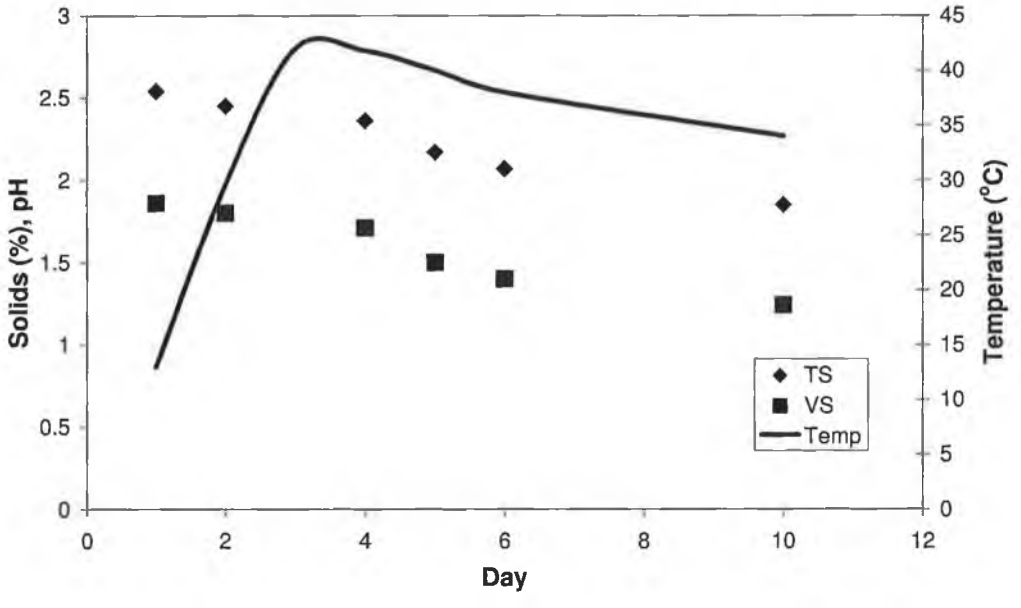


Figure 7.6 Solids (% v/v) and temperature within the pilot-plant during batch digestion (trial 2)

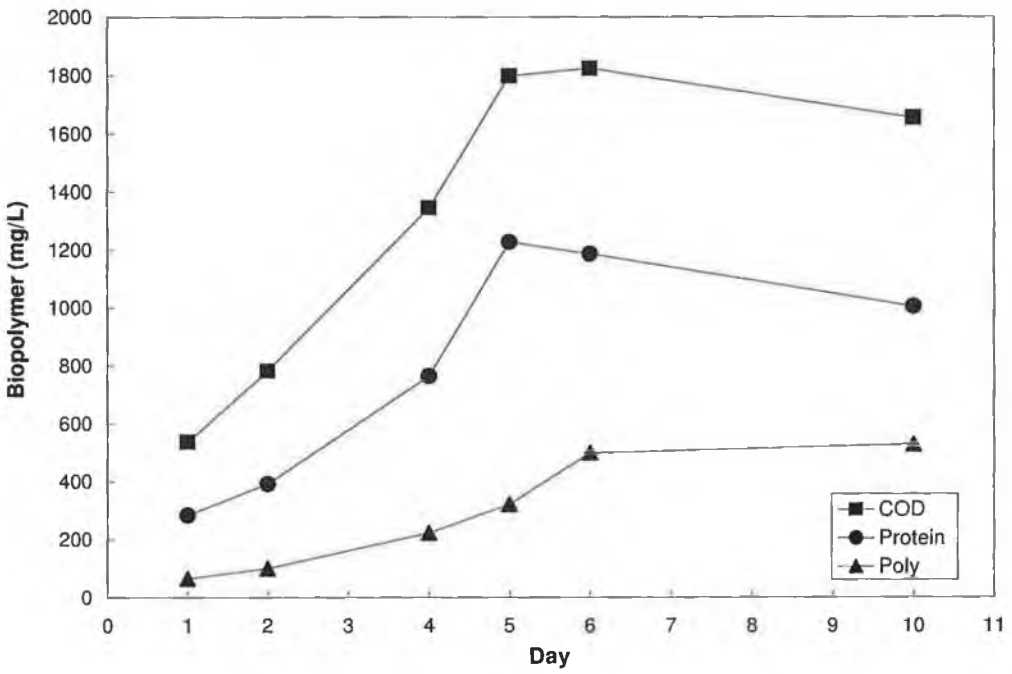


Figure 7.7 Solution COD, protein, and polysaccharide within the pilot-plant during batch digestion (Trial 2)

The concentration of solution COD, proteins and polysaccharides also increased during Trial 2. The increases were not as notable as those during Trial 1, and this is likely to have been the cause of the lower OPD. Soluble COD increased to a maximum of 1823 mg/L following 6 days of digestion, and then decreased to 1654 mg/L by Day 10 of digestion. Solution COD, solution polysaccharide and proteins all corresponded positively with the OPD (Figure 7.3). The strongest correlation was solution COD (R^2 = 0.9575).

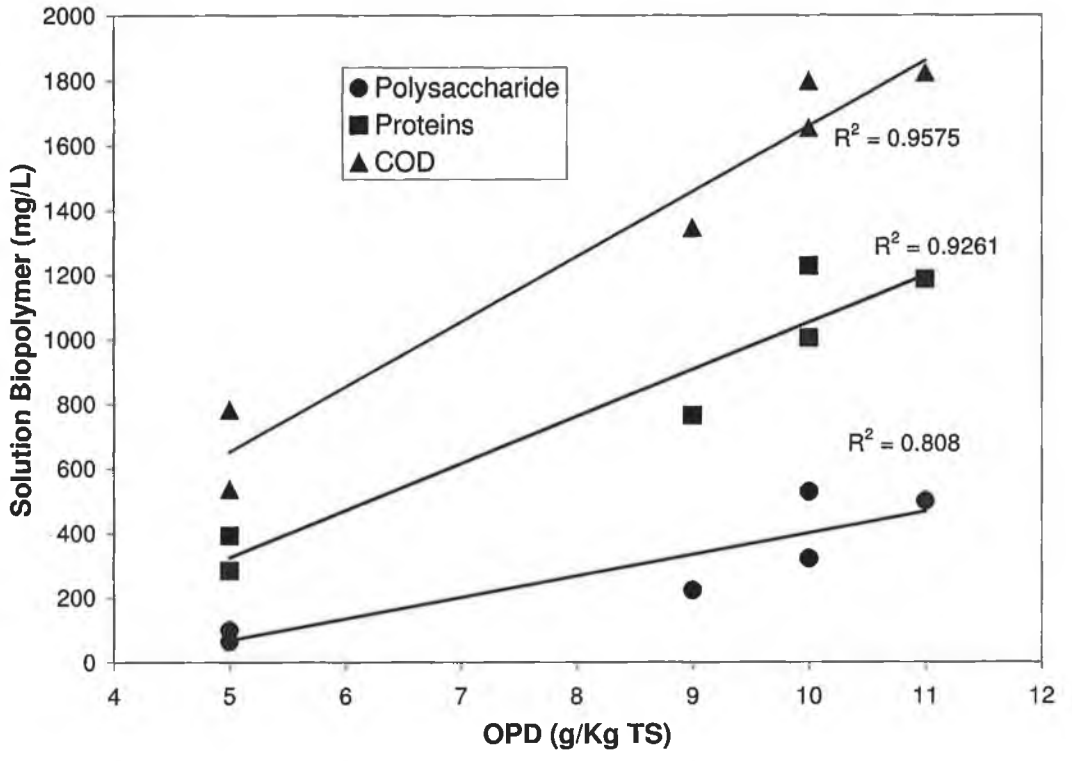


Figure 7.8 Solution COD, protein, and polysaccharide plotted against the optimum polymer dose (OPD) for pilot-plant sludge (Trial 2)

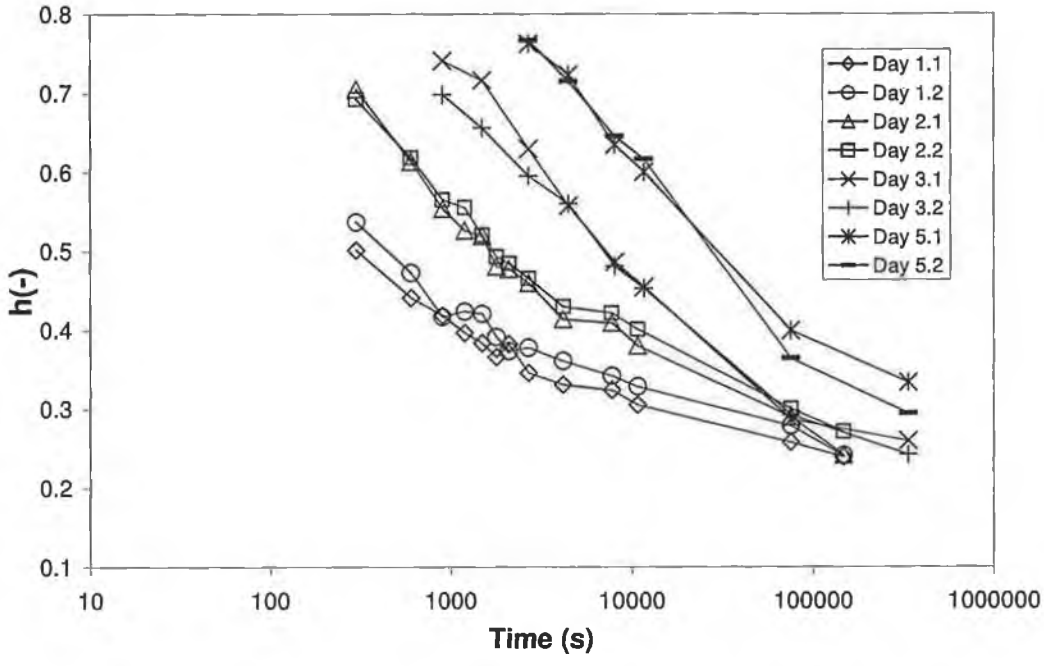


Figure 7.9 Transient centrifugal settling data (1000 rpm) for batch digestion pilot-plant sludge (Trial 2).

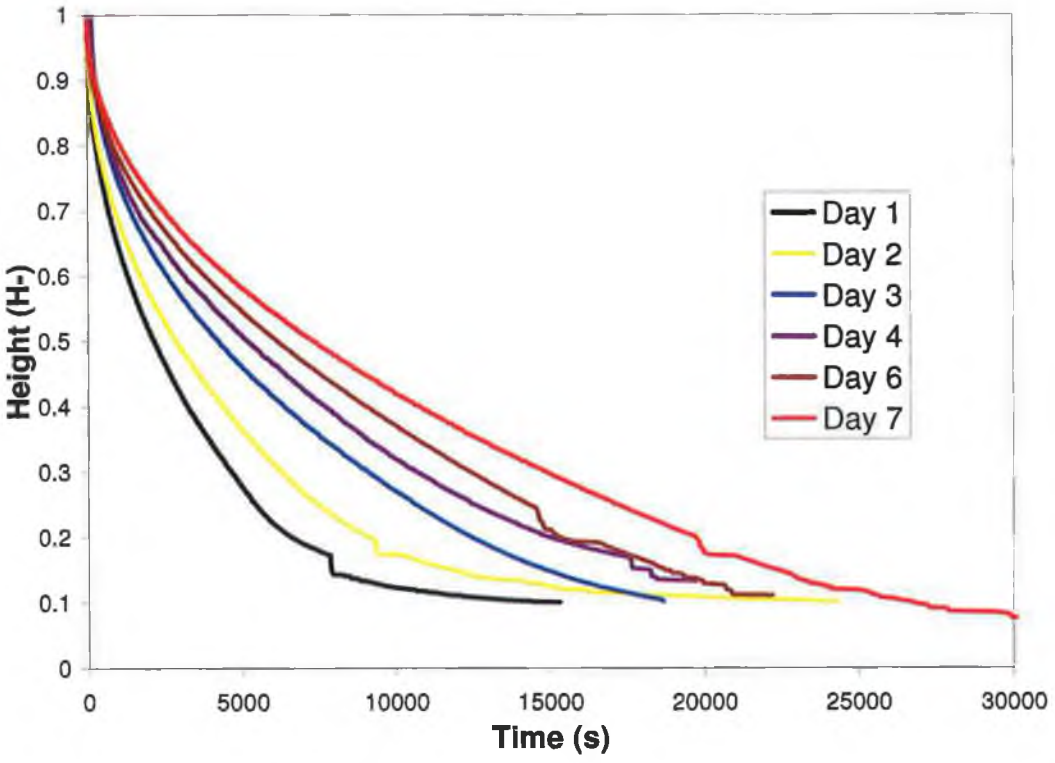


Figure 7.10 Dimensionless suspension height (h-) as a function of time for pressure-filtration testing at 200 kPa during Trial 2

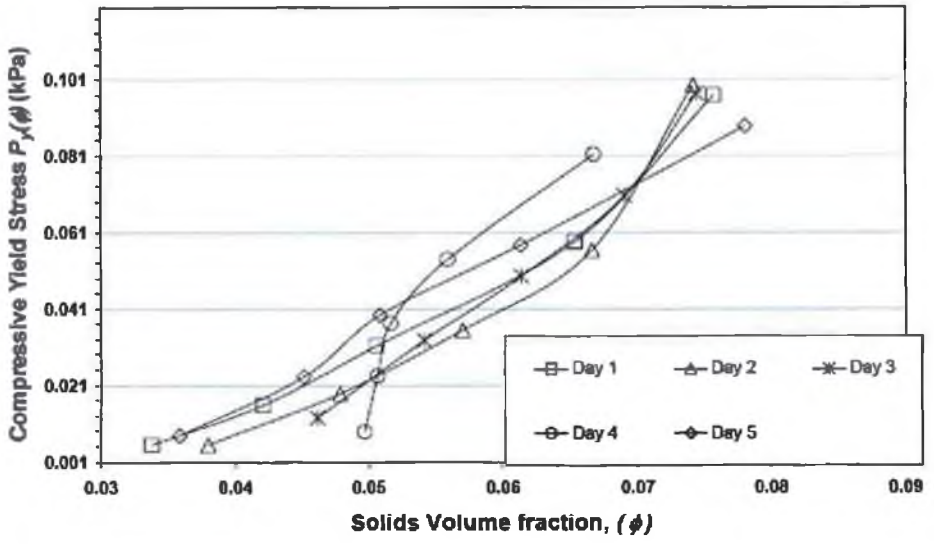


Figure 7.11 $P_y(\phi)$ versus ϕ for batch digestion pilot-plant sludge (trial 2)

More extensive dewatering tests were conducted on the sludge during Trial 2. Centrifugation at 1000 rpm was introduced to give a measure of settling rate and to provide data to calculate $P_y(\phi)$. Figure 7.9 gives the settling rate of the solid-liquid interface (at 1000 rpm) as a function of digestion time for the sludge during Trial 2. The duplicate tests show good agreement. Overall there was a significant decrease in the settling rates of the pilot-plant sludge as a function of digestion time. This was expected. It is known that the settling properties of sludge worsen as a function of digestion time in secondary sludge treatment (Novak *et al.*, 2003), and the poor settling properties corresponded with an increase in solution biopolymers and the OPD.

Following a prolonged period of settling, the sludges converge towards a single height which suggested that the $P_y(\phi)$ of the sludges would not differ significantly. This shows that settling behaviour, and by inference $R(\phi)$, is a better indicator of biosludge dewatering behaviour.

Pressure-filtration tests were also conducted on the sludge at 200kPa during the batch digestion (Figure 7.10 and Table 7.2). Figure 7.10 shows the calculated dimensionless height of the sediment in the filtration chamber. It must be noted that this does not reflect the rate of settling of the sludge, but rather the rate of expression of filtrate through the filter membrane. As with the centrifugation settling tests, a trend of deteriorating dewatering properties was evident as a function of digestion time. When corrected for solids concentrations (decreasing as digestion progressed), the deterioration in dewatering properties is further emphasised.

Figure 7.11 outlines $P_y(\phi)$ as a function of digestion during Trial 2. There was little variation in $P_y(\phi)$. This suggested that for an unconditioned sludge like this, which had gone through

significant structural change, due to cell lysis and solubilisation, the ultimate compressibility was independent of these factors. Table 7.2 presents the ϕ_f and fitted ϕ_∞ obtained from pressure-filtration tests conducted on the sludge on consecutive days.

Table 7.2 ϕ_f and predicted ϕ_∞ from pressure-filtration (200kPa) of sludge during Trial 2

Day	1	2	3	4	5	7
ϕ_f	0.1477	0.1554	0.1642	0.181	0.164	0.133
ϕ_∞	0.1692	0.1566	0.1669	0.2183	0.2191	0.1683

7.2.3 Conclusions

- During two batch digestion trials the settling properties of sludge resulting from the ATAD pilot plant deteriorated as a function of digestion. The quantity of biopolymeric material in solution also increased as a function of digestion during both trials, and this correlated strongly with an increase in the OPD.

- The batch digestion of thickened WAS sludge generated thermophilic temperatures (as high as 60 °C) and resulted in a marked deterioration in dewatering properties over a short period of time. The digestion of unconditioned WAS generated mesophilic temperatures (~ 40 °C) and a more gradual deterioration in dewatering properties. Both digestions resulted in the release of large quantities of biopolymeric materials into the solution phase; COD, proteins, and polysaccharides, and these correlated strongly with the OPD.

- Overall, digestion at 60 °C caused a greater deterioration in dewatering properties than digestion at 40 °C. It is possible that thermophilic temperatures resulted in a heat-shock effect releasing intractable material into solution which increased the OPD, and thermophilic aerobic bacteria may be less adapted to utilising complex substrates than mesophilic aerobic digestion (laPara *et al.,* 2001). However, it must be noted that the sludge used in Trial 2 had been conditioned with polyelectrolyte before digestion, and had a higher concentration of solids than that used in Trial 1, and these factors may also have contributed to poor dewatering.

7.3 Centrifugation analysis of post-storage ATAD sludges

7.3.1 Introduction

In this section centrifugation tests are described which were conducted on post-storage ATAD sampled from product storage tank 4 (PS4). Scrape-tests were conducted on sludge which had been centrifuged at 1000, 2000 and 4000 rpm to extend the range of the $Py(\phi)$ data to include higher ϕ. Centrifugation scrape-tests and settling tests were also conducted on post-storage ATAD which had been conditioned using ferric sulphate, and ZETAG 7869 cationic polyacrylamide.

7.3.2 Scrape-tests at 1000, 2000 and 4000 rpm on unconditioned sludge.

To extend the range of ϕ determined by centrifugation scrape-tests, equilibrium settling was conducted on a post-storage ATAD at 2000 and 4000 rpm in addition to 1000 rpm. A sample from PS4 with an assumed solid density of 1300 kg/m^3 was used in the scrape-tests. ϕ_0 was 0.0176. Figure 7.12 gives the $P_y(\phi)$ data that was obtained from the tests. The data shows a well described curve, with the data obtained from the 1000, 2000 and 4000 rpm tests showing approximate agreement.

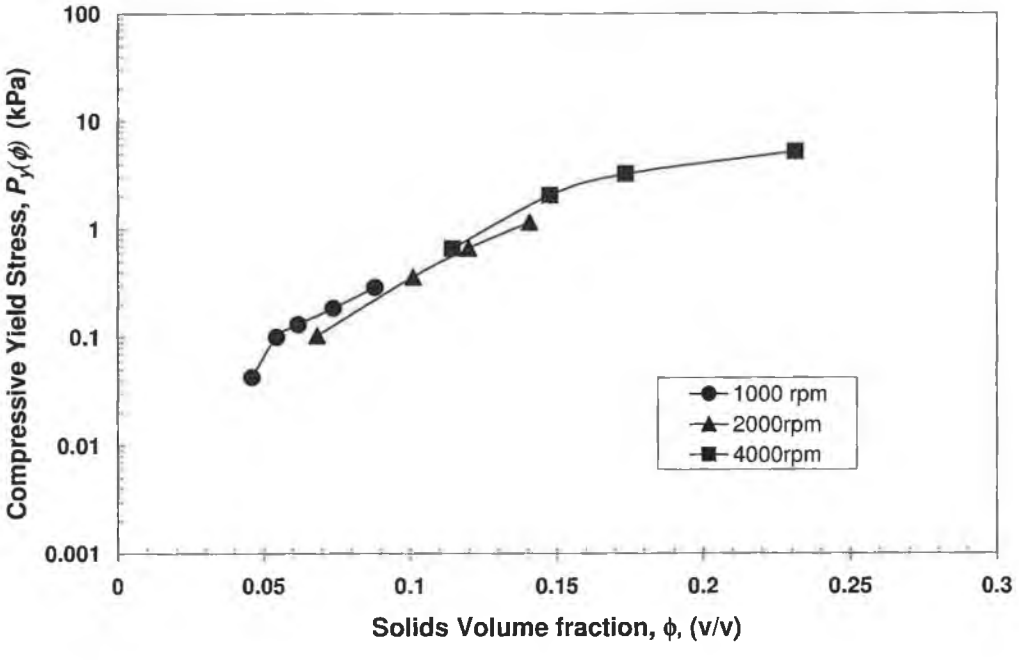


Figure 7.12 $P_y(\phi)$ as a function of ϕ for PS4 sludge. Data obtained from centrifugation scrape-tests at 1000, 2000 and 4000 rpm.

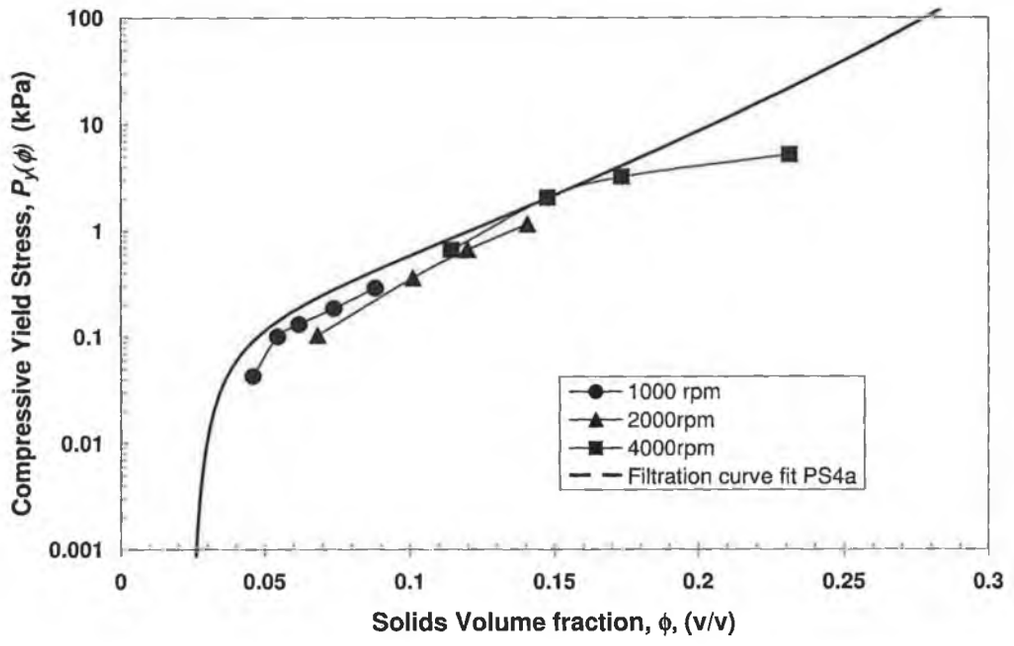


Figure 7.13 $P_y(\phi)$ as a function of ϕ for PS4 sludge. Data obtained from centrifugation scrape-tests at 1000, 2000 and 4000 rpm, also shown $P_y(\phi)$ curve fit obtained from previous filtration testing.

The data obtained from centrifugation scrape tests is compared with a curve-fit obtained from pressure-filtration of PS4 (described in Chapter 5). The filtration curve-fit and the centrifugation data describe a similar $P_y(\phi)$ functional form, however, either the centrifugation scrape-tests are over estimating $P_y(\phi)$ or the filtration tests are underestimating it. The sludge used in filtration testing was conditioned with ZETAG 7869 at a concentration of 24 kg/tDS. This may have also have affected the compressibility, due to steric effects.

7.3.3 Centrifugation tests on ferric-conditioned and polyelectrolyte-conditioned ATAD

Figure 7.14 gives centrifugal settling data for post-storage ATAD conditioned using ferric sulphate. The sludge was sampled from PS4. The data are presented on semi-logarithmic co-ordinates, due to the long settling times which occurred. Ferric sulphate was added at four different concentrations; 0.039, 0.052, 0.06 and 0.1g/gDS.

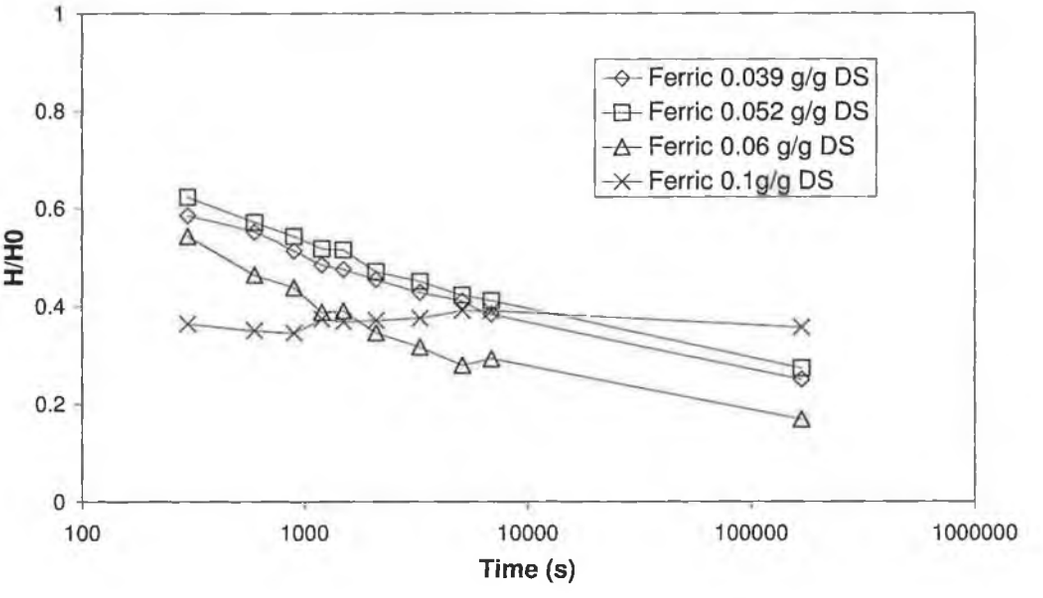


Figure 7.14 Transient centrifugal settling data (1000 rpm) for post-storage ATAD conditioned using ferric sulphate.

The sludge settled fasted when dosed with ferric at a concentration of 0.1 g/g DS. However, such a high dose of ferric added significantly to the solids concentration of the

sludge, impacting the height the sludge finally settled to. A ferric concentration of 0.06 g/g DS improved the extent of sludge settling; in comparison to the other doses.

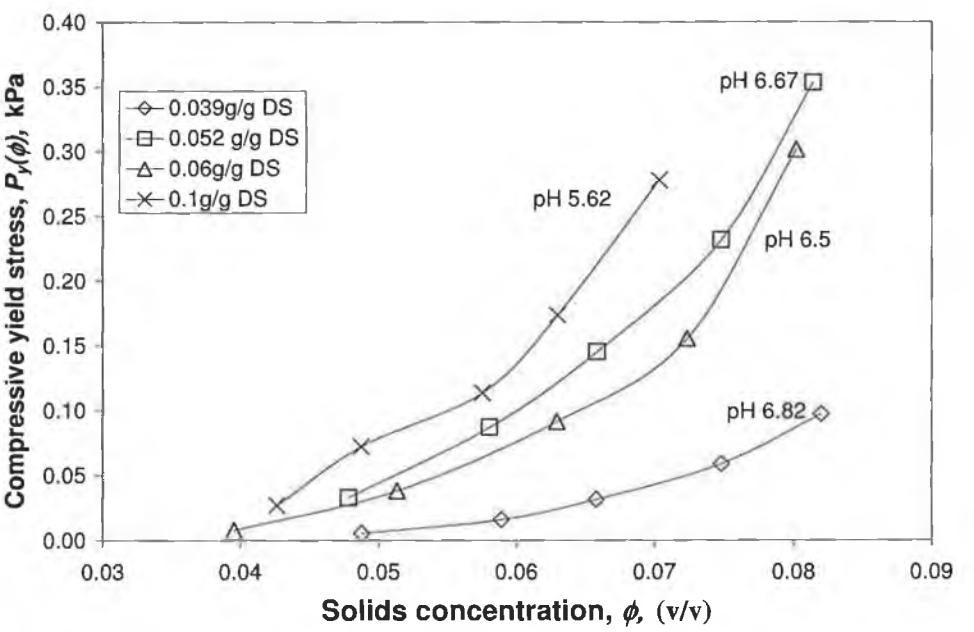


Figure 7.15 $P_y(\phi)$ versus ϕ for post-storage ATAD conditioned with ferric sulphate at different concentrations. The pH of the sludge is also shown.

Figure 7.15 gives $P_y(\phi)$ for post-storage ATAD which was conditioned with ferric sulphate. The use of ferric sulphate as a conditioning agent had a notable impact on the sludge compressibility. Generally, the greater the quantity of ferric sulphate used, the poorer the sludge compressibility. The use of another ferric salt, ferric chloride, as a conditioning agent for ATAD biosolids, was investigated by Murthy (1998). When used in conjunction with a high weight cationic polyeletrolyte, relatively small amounts of

ferric chloride were found to greatly reduce the quantity of polyeletrolyte required to obtain the OPD.

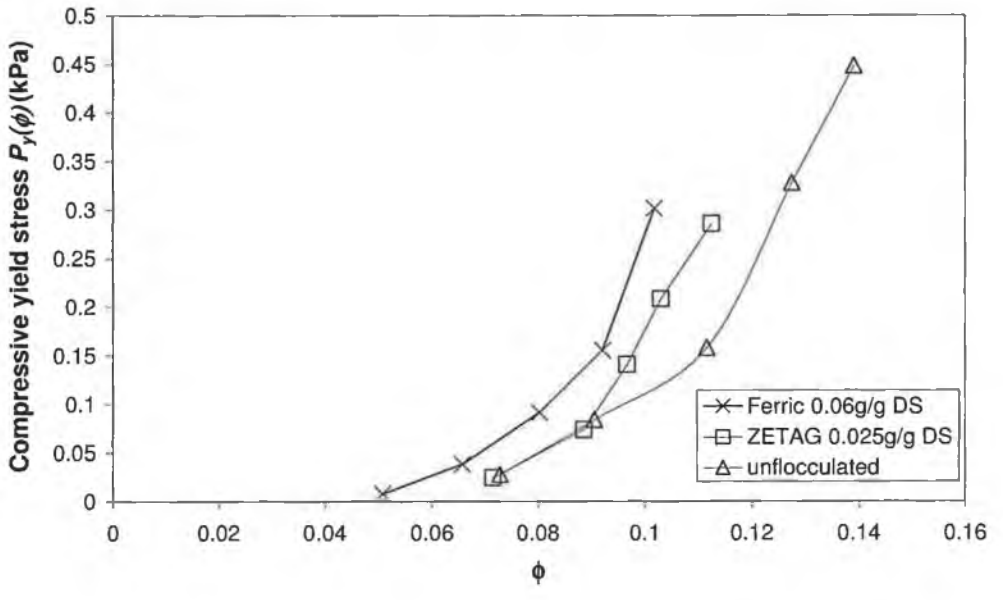


Figure 7.16 $P_y(\phi)$ versus ϕ for post-storage ATAD (PS4); unconditioned, conditioned with ferric sulphate, and conditioned with ZETAG 7869 polyelectrolyte.

Ferric sulphate conditioning impacted on sludge compressibility and this is shown in Figure 7.16 in which $P_y(\phi)$ (obtained from centrifugation at 1000rpm) is compared for unconditioned sludge, sludge conditioned with ZETAG 7869, and ferric sulphate-conditioned sludge. Sludge conditioned at 0.06g/g DS ferric sulphate was selected, as this was found to be the optimum dose in the dewatering tests. The ferric sulphate conditioned sludge had the poorest compressibility of the three sludges, as measured as $P_y(\phi)$. The unconditioned sludge had the best compressibility, but this would have been offset by long settling times.

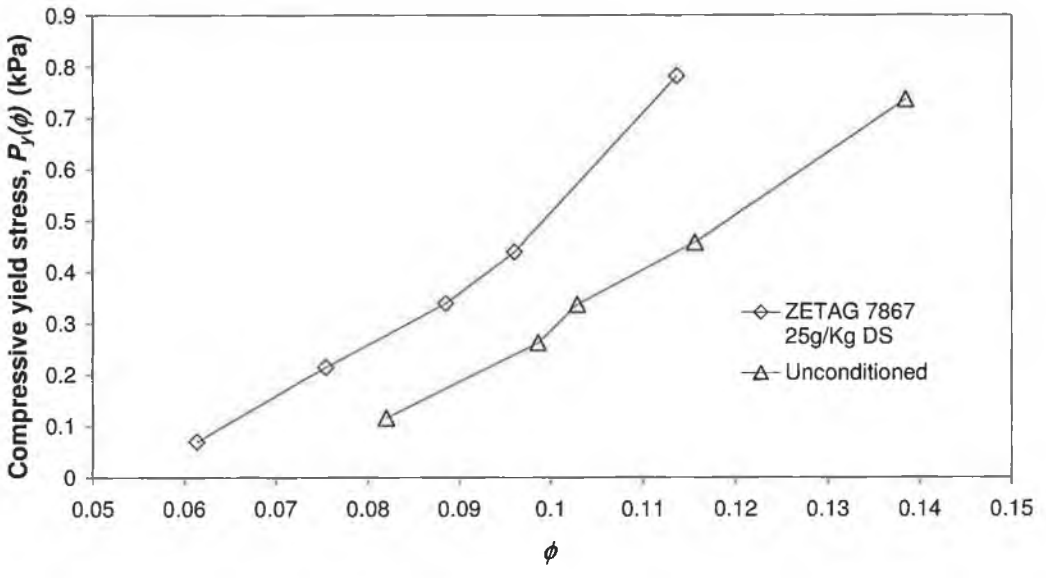


Figure 7.16 $P_y(\phi)$ versus ϕ for unconditioned and conditioned post-storage ATAD sludge. Data obtained from equilibrium scrape test at 1000rpm

Conditioning with ZETAG 7867 was also found to impact on sludge compressibility (Figure 7.16). Unconditioned sludge was significantly more compressible than conditioned sludge.

7.3.4 Conclusions

- Centrifugation scrape tests at 1000 rpm, 2000 rpm and 4000 rpm were used to describe $P_y(\phi)$ for a post-storage ATAD. The resulting data described a ϕ curve ranging from 0.04 to 0.25 (v/v). This was compared to a functional form obtained

from filtration testing of conditioned post-storage ATAD (ZETAG 7869 at 24 kg/tDS). The conditioned sludge was slightly less compressible.

- Ferric sulphate conditioning improved ATAD sludge settling characteristics. However, it had a significant impact on sludge compressibility.

- Post-storage ATAD was less compressible following conditioning with ZETAG 7869 polyeletrolyte.

CHAPTER EIGHT: Conclusions and further work

8.1 Conclusions and major outcomes

The work presented in this thesis involved the application of novel suspension characterisation dewatering techniques to various types of sewage sludge (which exhibit non-traditional filtration behaviour). The experimental techniques allowed for sewage sludge dewatering to be quantified directly in terms of compressive-rheology parameters. The properties examined were the compressive yield stress, $P_y(\phi)$, the hindered settling function $R(\phi)$, and diffusivity, $D(\phi)$. These are fundamental material dependent properties, and they represent a much sounder scientific basis for evaluating dewatering characteristics than other empirically and non-material dependent properties such as the capillary suction time (CST). A range of experimental and modelling techniques were employed to determine these properties for sludges across a range of solids concentrations, from the low solids regime (batch settling) to the intermediate (centrifugation and pressure filtration) and the high solids regime (pressure filtration).

The primary focus was on ATAD dewatering, though several other types of sewage sludge were also investigated. This work encompassed the first application of compressive rheology tools in the characterisation of ATAD sludges. ATAD dewatering was investigated in depth, and a 500 litre ATAD pilot-plant was operated under controlled process conditions on site at Killarney WWTP. This allowed comparison of the pilot-plant ATAD with ATAD produced at the full-scale works in Killarney, and furthermore, ATAD sludges from treatment plants in Germany and Luxembourg were

also investigated. The characterisation results were brought together to illustrate the generic properties of ATAD sludges. In addition to ATAD sludges, activated sludges and mesophilic anaerobic sludges were also characterised as part of this work. Sludge conditioning methods such as freeze-thaw conditioning and the application of cationic polyelectrolytes (for flocculation) and ferric sulphate (for coagulation) were also evaluated.

Overall the results showed that ATAD varied widely in terms of dewatering properties. Most ATAD sludges examined had similar compressive properties to other wastewater treatment sludges, but were exceptionally impermeable to varying degrees. ATAD resulting from the pilot-plant and directly from the ATAD digesters at Killarney exerted an exceptionally high polymer demand, and could not be realistically conditioned or dewatered. However, ATAD which had been stored in the large post-process storage tanks at Killarney was readily dewaterable at polymer doses of 22-33 kg/tDS cationic polymer. Once conditioned, the post-process ATAD was roughly comparable, and sometimes had better properties, than mesophilic anaerobic sludges in terms of its permeability. ATAD from treatment plants in Germany and Luxembourg was shown to be much more readily dewaterable, with lower polymer doses required than the ATAD from Killarney. It is thought the presence of primary sludge in the feed to these ATAD plants resulted in a more dewaterable product.

Endeavours were made to correlate specific types of solution phase biopolymers to sludge dewatering properties. For all types of sludge these were shown to correlate

strongly with polymer requirements. In particular strong correlations were shown to exist between the presence of polysaccharides in solution and the polymer requirements of sludge. Polysaccharides were also shown to be recalcitrant in solution at different retention times for ATAD and resistant to digestion. Post-process storage effected a marked improvement in ATAD dewaterability at Killarney and this was linked to a decrease in solution biopolymers during storage. Storage of mesophilic anaerobic sludge at 5 ^{o}C resulted in a linear increase of protein in solution. This however, could not be linked to a change in dewatering properties.

The level of biopolymers in solution for ATAD sludges was shown to be dependent on temperature and digestion time, and this was also linked to the optimum polymer dose. Batch digestions illustrated a temporal accumulation of solution biopolymer, and this correlated with increasing polymer dose and poorer dewatering properties. Overall, it is concluded that the ATAD process should not be employed in situations where dewatering of the final product is a necessity. Poor dewatering appears inherent to the ATAD process and the associated conditioning costs to achieve a readily dewaterable ATAD sludge offset the economic benefits of the process.

As solution biopolymers were clearly linked to poor sludge dewatering, one logical approach to offsetting this is to supplement the enzymatic activities of sludge biomass by the addition of commercial enzymes. A series of trials were devised to investigate whether the addition of protease, glucosidase, and cellulase to mesophilic anaerobic sludge would enhance sludge dewatering properties and reduce the level of solution

biopolymers. The addition of these enzymes was not shown to affect anaerobic sludge dewatering properties.

8.2 Further work and future directions

- Farther development and refinement of the biosludge characterisation protocol. At present the methods involved are exceptionally time consuming. A full characterisation of a single sewage sludge, across the full range of solids concentrations (from the gel-point to concentrations obtained from pressure filtration) currently involves at least two batch settling tests, several pressure-filtration tests and several centrifugation tests. This takes several weeks. Improved modelling techniques allowing fitting of end-points to limited data (obtained from truncated tests) would be of much use.

- Investigations into the cause of the improvements in dewatering properties that resulted during the post-porcess storage of ATAD sludge. It was shown that solution biopolymers decreased during storage. It needs to be established whether active digestion was occurring in these tanks (and if so what sort of biomass was responsible for it) or whether it was caused by the presence of enzymes which may be reactivated during the cooling regime.

8.3 Overview

The work presented in this thesis has set a new benchmark for the understanding of ATAD dewatering. It has quantified the poor dewatering of ATAD sludges in unequivocal terms, and also gives firm direction for future research efforts in the area.

REFERENCES

Adamson, A., W. *Physical chemistry of surfaces* (5th ed.), Wiley, New York (1990).

Agarwal, S., Abu-Orf, M. and Novak, J. T. (2005) Sequential polymer dosing for effective dewatering of ATAD sludges, *Water Research*, **39**, 1301-1310.

Allen, M. (1950) The dynamic nature of thermophily, *Journal of General Physiology*, **33**, 205-214.

Al-Muzaini, S. and Hamoda, M. F. (1999) Selection of an effective sludge dewatering system for a small wastewater treatment plant, *Environment International*, **25**, 983-990.

Amend, J. P. and Shock, L. S. (2001) Energetics of overall metabolic reactions of thermophilic and hyperthermophilic Archae and Bacteria, *FEMS Microbiology Reviews*, **25**, 175-243.

Ardern, E. and Lockett, W. T. (1914) Experiments on the Oxidation of Sewage without the Aid of Filters, *J. Soc. Chem. Ind*, **33**, 523.

Bartlett, J. and Killelea, E. (2001) The characterisation, treatment and sustainable use of biosolids in Ireland, *Wastewater Science and Technology*, **44,** 35 – 40.

Bitton, G. (2005) *Wastewater Microbiology*, John Wiley & Sons, Inc., Hoboken, New Jersey.

Bomio, M. (1990). *PhD Thesis*: *Bioprocess development for aerobic thermophilic sludge treatment*, ETH Zurich, Zurich.

Borowski, S. and Szopa, J. S. (2007) Experiences with the dual digestion of municipal sewage sludge, *Bioresource Technology*, **98**, 1199-1207.

Brock, T. D. (1986) *Thermophiles: General, Molecular and Applied Microbiology*, Wiley-Interscience, New York.

Buscall, R. and White, L. R. (1987) The Consolidation of Concentrated Suspensions. Part 1.-The Theory of Sedimentation, *Journal of the Chemical Society. Faraday Transactions. I, Physical Chemistry in Condensed Phases*, **83**, 873-891.

Campbell, H. W. (2000) Sludge management - future issues and trends, *Water Science and Technology*, **41**, 1-8.

Chen, Y., Chen, Y.-S. and Gu, G. (2004) Influence of pretreating activated sludge with acid and surfactant prior to conventional conditioning on filtration dewatering, *Chemical Engineering Journal*, **99**, 137-143.

Cheremisinoff, N. P. (1996) *Biotechnology for Waste and Wastewater Treatment*, Noyes Publications, New Jersey.

Chmelir, M., Kunschner, A. and Barthell, E. (1980) Water soluble acrylamide polymers: 2. Ageing and viscous flow of aqueous solutions of polyacrylamide and hydrolysed polyacrylamide, *Angew. Makromol. Chem*, **89**, 145-165.

Christensen, G. L. and Dick, R. I. (1985) Specific resitance measurements: Methods and procedures, Journal of Environmental Engineering, **111**, 3, 258-271.

Chu, A., Mavinic, D. S., Kelly, H. G. and Ramey, W. D. (1994) Volatile fatty acid production in thermophilic aerobic digestion of sludge, *Water Research*, **28**, 1513-1522.

Chu, C. P., Lee, D. J., Chang, B.-V., You, C. H., Liao, C. S. and Tay, J. H. (2003) Anaerobic digestion of polyelectrolyte flocculated waste activated sludge, *Chemosphere*, **53**, 757-764.

Colin, F. and Gazbar, S. (1995) Distribution of water in sludges in relation to their mechanical dewatering, *Water Research*, **29**, 2000-2005.

Cousin, C. P. and Ganczarczyk, J. J. (1998) Effects of salinity on physical characteristics of activated sludge flocs, *Water Quality Resource Journal Canada*, **33**, 565.

Darcy, H. P. G. (1856) *Les fontaines publiques de la ville de Dijon*, Dalamont, Paris.

de Kretser, R. G., Scales, P. J. and Boger, D. V. (2002) Compressive rheology: An Overview, *Annual Rheology Reviews: 2002 (British Society of Rheology).*

Dentel (2002) Conditioning: In *Sludge into Biosolids: Processing, Disposal, Utilization* (Ed, Vesilind, P. A.) IWA, London.

Dignac, M. F., Urbain, V., Rybacki, D., Bruchet, D., Snidaro, D. and Scribe, P. (1998) Chemical description of extracellular polymers: Implication on activated sludge floc structure, *Water Science and Technology*, **38**, 45-53.

EC Directive 86/278/EEC (On the protection of the environment and in particular the soil when sewage sludge is used in agriculture)

EC Directive 91/271/EEC (Concerning urban wastewater treatment)

Eloff, J., Pressley, R., Staton, K. M. and and Alleman, J. E. (2000) In *Biosolids Research Needs Conference*, National Science Foundation, Maryland, pp. 120-125.

Fehily, Timony and Co (1998) The Inventory of Non-hazardous Sludges in Ireland Department of the Environment and Local Government.

Fehily, Timony and Co. (1999). Code of Good Practice for the Use of Biosolids in Agriculture-Guidelines for Local Authorities and Wastewater Treatment Plant Operators, Department of the Environment and Local Government.

Forster, C. F. (1971) Activated sludge surfaces in relation to the sludge volume index, *Water Research*, **5**, 861-870.

Forster, C. F. (1985) Factors involved in the settlement of activated sludge--I : Nutrients and surface polymers, *Water Research*, **19**, 1259-1264.

Forster, C. F. (2002) The rheological and physico-chemical characteristics of sewage sludges, *Enzyme and Microbial Technology*, **30**, 340-345.

Frolund, B., Palmgren, R., Keiding, K., and Nielsen, P., H. (1996) Extraction of Extracellular Polymers from Activated Sludge using a Cation Exchange Mechanism, *Water Research*, **30**, 1749-1758.

Gale, R. S. and Baskerville, R. C. (1967) Capillary suction method for the determination of the filtration properties of a solid/liquid suspension, *Chem. Inc.*, **9**, 355-356.

Garnier, C., Gorner, T., Lartiges, B. S., Abdelouhab, S. and de Donato, P. (2005) Characterization of activated sludge exopolymers from various origins: A combined size-exclusion chromatography and infrared microscopy study, *Water Research*, **39**, 3044-

3054.

Gomez, J., Gracia, M. de, Ayesa, E., Garcia-Heras, J. L. (2007) Mathematical modelling of thermophilic aerobic digesters, *Water Research*, **41**, 959-968.

Haas, H. C. and MacDonald, R. L. (1972) Dichotomies in the viscosity stability of polyacrylamide solutions, *Journal of Polymer Science B*, **10**, 461-467.

Harbour, P. J., Aziz, A. A. A., Scales, P. J. and Dixon, D. R. (2001) Prediction of the dewatering behaviour of selected inorganic sludges, *Water Science and Technology*, **44**, 191-196.

Higgins, M. and Novak, J., T. (1997a) Characterisation of exocellular proetein and its role in bioflocculation, *Journal of Environmental Engineering*, **123**, 479-485.

Higgins, M. and Novak, J., T. (1997b) Dewatering and settling of activated sludges: the case for using cation analysis, Water *Environment Research*, **69**, 225-232.

Holbrook, R., D., Hong, S. N., Murthy, S., N. and Surovik, F. (2000) Full-Scale Experience with Conditioning and Dewatering of Thermophilic Aerobically Digested Biosolids, *Florida Water Resources Journal.*

Houghton, J. I. and Stephenson, T. (2002) Effect of influent organic content on digested sludge extracellular polymer content and dewaterability, *Water Research*, **36**, 3620-3628.

Howells, I., Landman, K. A., Panjikov, A., Sirakoff, C. and White, L. R. (1990) Time dependent batch settling of flocculated suspensions, *Applied Mathematical Modelling*, **14**, 77-86.

Hunter, J. V., Genetelli, E. J. and Gilwood, M. E. (1966) In *37th Purdue Industrial Waste Conference* (Ed, Bloodgood, D. E.) Purdue University Publishing, Lafayette, IN, USA.

Jin, B., Wilen, B., and Lant, P. (2003) A comprehensive insight into floc characteristics and their impact on compressibility and settleability of activated sludge, *Chemical Engineering Journal*, **95**, 221-234.

Johnson, S. B., Scales, P. J., Dixon, D. R. and Pascoe, M. (2000) Use of a superthickener device to concentrate potable water sludge, *Water Research*, **34**, 288-294.

Jorand, F. J., Zartarian, F., Thomas, F., Block, J. C., Bottero, J. Y., Villemin, G., Urbain, V. and Manem, J. (1995) Chemical and structural (2D) linkages between bacteria within activated sludge flocs, *Water Research*, **29**, 1639-1647.

Kapur, P. C., Laha, S., Usher, S., de Kretser, R. G. and Scales, P. J. (2002) Modelling of the consolidation stage in pressure filtration of compressible cakes, *Journal of Colloidal and Interface Science*, **256**, 216-222.

Katsiris, N. and Kouzeli-Katsiri, A. (1987) Bound water content of biological sludges in relation to filtration and dewatering, *Water Research*, **21**, 1319-1327.

Keiding, K. and Rasmussen, M. R. (2003) Osmotic effects in sludge dewatering, *Advances in Environmental Research*, **7**, 641-645.

Keiding, K., Wybrandt, L. and Nielsen, P. H. (2001) Remember the water-a comment on eps colligative properties, *Water Science and Technology*, **43**, 17-23.

Kelly, H. G. (2003) Emerging Processes in Biosolids Treatment 2003, In *2nd Canadian Organic Residuals Conference.*

Kelly, H. G. and Mavinic, D. S. (2003) Autothermal Thermophilic Aerobic Digestion Research: Application and Operational Experience *In Thermophilic Digestion: Hot Update!* WEFTEC, Los Angeles.

Kim, Y.-K., Bae, J.-H., Oh, B.-K., Hong Lee, W. and Choi, J.-W. (2002) Enhancement of proteolytic enzyme activity excreted from Bacillus stearothermophilus for a thermophilic aerobic digestion process, *Bioresource Technology*, **82**, 157-164.

Klein, J. and Westerkamp, A. (1981) Peculiarities of polyacrylamide analysis by aqueous GPC., *Journal of Polymer Science*, **19**, 707-718.

La Heij, E. J., Kerkhof, P. J. A. M., Herwijn, A. J. M. and Coumans, W. J. (1996) Fundamental aspects of sludge filtration and expression, *Water Research*, **30**, 697-703.

Landman, K. A., Stankovitch, J.M., and White, L.R. (1999) The Measurement of Filtration Diffusivity D(phi) of a Flocculated Suspension, *American Institute of Chemical Engineering Journal*, **45**, 1875.

Landman, K. A. and White, L. R. (1994) Solid/liquid separation of flocculated suspensions, *Advances in Colloid and Interface Science*, **51**, 175-246.

Landman, K. A. and White, L. R. (1997) Predicting filtration time and maximizing throughput in a pressure filter, *American Institute of Chemical Engineers Journal*, **43**, 3147-3160.

LaPara, T. M. and Alleman, J. E. (1999) Thermophilic aerobic biological wastewater treatment, *Water Research*, **33**, 895-908.

Lapara, T. M., Konopka, A. and Alleman, J. E. (2001) Aerobic biological treatment of a pharmaceutical wastewater: Effect of temperature on COD removal and bacterial community development, *Water Research*, **35**, 4417-4425.

LaPara, T. M., Konopka, A., Nakatsu, C. H. and Alleman, J. E. (2000a) Effects of elevated temperature on bacterial community structure and function in bioreactors treating a synthetic wastewater, *Journal of Industrual Microbiology and Biotechnology*, **24**, 140-145.

LaPara, T. M., Nakatsu, C. H., Pantea, L. M. and Alleman, J. E. (2000b) Phylogentic analysis of bacterial communities in mesophilic and thermophilic bioreactors treating pharmaceutical wastewater, *Applied Environmental Microbiology*, **66**, 3951-3959.

Lapsidou, C. S. and Rittmann, B. E. (2002) A unified theory for extracellular polymeric substances, soluble microbial products, and active inert biomass, Water Research, **36**, 2711-2720.

Lee, D. J. (1994) A dynamic model of the capillary suction apparatus, *Journal of Chemical Engineering of Japan*, **27**, 216-221.

Lee, D. J. (1995) Moisture distribution and removal efficiency of waste activated sludges, Water Science and Technology, **33**, 269-272.

Lee, D. J. and Wang, C. H. (2000) Theories of cake filtration and consolidation and implications to sludge dewatering, *Water Research*, **34**, 1-20.

Li, D. H. and Ganczarczyk, J. J. (1990) Structure of activated sludge flocs, *Journal of Biological Chemistry*, **193**, 365-275.

Liao, B. G., Allen, D. G., Leppard, G. G., Droppo, I. G. and Liss, S. N. (2002) Interparticle Interactions Affecting the Stability of Sludge Flocs, *Journal of Colloidal and Interface Science*, **249**, 372-380.

Liu, H. and Fang, H., P. (2002) Extraction of extracellular polymeric substances (EPS) of sludges, *Journal of Biotechnology*, **95**, 249-256.

Mavinic, D. S. and Koers, D. A. (1979) Performance and kinetics of low-temperature, aerobic sludge digestion, *Canadian Journal of Civil Engineering*, **4**, 445-454.

Matthews, P. (2002) Options for Biosolids Utilization and Sludge Disposal: Agricultural and Other Land Uses, In *Sludge into Biosolids: Processing, Disposal, Utilization* (Eds Vesilind, P.A. and Spinosa, L.) IWA Publishing, London

Metcalf, Eddy, Tchobanoglouos, G., Stensel, H. D. and Burton, F. (2001) *Wastewater Engineering: Treatment Disposal, Reuse*, McGraw-Hill, Toronto.

Mihaltz, P., Kovacs, R., Csikor, Z. and Dahab, M. F. (2003) Degredation rates in thermophilic sludge processing: the liquid and the solid way, In *Wastewater sludge as a resource, Biosolids 2003*(Ed, Odegaard, H.) IWA, Trondheim, Norway.

Mikkelsen, L., H. and Keiding, K. (2002) Physico-chemical characteristic of full scale sewage sludges with implications to dewatering, *Water Research*, **36**, 2451-2462.

Milenko, R. and Zupancic, G. D. (2002) Thermophilic aerobic digestion of waste activated sludge, *Acta. Chim. Slov.*, **49**, 931-943.

Murthy, S., N. , Novak, J., T. and Holbrook, R., D. (2000) Optimizing dewatering of biosolids from autothermal thermophilic aerobic digesters (ATAD) using inorganic conditioners, *Water Environment Research*, **72**, 714-721.

Murthy, S., N., Novak, J., T., Holbrook, R., D. and Sukovitz, F. (1998) Mesophilic aeration of autothermal thermophilic aerobic digester (ATAD) biosolids to improve plant operations, In *Civil Engineering*, Virginia Polytechnic Institute, Blackburg.

Neyens, E., Baeyens, J., Dewil, R. and De heyder, B. (2004) Advanced sludge treatment affects extracellular polymeric substances to improve activated sludge dewatering, *Journal of Hazardous Materials*, **106**, 83-92.

Nielsen, P. H., Thomson, T. R. and Nielsen, J. L. (2003) Bacterial composition of activated sludges- importance for floc and sludge properties, In *Wastewater sludge as a resource, Biosolids 2003* (Ed, Odegaard, H.) IWA, Trondheim, Norway.

Novak, J., T. (2002) Dewatering, In *Sludge into Biosolids: Processing, Disposal, Utilization* (Ed, Vesilind, P. A.) IWA, London.

Novak, J., T. and Park, C. (2003) Chemical conditioning of sludge, *Water Science and Technology*, **49**, 73-80.

Novak, J., T., Sadler, M. E. and Murthy, S., N. (2003) Mechanisms of floc destruction during anaerobic and aerobic digestion and the effects on conditioning and dewatering of biosolids, *Water Research*, **37**, 3136-3144.

Odegaard, H. (2004) Sludge minimization technologies - an overview, *Water Science and Technology*, **49**, 31-40.

Owen, A. T., Fawell, P. D., Swift, J. D. and Farrow, J. B. (2002) The impact of polyacrylamide flocculant solution age on flocculation performance, *International Journal of Mineral Processing*, **67**, 123-144.

Pan, J. R., Huang, C., Cherng, M., Li, K.-C. and Lin, C.-F. (2003) Correlation between dewatering index and dewatering performance of three mechanical dewatering devices, *Advances in Environmental Research*, **7**, 599-602.

Piirtola, L., Uusitalo, R. and Vesilind, A. (2000) Effect of mineral materials and cations on activated and alum sludge settling, *Water Research*, **34**, 191-195.

Piterina, A., McCausland, C., Bartlett, J. and Pembroke, J. T. (2006) Microbial ecology of autothermal aerobic digestion (ATAD): diversity, dynamics and activity of bacterial communities involved in treatment of a municipal wastewater

Ponti, C., Sonnleitner, B. and Fiechter, A. (1995a) Aerobic thermophilic treatment of sewage sludge at pilot plant scale. 1. Operating conditions, *Journal of Biotechnology*, **38**, 173-182.

Ponti, C., Sonnleitner, B. and Fiechter, A. (1995b) Aerobic thermophilic treatment of sewage sludge at pilot plant scale. 2. Technical solutions and process design, *Journal of Biotechnology*, **38**, 183-192.

Rudolfs, W. and Amberg, H. R. (1953) White water treatment. V. Aeration with nonflocculent growths, *Sewage Industrial Wastes*, **25**, 70-78.

Rulkens, W. H. (2003) Sustainable sludge management: What are the challenges for the future? In *Wastewater Sludge as Resource, Biosolids 2003* (Ed, Odegaard, H.) IWA, Trondheim, Norway, pp. 13-20.

Ruth, B. F. (1946) Correlating filtration theory with industrial practice, *Industrial Engineering Chemistry*, **38**, 564-571.

Scisson, J. P. (2003) ATAD, the next generation: design, construction, start-up and operation of the first municipal 2nd generation ATAD, In *Joint Residuals and Biosolids Conference and Exhibition* WEF/AWWA/CWEA.

Smiles, D. E. (1998) Water flow in filter paper and capillary suction time, *Chemical Engineering Science*, **53**, 2211-2218.

Smollen, M. (1990) Evaluation of municipal sludge drying and dewatering with respect to sludge volume reduction, *Water Science and Technology*, **22**, 153-161.

Sobeck, D. C. and Higgins, M. J. (2002) Examination of three theories for mechanisms of cation-induced bioflocculation, *Water Research*, **36**, 527-538.

Sonnleitner, B. and Fiechter, A. (1983) Bacterial diversity in thermophilic aerobic sewage sludge. II. Types of organisms and their capacities, *European Journal of Applied Microbial Biotechnology*, **18**, 174-180.

Spinosa, L. and Lotito, V. (2003) A simple method for evaluating sludge yield stress, *Advances in Environmental Research*, **7**, 655-659.

Sponza, D., T. (2003) Investigation of extracellular polymer substances (EPS) and physiochemical properties of different activated sludge flocs under steady-state conditions, *Enzyme and Microbial Technology*, **32**, 375-385.

Stentiford, E. I. (2002) Sludge Treatment Options: Aerobic Digestion, In *Sludge into Biosolids: Processing, Disposal, Utilization*, (Ed, Vesilind, P. A.) IWA, London.

Stickland, A. D. (2005) *PhD thesis: Solid-liquid separation in the water and wastewater industries*, In Department of Biomolecular and Chemical Engineering, University of Melbourne, Melbourne.

Streebin, L. E. (1968) *PhD thesis*: *Comparison between thermophilic and mesophilic aerobic biological treatment of a synthetic organic waste,* Oregon State University.

Surucu, G. A. (1975) *PhD thesis: Thermophilic aerobic treatment of high strength wastewaters with recovery of protein*, University of Illinois, Illinois.

Suvilampi, J., Lehtomaki, A. and Rintala, J. (2003) Comparison of laboratory-scale thermophilic biofilm and activated sludge processes integrated with a mesophilic activated sludge process, *Bioresource Technology*, **88**, 207-214.

Tezuka, Y. Cation-dependent flocculation in a *Flavobacterium* species predominant in activated sludge (1969) *Applied Microbiology*, **17**, 222-226

The Dumping at Sea Act (no.14 of 1996)

The Waste Management (Use of Sewage Sludge in Agriculture) Regulations (1998)

Tiirola, M. A., Suvilampi, J. E., Kulomaa, M. S. and Rintala, J. A. (2003) Microbial diversity in a thermophilic aerobic biofilm process: analysis by length heterogeneity PCR (LH-PCR), *Water Research*, **37**, 2259-2268.

Tiller, F. M. (1955) The role of porosity Part II: Analytical equations for constant rate filtration, *Chem. Eng. Prog.*, **51**, 282-290.

Tiller, F. M. (1975) In *Scientific Basis of Filtration* (Ed, Ives, K.) Noordhoff, London, 315-397.

Tiller, F. M. and Shirato, M. (1964) The role of porosity in filtration: VI. New definition of filtration resistance, *AIChE J*, **10**, 61.

Ugwuanyi, J. O., Harvey, L. M. and McNeil, B. (2004) Development of thermophilic populations, amylase and cellulase enzyme activities during thermophilic aerobic digestion of model agricultural waste slurry, *Process Biochemistry*, **39**, 1661-1669.

Urbain, V., Block, J. C. and Manem, J. (1993) Bioflocculation in activated sludge: an analytical approach, *Water Research*, **27**, 829-838.

US EPA Rule 503 regulations (EPA, 1993)

Usher, S. P., De Kretser, R. G. and Scales, P. J. (2001) Validation of a New Filtration Technique for Dewaterability Characterisation, *American Institute of Chemical Engineering Journal,* **47**, 1561-1570.

Vaxelaire, J. and Cezac, P. (2004) Moisture distribution in activated sludges: a review, *Water Research*, **38**, 2215-2230.

Vesilind, P. A. (1979) *Treatment and Disposal of Wastewater Sludges*, Ann Arbor Science, Ann Arbor.

Vesilind, P. A. (1988) Capillary suction as a fundamental measure of sludge dewaterability, *J. Wat. Pollut. Con.*, 60.

Vesilind, P. A. and Hsu, C.-C. (1997) Limits of sludge dewaterability, *Water Science and Technology*, **36**, 87-91.

Vesilind, P. A. and Ormeci, B. (2000) A modified capillary suction time apparatus for measuring the filterability of super-flocculated sludges, *Water Science and Technology*, **42**, 135-139.

Vesilind, P. A. and Spinosa, L. (2001) In *Sludge into biosolids: processing, disposal, utilization* (Eds, Spinosa, L. and Vesilind, P. A.) IWA Publishing, London.

Visvanathan, C. and Nhien, T. T. H. (1995) Study on aerated biofilter process under high temperature conditions, *Environmental Technology*, **16**, 301-314.

Vogelaar, J. C. T., Klapwijk, A., van Lier, J. B. and Rulkens, W. H. (2002) Temperature effects on the oxygen transfer rate between 20 and 55 °C, *Water Research*, **34**, 1037-1041.

Wagner, M., Loy, A., Nogueira, R., Purkhold, U., Lee, N. and Daims, H. (2002) Microbial community composition and function in wastewater treatment plants, *Antonie Van Leeuwenhoek*, **81**, 665-680.

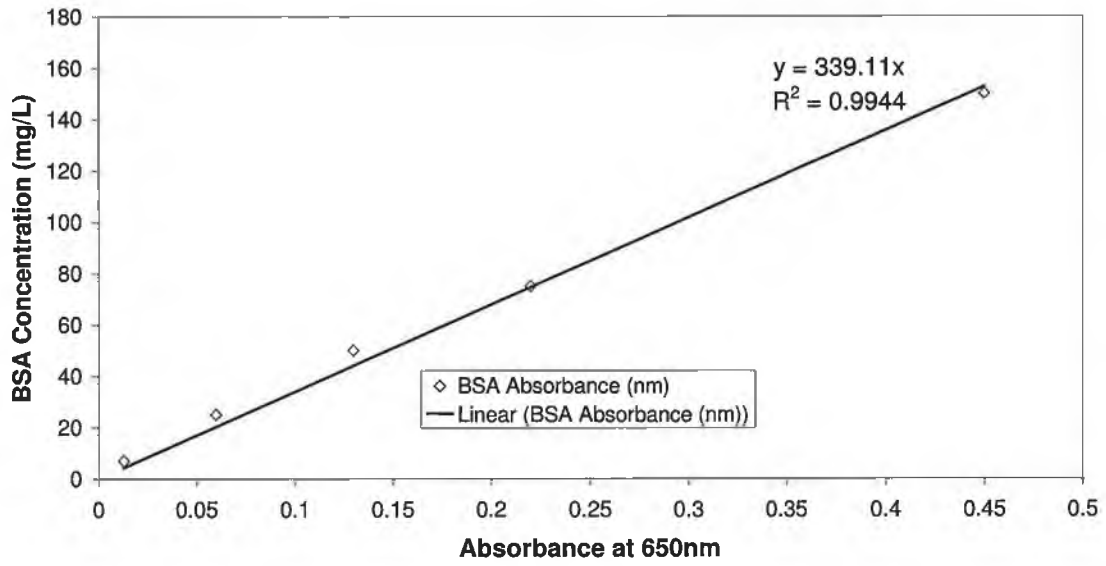
Wilén, B., Jin, B. and Lant, P. (2003) The influence of key chemical constituents in activated sludge on surface and flocculating properties, *Water Research*, **37**, 2127-2139.

Wu, R. M., Lee, D. J., Wang, C. H., Chen, J. P. and Tan, R. B. H. (2001) Novel cake characteristics of waste-activated sludge, *Water Research*, **35**, 1358-1362.

Zhou, J., Mavinic, D. S., Kelly, H. G. and Ramey, W. D. (2002) Effects of temperature and extracellular proteins on dewaterability of thermophilically digested biosolids, *Journal of Environmental Engineering and Science*, **1**, 409.

Zhou, J., Mavinic, D. S., Kelly, H. G. and Ramey, W. D. (2003) Experimental assessment of factors influencong the dewatering properties of thermophilically digested biosolids In *Specialist group on sludge management* (Ed, Odegaard, H.) IWA, Trondheim, Norway, pp. 111-118.

APPENDIX I



APPENDIX II