

STUDIES ON THE CLARIFICATION OF SUGARCANE JUICE CONTAINING SLOW SETTLING MUD

Cumhur Hakan Bakir
BE (Chem)

Submitted in fulfilment of the requirement for the degree of
Master of Engineering (Research)



Centre for Tropical Crops and Biocommodities

School of Chemistry, Physics and Mechanical Engineering

Science and Engineering Faculty

Queensland University of Technology

2018

Keywords

Sugarcane juice

Clarification

Aggregation

Coagulation

Flocculation

Settling rate

Turbidity

Colloids

Clays

Surface chemistry

Zeta potential

Floc structure

Porosity

DLVO theory

Abstract

To remain globally competitive the Australian sugar industry must achieve high clarification standards irrespective of the quality of the cane supply in order to maintain sugar quality and minimise sugar losses in the mud cake. The presence of soils and colloidal particles such as clay minerals in the cane supply of raw sugar manufacturing process presents challenges in the clarification process which ultimately affect throughput, efficiency and yield and quality of the product raw sugar. The juices expressed from canes originating from the soils of Meringa, Pioneer River and Victoria Plains, to name a few, are difficult to clarify and hence reduce the profitability of Australian sugar mills. In this present study soil samples received from three different sugar cane growing regions in Queensland, Australia are characterised in terms of their physico-chemical properties to investigate the relationship between impurities in the soils and the impact on clarification performance, namely its settling behaviour.

The investigations undertaken in this study supports the anecdotal evidence that Mt Mackay is a 'good' soil exhibiting good settling and clarification properties and Gluepot is a 'bad' soil exhibiting poor settling and clarification properties. Gluepot had the lowest true particle density, the highest proportion of fine particles (*i.e.*, $<1\ \mu\text{m}$ size range), lowest proportion of particles in the $>100\ \mu\text{m}$ size range, highest clay and organic fractions. Gluepot also contained clay minerals of the montmorillonite type, a known expandable clay which have the ability to absorb more water which reduces its bulk density and hence its settling rate. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) analyses showed the dominance of NH_4 and relatively higher proportion of hydrocarbon species, total organics and Na ions in the wet soil samples. Sodium ions are effective in particle stabilisation, and hence will not encourage coagulation/flocculation. The proportion of Na ions in Gluepot (the bad soil) is 4 times that of Mt Mackay.

High proportions of fine particles (*i.e.*, $<200\ \text{nm}$) found in the soil samples that are difficult to settle were classified as amorphous by X-ray powder diffraction (XRD) analysis because no diffraction patterns could be obtained and broadening of clay mineral peaks showed high imperfection in their internal structure and high particle

dispersion. Electron microscopy confirmed the presence of this highly dispersed phase, and the electron diffraction patterns from films of these particles indicated the crystalline nature of these nano-clays. Erosion of clay particles as observed in Transmission electron microscopy (TEM) micrographs and especially the expandable smectite-like minerals were probably the best candidates for the origin of the nano-clays.

Significant differences in the electrochemical properties of the soils were identified and there was poor dependence between ζ values and electrolyte concentration in mono-valent salt solutions for the difficult to clarify soils. Structure building phenomenon (as shown by Transmission X-ray microscopy (TXM)) by the nano-clay particles may be responsible for the problems with poor juice clarification by hindering floc aggregates from settling, despite changing environmental chemistry.

Batch settling tests using soil electrolyte suspensions showed that flocs produced from Gluepot soils consistently performed poorly compared to flocs produced from Mt MacKay soils regardless of the type and dosing rate of the flocculant used. This provided further evidence of the anecdotal evidence that Gluepot soils have inherently poor flocculation properties. The addition of pre-flocculated bagasse fly ash improved the settling rate of all three soils. However the improvements were only significant for the Gluepot and Invicta 255B soils. The benefits of pre-flocculated ash for the Mt Mackay soil was only significant when the soil to ash ratio was greater than 1:1. The addition of gypsum to a mixture of soil and pre-flocculated ash slightly reduced the final settling times for Mt Mackay and Invicta 255B flocs. For Gluepot on the other hand when a small portion of gypsum is added (*i.e.*, at a ratio of 19:1) the final settling time increased by ~90 %.

Increasing the mixing time during coagulation significantly improved the initial settling rate of the flocs. Increasing the mixing speed from 500 to 750 r/min at each of the three mixing times improved the initial settling rate as well. However, when the mixing speed was increased further to 1000 r/min the initial settling rates generally reduced.

The method of comparing the settling behaviour of flocs produced from flocculating the soils in centrifuged factory incubated juices did not prove to be successful. All three soils behaved similarly in contrast to the results achieved in the previous sections where all three soils behaved differently with Gluepot consistently

being slowest settling soil and Mt MacKay being the fastest settling soil. It was not possible to come up with a new method that could be used to compare the settling behaviour of the soils in factory juice. The lack of any significant differences between the soil settling rates indicate that the composition of the soils do not affect the flocculation mechanisms. It is possible that the colloidal particles that remain in the factory incubated juices after centrifuging dominate the flocculation mechanisms.

Tests with and without fibre showed that the flocs which do not contain fibre settle at up to 100 % faster and produce half the volume of mud. This is a significant result as it means that the capacity of an existing clarifier can potentially be doubled if the fibres are removed from the mixed juice at the rotary juice screens. In addition it provides the option for factories to reduce the amount of fibre in the mixed juice prior to clarification when there is an indication that the incoming cane is from an area/farm containing bad soil. The main reason for allowing fibre to enter the mixed juice stream via the perforations in the rotary juice screens is because they are used as a filter aid during mud filtration at the filter station. However there are alternative processes that can collect and deliver the fibres directly to the filter station without it passing through with the juice.

The addition of gypsum produced slight increases in settling rate but these were not significant.

Publication

Journal article

Bakir, H., Zhangying, Z., Zbik, M., Harrison, M. and Doherty, W.O.S. (2016). Understanding flocculation properties of soil impurities present in the factory sugarcane supply. *Journal of Food Engineering*, 189 (2016), 55-63.

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List of Abbreviations and Nomenclature

Acronyms

| | |
|----------|--|
| ASMC | Australian Sugar Milling Council |
| CEC | Cation exchange capacity |
| CJ | Clarified juice |
| CPS | Counts per second |
| CTCB | Centre for Tropical Crops and Biocommodities |
| DLVO | Derjaguin and Landau, Verwey and Overbeek |
| EDL | Electric double layer |
| EDX | Energy dispersive X-ray |
| ESJ | Evaporator supply juice |
| IEP | Iso-electric point |
| MJ | Mixed juice |
| NG | New Generation |
| PCA | Principal Component Analysis |
| ppm | Parts per million |
| QUT | Queensland University of Technology |
| RT | Residence time |
| RVF | Rotary vacuum filter |
| SEM | Scanning electron microscopy |
| SRI | Sugar Research Institute |
| SRL | Sugar Research Limited |
| TEM | Transmission electron microscopy |
| TOF-SIMS | Time-of-flight secondary ion mass spectrometry |
| TXM | Transmission X-ray microscopy |

| | |
|-----|----------------------------------|
| UQ | University of Queensland |
| XPS | X-ray photoelectron spectroscopy |
| XRD | X-ray powder diffraction |

Nomenclature

| | |
|----------|---|
| c_K | Critical coagulation concentration |
| d_f | Diameter of mud floc |
| g | Gravitational acceleration constant |
| M | Molarity |
| pzc | Point of zero charge |
| V_{ER} | Repulsive EDL interactive energy |
| V_T | Total interactive (or potential) energy |
| V_{VA} | Attractive van der Waals interactive energy |

Greek Letters

| | |
|------------|---|
| μ_j | Dynamic viscosity of juice |
| ϵ | Dielectric constant within the EDL surrounding a particle |
| ζ | Zeta potential (or electrokinetic potential) |
| v_o | Terminal settling rate (or speed) |
| ρ_f | Bulk density of the mud floc |
| ρ_j | Density of juice |
| β | Electrophoretic mobility |

RESEARCH CONTRIBUTIONS

This study is on the clarification of sugarcane juice containing different types of soils, and has added a body of knowledge on coagulation-flocculation processes through the following contributions:

- Soils that impact on poor coagulation/flocculation processes and those that have slow settling floc characteristics are likely to have some or all of the following features when compared to ‘good soils’:
 - contain a higher proportion of low density particles;
 - contain a higher proportion of organic and other amorphous materials;
 - contain higher specific surface area, cation exchange capacity and ζ ; and
 - contain nano-clays with montmorillonite type composition. These expandable clays have the ability to absorb water which reduces the particle bulk density and hence settling rate of the floc
- Structure building phenomenon of some soils present in sugarcane juice may be responsible for poor clarification and slow settling flocs.
- There are significant differences in the clarification performance between a dry and wet soil because of differences in surface chemistry. The dry soil has been shown to have faster settling characteristics compared to the set soil.
- The addition of flocculated bagasse fly ash as a ballasting agent enhancing the settling rate of flocs.
- Gypsum affects the coagulation/flocculation behaviour of slow settling soils.
- The removal of fine fibre (*i.e.*, bagacillo) from mixed juice significantly improves the settling rate of flocs, and therefore provides opportunity for significantly increasing throughput, and reduces the footprint of industrial clarifiers. This is a corollary to soils that contain higher proportions of organics that show slow settling rates.

Statement of Original Authorship

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signature: [QUT Verified Signature](#)

Date: 23rd October 2018

Acknowledgements

I would like to sincerely thank my principal supervisor, Prof. William Doherty, for his continuous support, patience, motivation, and extensive knowledge. His guidance helped me immensely to complete my research study and during the writing of my thesis.

I would also like to thank the generous financial support provided by Sugar Research Limited (SRL).

Thank you to the production staff at Rocky Point Mill for providing me access to their on-site facilities.

The assistance provided by my colleagues Adrian Baker and Dr Floren Plaza for assisting me with the batch settling tests undertaken at Rocky Point Mill and Queensland University of Technology (QUT) is greatly appreciated. I would also like to thank the assistance provided by Wanda Stolz in the laboratory and Neil McKenzie with juice testing equipment over the course of my Master's program. I would also like to thank many of my other colleagues at Centre for Tropical Crops and Biocommodities (CTCB) for their assistance and encouragement.

Many thanks also goes to: QUT staff - Gus Luthje for soil preparation; Tony Raftery for XRD; Sanjleena Singh for electron microscopy; Shane Russell with the loss on ignition tests, University of Queensland (UQ) staff - Marek Zbik for helping me to understand the fundamental science on colloidal particles and separation phenomenon, Prof. (emeritus) Edward White with assistance with the pycnometer tests; Barry Wood for X-ray photoelectron spectroscopy (XPS) testing and University of South Australia staff - John Denman for the TOF-SIMS tests.

Last but not least I would like to thank my dear wife Suzie, my daughters Yaren and Seren, and son Taylan for their continued support and encouragement.

I would like to dedicate this thesis to my beloved parents and family.

Chapter 1: Introduction

1.1 BACKGROUND

The Australian sugarcane industry is one of Australia's largest and most important rural industry utilising approximately 380,000 hectares of farmland yielding up to 35 million tonnes of sugarcane from which approximately 4.5 million tonnes of raw sugar, 1 million tonnes of molasses and 10 million tonnes of bagasse (cane fibre by-product) is produced annually (Australian Sugar Milling Council (ASMC) website, www.asmc.com.au accessed 4 December 2013). Queensland produces and exports approximately 85 % of the total raw sugar production in Australia, generating up to \$2.0 billion in export earnings and the balance which is produced in New South Wales is refined and sold in the domestic market (www.asmc.com.au (accessed on 4 December 2013)). As a whole, the industry employs approximately 16,000 people across the growing, harvesting, milling and transport sectors (www.asmc.com.au (accessed on 4 December 2013)).

Solid-liquid separation processes are used in many industrial and chemical processes such as sugarcane, water and wastewater treatments, mining, drilling and extraction processes such as coal mining and oil sands (Doherty and Edye, 1999), (Gregory, 2006), (Oliveira and Rubio, 2012) and (Meadus *et al.*, 1982). The raw products fed to these processes all contain soil and water forming an aqueous solid-liquid suspension having particles with various sizes (Singer and Munns, 2006). Current solid-liquid separation technologies rely heavily on an initial pre-treatment process to coagulate and flocculate suspended particles to form larger "floc" clusters which are more efficiently separated (Somasundaran and Runkana, 2005). Therefore, the destabilisation of colloids (1 nm to 1000 nm particle sizes) to achieve aggregation of particles (coagulation and flocculation) is a key governing factor in solid-liquid separation processes (Pefferkorn, 1995), (Sabah and Cengiz, 2004).

1.2 RESEARCH PROBLEM

Clarification of sugarcane juice containing slow settling muds reduces throughput, efficiency and yield and quality of the product raw sugar. The total industry cost associated with poor settling muds is estimated at ~\$1 M per annum.

Most of this cost is due to lost production time as a consequence of reduced throughput and/or short term production stoppages. Slow settling mud problem is much more prevalent during periods of rainfall when high dirt loadings come in with the cane supply and when clay minerals are present in the soil.

The quantity of soil in the cane supply is highly variable and is dependent on a number of factors including harvesting method, growing and climatic conditions, quality of the cane crop, burnt or green cane and condition of the farm ground. The quantity of soil entering the cane supply has tended to increase significantly with the introduction of mechanical harvesting (Steindl, 1998, Kroes and Forsell, 1999) through the 1960's and more recently, as a result of green cane harvesting (Moller *et al.*, 2010, Thai and Doherty, 2011). In Australia, cane is harvested mechanically and the quantity of the soil is typically ~2 % by weight of the cane supply to the factory (Olson *et al.*, 1999).

After juice is extracted from the cane, soil and other impurities are removed from the process using hot clarification followed by filtration. During clarification the juice is heated and limed to form micro-flocs. The juice is then flashed to remove dissolved air from the juice as well as dispersed air bubbles. The juice is then flocculated using an anionic polyacrylamide polymer to form large macro-flocs (mud flocs) and clarified in a continuous gravity settling clarifier.

The mud flocs settle to the floor of the clarifier forming a mud layer which is removed as mud underflow whilst the clarified juice flows upwards to the upper sections of the clarifier and is collected via overflow channels (Rein, 2007). The rate at which the mud flocs settle (settling velocity) is of great practical importance in solid-liquid separation processes involving the design and sizing of gravity settling clarifiers (Rein, 2007). If the settling rate of the mud flocs is not sufficiently faster than the bulk upward velocity of the juice then there is a risk that the mud flocs will be retained in the clarified juice stream and cause high turbidity (Rein, 2007). Under such circumstances, it is necessary to reduce the crushing rate and juice processing rate of the factory until improved clarification conditions are restored. Slow settling mud flocs also have the undesirable effect of producing light fluffy mud that is difficult to separate and wash which can cause bottlenecking at the filter station. In extreme cases a build-up of this light fluffy mud will require cane crushing to be stopped to allow processing of the high levels of mud in the factory. This is now an increasing problem

due to a change in the cultivated area from rich alluvial flood planes to marginal soil types as a result of urban encroachment and competition from other crops.

Currently, there is insufficient knowledge on how clay minerals affect the coagulation and flocculation mechanisms that take place during sugar cane juice clarification. Whilst many researchers have studied the implications of clay particles on clarification in other industries such as water treatment, very little research has been undertaken specifically for sugar cane juice clarification.

1.3 AIMS AND OBJECTIVES

The overall objective of this research was to find a practical solution to overcome poor clarification experienced by sugar mills from time to time as a result of clay rich soils entering the process with the cane supply. More specifically the project aimed to identify what factors lead to poor and good coagulation and flocculation processes. Specific objectives were:

- Characterisation of soils from sugarcane growing regions.
- Evaluating the coagulation and flocculation behaviour of the soils in aqueous and synthetic juice systems.
- Identifying strategies to overcome poor clarification performance.
- Developing a practical process for treating juices that contain clay rich soils that have poor clarification performance.

1.4 SCOPE OF THE THESIS

Figure 1.1 provides the relationship between the various chapters and project objectives.

Chapter 1 provides the background of the study, the research problem and the specific objectives of the project.

Chapter 2 provides a comprehensive literature review on sedimentation theory and the important parameters that affect the stability of soils in aqueous solutions.

Chapter 3 reports on studies of the physical properties of ‘good’ and ‘bad’ soils that influence clarification properties.

Chapter 4 provides the results on the settling rate of soils in synthetic juices, and the effect of various additives on the settling behaviour of the soils.

Chapter 5 provides the results on the settling behaviour of the soil particles with factory juices.

Chapter 6 provides a summary of the findings from the study and recommendations for future work.

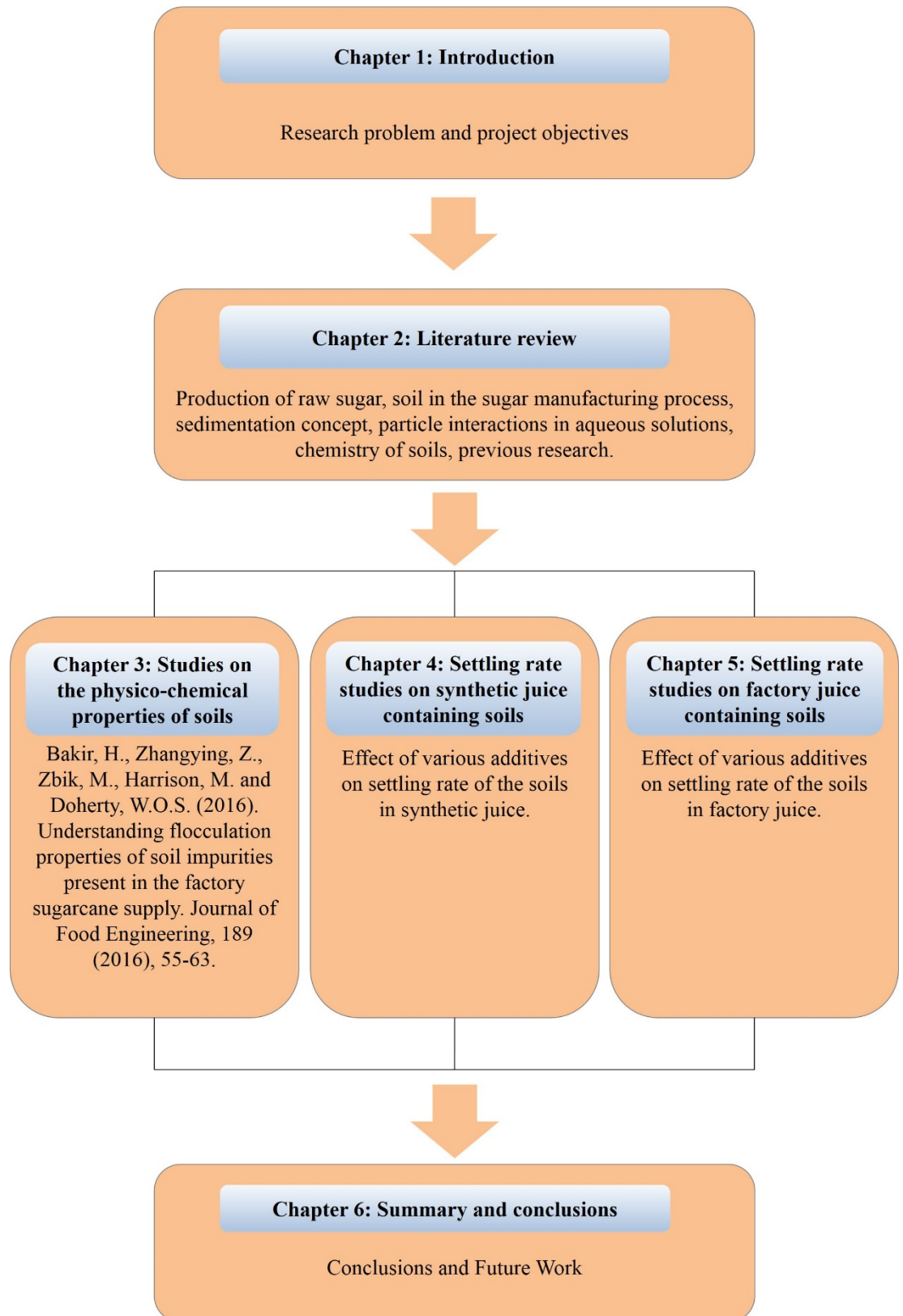


Figure 1.1 Flow diagram of the relationship between various chapters and project objectives

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Chapter 2: Literature review

2.1 INTRODUCTION

The destabilisation of colloidal suspensions is a common aspect of solid liquid separation processes in clarification and filtration (Koohestanian *et al.*, 2008). The presence of soils and colloidal particles such as clay minerals in the cane supply of raw sugar manufacturing process presents challenges in the clarification and filtration unit process which ultimately affect throughput, efficiency and yield and quality of the product raw sugar (Wright, 2006; Steindl, 1998). This chapter provides an overview of the unit processes in the raw sugar manufacturing process from harvesting, where soil impurities enter the cane supply, through to the final product sugar. The principles in sedimentation theory, colloid interactions and their stability as well as the chemistry of soils are presented. Previous research in the area of destabilisation of aqueous colloidal suspensions that cause poor coagulation and flocculation is presented.

2.2 PRODUCTION OF RAW SUGAR

Figure 2.1 is a process flow diagram depicting the Australian raw sugar manufacturing process. The diagram shows the various product streams exiting from the factory and the distribution of sucrose to each stream on a weight % (*i.e.*, wt%) basis based on information retrieved from Anon., (2015). The numbers in the brackets refer to the rates of the stream and the sucrose component in the various streams in units of tonnes per hour (*i.e.*, t/h). The process consists of cane harvesting and transport to the sugar mill, milling to extract juice from the cane, clarification of the extracted juice and mud filtration, evaporation, crystallisation of sugar, centrifugation and sugar drying.

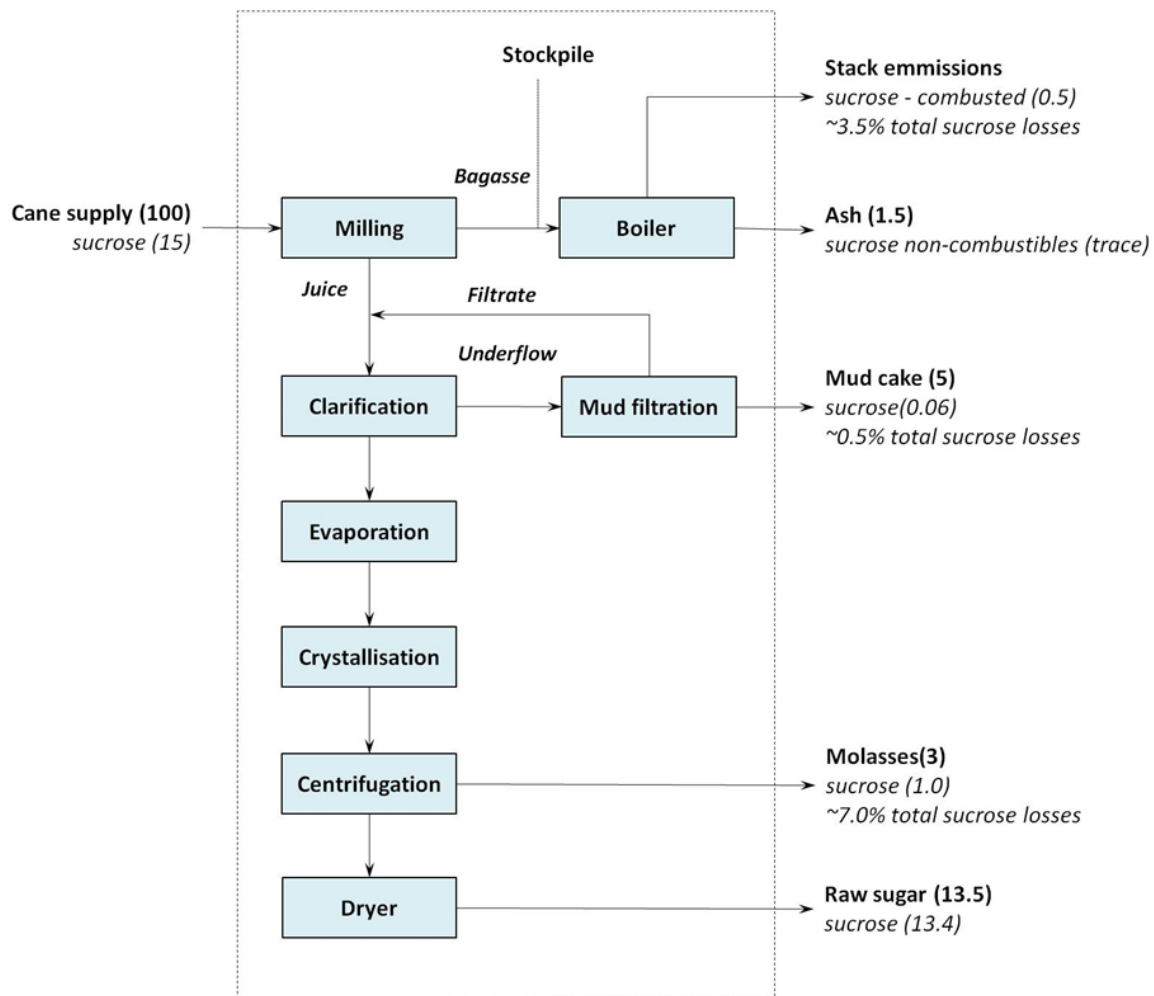


Figure 2.1 Process flow diagram of an Australian raw sugar manufacturing process

2.2.1 Harvesting and transport

Mechanical harvesters are used to harvest the cane as illustrated in Figure 2.2 (<https://asmc.com.au/>). The key components of a modern mechanical harvester are shown in Figure 2.3 (Kroes, 1997). The cane is topped to remove the sucrose scarce tops of the cane plant. The crop dividers separate cane from the rows on either side of the harvested row. The knockdown and fin rollers guide the cane into the path of the base cutter. The base cutter is a set of counter-rotating disks with replaceable blades designed to cleanly cut the cane at ground level. The two cutters are spaced out and slightly angled forward so that there is minimal contact with the top of the mound where the base of the cane is. The height of the base cutter relative to the frame of the harvester is set by the operator. However, due to inconsistencies in the topography of the farm ground cutting beneath the ground level occurs which picks up soil.

The cut cane is directed into the feed rollers with the help of the lifting roller. The feed roller directs the cane into the path of choppers where they are cut into smaller lengths of ~20 to 30 cm (termed billets). The primary and secondary extractors are used to separate any unwanted sucrose scarce trash (green and dried leaves and tops) components, from the cane supply. Cane is transported to the mills by road and/or rail. The supply of cane from a particular farm and from a particular harvesting event is termed a rake. Each rake is weighed at the factory for cane payment purposes.



Figure 2.2 Photo showing mechanical harvesting of sugarcane
(<https://asmc.com.au/>)

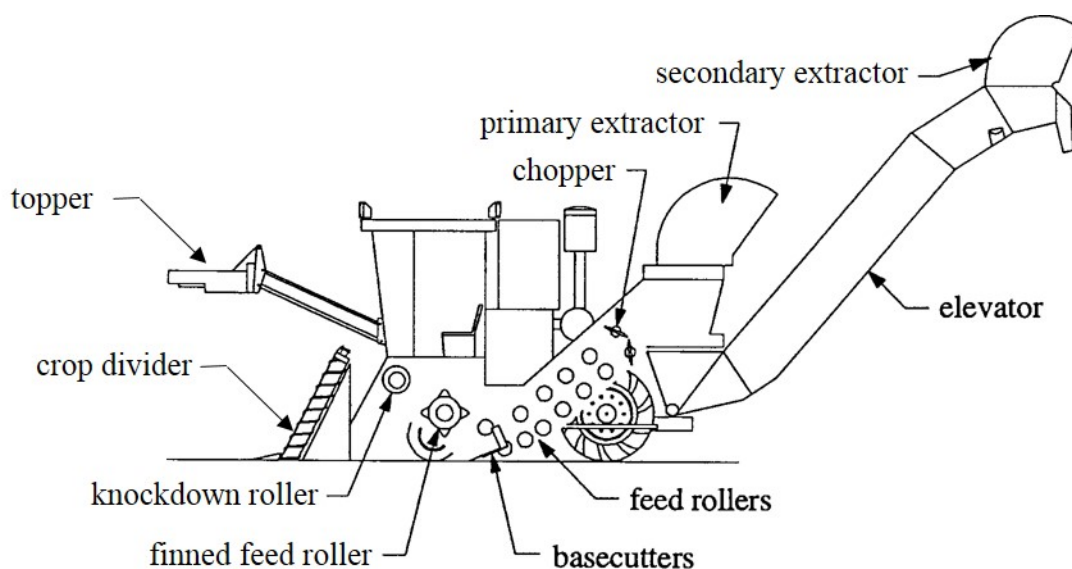


Figure 2.3 Key components of a modern mechanical cane harvester (Kroes, 1997)

2.2.2 Milling

At the sugar mill the cane is shredded to produce a continuous cane fibre mat which is then squeezed under high pressure through a series of paired mill rollers (milling train) to express the juice (Rein, 2007). Imbibition (or maceration) water is used during milling to maximise sucrose extraction from the cane fibres (Rein, 2007). The total quantity of juice generated by the milling process is ~110 wt% on cane (Rein, 2007). Samples of the cane from each bin and first expressed juice (juice prior to application of imbibition water) from each rake are collected using a tracking system and analysed in the laboratory. The cane weight and analysis results are used for cane payment purposes.

Approximately, one third of the soil in the cane supply is washed into the juice stream with the balance remaining in the cane fibres (Muller *et al.*, 1982). This number is confirmed by experience in Louisiana, although it can be quite variable (Wright, 2006). A typical value across the industry for the soil in the cane supply is ~2 wt% by weight of the cane supplied to the factory (Olson *et al.*, 1999). The soil washed to the juice becomes mud solids (Rein, 2007). Hence, assuming 110 wt% juice on cane and 2 wt% soil in cane, the quantity of mud solids (from washed soil) would be ~0.6 wt%. The mud solids from washed soil is in addition to the base load of mud solids in juice (*i.e.*, that for soil free cane) (Wright, 2006). The base load of mud solids in juice are generated by the physico-chemical reactions of clarification, and is usually ~0.2 to 0.4

wt% on juice (Wright, 2006). Therefore, the total mud solids in juice would be ~0.8 to 1.0 wt%.

The juice is screened through rotary juice screens to remove and redirect the coarse cane fibres back onto the milling train (Rein, 2007). The screens allow fine cane fibre particles (bagacillo) produced as a result of the shredding, other fine particles including soil to pass through and remain in the juice stream. The bagacillo assists as a filter aid during mud filtration (Rein, 2007). The screened raw juice termed mixed juice (MJ) undergoes clarification to remove non-sucrose impurities.

The cane fibres exiting the final mill rollers are termed bagasse. The bagasse is used as a fuel supply for the boiler which raises steam for process heating as well as electricity generation to power the process. Excess electricity is sold off to the local electricity grid.

After the bagasse is burnt the produced ash is conveyed to the mud storage bins. Mud cake from the filters is also stored in the same mud storage bins. Collectively, the ash and mud mixture is transported by trucks and redistributed back to the cane farms as a fertiliser supplement (Rein, 2007).

2.2.3 Clarification

The MJ is clarified in a continuous process using gravity settling clarifiers to remove solids and precipitates. A variety of clarifier designs are available but a very popular design is the short retention time (SRT) clarifier designed by Sugar Research Institute (SRI). The most recent SRI design is called the New Generation (NG) clarifier which incorporates perforated plates to maximise throughput and minimise juice residence time (RT) in the clarifier (Rein, 2007). Other designs such as multi-trays have higher RT's (~3 h) compared to the NG design which has a RT of ~20 to 45 min (Rein, 2007). High RT under hot conditions can lead to sucrose degradation and colour formation in the juice (Rein, 2007).

The typical process for clarification of mixed juice in Australian sugar mills is illustrated in Figure 2.4 (Anon., 2015). The process is based on the addition of lime saccharate to heated juice at ~76 °C in order to raise the juice pH from ~5.5 to ~7.8 to prevent hydrolysis of sucrose (Doherty and Edye, 1999). At the same time the lime saccharate delivers calcium ions which react with the phosphates in the juice to form a calcium phosphate precipitate (Doherty and Edye, 1999). The heating denatures

proteins in the juice. These precipitates are termed mud solids and are usually around 0.2 to 0.4 wt% on juice (Wright, 2006).

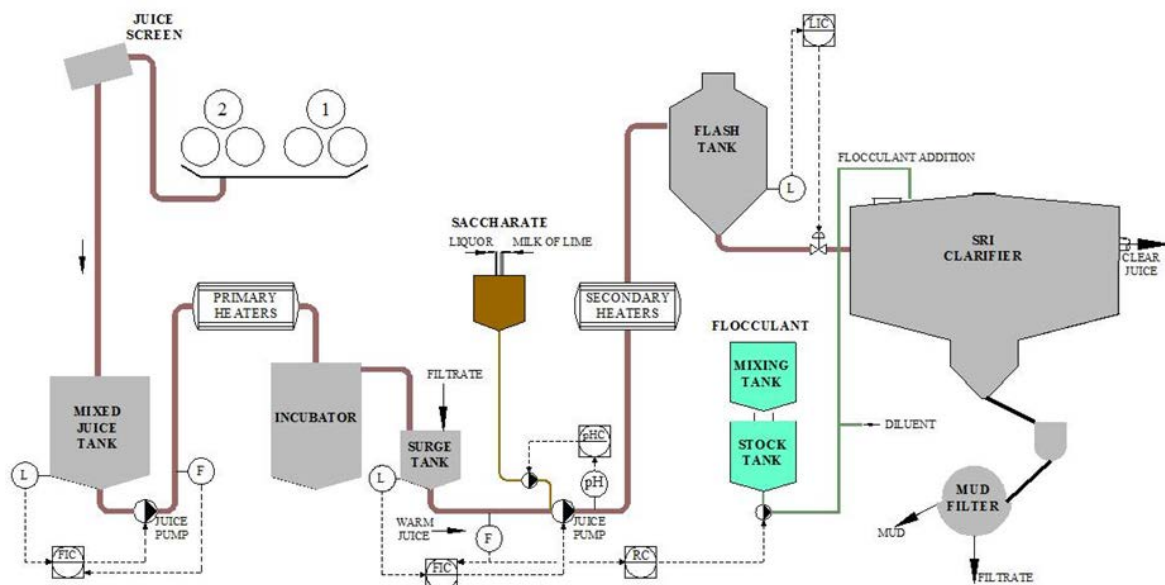


Figure 2.4 Typical raw sugar cane juice clarification process in Australia (Anon., 2015)

The calcium phosphate precipitate acts as a sweep flocculant by removing suspended matter from the juice and adsorbing dissolved molecules and ions (Doherty and Edye, 1999). The juice is then superheated to $\sim 103\text{ }^{\circ}\text{C}$ and flashed in a flash tank under atmospheric conditions to remove dissolved air and air bubbles which may be entrapped between fibre particles (Rein, 2007).

The flashed juice then flows to the clarifier where the original soil particles, denatured proteins, calcium phosphate precipitate, soil and other suspended matter are flocculated to form “mud floc” clusters using high molecular weight anionic polymers to increase their settling rate in the clarifier (Doherty and Edye, 1999). There are many different clarifier designs but in principle they all involve channelling the mud floc/juice suspension into separation zones in the main body of the clarifier. In the separation zones the mud floc/juice suspensions flow horizontally over a given distance which provides an opportunity for the mud flocs to settle out of the juice stream under the force of gravity.

The clarified juice (CJ), which is mostly free of suspended matter, flows from the separation zone to the top upper section of the clarifier and is collected via overflow

channels and is then piped to the evaporator supply tank. The juice in the evaporator supply tank is termed evaporator supply juice (ESJ) which is commonly used interchangeably with CJ.

The mud flocs settle to the floor of the clarifier to form a mud layer. Although, clarifiers have a certain mud storage capacity in the lower section of the clarifier (*i.e.*, below the separation zone) the 'mud interface' (interface between the settled mud layer and the juice above it) height is visually monitored (though mud windows) and controlled by the operator to keep the mud upper level in the clarifier close to a desired target (Wright, 2006). The floor of clarifiers are continuously and gently scraped to assist with mud thickening and to direct the mud to the mud outlet of the clarifier. This mud stream is typically referred to as the underflow (or mud underflow). For NG clarifiers, the CJ and mud underflow flowrates are typically ~90 % and 10 % of the clarifier inlet flowrate respectively. The CJ is directed to the ESJ, tank which feeds the evaporators and subsequently is used for sugar crystallisation. The mud underflow on the other hand is directed to the mud filter station where the insoluble solids (*i.e.*, mud and fibre solids) are removed from the process in the form of a washed and dewatered cake (commonly termed mud or filter cake).

2.2.3.1 Mud filtration

The mud underflow from the clarifier flows to the mingler (or mixer) where the mud is conditioned to improve its filtration characteristics. Conditioning involves the addition and mixing of mud filtrate to dilute the mud and filter aids such as bagacillo, lime (or lime saccharate) solution and flocculant solution (Rein, 2007). Lime and flocculant are not always added but bagacillo is a key requirement for most filter technologies such as the rotary vacuum filters (RVF) which is almost universally used in Australia. For RVFs the quantity of bagacillo required to achieve good filtration is typically ~0.4 to 0.5 times the amount of mud solids present in the mud cake (Rein, 2007). Typically, a portion of the total bagacillo requirement is in the mixed juice via the rotary juice screen and the balance is obtained from the final mill bagasse using a pneumatic system from the final mill bagasse.

During filtration, hot water is added to wash the juice from the mud cake. The washed mud cake is then dewatered to remove as much liquid as possible to minimise sucrose losses. The recovered juice/hot water mixture is termed filtrate and is recycled back to MJ (upstream of the clarification stage). Mud solids that pass through the filter

screen holes during filtration with the filtrate are also recycled with the filtrate adding to the overall mud solids loading on the clarifier. It is therefore desirable to retain as much mud solids as possible on the filter cake. This aspect of the filtration is termed mud solids retention and is used as a key performance indicator for mud filtration. For RVFs the mud solids retention is typically ~85 wt% (Rein, 2007).

Analyses on subsamples of the mud cake and the cake rates are used to determine the quantity of sucrose that is lost with the mud cake. At regular intervals samples of the mud cake are collected from the surfaces of each filter and weighed. The samples are taken from a known surface area of the filter. The cake weight, average rotational speed of the RVFs and the surface areas are used to calculate the average mud cake rate from each filter. The mud cake typically contains ~1.2 wt% sucrose which represents ~0.3 to 0.6 wt% of the overall factory sucrose losses.

The mud cake is transported and redistributed back to the cane farms as a fertiliser supplement (Rein, 2007). The total mud cake rate is used as a guide for determining the overall quantity of soil that enters the factory with the cane supply.

2.2.4 Evaporation, crystallisation and sugar drying

The aim of evaporation is to reduce the water content of the clarified juice to form a syrup. The syrup is then processed through three evaporative/crystallisation pans A, B and C with each pan evaporating a lower quality syrup (Rein, 2007). The boiled syrups are seeded with fine sugar crystals initiating crystallisation thus growing the seed crystals (Rein, 2007). The resulting mixture of sucrose crystals and syrup is termed massecuite.

The sugar crystals are separated from the massecuite in centrifuges and are then sent on to drying and storage/packing (Rein, 2007). The remaining syrup is passed to the next evaporation pan or passed out of the C pan as molasses (Rein, 2007). The exhaustion of sucrose from the molasses is limited by the high viscosity of the massecuite which restricts boiling and its handling properties. The sucrose loss in molasses represents the largest loss in the process being approximately 7 wt% of the total sucrose losses.

2.3 SOILS IN THE SUGAR MANUFACTURING PROCESS

Soil can be defined as any loose farm ground material that enters the cane supply. The main components of a typical farm soil mixture has been divided into three main size separates by the U.S. Department of Agriculture which can be further subdivided as shown in Table 2.1.

Table 2.1 Size fractions of soil particles (Singer and Munns, 2006)

| Fraction | Diameter (mm) |
|-----------------|----------------------|
| Sand | 2.00 – 0.05 |
| Very coarse | 2.00 – 1.00 |
| Coarse | 1.00 – 0.50 |
| Medium | 0.50 – 0.25 |
| Fine | 0.25 – 0.10 |
| Very fine | 0.10 – 0.05 |
| Silt | 0.05 – 0.002 |
| Coarse | 0.05 – 0.02 |
| Medium | 0.02 – 0.005 |
| Fine | 0.005 – 0.002 |
| Clay | <0.002 |
| Coarse | 0.002 – 0.0002 |
| Fine | <0.0002 |

Since the introduction of mechanical harvesting (1960 to 1965) the amount of soil in the cane supply has tended to increase significantly (Steindl, 1998; Kroes and Forsell, 1999) and more recently, as a result of green cane harvesting which takes place in many areas (Moller *et al.*, 2010; Thai and Doherty, 2011). Moller *et al.*, (2010) reported soil loadings that were between 40 to 60 wt% higher when harvesting green unextracted cane compared to burnt extracted cane. A typical value across the industry for the soil in the cane supply is ~2 wt% by weight of the cane supplied to the factory (Olson *et al.*, 1999).

Soil is a major problem to the sugar industry. Kroes and Forsell (1999) grouped the problems caused by soil as follows:

- Increased wear and tear of harvesting equipment;
- Increased wear and tear of equipment throughout the sugar factory, particularly within the milling train and boilers;
- Reductions in extraction due to roller wear;
- Combustion problems and shutdowns of bagasse fired boilers;
- Process inefficiencies; and
- Increased loading of stack emissions.

Despite these adverse effects some of the soil particles play a key role in increasing the settling rate of the mud flocs and hence increase the separation efficiency during clarification because their densities are greater than that of the other constituents of the mud floc. This is outlined in greater detail further below in section 2.4.1.

2.4 THE SEDIMENTATION CONCEPT

Sedimentation is the process where particles dispersed in a fluid settle under the force of gravity (or an applied force) due to a density difference between the dispersed particles and the fluid they are suspended in. When this process is performed under a controlled environment it is commonly known as a batch settling test or jar test. A simplified history of the batch settling of a flocculated suspension is shown in Figure 2.5 (Svarovsky, 2013). The upper section of Figure 2.5 is a continuous plot of the four zones that have been observed to develop during sedimentation and the lower sections show the cylinders (A to E) at various stages of settling according to Comings *et al.*, 1954. The contents of each cylinder (A to E) at the various stages can be summarised as follows:

Cylinder A

A uniform suspension of the flocculated particles (zone 2). This is representative of the clarifier feed stream.

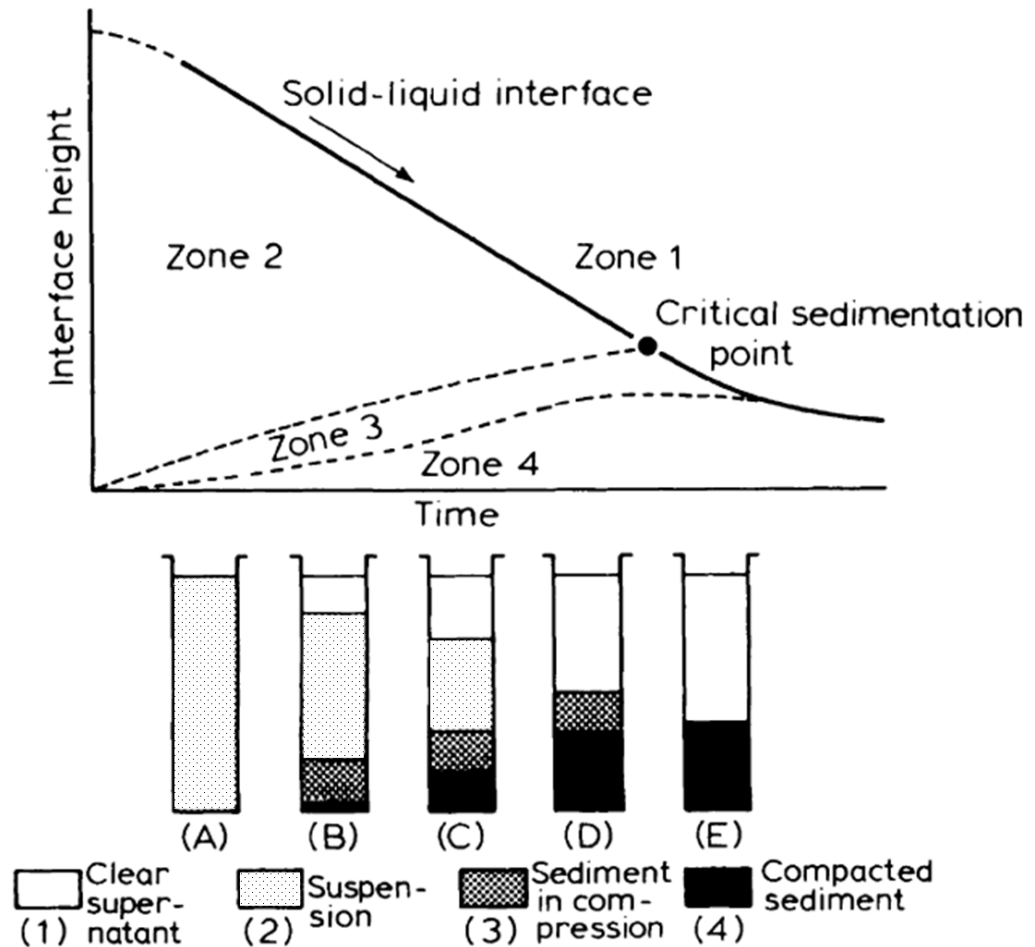


Figure 2.5 Sedimentation of a flocculated suspension (Svarovsky, 2013)

Cylinder B

After a short time zone 4 develops at the base of the cylinder. Zone 4 is a mixture of flocs and comparatively large particles that have settled and are resting at the bottom upon one another. This zone has formed from flocs that were initially very close to the bottom of the cylinder. Zone 3 develops immediately above zone 4. Zone 3 represents a transition layer that is intermediate in density between the deposit (zone 4) and the suspension (zone 2). In this transition layer the liquid is being squeezed out from among a network of flocs. Hence it is called the ‘sediment in compression’ zone. Zone 2 maintains the concentration of the original suspension. The clarity of zone 1 depends on how well the suspension is flocculated. The better the flocculation the lower the turbidity of the liquid zone and the more distinct the interface between zone 1 and zone 2 will be.

Cylinder C

Shows the effect of continued settling where the upper and lower zones increase in volume whilst the volume of the suspension zone decreases. The compression zone remains the same in volume but moves upwards.

Cylinder D

Shows the effect when all the solids have settled out of the suspension zone and exist as a sediment layer. This condition is known as the 'critical sedimentation point'. Up to this point the solid-liquid interface follows an approximately linear relationship with time as shown by the plot in the upper section of Figure 2.5.

Cylinder E

Shows the effect where the sediment in compression zone (zone 3) has disappeared through compression to form the compacted sediment. During compression the liquid that accompanies the flocs in the sediment is slowly released due to the weight of the sediment above it until an equilibrium is established between the weight of the flocs and their mechanical strength. The time taken to reach this equilibrium point constitutes the major part of the time involved for the total process. The overall process time usually depends on the type of settling aids used. Coagulants may give process times of several hours whereas acrylic-based polymer flocculants can achieve process times of a fraction of this.

At the commencement of settling the flocs settle freely at various velocities and therefore lead to collisions occurring between fast and slow settling neighbouring flocs. These collisions as well as the displacement of liquid in an upward direction have a slowing effect on the settling rate of the flocs in reference to a fixed point of the cylinder. Collectively these interactions cause what is known as hindered settling. Hindered settling occurs in the original suspension zone as well as in the initial compaction zone. The higher the concentration of the flocs the more the extent of hindered settling becomes.

The plot in Figure 2.5 can be developed from a batch settling test. In general the interface between clear liquid above and the settling layer below is recorded over time. The tangent at any point along an interface height versus time plot represents the settling rate of the interface at that time. Since the beginning of the 1900's many researchers have studied the behaviour of both granular and flocculated solids using

batch settling tests (Coe and Clevenger, 1916; Kynch, 1952; Richardson and Zaki, 1954; Talmadge and Fitch, 1955; Michaels and Bolger, 1962) as a basis for developing design theories for clarifiers and/or thickeners. These theories are based on the use of multiple construction lines drawn at specific points along the interface height versus time plots. This aspect of batch settling tests is not in the scope of the present study and therefore will not be covered any further.

In the present study batch settling tests are used as a basis for quantifying and comparing the settling behaviour of the soil samples in different liquid suspensions. The initial linear settling period represents the free settling period. During this period the flocs settle freely before reaching the settled layer. The settling rate during this period is often referred to as the ‘initial settling rate’. The initial settling rate provides an indication of how quickly or easily the flocs can settle out of the separation zone of clarifiers without being entrained with the flowing liquid. The initial settling rate is used to determine the required cross sectional area (hence the diameter) of SRI’s SRT clarifier designs. The final mud height provides information about how well the mud thickens and how much storage capacity is required in the lower section of clarifiers for the settled mud. The desired results from a batch settling test are:

- High initial settling rate,
- Low turbidity clarified juice, and
- Low mud volume.

2.4.1 Factors affecting floc settling rate based on Stokes law

Due to the complex nature of liquid suspensions containing particles with a large size distribution it has been difficult to examine sedimentation processes theoretically. In 1851, George Gabriel Stokes derived an expression (Stokes’ Law), for the terminal velocity of a single spherical particle with negligible charge falling through a fluid under the force of gravity.

If it is assumed that a single spherical floc with negligible charge falls through a liquid such as sugarcane juice its terminal velocity (settling rate) can be approximated by Stokes’ Law as:

$$v_o = \frac{(\rho_f - \rho_j)d_f^2}{18\mu_j}g \quad 2.1$$

where v_o is the terminal settling rate,
 d_f is the diameter of the floc,
 ρ_f is the bulk density of the floc,
 ρ_j is the density of the juice,
 μ_j is the viscosity of the juice,
 g is the gravitational acceleration constant.

Therefore to maximise the settling rate of the floc requires a:

- larger differences between the bulk density of the floc and the density of the juice ($\rho_f - \rho_j$)
- larger floc diameter (d_f), and
- lower viscosity of the juice (μ_j)

In sugarcane juice clarification both density and viscosity of the juice are dependent on the temperature and the quantity of total solids in the juice. Clarification temperature is set at $\sim 100^\circ\text{C}$ and the amount of dissolved solids in the juice is dependent on the cane quality and the amount of imbibition water used during juice extraction. The amount of imbibition water added during extraction is limited by the capacity of the evaporators so there is no real opportunity to lower the density and viscosity of the juice. The density of the juice at $\sim 98^\circ\text{C}$ and 15 brix is typically $\sim 1025\text{ kg/m}^3$ and the viscosity is $\sim 4.0 \times 10^{-4}\text{ Pa}\cdot\text{s}$ (Rein, 2007). Hence to achieve rapid settling rates based on density difference alone would require that the bulk density of the mud floc is somewhat larger than $\sim 1025\text{ kg/m}^3$.

The floc size (or diameter) and bulk density are dependent on many factors that affect the underlying mechanisms that lead to floc formation. In sugarcane juice clarification, floc formation is a two-step process involving aggregation of individual suspended particles followed by bridging flocculation with the addition of high molecular weight polymers (or flocculants). The initial aggregation step occurs as a result of destabilisation of the suspension by eliminating any repulsive interactions that prevent individual particles from coming into contact and adhering (Hogg, 2013). Factors that affect floc formation (and hence floc size and bulk density) include type and dosage of coagulants/flocculants, applied shear force, and the physical and surface

properties of the individual particles (Yu *et al.*, 2009; Ehrl *et al.*, 2008). A more detailed review of these factors is presented further below in sections 2.5 and 2.6.

Mud flocs are largely occupied by juice and varying quantities of air bubbles, soil particles, bagacillo, starch, waxes, and calcium phosphate and denatured protein precipitates formed during clarification reactions (Doherty and Edye, 1999). Soil particles are the main insoluble solids in juice making up ~45 wt% of the insoluble solids content (Rein, 2007; Wright, 2006). The true particle density of soils represents the average particle density of the silicates, organics and metal oxides however it is generally accepted as being ~2,650 kg/m³ due to the high quartz content in most soils (Alexandrou and Earl, 1998). However, the bulk density of the mud floc is much smaller, due to the high liquid to insoluble solid ratio (Knix and White, 2001). It then follows that the bulk density of a given mud floc should be able to be increased if the individual particles making up the floc:

- consisted of a higher proportion of high density particles, and
- were able to pack tightly to minimise the void fraction (and hence liquid volume) of the mud floc.

These are the main reasons why air bubbles are removed from juice during flashing (*cf.* Section 2.2.3) and prior to flocculant addition. The density of air is ~1000 times lower than the density of the juice. Even one air bubble can have a significant lowering effect on the bulk density of the mud floc. Figure 2.6 is a micro photo of aerated kaolin and carbon flocs showing the incorporation of air bubbles within a kaolin and carbon flocs. In these cases the flocs have been deliberately aerated for flotation clarification.

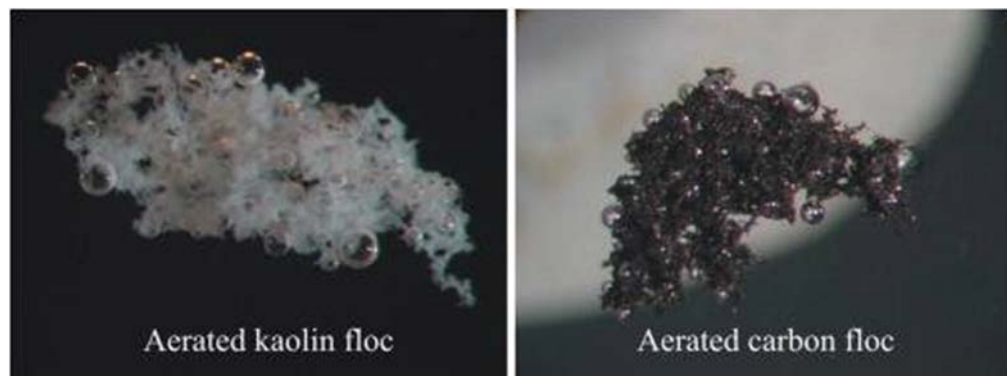


Figure 2.6 Examples of how air bubbles attach to floc clusters (Oliveira and Rubio, 2012)

The quantity of bagacillo present in juice is dependent on the quantity of mud solids and the amount of bagacillo that is acquired through the rotary juice screens as opposed to collection and delivery through the pneumatic system. The portion collected via the rotary juice screens is typically 50 % of the total requirement but due to the high maintenance costs and poor control pneumatic systems are being decommissioned and all the bagacillo is acquired through the rotary screens. Under these circumstances the quantity of bagacillo in juice and hence what would be present in mud flocs is ~0.2 wt% (based on a fibre ratio of 0.4 to 0.5 and a mud solids content of 1.0 wt%).

According to work done by Perez *et al.*, (2017) the true particle density of sugarcane bagasse particles ranging in size from 9.5 to 0.075 mm ranged between ~460 and 605 kg/m³ respectively. Bagacillo is considered to be the smaller size fraction of bagasse particles so their particle density would be ~605 kg/m³ which is significantly lower than the juice density (*viz.*, ~1025 kg/m³). Hence the removal of most of the bagacillo from juice should significantly increase the bulk density and settling rate of the mud floc provided the packing arrangement of the remaining particles does not change. Surprisingly, there were no literature found on the impact of bagacillo fibres on the bulk density or settling rate of mud flocs even though most of the bagacillo can be removed from the juice relatively easily by installing finer aperture screens on the rotary juice screens (*cf* Section 2.2.3.1). However, as bagacillo is a readily available and effective filter aid for mud filtration it would be necessary to collect and deliver the bagacillo directly to the filter station as opposed to allowing a portion of it to flow through the clarification streams.

The incorporation of soil particles would be expected to increase the bulk density due to their densities being significantly higher than the juice density. Wright (2006a) suggested, that the mud solids content in the underflow increases by ~0.45 units for each 0.1 unit rise in the proportion of soil constituting the mud solids. As a consequence, the mud flocs thicken to a greater extent and therefore increase the mud solids concentration in the underflow. However clay and other colloidal particles in the soil can produce stable colloidal suspensions that are difficult to coagulate and flocculate. For example, most clay minerals are alumino-silicates, which have two dimensional sheet lattice structures that are platy in natural occurrence (Singer and Munns, 2006). The aspect ratio of kaolinite is ~10 with an equivalent diameter of ~200

to 1000 nm and montmorillonite has an aspect ratio of ~80 to 500 with an equivalent diameter of 5 to 200 nm. The presence of these particles (clays, for example) can lead to no coagulation or flocculation at all or produce mud flocs that are loosely packed which reduces the bulk density of the mud flocs and therefore their settling rates considerably. The impact of clay particles on bulk density and settling rate is discussed in greater detail in section 2.6.

A potentially applicable method for increasing the bulk density of mud flocs in sugarcane juice clarification is the incorporation of high density particles such as sand, bagasse fly ash or metal oxides to the juice prior to flocculation. This concept is more commonly known as floc ballasting. The use of ballasting agents to increase bulk density and hence the settling rate of flocs have been studied at laboratory and pilot plant scale since approximately 1977 (Young and Edwards, 2003). In raw sugar production bagasse fly ash is readily available as a result of burning bagasse in the boiler. The particle density of bagasse fly ash is $\sim 1390 \text{ kg/m}^3$ (Lima *et al.*, 2012).

Also, the quantity of suspended particles in the juice has an effect on the settling rate of the mud flocs. When the suspended particle concentration in the juice is high it leads to what is known as hindered settling. Hindered settling occurs when the individual mud flocs come into close contact during settling and hence settle collectively as a layer rather than settle freely as individual mud flocs (Gregory, 2006). Crees *et al.*, (1978) showed that, at high mud solids load ($>0.8 \text{ wt}\%$), the settling rate was a function of the flocculant dose rate and determined that the effects of hindered settling predominated at higher mud solids loading. In net the overall settling rate is limited by the settling rate of the mud layer. Therefore soil loadings to the clarifier should be minimised. This includes the mud solids that are recycled to the clarification stage with the filtrate from the filter station.

The proportion of starch, precipitated calcium phosphate, denatured proteins, waxes and other precipitated organic matter in juice is typically ~ 0.2 to $0.4 \text{ wt}\%$ (Wright, 2006). Due to their complex nature and the fact they are formed via chemical and heating reactions it would be difficult to assess the impact of their presence based on their densities alone. In addition there were no literature found on the true particle densities of these components. As an example, starch concentration in juice can be as high as 4,000 ppm on brix (Figueira *et al.*, 2010). Starch granules are approximately spherical in shape with diameters ranging between $1\text{-}3 \mu\text{m}$ (Figueira *et al.*, 2010).

Kampen *et al.*, (1998) reported diameters ranging between 1-10 μm whilst Stevenson and Whayman (1976) and Park *et al.*, (1985) reported diameters of 1-5 μm . However, during clarification the heating and incubation causes most of the starch granules in suspension to solubilise and then be broken down into smaller molecules by the action of naturally occurring Amylase (Zhou *et al.*, 2008). Therefore their presence in granular form and based on its particle density alone is unlikely to have a significant impact on the bulk density of the mud floc.

2.5 PARTICLE INTERACTIONS IN AQUEOUS SOLUTIONS

An understanding of how particles interact in aqueous solutions is fundamentally important in solid liquid separation processes. Due to the effects of Brownian motion and gravity particles in solution collide with one another. During these collisions particles may adhere together to form aggregates and enable sedimentation. In this case the particles are said to be unstable. If aggregation does not occur the particles remain dispersed throughout the suspension and the particles are said to be stable.

The stability of the particles is influenced by short range forces that exist between the particles. The two forces that play a significant role during particle interactions are van der Waals attractive forces and repulsive forces that exist as a result of particles with like charge. The development of these charges and their influence on particle interactions are described in the following sections.

2.5.1 Surface charge

The surfaces of particles in aqueous solutions are likely to acquire a charge due to ionisation of chemical groups (Gregory, 2006). These charged surfaces become surrounded by a cloud of counter ions extending from the surface into the solution. The larger the surface charge and the higher the concentration of counter ions the larger the cloud of counter ions will be. The cloud of counter ions has the effect of reducing the net charge of the particles. Surfaces can also acquire a charge through the protonation and deprotonation of oxygen and nitrogen atoms which are often contained in functional groups attached to the surfaces of particles. Therefore the magnitude of the net charge can be influenced by the type and concentration of counter ions as well as the solution pH.

The point at which the net charge of the particles is zero is termed the 'point of zero charge' (pzc) (Gregory, 2006). This is the point at which the repulsive forces are

non-existent so the particles are able to approach each other close enough for van der Waals attractive forces to dominate and initiate aggregation. If the cation concentration is greater than that at the pzc then the surface charge is positive and vice versa (Gregory, 2006).

2.5.2 Electrical double layer

A charged surface in solutions containing ions affects the distribution of ions in the surrounding interfacial region. A higher concentration of counter ions exist around the charged surface while the like ions are distributed in solution away from the charged surface. The combined system of surface charge and the excess charge in solution is known as the electrical double layer (EDL) as illustrated in Figure 2.7 (Kopeliovich, 2009). The inner layer around the surface of the particle is known as the Stern layer, where the counter ions are strongly attracted to the particle. The outer layer is known as the diffuse layer, where the ions are loosely bound to the particle. Within the diffuse layer there is a boundary known as the slipping plane, where the particle and the counter ions contained within it exist as a single entity.

Figure 2.7 also shows a plot of potential energy as a function of distance from the particle surface. The potential energy at any given distance represents the energy that is required to force two particles together so that they are separated by that given distance. There is an exponential decrease in the potential energy as the distance from the surface increases. The potential energies at the particle surface, the stern plane and the slipping planes are denoted by the surface, stern and ζ respectively. The ζ which is also known as the electrokinetic potential is an important parameter in terms of particle stability. Particle stability and ζ are covered in greater detail in section 2.5.4.

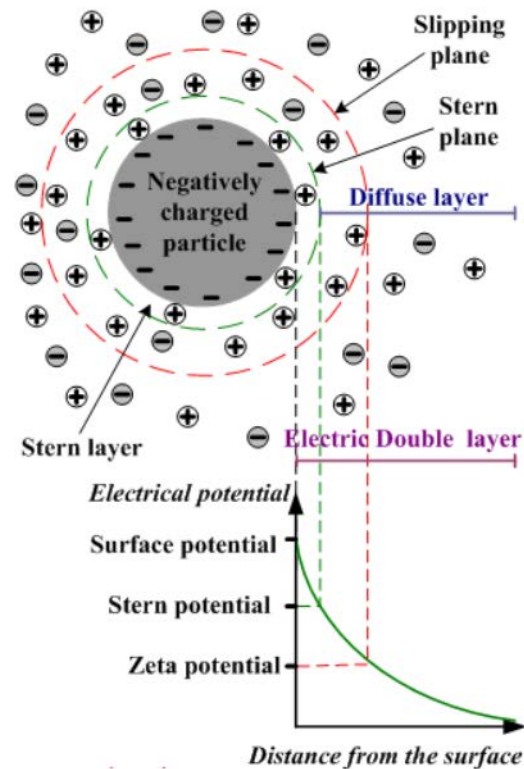


Figure 2.7 Electric double layer of negatively charged colloid in a liquid medium (Kopeliovich, 2009)

2.5.3 DLVO theory

A quantitative theory on colloid stability was developed by Derjaguin and Landau, (1941) and Verwey and Overbeek (1948) (DLVO theory). The DLVO theory describes aggregation of dispersed particles in terms of two contributing forces at the EDL (*cf.* Section 2.5.2) and the inter-particle distance. These two forces are van der Waals forces of attraction and electrostatic forces of repulsion between particles of similar charge as illustrated in Figure 2.8. The theory assumes that the contributions of these two forces are additive and hence provides the basis for the stability of colloids to be assessed quantitatively.

On this basis the total interactive (or potential) energy between two surfaces (V_T) is calculated by summing the repulsive EDL interactive energy (V_{ER}) and the attractive van der Waals interactive energy (V_{VA}), thus:

$$V_T = V_{VA} + V_{ER} \quad 2.2$$

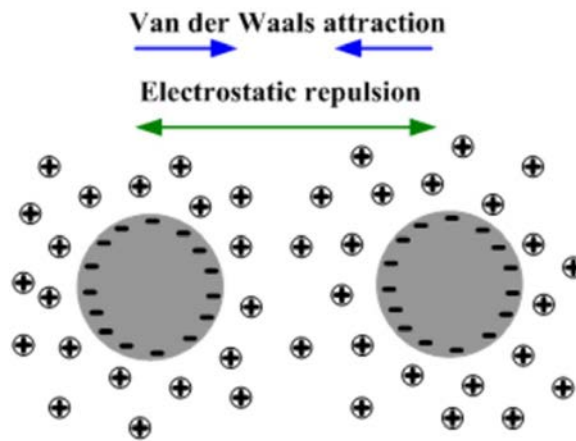


Figure 2.8 van der Waals attraction and electrostatic repulsion between two colloids (adopted from Kopeliovich, 2009).

Figure 2.9 shows the variations in the repulsive (V_{ER}), attractive (V_{VA}) and the total (V_T) interactive energies as a function of the distance between two particles that have the same charge. The EDL interactive energy (V_{ER}) results from the overlapping of the diffuse layers and hence for like charge particles the forces are repulsive. For oppositely charged particles the forces as a result of the EDL interactions would be attractive. When the particles are very close the van der Waals forces dominate with a resultant negative interactive energy that leads to aggregation. At close contact the interactive energy is known as the primary minimum. There is a second region where the resultant interactive energy is negative and this is known as the secondary minimum. Compared to the primary minimum the aggregation in the secondary minimum is not stable and reversible.

As the particles move further away from each other past the primary minimum region the van der Waals attractive forces decrease more sharply compared to the repulsive EDL forces. Therefore within this region the EDL repulsive forces dominate creating a net repulsive energy barrier. The height of this energy barrier determines the stability of the suspension. For aggregation to occur the height of this energy barrier needs to be lowered or removed and this can only be done by changing the EDL repulsive forces as it is impossible to change the van der Waals forces. The EDL repulsive forces can be manipulated by changing the ζ of a suspension. The effect of ζ on particle stability is covered in the following section.

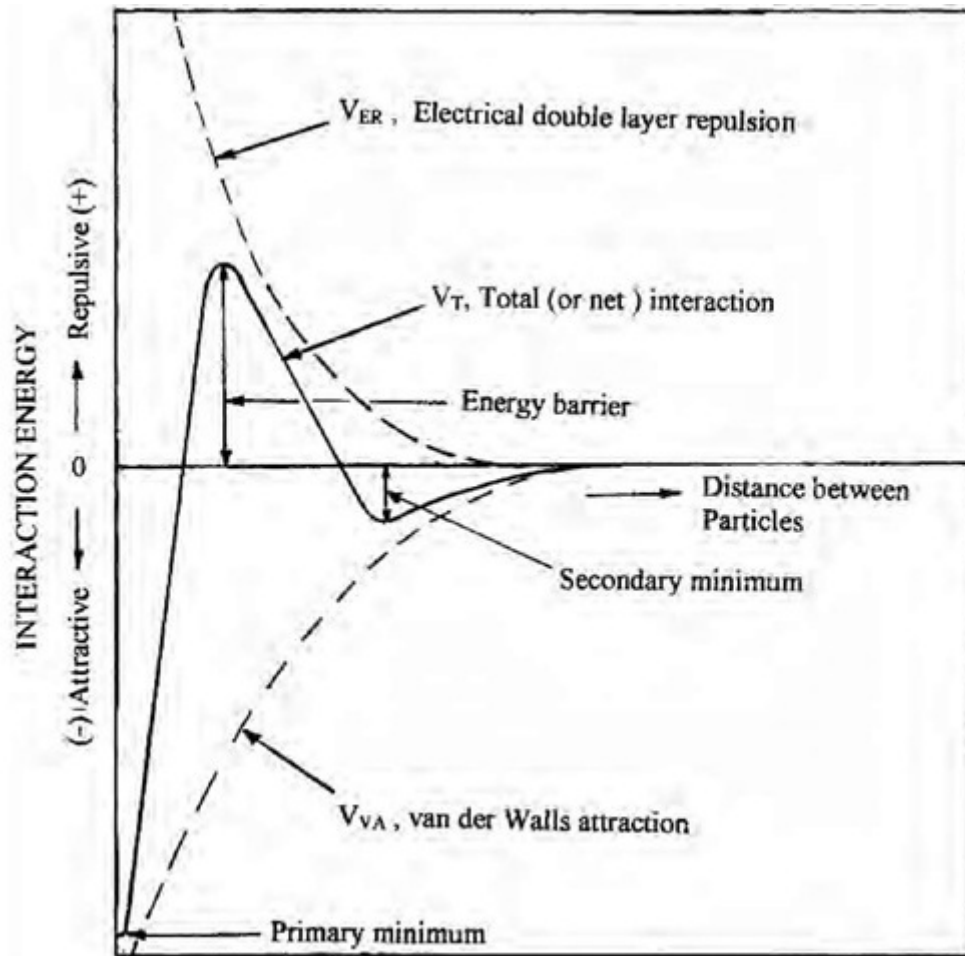


Figure 2.9 The variation in interactive energies with particle distance based on DLVO theory (Celik and Ersoy, 2004)

2.5.4 Zeta potential and stability

The ζ is the potential energy at the surface of the slipping plane as shown in Figure 2.7. It is an important property of a particle suspension that determines the strength of the EDL repulsive forces between particles and therefore identifies the stability of a colloid system. The concentration (or availability) of counter ions and temperature influence the nature of the EDL and hence the ζ (*cf.* Section 2.5.2). Therefore the stability or ζ of the suspension may be manipulated by the addition of an electrolyte containing counter ions or by changing its pH or temperature.

ζ can be calculated from the Helmholtz-Smoluchowski equation (Bennett, 1959) for large solid particles:

$$\zeta = \frac{4\pi\mu}{\epsilon}\beta \quad 2.3$$

where β is the electrophoretic mobility,

μ is the dynamic viscosity of the solution,

ϵ is the dielectric constant within the electrical double layer surrounding the particles.

If the particles have a large positive or negative ζ (e.g., $> \pm 100$ mV) a sufficiently large repulsive force exists between the particles and aggregation is prevented. However, at lower ζ there is usually sufficient kinetic energy available to overcome the energy barrier to allow particles to approach close enough for the attractive forces to dominate and initiate aggregation. For the case where the ζ is equal to zero corresponds to the isoelectric point (IEP) which represents the least stable point possible and aggregation occurs readily.

2.5.5 Coagulation and flocculation

Although the terms coagulation and flocculation are sometimes used interchangeably to describe aggregation a distinction can be made between the two terms. In the field of colloid science the term coagulation describes the case where particles in an aqueous solution are destabilised by the addition of salts (coagulants) or by charge neutralisation to form small and dense aggregates (Gregory, 2006). Flocculation on the other hand is used to describe the process where the aggregates formed during coagulation cluster together through polymer bridging to form ‘flocs’ that are generally larger and more open in terms of structure (Gregory, 2006).

The addition of coagulants followed by polymers (flocculants) has been used widely since their development in the 1950’s to improve the performance and efficiency of clarification and filtration processes. In most aqueous solutions particles carry a negative charge and in sugar cane juice clarification for example lime saccharate is typically used to deliver Ca^{2+} ions to the juice to induce destabilisation of the particles and to form cation bridging between the particles and the flocculant.

The flocculants used in the sugar industry belong to the class known as partially hydrolysed polyacrylamides which are linearly chained high molecular weight molecules consisting of acrylate and acrylic acid monomers as illustrated in Figure 2.10 (Anon., 2015).

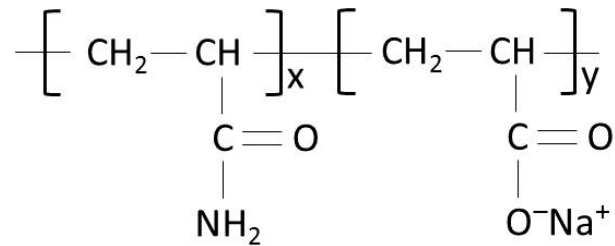


Figure 2.10 Structure of poly (acrylamide-co-sodium acrylate) (Anon., 2015)

In solution, the Na^+ ions (see Figure 2.10) dissociate from the acrylate group resulting in a negative charge on the COO^- branch (Anon., 2015). The number of charged sites along the polymer chain is dependent on the acrylate content (*i.e.*, mol of x) or degree of hydrolysis which represents the mol% of acrylate and acrylic acid monomers, thus (Anon., 2015):

$$\text{Degree of hydrolysis (mol\%)} = \frac{y}{(x + y)} \times 100 \quad 2.4$$

Figure 2.11 (Anon., 2015) shows a schematic of a flocculant structure at 25 and 50 mol% hydrolysis. The charged sites along the chain provide linkage points for the attachment of particles through a divalent cation bridge (Figure 2.12 (a)) (Anon., 2015). Due to its linear structure the higher the molecular weight of the flocculant the longer the polymer chain will be. If only short sections of the polymer chain attach to any one particle several particles can be linked to each polymer chain and an extensive network (flocs) can be built (Figure 2.12 (b)) (Anon., 2015).

The degree of hydrolysis is an important parameter that needs to be considered when selecting the suitability of a flocculant for a given suspension. This is due to the repulsive forces that exist between the negative charges on nearby free linkage points along the polymer chain and the negative charges on the particle surface (Anon., 2015). If the particle surface charge is very low then strong cation bridges can be formed as there is little repulsion from the negative charges on nearby linkage points. In this case a low degree of hydrolysis is required (Anon., 2015). If the degree of hydrolysis is too high then too much of each chain becomes adsorbed on individual particles for extensive inter-particle bridging and floc growth to occur (Anon., 2015). The flocs that are formed will be small and have low settling rates but the supernatant juice will be clear (Anon., 2015).

As the charges on the particle surface increases, the strength of the bond across the cation bridges between the polymer and the particle decreases due to stronger repulsive forces (Anon., 2015). In this case a higher degree of hydrolysis is required to hold the chain on the particle surface (Anon., 2015). If the degree of hydrolysis is too low then some particles are easily dislodged from the chain. However, overall there can still be reasonable floc growth but the main problem is a residual haze in the supernatant juice (Anon., 2015).

In the Australian sugar industry Crees *et al.*, (1991) showed that flocculants with a degree of hydrolysis of between 22 and 35 mol% typically produced improved clarification performance through more rapid settling rates and lower clarified juice turbidities.

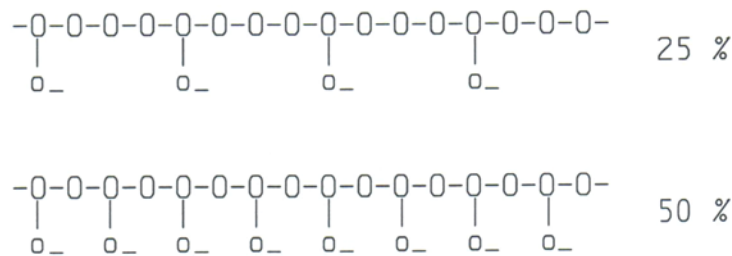


Figure 2.11 Schematic showing two levels (25 mol% and 50 mol%) of flocculant hydrolysis (Anon., 2015)

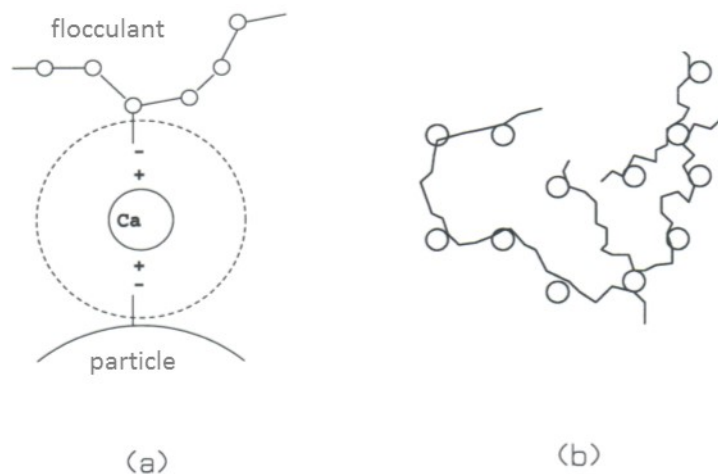


Figure 2.12 Schematic showing the concept of cation bridging (a) and floc formation (b) (Anon., 2015)

2.6 CHEMISTRY OF SOILS

The main colloidal component of soil matter is made up of clay particles that have formed through the process of chemical weathering (mainly through hydrolysis) of silicate minerals at the earth's surface (Harpstead *et al.*, 2001). As with other colloids clay particles have a large ratio of surface area to volume which magnifies the effects of surface forces (*cf.* Section 2.8) in aqueous solutions. Some of the most common clay minerals found in soils are kaolinite (a 1:1 mineral type), illite (a 2:1 mineral type) and smectite (a 2:1 mineral type). The presence of these clays in aqueous systems is the primary cause of slow settling of floc aggregates and poor solution turbidity.

The principal structural elements of clay minerals are two dimensional arrays of silica (silicon-oxygen tetrahedral) and two dimensional arrays of alumina (aluminium or magnesium-oxygen-hydroxyl octahedral) (Harpstead *et al.*, 2001). Their structures include water molecules as well and hence clay minerals are called hydrated aluminosilicates. Structurally, clay particles differ to most other particles due to their platy or layered structure. The structure of most silicate clay particles comprise of silica and alumina layers that are stacked on top of one another in two distinct sequences (Harpstead *et al.*, 2001). In most cases the stacking sequence consists of one alumina layer that is sandwiched between two silica layers in which case the mineral is said to be a 2:1 mineral and in the other case the silica and alumina layers alternate in sequence and in this case the mineral is said to be a 1:1 mineral (Harpstead *et al.*, 2001).

In aqueous solutions clay minerals develop a negative charge on their surfaces due to (1) the presence of oxygen ions with one negative charge unsatisfied along the edge of the crystal (called edge charge) and (2) isomorphous substitution (Harpstead *et al.*, 2001). The edge charge is pH dependent and can be nullified by H^+ ions under acidic conditions and therefore is not a permanent charge. In the case of isomorphous substitution the charge is permanent and is caused in some clays by the substitution of an aluminium ion (Al^{3+}) for a silicon ion (Si^{4+}) in the outer silica layers, and in other clays by the substitution of a magnesium ion (Mg^{2+}) for a Al^{3+} in the alumina layer (Harpstead *et al.*, 2001).

Due to their layering arrangement, clay particles tend to have high aspect ratios (width to height ratio) and for kaolinite, this aspect ratio is usually ~ 10 but can vary widely for very thin platelets (Zbik and Smart, 1998). The aspect ratios of smectite

minerals, such as montmorillonite, are generally much larger (e.g. 80-500) and hence the area of the basal planes is most dominant in smectites (Zbik *et al.*, 2010). As a consequence of the platelet-like shape, the electric charges are present at the mineral surfaces (basal and edge sites), the clay particles have the ability to form complex aggregates and network assemblies in aqueous solutions. This behaviour is dependent on water and clay chemistry as well as the clay particle packing density (Bowles, 1968). In the presence of water, the adsorbed cations in the clay sorption complex can be exchanged with cations of other species in the water environment, and they are therefore known as exchangeable cations.

2.7 PREVIOUS RESEARCH

A large body of literature exists on destabilisation of aqueous colloidal suspensions that cause poor coagulation and flocculation (Davis and Maffia, 1995; Lagaly and Ziesmer, 2003; Tombacz and Szekeres, 2006; Ma, 2011; Szilagy *et al.*, 2012; Lee *et al.*, 2012; Liu *et al.*, 2013). The main focus of their work was to characterise the colloidal particles in terms of their physical and morphological properties, electrokinetic's and investigate their coagulation behaviour in aqueous solutions on the basis of the DLVO theory and the characterisation.

Szilagy *et al.*, (2012) studied the destabilisation of colloidal suspensions in the presence of polyelectrolytes and the corresponding oligomers. They investigated negatively charged particles in the presence of polyamines and positively charged particles in the presence of polycarboxylates and found that:

- multivalent oligomers of low valence destabilize the particles by screening according to the Schulze-Hardy rule,
- polyelectrolytes induce destabilisation by overcharging, and
- both regimes can be observed for oligomers of intermediate valence.

Lagaly and Ziesmer (2003) reviewed the coagulation of sodium montmorillonite dispersions by inorganic and organic cations and the influence of compounds of practical interest such as phosphates, cationic and anionic surfactants, alcohols, betaine-like molecules and polymers like polyphosphates, tannates, polyethylene oxides with cationic and anionic end groups, and carboxy methylcellulose. Their studies revealed various destabilisation processes such as:

- The influence of the counter ion valence corresponded to the DLVO theory.
- Adsorption of multivalent anions, especially of several phosphates increases the density of the negative edge charges and transforms the edge (-)/face (-) coagulation into face (-)/face (-) coagulation with distinctly higher critical salt concentrations.
- In dispersions of high montmorillonite contents (>1%) the coagulation is, probably, initiated by edge (-)/edge (-) aggregation. Coagulation between the positive edges and the negative faces (card house structure) only occurs at $\text{pH} < 6$.
- Adsorption of the inorganic counter ions at the surface plays an important role and is still more pronounced for organic cations which show very low coagulation concentrations. In these cases, the effect of the valence on the critical coagulation concentration is obscured by the Stern layer adsorption, the different orientation of the organic counter ions on the surface, and their influence on the solvent structure near the surface. As a consequence of the adsorption of inorganic and organic counter ions on the clay mineral surface the critical coagulation concentration (cK) value depends on the montmorillonite content in the dispersion.
- The substitution of the exchangeable cations by betaines provides an example of lyosphere stabilization: the betaine molecules anchored at the surface immobilize large amounts of water around the particles so that the van der Waals attraction between the particles in the aqueous dispersion become weak, the electrostatic repulsion dominates and increases the salt stability.
- Polyethylene oxides with cationic and anionic end groups show the interplay between flocculation by charge neutralisation or by bridging and steric stabilization. However, pronounced stabilization of the sodium montmorillonite dispersions (cK values of NaClG500 mmol/l) was only attained for polyethylene oxides with smaller molecular masses (F4000) and hexadecyl dimethylammonium end groups.

Despite these studies very little work has been done to investigate the effects of colloidal suspensions in sugarcane juice clarification and filtration. However, it should

be noted that a reasonable amount of work has been undertaken on the effects of high mud solids loading on clarification and filtration.

Steindl (1998) showed that high mud solids (>0.8 wt%) loading in the clarifier feed usually resulted in:

- Reduced settling rates of flocculated mud particles;
- Poor clarification performance as evidenced by hazy clarified juice and carryover of mud particles with the clarified juice; and
- Rapidly rising mud levels in the bottom of the clarifier.

Wright (2006) studied the effects of soil and other factors on mud filtration. The quantities of mud to be handled and the filter performance criteria (the filter area requirement, pol loss in mud cake, and fibre ratio) are strongly related to the level of mud solids in juice, and hence are strongly influenced by the soil level in the cane. His work showed that for a one percent unit rise in soil in the cane supply the mud underflow rate rose by approximately 4 vol%. Therefore as the soil rate in the cane supply increased the mud cake rate also increases leading to higher sucrose losses.

These studies did not however look at the underlying causes of poor clarification and mud filtration based on the soil properties.

Kampen (1974) on the other hand studied the effects of three different types of field soil typically found in the Louisiana (USA) cane growing region. The soils were classified as sandy, silty and clayey. In the tests varying quantities of these soils were added to clean hand cut juices from three different cane varieties. Kampen (1974) concluded that:

- All three soil types increased the final mud height. The clayey soil significantly increased the final mud height compared to the silty and sandy soil types;
- The turbidity of the clarified juices were somewhat improved when field soil was present. This was usually much more so for the clayey soil compared to the silty and sandy soils;
- The clarification effect, which is non-sugars removed/original non-sugars present (x) 100, is lower when the juice contained field soil, more so for the clayey soil;

- The true purity is also slightly lowered when field soils are present, and, again, more so for the clayey soils;
- From analyses of the clarified juice with an atomic absorption flame emission apparatus, it was found that field soils increase the SiO₂ content slightly;
- The sodium and magnesium content in the clarified juice do not change significantly;
- The potassium and calcium content in the clarified juice are slightly lowered, more so by the clayey soil;
- The aluminium and iron content in the clarified juice are slightly lowered, more so by the clayey soil; and
- The phosphorus pentoxide (P₂O₅) content in the clarified juice increased slightly.

The present study builds on the work undertaken by Kampen (1974) to obtain a greater understanding of the effects of clay soils on clarification and filtration.

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Chapter 3: Studies on the Physico-Chemical Properties of Soils

3.1 INTRODUCTION

In this chapter soil samples received from three different sugar cane growing regions in Queensland, Australia were characterised in terms of their physico-chemical properties. The chapter is split into two sections, viz., sections 3.2 and 3.3. Section 3.2 presents the analyses work to determine some of the physical properties of the soils. Section 3.3 presents further characterisation of the soils in terms of their physico-chemical properties and settling tests to investigate the relationship between impurities in the soils and the impact on the settling behaviour.

3.2 CHARACTERISATION OF SOILS

3.2.1 Materials

3.2.1.1 Field soils

The soil sample name, its origin, moisture and typical factory clarification performance of the juices extracted from the different cane supply sources are shown in Table 3.1.

The soil samples were collected from multiple locations and from the top ~10 cm of the soil and then mixed to produce composite samples. The soils were then spread out on trays and allowed to dry as much as possible at room temperature in the laboratory. Any large fibrous materials present in the soil samples were removed by physical means. The larger soil aggregates were broken down to form fine loose soil using a Resch BB200 jaw crusher prior to mixing to form composites (Figure 3.1).

Table 3.1 Soil name, origin and typical factory clarification performance

| Sample name | Origin | Typical factory clarification settling rate, cm/min |
|---------------|---------|---|
| Mt Mackay | Tully | 30-60 (Good) |
| Invicta 255B | Invicta | 1-20 (Poor) |
| Gluepot 3522A | Mackay | 1-20 (Poor) |

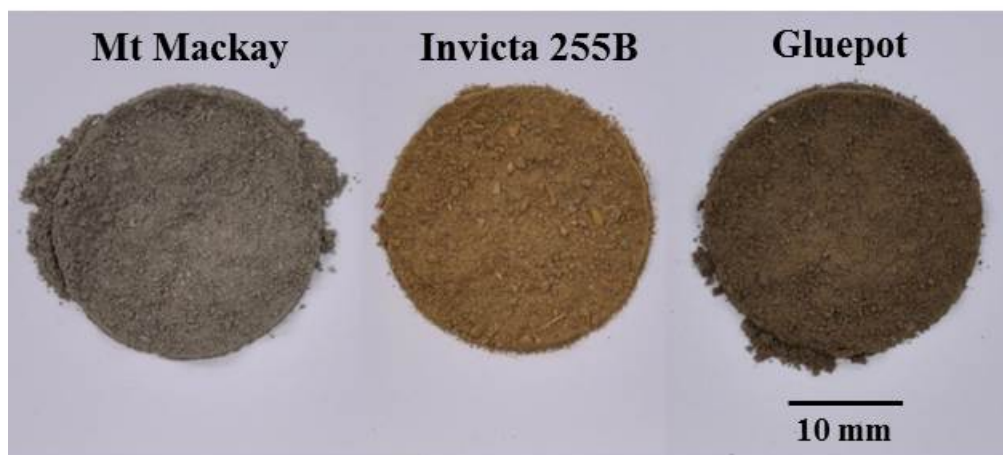


Figure 3.1 Photo showing the samples of the soils after they were processed through the Resch BB200 jaw crusher

3.2.2 Methods

3.2.2.1 Moisture content

The moisture content of the soils was determined by drying the samples in an oven at 65 °C to constant weight.

3.2.2.2 Helium pycnometer tests on soils

The true particle density of the soils was determined by the Helium Pycnometer test using an AccuPyc 1340. A 15 cm³ sample holding chamber was used and filled to ~75 % full.

3.2.2.3 Particle size distribution of the soils

A 1 wt% solution of the soil was prepared using Milli-Q water. The solution was sonicated for a total of 6 min prior to analysis in the Malvern Mastersizer 3000E.

3.2.2.4 Clay fraction analysis

Prior to clay fraction analysis, 2.5 g of each soil sample was dried in an oven overnight at 110 °C to constant weight. Each of the dry soil samples were transferred into separate 110 mL plastic jars followed by the addition of 100 mL of Milli-Q water and 1 mL of 30% ammonia solution to each jar. The suspensions were sonicated for 1 minute using a probe sonicator. After sonication, the solutions were transferred to 1000 mL measuring cylinders and a further 2 mL of the ammonia solution was added. The contents were mixed by inverting 10 times and then left standing to allow particles >2 µm (non-clay fraction) to settle sufficiently below the liquid surface so that 10 mL

aliquots of the supernatant could be syphoned out from the upper region of the supernatant using a pipette.

The clay size fraction is considered to be particles of $<2 \mu\text{m}$. Stokes law was used to determine the time required for particles $>2 \mu\text{m}$ (density of 1.65 g/cm^3) to settle $\sim 80 \text{ mm}$. Each 10 mL aliquot was collected after allowing suspension to stand for $\sim 6 \text{ h}$. The 10 mL aliquots were then transferred into separate 25 mL pre-weighed beakers. Each solution was placed in an oven at $\sim 65 \text{ C}$ under vacuum until the bulk of the water was evaporated. The partially dried samples were then transferred to a $110 \text{ }^\circ\text{C}$ oven and dried to constant weight. The difference in weight between the empty beaker and the dried sample plus beaker is the clay content in the 10 mL portions of the original 1 L suspensions. Thus, the total clay weight in the original soil sample is the clay weight multiplied by $(1000/10)$. The clay fraction (wt%) is the total clay weight divided by the weight of the original sample.

3.2.2.5 Organic fraction analysis using hydrogen peroxide method

Prior to organic fraction analysis 2.5 g of each soil sample was dried in an oven overnight at $110 \text{ }^\circ\text{C}$ to constant weight. Approximately 2.5 g of the pre-dried soil samples were weighed and transferred into pre-weighed 250 mL glass beakers. To each beaker 100 mL of Milli-Q water was added. Using a burette, hydrogen peroxide ($3 \text{ v/v}\%$) was added slowly and incrementally to the soil suspensions whilst stirring to allow it to react with the organics in the samples. The addition of hydrogen peroxide breaks down organics to CO_2 . The reaction was presumed complete when no CO_2 gas bubbles were visible by further addition of hydrogen peroxide. Approximately, 10 to 20 mL of peroxide was added to each suspension.

The beakers including the reacted samples were then placed in a vacuum oven set to $65 \text{ }^\circ\text{C}$ and dried to constant weight. The samples were then dried to constant weight at $110 \text{ }^\circ\text{C}$. The weight of the organic component is the difference between the original sample weight and the weight of the sample after it was dried to constant weight at $110 \text{ }^\circ\text{C}$. The organic fraction (wt%) is the weight of the organic component divided by the original sample weight.

3.2.2.6 Total organic carbon, organic C, and carbonate by loss on ignition

The total organic carbon, organic C and carbonate by loss on ignition were determined based on method 6G1 in Rayment and Lyons (2011).

Soil samples (~3 g) dried overnight in an oven at 105 °C were placed into a furnace set at 550 °C for 2 h. The samples were cooled and then transferred to the desiccator before being weighed. The difference in weight represents the organic matter in the soil samples.

The samples were then placed back into the furnace set at 950 °C for 2 h. The samples were cooled and then transferred to the desiccator before being weighed. The difference in weight between the 550 and 950 °C drying periods represents the organic carbonate content of soils.

The difference in weight before drying at 550 °C and after drying at 950 °C represents the total organic carbon content of the soils.

3.2.2.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a valuable technique, which provides qualitative information on the surface chemistry and elemental composition of substances. Survey (*i.e.*, wide) scans were taken with pass energy of 160 eV and multiplex (*i.e.*, narrow) high-resolution scans were taken at 40 eV. Survey scans were carried out over a binding energy range of 1200 eV to 0 eV with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure was 1.0×10^{-9} torr and 1.0×10^{-8} torr in the analysis chamber and during sample analysis, respectively. Peak fitting of the high-resolution data were also carried out using the CasaXPS software.

3.2.2.8 Time of flight secondary ion mass spectrometry (TOF-SIMS)

The analysis were carried out at the Australian Microscopy and Microanalysis Research Facility, Ian Wark Research Institute, University of South Australia.

Surface analysis was carried on dry loose soil samples and wet samples obtained from a suspension in Milli-Q water. The wet samples were prepared by adding soil material to Milli-Q water, sonicating for 5 min and allowing it to settle for 30 min. Aliquots were extracted from the suspension near the top of the solution. A droplet of this sample was then placed on a clean silicon wafer and the sample placed in a desiccator and pumped down to remove the liquid phase. The soil residue on the wafer was then loaded for surface analysis.

In all cases, the mass spectra collected from the analysis contained high responses from inorganic elemental species (*i.e.*, Na, Al, Si, K, Ca and Fe). Organic peaks were also detected, but in much lower intensity and with complex fragmentation patterns. These data were normalised to total selected counts per spectra, to help correct for changes in ion yield between experiments. This then allows qualitative comparisons to be made between different measurement and different samples.

Principal component analysis (PCA) was used to help highlight and identify variation in the data set, and hence differences between samples. Principal component analysis is a statistical procedure that transforms data to a set of values of linearly uncorrelated variables called principal components which is ordered in terms of their variance. The lack of correlation is important as it indicates that the components are measuring or representing different aspects in the data.

3.2.3 Results and discussion

3.2.3.1 Moisture content of the soils

Table 3.3 shows the moisture contents for each of the soils after drying. Mt Mackay and Gluepot contained the highest proportion of adsorbed water.

Table 3.2 Moisture content of soil samples

| Sample name | Moisture content, wt% |
|---------------|-----------------------|
| Mt Mackay | 10.44 |
| Invicta 255B | 2.70 |
| Gluepot 3522A | 7.89 |

3.2.3.2 True particle densities of the soils

The true particle density is the weight per unit volume of the solid portion of the soil as described by Webb (2001). It should not be confused with the bulk density which also includes the volume occupied by voids between neighbouring particles and voids within each particle. The true particle density is most relevant in relation to settling rates of flocs formed from soil suspensions. Because soils are typically made up of varying quantities of silicates, organics and metal oxides the true particle density measured here represents the average true particle density of all the particles that make up the soil. The true particle density is high if large amounts of heavy minerals such

as magnetite; limonite and hematite or metal oxides are present in the soil. With increase in organic matter of the soil the particle density decreases. As most soils contain relatively high quantities of quartz their true particle densities are commonly quoted as being $\sim 2.650 \text{ g/cm}^3$ (Schjonning *et al.*, 2017).

The true particle densities of the soil samples are shown in Table 3.3. The results show that the particle densities vary between 2.3 and $\sim 2.5 \text{ g/cm}^3$. Gluepot has the lowest particle density at 2.324 g/cm^3 and Invicta 255B has the highest particle density at 2.539 g/cm^3 .

Table 3.3 True particle density of soil samples

| Soil sample | True particle density (g/cm^3) |
|---------------|--|
| Mt Mackay | 2.509 |
| Invicta 255B | 2.539 |
| Gluepot 3522A | 2.324 |

3.2.3.3 Particle size distribution

Figure 3.2 shows the particle size distribution of the three soils. Mt Mackay which is known to be a good settling soil has the lowest proportion of particles less than $1 \mu\text{m}$. It also has the highest proportion of particles in the 10 to $100 \mu\text{m}$ range. For particles in the 5 to $15 \mu\text{m}$ range Gluepot has a lower proportion than the Mt Mackay sample. Particles with sizes in the range 100 to $1000 \mu\text{m}$ predominate in the Invicta 255B sample compared to the other soils. These may be related to the organic matter fraction.

The specific surface areas, the mean volume diameter ($D[4,3]$) and the particle sizes at 10, 50 and 90 wt% volume densities are summarised in Table 3.4.

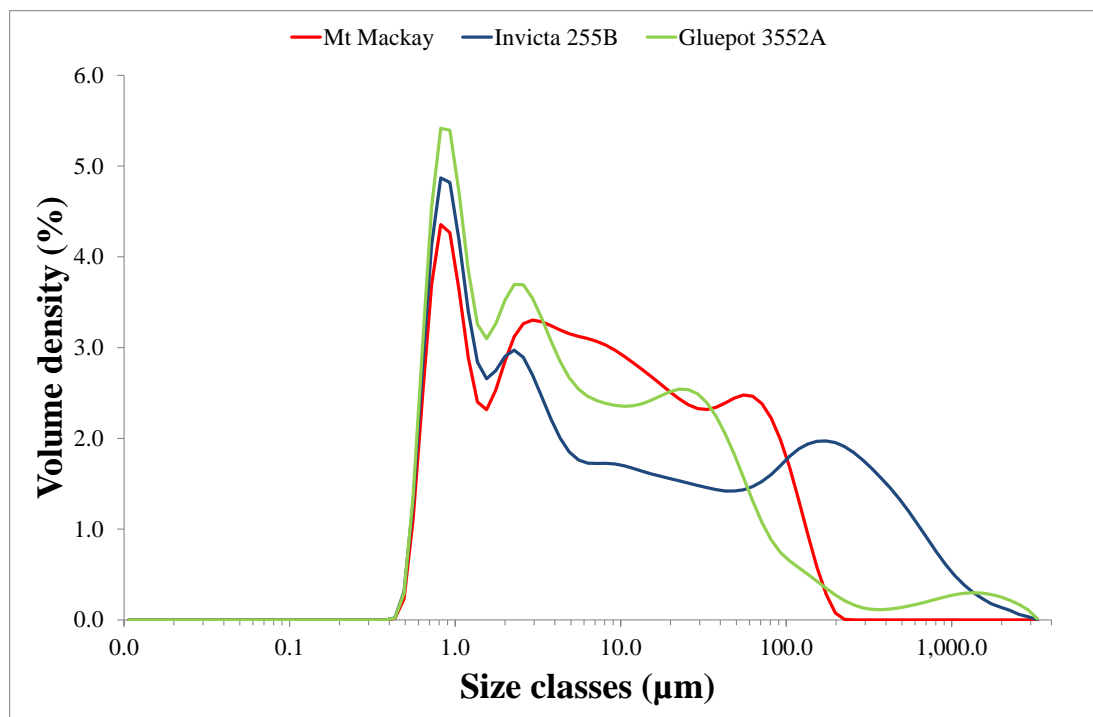


Figure 3.2 Particle size distribution of the soils

Table 3.4 Particle size data

| Soil | Specific surface area m ² /kg | D[4,3] µm | Volume, % | | |
|---------------|--|--------------|---------------|---------------|---------------|
| | | | Dx (10) µm | Dx (50) µm | Dx (90) µm |
| Mt Mackay | 2221 | 20.6 | 0.875 | 6.30 | 65.2 |
| Invicta 255B | 2293 | 106 | 0.840 | 8.04 | 321.0 |
| Gluepot 3522A | 2645 | 54.7 | 0.819 | 4.19 | 54.3 |

3.2.3.4 Clay and organic fractions

Figure 3.3 shows the proportion of the clay and organic fractions (based on the peroxide method) in the soils. Both the Invicta and Gluepot soils have relatively higher proportions of clay compared to the Mt Mackay soil. The Gluepot soil also has significantly higher proportions of organic matter compared to the other two soils.

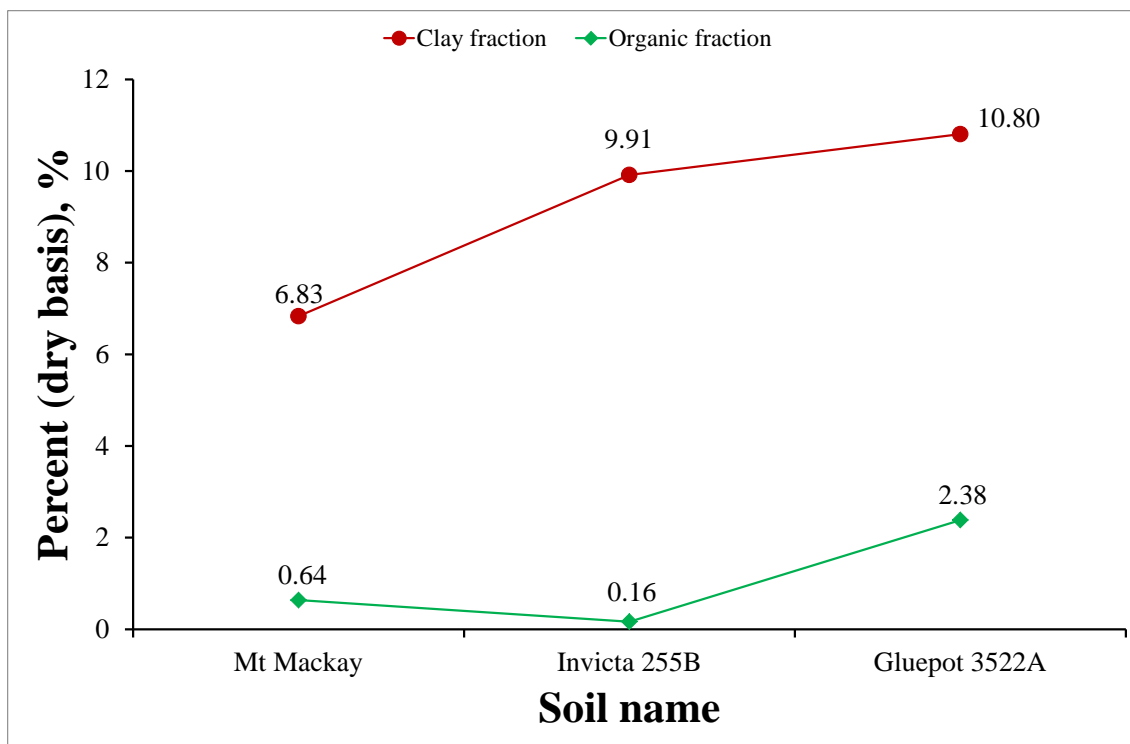


Figure 3.3 Clay and organic fractions of the soils

3.2.3.5 Loss on ignition

Results of the carbon content in the soil samples are presented in Table 3.5. The results show that approximately 90 % \pm 5 % of the total carbon is released at 550 °C (organic material). Gluepot has the highest % carbon in organic matter as well as carbonates. This soil is regarded as having a low settling velocity during factory clarification.

The results presented in Figure 3.3 were determined using the hydrogen peroxide method, and follow a similar trend to the ignition method. The results show that organic carbon determined by the peroxide method aligns with carbon associated with carbonates.

Table 3.5 Carbon content of soil samples

| Sample | Organic material (loss on ignition @ 550 °C) | | Carbonates (loss on ignition @ 950 °C) | | Total loss (wt%) |
|---------------|--|---------------|--|---------------|---------------------|
| | Loss (wt%) | % of total | Loss (wt%) | % of total | |
| | Mt Mackay | 8.02 | 94.95 | 0.43 | |
| Invicta 255B | 4.39 | 88.67 | 0.56 | 11.33 | 4.95 |
| Gluepot 3522A | 12.93 | 93.94 | 0.83 | 6.06 | 13.76 |

3.2.3.6 X-ray photoelectron spectroscopy (XPS)

Figure 3.4 to Figure 3.6 show the XPS survey scans for the colloidal soils of the Mt Mackay, Invicta 255B and Gluepot soil samples respectively. The scans show that there are relatively higher quantities of oxygen, carbon, Si and Al compared to Fe, N, Ca and K. The Si:Al ratio indicates the type of mineral present in the colloidal soils (Shainberg and Levy, 2005). The Si:Al ratio is 1:1 for the Mt Mackay sample indicating a clay mineral of kaolinite type, while the Si:Al ratio for the other two soils indicate a mixture of the 1:1 and 2:1 mineral types. The 2:1 mineral is of the montmorillonite type, a known expandable clay (Barton and Karathanasis, 2002). Expandable clays have the ability to absorb water (Karpinski and Szkodo, 2015) which would reduce their bulk density and hence their settling rates. Both Invicta 255B and Gluepot soils are known to have poor settling rates during factory clarification (Table 3.1).

The amount of Ca and Fe is least in the Mt Mackay sample, regarded as a soil with good clarification characteristics. Calcium and Fe ions are noted to assist coagulation, so there may well be a minimum concentration required. Hydrolysable cations such as Al^{3+} and Fe^{3+} can be highly effective in dispersion destabilisation and in addition to causing double-layer compression, these species are highly surface active and can reverse the ζ (Tripathy and De, 2006). These species can also promote aggregation by modifying dispersed particles through surface precipitation of colloidal hydroxides.

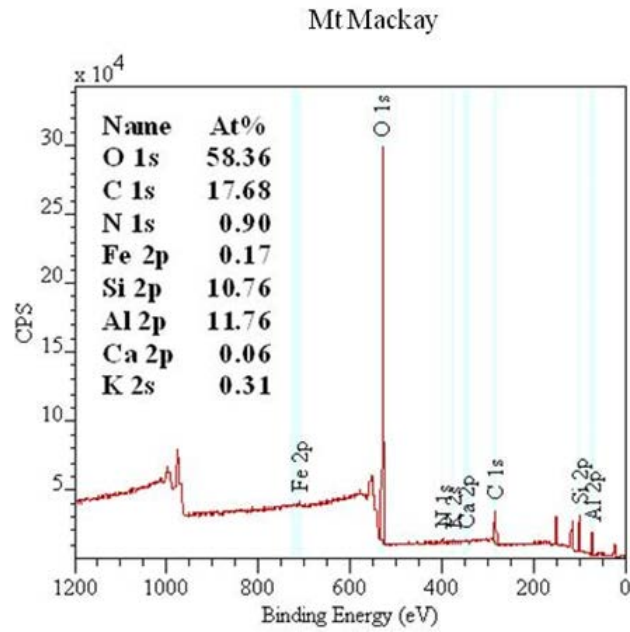


Figure 3.4 XPS survey scan for colloidal soil particles for Mt Mackay soil

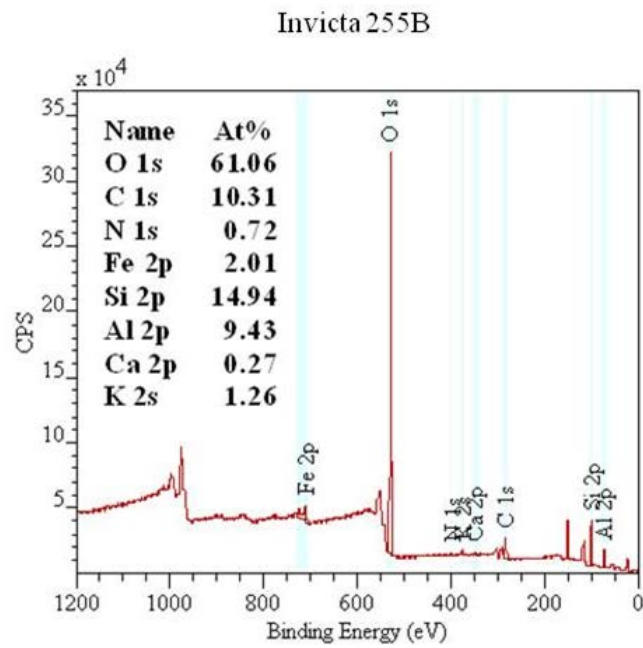


Figure 3.5 XPS survey scan for colloidal soil particles for Invicta 255B soil

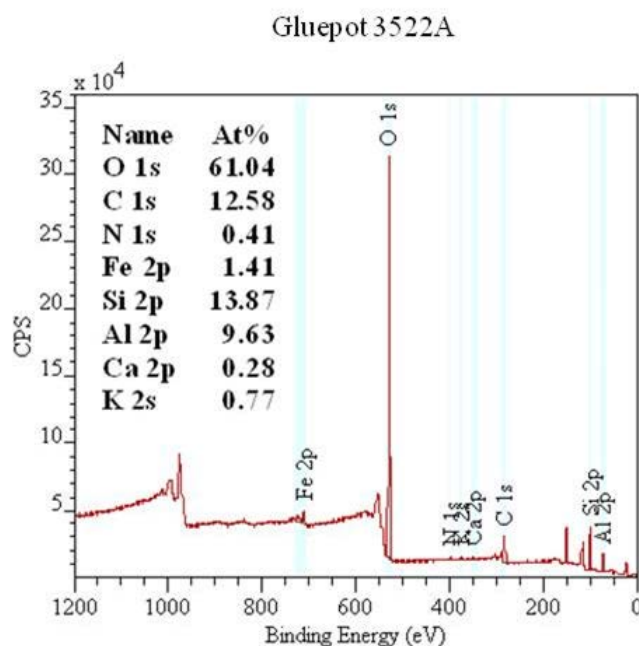


Figure 3.6 XPS survey scan for colloidal soil particles for Gluepot soil

To determine the chemical states associated with the C, O, N, Si and Al peaks, a high resolution scan was obtained for Mt Mackay, Invicta 255B and Gluepot (Table 3.6 to Table 3.8 and Figure 3.7 to Figure 3.9). The high resolution XPS spectra of the C 1s electrons obtained from the measurement of the samples clearly indicate four chemically shifted C 1s peak, of different chemical environments. The XPS analysis of the soil samples reveal the presence of hydrocarbons (C*-C), alcohol (C*-OH), carbonyl (C*-O) and organic ethers (C*-OC). These carbon functional groups suggest the presence of polysaccharides and organic acid compounds. The amide functional group suggests the presence of proteins, and that the surfaces are negatively charged due to the ionisation of the carboxyl and amino groups to give COO⁻ and NH₃⁺ ions (Miflin, 2014). It should be noted, however, that no ionisable carboxylic acid was detected from the binding energy results, perhaps indicating that at the pH the samples were analysed was not sufficient for this to occur.

As shown in Table 3.6 to Table 3.8, the proportions of the organic and also inorganic compounds are different among the three samples. The proportions of hydrocarbon and alcohol species are highest in the Mt Mackay samples, while the proportion of the carbonyl group is highest in the Gluepot sample. The ionisable species will have a strong bearing on the overall charge, *i.e.*, ζ associated with the soils.

Table 3.6 Binding energy values for Mt Mackay soil

| Bond | Binding energy (eV) | Atomic % |
|---------------------------|---------------------|----------|
| Fe 2p | 711.935 | 0.143 |
| Fe 2p | 714.560 | 0.034 |
| O 1s, some O*-amide | 531.941 | 57.790 |
| N*-H ₂ /N*-C-O | 400.080 | 0.778 |
| K 2p _{3/2} | 293.307 | 0.343 |
| K 2p _{1/2} | 296.184 | 0.180 |
| C*-C | 284.800 | 8.225 |
| C*-OH | 286.409 | 6.061 |
| C*-O | 287.694 | 1.707 |
| C*-OC | 288.877 | 1.478 |
| Si 2p | 102.798 | 11.130 |
| Al 2p | 74.467 | 12.130 |

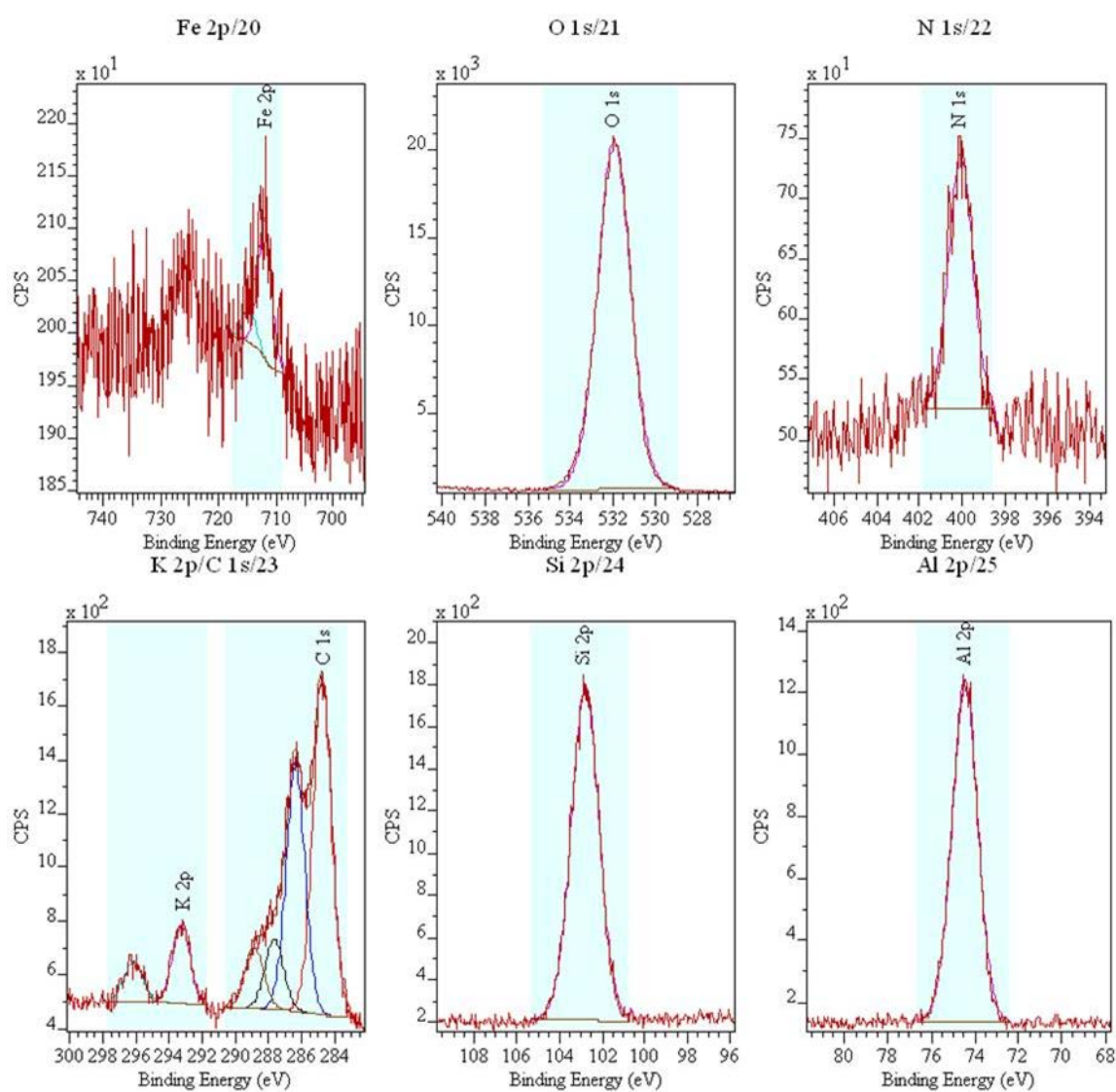


Figure 3.7 High resolution XPS spectra for Mt Mackay soil

Table 3.7 Binding energy values for Invicta 255B soil

| Bond | Binding energy (eV) | Atomic % |
|---------------------------|---------------------|----------|
| Fe 2p | 712.342 | 0.678 |
| Fe 2p | 714.677 | 0.174 |
| O 1s, some O*-amide | 531.941 | 62.430 |
| N*-H ₂ /N*-C-O | 400.234 | 0.462 |
| K 2p _{3/2} | 293.498 | 0.936 |
| K 2p _{1/2} | 296.282 | 0.419 |
| C*-C | 284.800 | 5.375 |
| C*-OH | 286.731 | 2.293 |
| C*-O | 285.847 | 0.876 |
| C*OC | 288.902 | 0.768 |
| Si 2p | 102.845 | 15.760 |
| Al 2p | 74.552 | 9.829 |

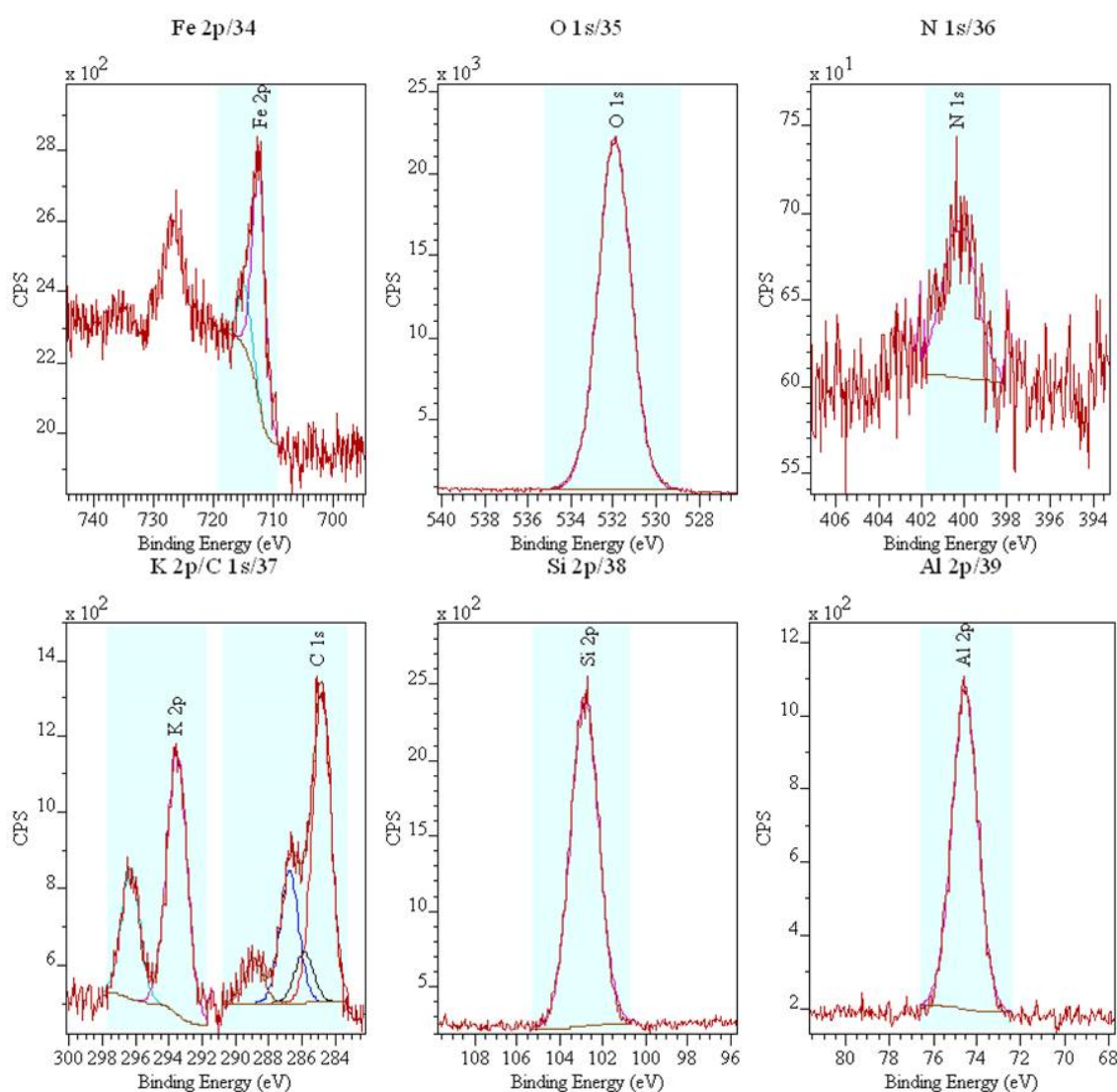


Figure 3.8 High resolution XPS spectra for Invicta 255B soil

Table 3.8 Binding energy values for Gluepot soil

| Bond | Binding energy (eV) | Atomic % |
|---------------------------|---------------------|----------|
| Fe 2p _{3/2} | 712.427 | 0.544 |
| Fe 2p _{3/2} | 714.983 | 0.190 |
| O 1s, some O*-amide | 531.931 | 60.450 |
| N*-H ₂ /N*-C-O | 400.164 | 0.407 |
| K 2p _{3/2} | 293.548 | 0.675 |
| K 2p _{1/2} | 296.309 | 0.353 |
| C*-C | 284.800 | 6.839 |
| C*-OH | 286.172 | 2.212 |
| C*-O | 286.958 | 2.226 |
| C*-OC | 288.928 | 1.232 |
| Si 2p | 102.831 | 14.33 |
| Al 2p | 74.5213 | 10.53 |

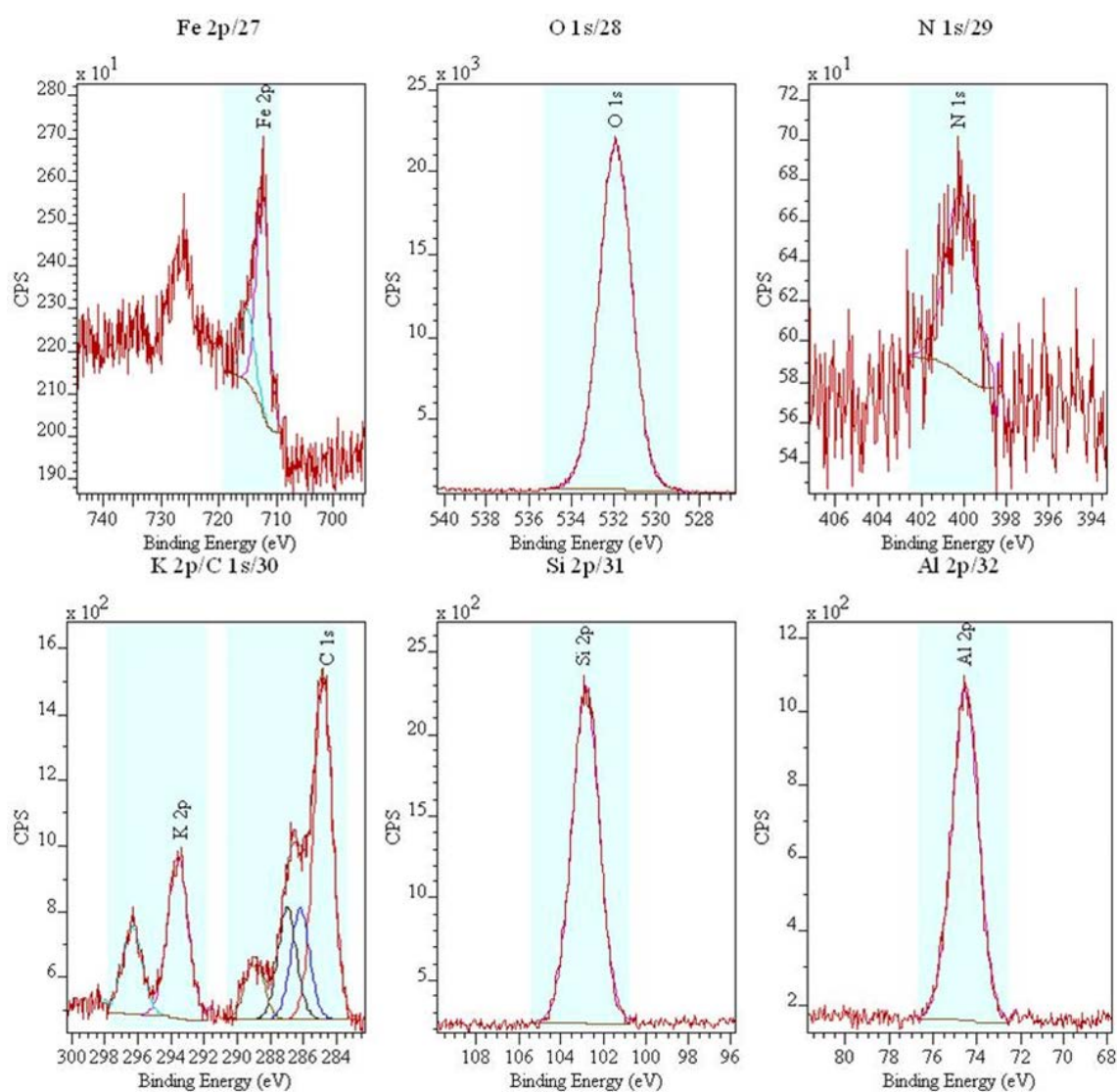


Figure 3.9 High resolution XPS spectra for Gluepot soil

3.2.3.7 Time of flight secondary ion mass spectrometry (TOF-SIMS)

The surface chemistry of the soil particles plays an important role in its coagulation and flocculation behaviour (*cf.*, Section 2.5). Time of flight secondary ion mass spectrometry (TOF-SIMS) is one of the most sensitive and reliable analytical techniques that assists with the identification of chemical species present on the outer most layer (~1-2 nm) of solid materials. TOF-SIMS has been used by many researchers to identify organic and inorganic species on the surfaces of particles (Cliff *et al.*, 2002; Grams and Bawolak, 2007; Chehreh Chelgani and Hart, 2014). The TOF-SIMS analysis was undertaken on the Mt Mackay and Gluepot soil samples.

Principal component analysis (PCA) was used to distinguish any differences in the surface chemistry between the Mackay and Gluepot soils as well as between wet and dry samples of the soils. Clustering of measurements in the PCA score plots suggests similar surface chemistry, and conversely measurements separated suggest significant variation (Holzweber *et al.*, 2014). Reference to the species in the loadings plots can help explain why measurements are either positively or negatively correlated to the principal component axes of the score plots.

3.2.3.7.1 Organic species

Figure 3.10 and Figure 3.12 show the principal component analysis (PCA) score plots for the wet and dry Mt Mackay and Gluepot samples respectively. Figure 3.11 and Figure 3.13 show the PCA loadings plots for the Mt Mackay and Gluepot samples respectively. The first principal component in the score plot for Mt Mackay (Figure 3.10), which represents ~93% of the variation in the original data set, shows that the wet and dry samples are separated on the PC1 axis. There is a larger spread in the 'dry' data points suggesting more surface heterogeneity. The loadings plot (Figure 3.11) shows a negative correlation with some hydrocarbon chain fragments as well as a strong correlation to NH_4^+ . The dry samples show strongest correlation to C_2H_4^+ and C_3H_5^+ .

The first principal component in the score plot for Gluepot (Figure 3.12), which represents ~66% of the variation in the original data set, shows that the wet and dry samples are roughly separated on the PC1 axis. There is however a larger spread in the 'dry' data points suggesting more surface heterogeneity. The loadings plot (Figure 3.13) shows an intense negative correlation to the first PC for NH_4 , as well as some

strong correlations for some hydrocarbon fragments. The most positively correlated, and hence associated with the dry samples, are signals for CH_3N and $\text{C}_3\text{H}_4\text{O}$.

Overall, there are a few trends apparent in the data. The spread in dry data points compared to wet data points suggest that the surfaces of the dry soils are more heterogeneous in comparison. The reason the surfaces of the wet samples appear more homogeneous after wetting may perhaps be due to the sample preparation method. When the soils were wet, any soluble material may have come out of the soil, and then upon drying in the vacuum redeposited on the surface of the soil particle in a more even manner. One of these species seems to be related to NH_4^+ , which exhibits a very strong correlation to all wet samples.

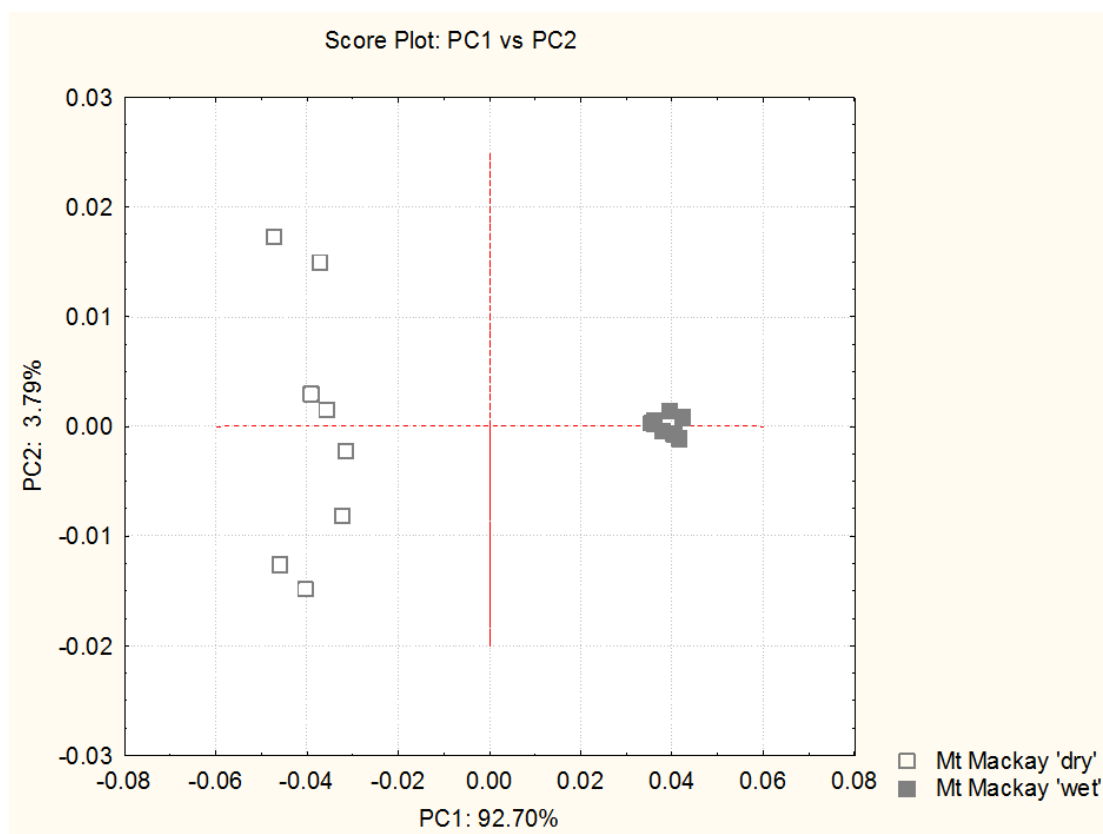


Figure 3.10 PCA score plot of Mt Mackay samples

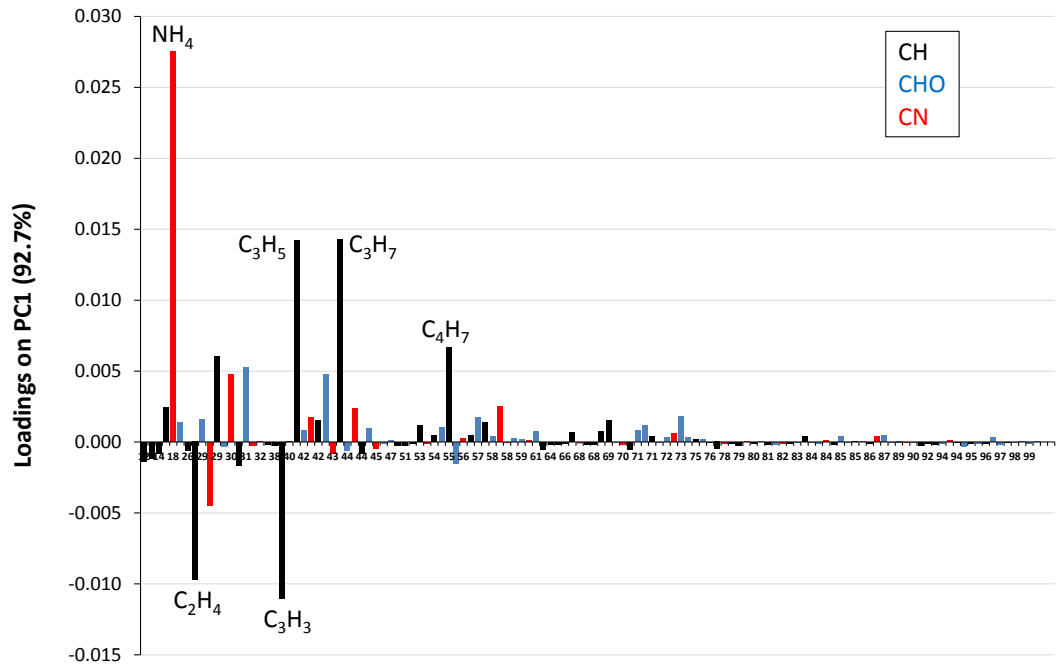


Figure 3.11 PCA loading of chemical species present in Mt Mackay samples

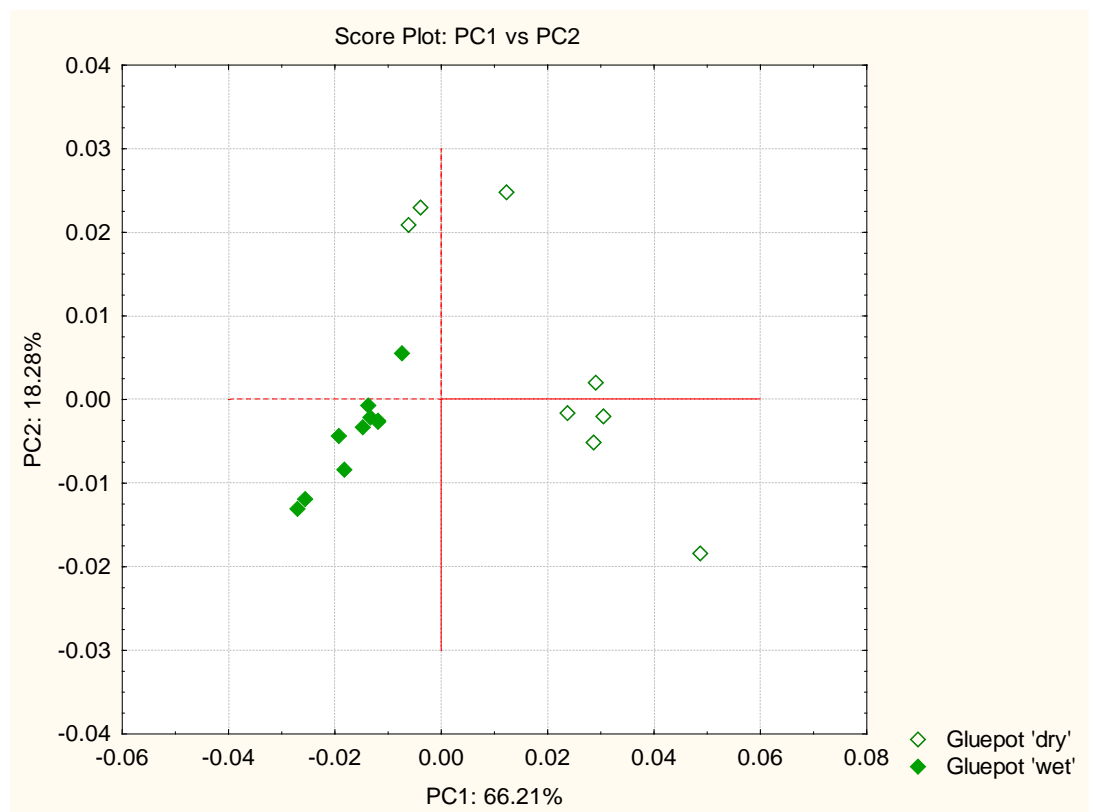


Figure 3.12 PCA score plot of Gluepot samples

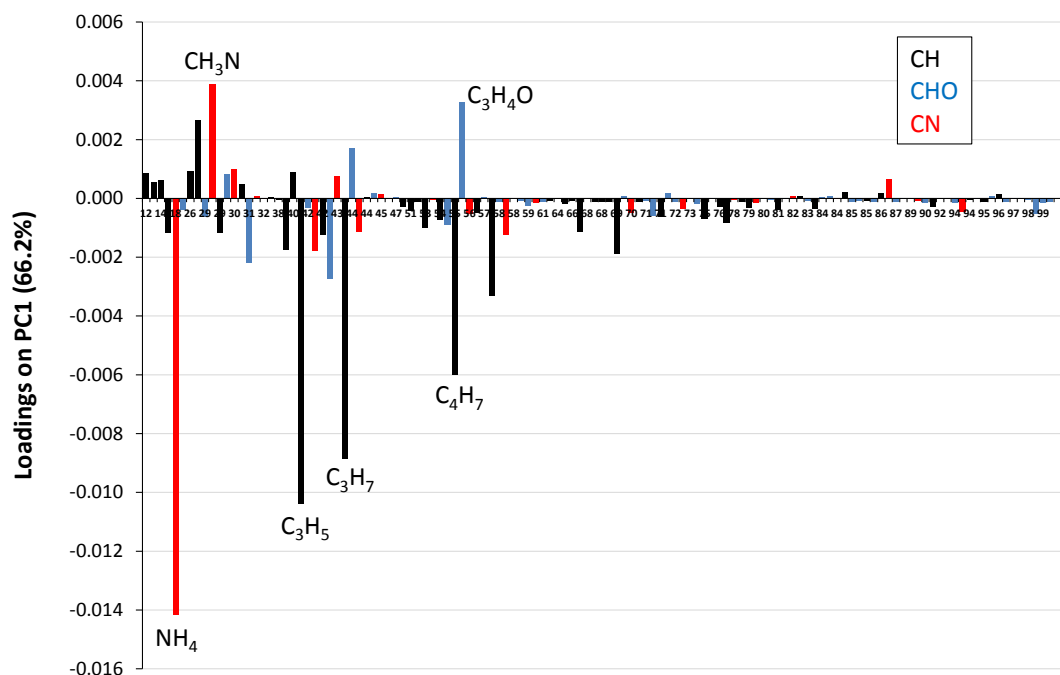


Figure 3.13 PCA loading of chemicals species present in Gluepot samples

3.2.3.7.2 Inorganic species

Figure 3.14 and Figure 3.15 detail the inorganic species and total organics present in the dry and wet Mt Mackay and Gluepot 3552A samples. In all cases the mass spectra collected from the analyses contained high responses from inorganic elemental species (*i.e.* Na, Al, Si, K, Ca and Fe). A significant difference between the wet and dry samples is the higher proportion of Na ions in the wet samples. There is also a higher proportion of total organics in the wet samples. In the dry samples the proportion of Al ions is higher. Sodium ions are known to be highly hydrated and are known to be good dispersants and hence poor coagulants (Sakuma *et al.*, 2011; Scholz, 2016). As such, looser flocs are expected to be formed with the wet samples compared to the dry samples. The higher organic content in the wet samples will to a certain extent, influence the floc density.

The soil from Mt Mackay is classed as good because juices expressed from sugarcane that originate from the soil have good clarification and settling characteristics. The proportion of Na ions on the surface of the wet particles of the Mt Mackay's soil is significantly less than the Gluepot 3552A sample.

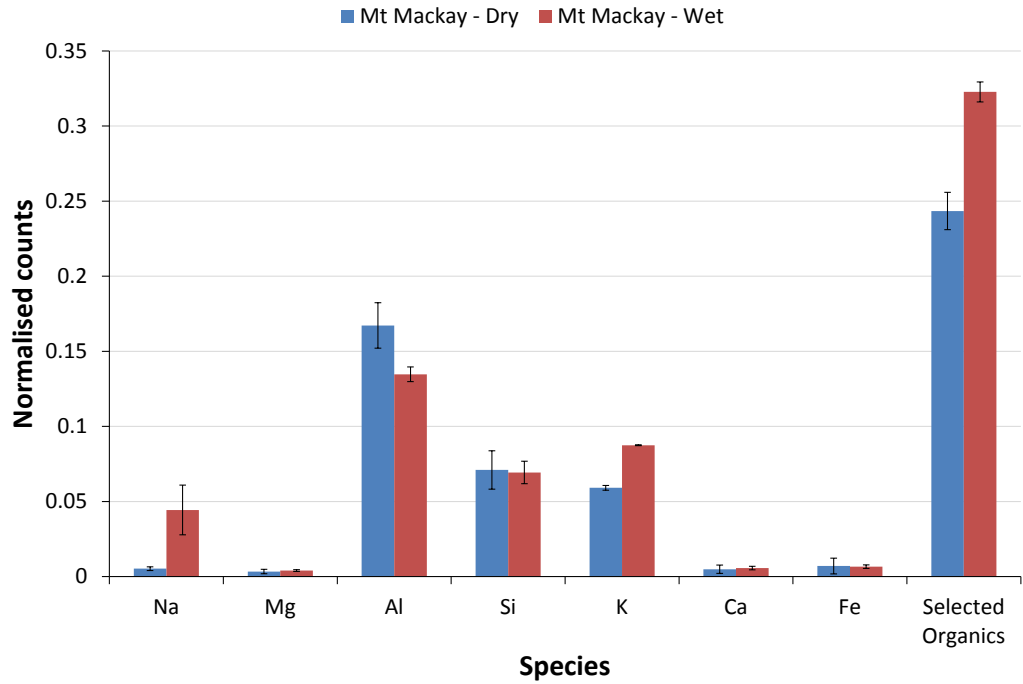


Figure 3.14 Distribution of inorganics and total organics on the surfaces of Mt Mackay particles

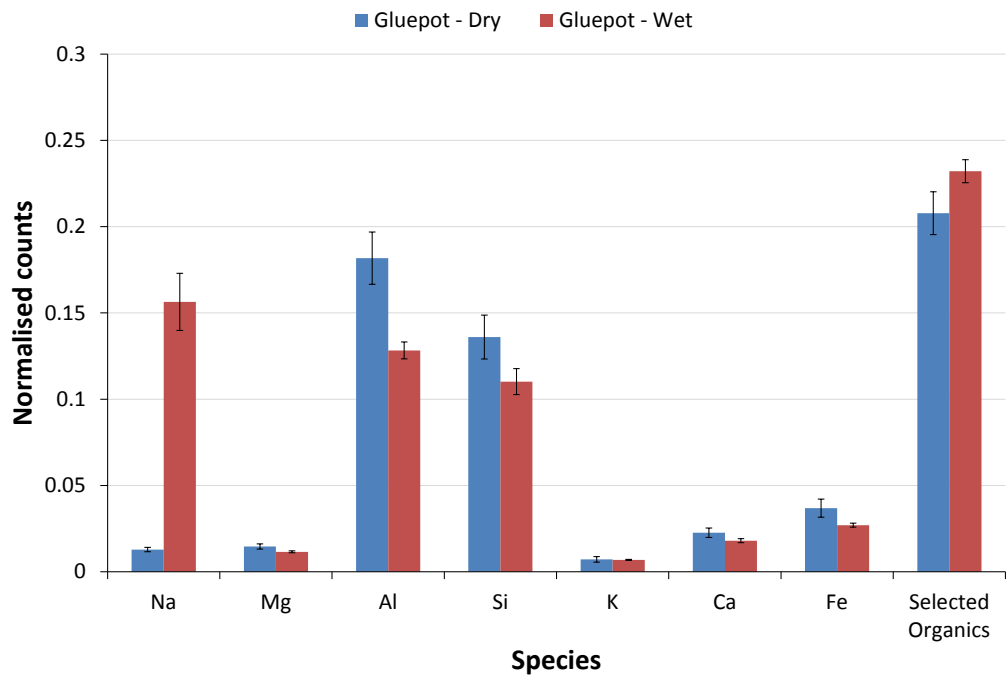


Figure 3.15 Distribution of inorganics and total organics on the surface of Gluepot particle

3.2.4 Conclusions

The investigations undertaken in this section supports the anecdotal evidence that Mt Mackay is a ‘good’ soil exhibiting good settling and clarification properties and Gluepot is a ‘bad’ soil exhibiting poor settling and clarification properties. Gluepot had the lowest true particle density, the highest proportion of fine particles (*i.e.*, <1 μm size range), lowest proportion of particles in the >100 μm size range, highest clay fraction and highest organic fraction for both the hydrogen peroxide and loss on ignition methods. Furthermore, the Si:Al ratio for the Gluepot and Invicta 255B soils indicate a mixture of the 1:1 and 2:1 mineral types. The 2:1 mineral is of the montmorillonite type, a known expandable clay. Expandable clays have the ability to absorb more water which reduces its bulk density and hence their settling rates.

Mt Mackay on the other hand had the lowest proportion of fine particles in the <1 μm size range, highest proportion of particles in the >100 μm size range and lowest proportion of clay fraction and lowest proportion of carbonates based on the loss on ignition method (*i.e.*, at 950 °C). The true particle density of Mt Mackay soil was similar to Invicta 255B and both were higher than Gluepot. The organic fraction in both the peroxide and loss on ignition method were lowest for the Invicta 255B soil.

TOF-SIMS analyses showed large differences between the wet and dry soil samples. The largest change between the surface chemistry of the dry and the wet soils appears to be the dominance of NH_4 and relatively higher proportion of hydrocarbon species in the wet samples. The NH_4 specie is likely to be associated with proteins/amino acids. The wet samples contain a higher proportion of total organics than the dry samples.

The inorganic elemental species responses were intense, and so are expected to play an appreciable role on the surface chemistry of the soils. The wet samples contain higher proportions of Na ions. Here, the adsorbed cations on the surface of the particles exchange with Na ions in the aqueous environment, thereby increasing the proportion of Na ions on particle surfaces. Sodium ions are effective in particle stabilisation, and hence will not encourage coagulation/flocculation. The results from the TOF-SIMS study also showed that the relative proportions of these ions are far less in the good soils compared with the bad soils. For example, the proportion of Na ions in Gluepot 3552A (the bad soil) is 4 times that of Mt Mackay.

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3.3 UNDERSTANDING FLOCCULATION PROPERTIES OF SOIL IMPURITIES PRESENT IN THE FACTORY SUGARCANE SUPPLY

Hakan Bakir ^a, Zhanying Zhang ^a, Marek S. Zbik ^b, Mark D. Harrison ^a,

William O.S. Doherty ^{a*}

^a*Centre for Tropical Crops and Biocommodities, Queensland University of Technology, GPO Box 2434, Brisbane, QLD, 4001, Australia*

^b*Geotechnical Engineering Centre, The University of Queensland, Australia*

Statement by the Author

The work presented in this section is a continuation of the work undertaken in Chapter 3.1 to 3.2. This section is based on the article titled: Understanding flocculation properties of soil impurities present in the factory sugarcane supply. Published in, *Journal of Food Engineering*, 189 (2016), 55-63.

The author is responsible for the sampling, analysis, data interpretation and the writing of the initial first draft of the paper, subsequent revisions and the final submission.

Dr Zhang assisted with the presentation of the paper and the initial submission.

Dr Zbik assisted with many of the analysis and the writing of the first draft of the paper.

Dr Harrison edited the drafts of the paper.

Prof. Doherty corresponded and supervised with the analysis, data interpretation and edited the drafts of the paper.

3.3.1 Abstract

Soil impurities in sugarcane supplies affect clarification and filtration unit operations in the raw sugar manufacturing process. Juices expressed from the sugarcane plant grown in certain soils display poor clarification and dewatering behaviours. In this study, the salient features of these soils were determined in order to understand why they influence flocculation and settling of juice particles (flocs). The soils were characterized by X-ray powder diffraction, transmission-, transmission x-ray-, and scanning electron microscopy, and their solution chemistries determined in electrolytes. In general, clay mineral composition, cation exchange capacity, and particle size contributed towards the poor settling characteristics of the soils. Fine

particles (*i.e.*, <200 nm) were found in difficult to clarify soil samples and were identified as nano-clays. The structure-building phenomenon of these clays if present in sugar juice are likely to impact on clarification, hindering the juice particles ability to settle despite changing environmental chemistry.

Keywords: Flocculation; Smectite; Soil; Sugarcane juice; Clarification; Dewatering

3.3.2 Introduction

Settling, dewatering, and filtration are important stages of solid/ liquid separation processes in many industries including the mining, water treatment, coal, and sugar industries. In many of these industries, settling is a low energy input process that can operate on a large scale. However, settling is not without its' challenges. For example, Fedorak *et al.*, 2002 reported a settling time for fine soil particles in tailing ponds of oil sand extraction of up to 150 years. In the sugar industry, many factories can experience very slow settling rates (<20 cm/min instead of >30 cm/min) of the flocced particles, low underflow mud solids content (<1-5 wt%), and high clarified juice turbidity (>50 turbidity @ 900 nm) caused by certain soils that come in with the cane supply (Crees *et al.*, 1978; Steindl, 1998; Cronje and Sahadeo, 2014). In some seasons, a 500 t/h Australian sugarcane factory can incur losses in excess of AU\$0.5 M/y due to sugar loss to the mud cake, lost time, and increased mud cake transport costs as a consequence of a 5 wt% increase in moisture (Qureshi *et al.*, 2001).

Kaolinite, illite, and smectite, are the most common clay minerals in soils and their presence in aqueous systems is the primary cause that prevents particle aggregation and increased settling speeds. They are sheet silicates, are platy and have a high platelet diameter to thickness ratio (*i.e.*, aspect ratio). For kaolinite, this aspect ratio is usually ~10 but can vary widely (Zbik and Smart, 1998). The aspect ratios for smectite minerals, such as montmorillonite, are generally much larger (e.g., 80-500). Hence, the area of the crystal basal planes is dominant over the edge area in expandable clay minerals like smectite in comparison to kaolinite.

Because of their platelet-like shape their equivalent diameters are 200-1000 nm for kaolinite and 5-200 nm for smectite particles. As a result of the electric charges present on the mineral surfaces (basal and edge sites), clay particles have the ability to form complex aggregates and network assemblies in aqueous solution. This behaviour is dependent on water and clay chemistry, as well as clay particle packing density (Bowles, 1968). The electric charge is compensated for by the adsorption of cations from solution (van Olphen, 1977). In the presence of water, the adsorbed cations in the clay sorption complex can be exchanged with cations of another species in the aqueous environment, and they are therefore known as the exchangeable cations.

Soil enters the raw sugar manufacturing process with the cane supply. Although, the cane plant has some soil particles adhered to it due to the effects of wind and rain

most of the soil enters as a result of mechanical harvesting. The height of the harvester's base cutters are adjusted and operated so that the cane stalk is cut just above ground level. Due to variations in the field topography, at times, the base cutters penetrate into the ground and pick up soil with the cut cane. Harvesting during wet weather and crops that are affected by cyclones during the growing season can significantly increase the level of soil in the cane supply. In Australia, the soil levels in the cane supply of around 2 wt% are typical and in extreme cases it can be above 10 wt% (Sandell and Agnew, 2002).

Kampen (1974) reported that the soil entering the sugar factory reduced the overall plant efficiency, including poor settling rates of the particles in the clarifier and higher mud volumes. In the work Kampen (1974) conducted on three different types of field soils (sandy, silt and clayey) typically found in the Louisiana (USA) cane growing region, clayey soils increased the final mud volume, increased non-sugar impurities and lowered juice purity in comparison to the two other soils.

Although the present study did not use real sugarcane juice, it builds on the work undertaken by Kampen (1974) to obtain a greater understanding of the effect of soil types on clarification. Therefore, the identification of the mineral composition of the soils from sugarcane regions, their macroscopic and morphological attributes and their physical and chemical properties in electrolytes will provide useful information for subsequent studies on the clarification properties of real sugarcane juices.

3.3.3 Materials

Field soil samples were obtained from three sugar cane growing regions in Queensland, Australia. The soil sample name, its origin, and typical factory clarification performance of the juices extracted from the different cane supply sources are shown in Table 3.9. The soil samples were collected from multiple locations and from the top ~10 cm of the soil and then mixed to produce composite samples. The larger soil aggregates were broken down to form fine loose soil using a Resch BB200 jaw crusher prior to mixing to form composites.

Chemicals, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Chem Supply, Gillman, Australia), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, Kilsyth, Australia), NaCl and KCl (Sigma- Aldrich, Sydney, Australia), were analytical grade.

The stock synthetic juice solution was prepared by dissolving 1.91 g of NaCl, 47.67 g of KCl, 18.34 g of CaCl₂ 2H₂O and 31.37 g of MgCl₂ 6H₂O in 1000 mL of Milli-Q water.

Table 3.9 Soil sample names, origins and historical factory clarification performances

| Sample name | Origin | Soil moisture (wt%) | Typical factory clarification settling rate, cm/min |
|--------------|---------|---------------------|---|
| Mt Mackay | Tully | 10.44 | 30-60 (Good) |
| Invicta 255B | Invicta | 2.7 | 1-20 (Poor) |
| Gluepot | Mackay | 7.89 | 1-20 (Poor) |

3.3.4 Methods

3.3.4.1 X-ray powder diffraction

The mineral composition of the samples was established using X-ray powder diffraction (XRD). The samples were oven dried at 60 °C and thoroughly mixed using an agate mortar and pestle before being pressed onto stainless steel sample holders.

A sub-sample (~1.5 g) was ground for 10 min in a McCrone micronizing mill with 2 mL of ethanol. The resulting slurry was oven dried at 60 °C then thoroughly mixed using an agate mortar and pestle before being pressed into a silicon sample holder prior to XRD analysis. The clay content was determined from a study of oriented samples, air dried on silicon wafer and mixed with ethylene glycol (Moore and Reynolds, 1997). XRD patterns were recorded using a PANalytical X'Pert Pro Multi-purpose diffractometer using Fe filtered Cu K_α radiation, auto-divergence slit, 2° anti-scatter slit and fast accelerator Si strip detector. Diffraction patterns were recorded in steps of 0.016° 2θ with a 0.4 s counting time per step, and logged to data files for analysis.

3.3.4.2 Structure characterisation by electron microscopes

Electron microscopy is the ‘tool of choice’ to study the microstructure of clays (Smart and Tovey, 1982; Smart *et al.*, 2004). Electron microscopy was undertaken using a JEOL-2100 Transmission Electron Microscope (TEM) with 200 kV

accelerating potential. Scanning Electron Microscope (SEM) JEOL 6040 with a featured energy-dispersive X-ray (EDX) spectroscopy was used to investigate the sample coated with platinum with accelerating voltage 15-20 kV. A known weight (1.00 g) was dispersed in 9 mL of Milli-Q water, sonicated for 1 minute, and then allowed to settle for 5 min. Using a Pasteur pipette, a droplet of the supernatant (*i.e.*, the clay fraction) was placed on a sticky stub and dried at room temperature. For TEM analysis, a droplet of the supernatant was deposited directly onto a carbon film before drying the sample in an oven at 45 °C. Transmission X-ray microscopy (TXM) with a photon flux of 5×10^{12} photons/s and an accelerating voltage of 200 kV was used to investigate the micro-morphology of the clays in the soils at National Synchrotron Radiation Research Centre (Taiwan). TXM samples were prepared by depositing a droplet of supernatant onto a silicon wafer plate and allowed to dry at room temperature.

3.3.4.3 Measurement of cation exchange capacity and settling rate of the soils

The preparation and analysis for cation exchange capacity (CEC) were carried out based on methods 15A1 and 15A2 respectively as described by Rayment and Higginson (1992).

Batch settling tests were carried out to determine the settling rates of the soil particles. The settling tests were conducted in 100 mL measuring cylinders using 1.0 wt % soil solution in an electrolyte mixture of chloride salts (Na^+ , 30 ppm; K^+ 1000 ppm; Ca^{2+} 200 ppm; and Mg^{2+} 150 ppm). The electrolyte composition was chosen to mimic the concentration of these ions present in a typical sugarcane juice solution. Prior to settling tests the soils were disintegrated in jars containing 1 g of the soil and 20 mL of Milli-Q water inside an ultrasonic water bath for 5 min. The soil solution was then transferred to a 150 mL beaker and stirred using a magnetic bar. A further 76 mL of Milli-Q water was added to the beaker followed by 4 mL of the stock synthetic juice solution to produce a 100 mL solution. The solution mixture was stirred for 1 minute before being transferred to a 100 mL measuring cylinder and allowed to settle.

The mud interface height (boundary line between solid and liquid phases) was measured via visual assessment at 1 minute intervals over a 30 minute period. A plot of mud interface height versus time was plotted. The initial settling rate (mL/min) was obtained from the initial linear part of the curve. The unit of the settling rate was

converted from mL/min to cm/min by dividing the height of the cylinder (cm) by the volume of the solution (mL). The average error in the measurements is $\pm 0.25\%$.

3.3.4.4 Measurement of physico-chemical properties of clay constituents

The physico-chemical properties of clay constituents (ζ , minerals surface chemistry, and water chemistry) were assessed. Samples of diluted suspension (~ 0.2 wt%) prepared from the clay fraction were used to determine the ζ using a Zetasizer (NanoSeries, Malvern Ltd., UK). The samples were measured in water and salt suspension as described previously (Hunter, 1981; Lyklema, 2003; Minor *et al.*, 1997).

Measurements of the ζ were conducted in electrolytes of Na, K, Ca, and Mg chlorides and a mixture of these metal ions (the mole ratio of Na^+ , K^+ , Ca^{2+} and Mg^{2+} was 3.4:67.2:13.1:16.2) at different ionic strengths. The average error for the determination of the ζ is $\pm 5\%$.

The specific surface areas of the clay fractions (below $2 \mu\text{m}$) of the soil samples were calculated from TEM images using the method described by a number of authors (Smart and Tovey, 1982; Zbik and Smart, 1998). Multiple TEM images were used and 100 randomly chosen particles from each sample were measured on grids. The aspect ratios of these were determined and the specific surface area calculate by the method of Zbik and Smart (1998). The average error for the measurement of the specific surface areas is $\pm 5\%$.

3.3.5 Results and discussion

3.3.5.1 Mineral composition by bulk X-ray powder diffraction

The major minerals in soil samples obtained from sugarcane fields were smectite, illite, and kaolinite, as well as some interlayer smectite-illite species. Figure 3.16 shows the XRD spectra of the three soil samples. Gluepot consists mostly of quartz and clay minerals comprising kaolinite, chlorite, and smectite. Relatively broad clay peaks indicate poor crystallinity with particles that are highly dispersed in nature. These crystallites are so small that they scatter X-rays, thereby broadening the major 001 peak. The formation of such particles may be a sign of severe erosion of the clays and may be an indication that the majority of the smaller particles are undergoing amorphisation.

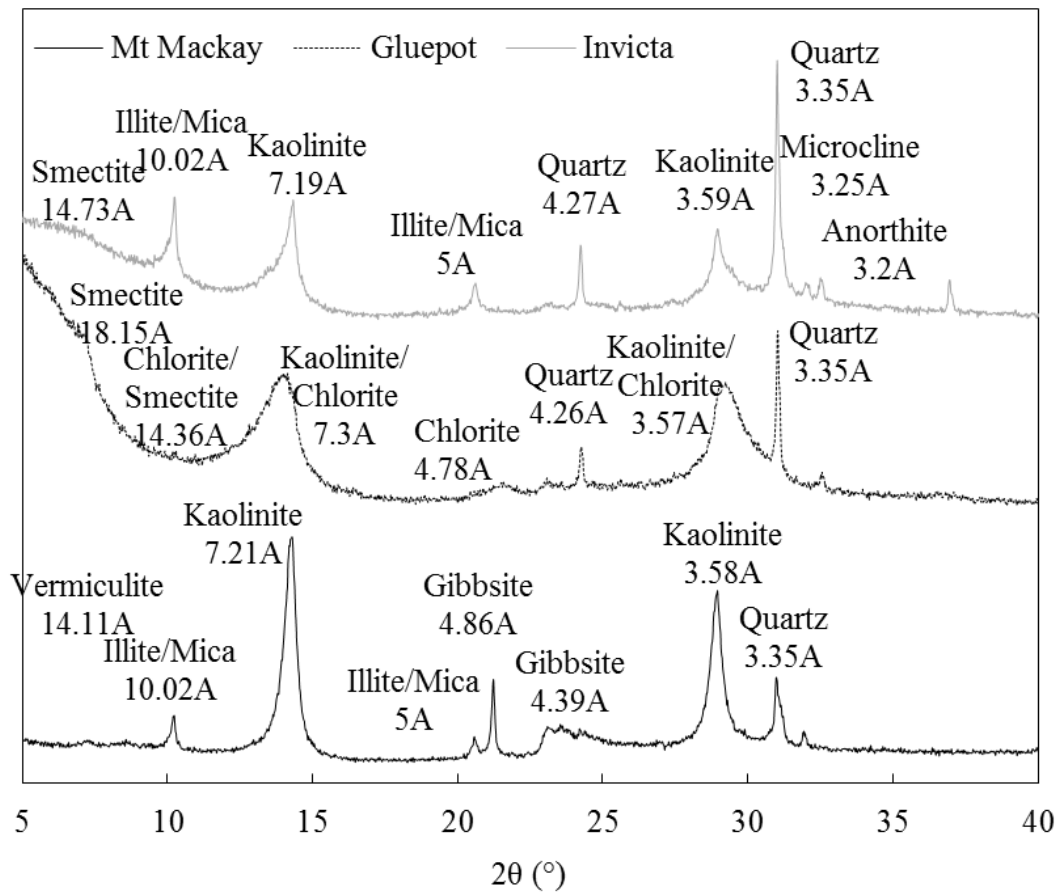


Figure 3.16 XRD spectra of soil samples

Invicta 255B consists of quartz, potassic and calcium feldspars, and micas, and clay minerals made up of kaolinite, smectite, and possibly illite. Peaks of 001 reflections of kaolinite show lesser broadening than in the Gluepot sample, which indicates higher crystallinity and therefore less erosion and amorphisation of the sample. Similarities in the broadening of the kaolinite and mica peaks may indicate that illite (hydromica), rather than mica, is the dominant constituent, along with kaolinite within the clay fraction of the Invicta 255B sample.

From the XRD results (Figure 3.16), the Mt Mackay sample contains quartz, potassic and calcium feldspars, kaolinite, illite or mica, and a small amount of gibbsite. The intensity of the kaolinite peaks from 001 reflection is stronger than those obtained for Invicta 255B and Gluepot, an indication of larger particle size for this mineral. It is worth noting that it is only Gluepot that contains smectite (a swelling clay mineral) in measurable quantities using XRD. The quantitative XRD analysis results indicate

that Gluepot contains the highest proportion of the amorphous component, while Mt Mackay contains the least amount (Table 3.10).

Table 3.10 Composition of soils (wt%) by bulk XRD analysis

| Mineral type | Gluepot | Invicta 255B | Mt Mackay |
|-------------------------|---------|--------------|-----------|
| Amorphous content | 71.2 | 38.9 | 5.3 |
| Quartz | 11.8 | 45.1 | 51.5 |
| Albite | 4 | 4.9 | - |
| Microcline (K-feldspar) | - | 6.4 | 9.3 |
| Anorthite | - | - | 1.1 |
| Kaolinite | 7.9 | 1.1 | 26.0 |
| Muscovite (Illite) | - | 3.6 | 5 |
| Smectite | 1.3 | - | - |
| Gibbsite | - | - | 1.7 |

3.3.5.2 Electron microscopy

Figure 3.17, Figure 3.18 and Figure 3.19 show the SEM and TEM images of the three soils. In Gluepot, kaolinite is present and is represented with relatively small platelets (mostly about 100 nm in diameter), some of which occasionally display pseudo-hexagonal symmetry. Crystals observed in the TEM and SEM micrographs (Figure 3.17A) show poor crystallinity and are consistent with the XRD results. The platelets edges are eroded and poorly defined. Most platelets are <200 nm in diameter but range between 10-250 nm. The platelets are single crystals but many of them form assembly of larger aggregates.

In contrast to kaolinite, thin smectite sheets are observed in different locations in the Gluepot sample and the flexible flakes constitute extremely dispersed phase particles (Lagaly and Ziesmer, 2003). The smectite sheet units are not held together by hydrogen bonding (as is the case in kaolinite) so such dispersion is very common, especially in a soil that is in a sodium-rich water environment. Sodium-based smectite sheets often defoliate to single units which are very thin (~1 nm) and flexible. The TEM micrograph shows the presence of extremely small particles (classed as amorphous by XRD) which form a blanket of larger crystal aggregates when dry. A film of small, submicron platelets is presented in Figure 3.17B.

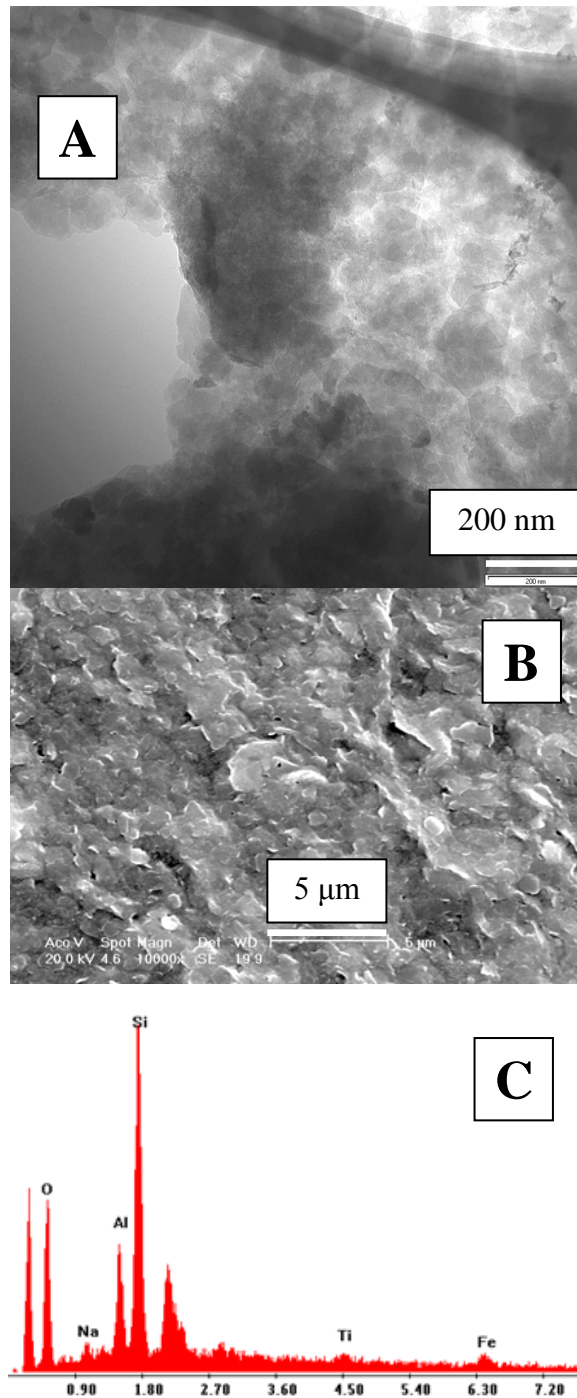


Figure 3.17 Results from electron microscope investigation of Gluepot. A- TEM micrograph, B- SEM micrograph and C- EDX results.

The EDX spectrum (Figure 3.17C) indicates the presence of Na, Al, Si, Ti, and Fe. The (2:1) Al to Si ratio is typical of smectites and illites in which the silicate sheet has two siloxane tetrahedral layers attached to the alumina rich octahedral layer. Although, this ratio is not diagnostic it may indicate the type of prevailing clay

component. Clay platelets seen in TEM and SEM micrographs of the Gluepot samples (Figure 3.17A and Figure 3.17B) are most dispersed in comparison to the other two soils.

The TEM micrograph of the Invicta 255B sample (Figure 3.18A) displays extremely small kaolinite and mostly illite platelets. The majority of the platelets are 80 nm in average diameter, so they fall into nanomaterial size classification. The smaller kaolinite particles are down to 50 nm in diameter and some mineral edges display a pseudo-hexagonal symmetry. The illite platelets observed in this sample are similar to poorly defined kaolinites, display shapeless edges and have lateral dimensions that are as small as 10 nm in diameter. Amorphous spongy-looking spherical aggregates up to 360 nm in diameter and a few kaolinite stacks of 120 nm in diameter with an aspect ratio ~4 are observed. Numerous irregularly shaped flakes of illite with an average diameter of 55 nm and amorphous aggregates in globular form with diameters up to 250 nm are observed (Figure 3.18A). Some halloysite in a twisted tube arrangement were observed to form complex aggregates up to 500 nm in diameter. The SEM micrograph for the Invicta sample (Figure 3.18B) displays a continuous blanket of irregular shaped illite sheets, kaolinite pseudo-hexagonal crystals and irregular shaped 'probably' illite platelets (Figure 3.18A). The EDX results presented in Figure 3.18C indicate the presence of Na, Al, Si, and Fe elements, the Al to Si ratio is most similar to 2:1 sheet silicates.

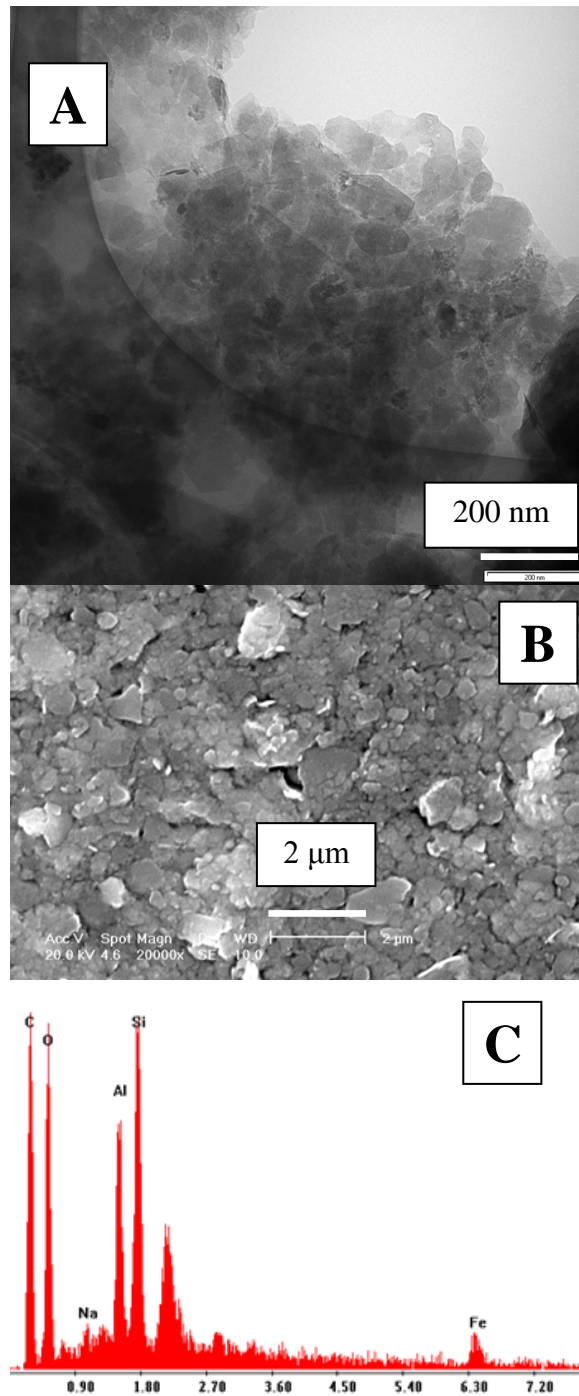


Figure 3.18 Results from electron microscope investigation of Invicta 255B. A-TEM micrograph, B- SEM micrograph and C- EDX results

The TEM of Mt. Mackay (Figure 3.19A) shows that kaolinite crystals and stacks with a broad diameter range in the lateral dimension dominate the clay fraction. Stacks are primary crystals which are in the process of defoliation which can be seen occasionally in the Mt. Mackay soil.

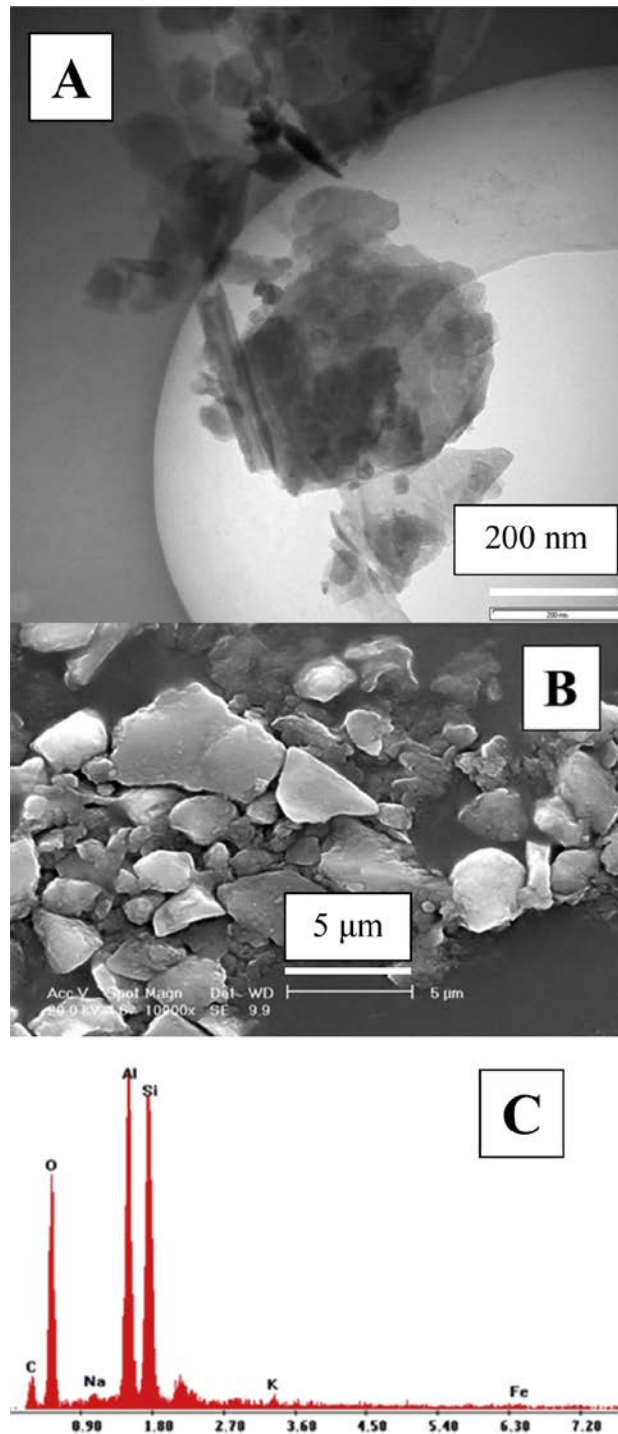


Figure 3.19 Results from electron microscope investigation of Mt Mackay. A- TEM micrograph, B- SEM micrograph and C- EDX results.

Such stacks are 180-200 nm in diameter and 50-100 nm thick giving an aspect ratio (ratio of diameter to thickness) of 2-4, which is much smaller compared to aspect ratios that are typical for kaolinite and illite crystals (~10). The presence of such stack in soil samples may indicate insitu mineral growth. In the Mt. Mackay soil, numerous

tubular halloysite minerals or transition from halloysite to gibbsite is common. The presence of gibbsite was confirmed by XRD (Figure 1C). Halloysite is a disordered mineral from the kaolinite group that is tubular in morphology; the length of halloysite tubes in the sample ranged from 400-1560 nm and with diameters of ~100 nm. The average diameter of most clay platelets observed and calculated from TEM micrographs was ~250 nm, which is relatively large compared with those observed in the other two soil samples. Other minerals identified in the TEM micrographs were assemblies of larger plates of mica and numerous aggregates of extremely small nano-clay platelets assembled into aggregates of up to 400 nm in diameter. Unlike the other two samples, there is no evidence of significant amounts of a highly dispersed phase in the Mt. Mackay sample. The SEM micrograph (Figure 3.19B) shows a mixture of grains (up to 5 μm in diameter) and a dispersed phase which is composed mostly of kaolinite. The EDX results (Figure 3.19C) indicate the presence of Na, Al, Si, and Fe elements, the Al to Si ratio in this case is mostly equal, which is typical of kaolinite (1:1) sheet silicates where one siloxane tetrahedral layer is connected to one alumina rich octahedral layer.

A larger proportion of extremely small particles, about a few nanometers in dimension were observed in TEM micrographs from Gluepot and Invicta, but more so from Gluepot. The origin of these particles is not clear but the micrographs suggest that they are eroded smectite flakes. The high amorphous contents of these soils are associated with high smectite and illite contents. The Mt. Mackay soil with relatively low amorphous content (determined by XRD) also has the lowest amount of the 2:1 type minerals. These fundamental differences in clay type between these samples may influence their microstructure and physical behaviour in an aqueous environment.

3.3.5.3 Soil chemistry

Correlations between mineral composition and other physical parameters are complex. Usually many more factors are involved than those that have been measured in the present study, including the amount and type of organic components that interact with the particles and the aqueous system. However, taking into consideration the results of the XRD analysis (Figure 3.16) and the morphological data, we hypothesised that only the smectite and the amorphous phase are the major mineral components that influence the clarification performance of the soils.

It is well known that specific surface area increases as particle size decreases in highly dispersed systems (Grim, 1968). Further, with increasing surface area the sorption capacity of such dispersed systems increases. As a consequence, the ion exchange capacity (which represents ions adsorbed from the natural soil pore water environment) increases in proportion to clay fraction size in a sample as well as the surface area of the clay component in soil. The surface areas for kaolinites is up to 15 m²/g and for illite they are up to 100 m²/g (Grim, 1968). Smectites on the other hand have much higher surface areas (up to 900 m²/g) due to their larger interlayer spaces that are open for water and counter-ion penetration. As such, the quantity of counter ions within a given clay soil system depends on the mineral composition and will approach 3-15 meq/100 g, 10-40 meq/100 g, and 80-150 meq/100 g for kaolinite, illite, and smectite, respectively (Grim, 1968). From the results of the mineral composition analysis (Figure 3.16), smectite is present in Gluepot and Invicta soil samples.

The XRD results also indicated that the amorphous component is likely to be associated with illite and smectite contents in samples. There is little or no amorphous phase in samples where kaolinite was the main clay mineral component, as shown with the Mt Mackay sample. In the TEM micrographs, extremely small particles of a few nm in diameter were observed and it seems that these particles are likely to have broken off from the smectite sheet edges. These particles may be an important component of the amorphous phase in the samples. Other amorphous phase components may include amorphous silica, oxides and coal particles which were observed in some SEM micrographs (probably resulting from burning sugarcane leaves prior to harvesting).

Figure 3.20 shows the CEC of the three soil samples. High CEC corresponds with high specific surface area and amorphous content (Table 3.10). This correlation is mostly due to high surface area of the dispersed minerals, illite and smectite. Higher illite and smectite contents in the soil samples adsorbs higher proportions of exchange ions which can be retained on the clay surface and affect the electric double layer after the soils are wetted. Ions are usually hydrated, and with larger electric double layer surrounding the mineral particles water retention increases.

It is then not surprising that clay soils with higher smectite content, characterized by higher surface area and correlated with higher CEC also correlate positively with the plastic properties which describe water retention capability in the soils. Data variation reflects exchangeable cation composition differences within the natural

sorption complex of the studied soil samples. The results obtained from this study are similar to those obtained in a previous study (Grabowska-Olszewska, 1968) on model soil mixtures in which a linear relationship between liquid retained, smectite content, and the sorption complex was observed.

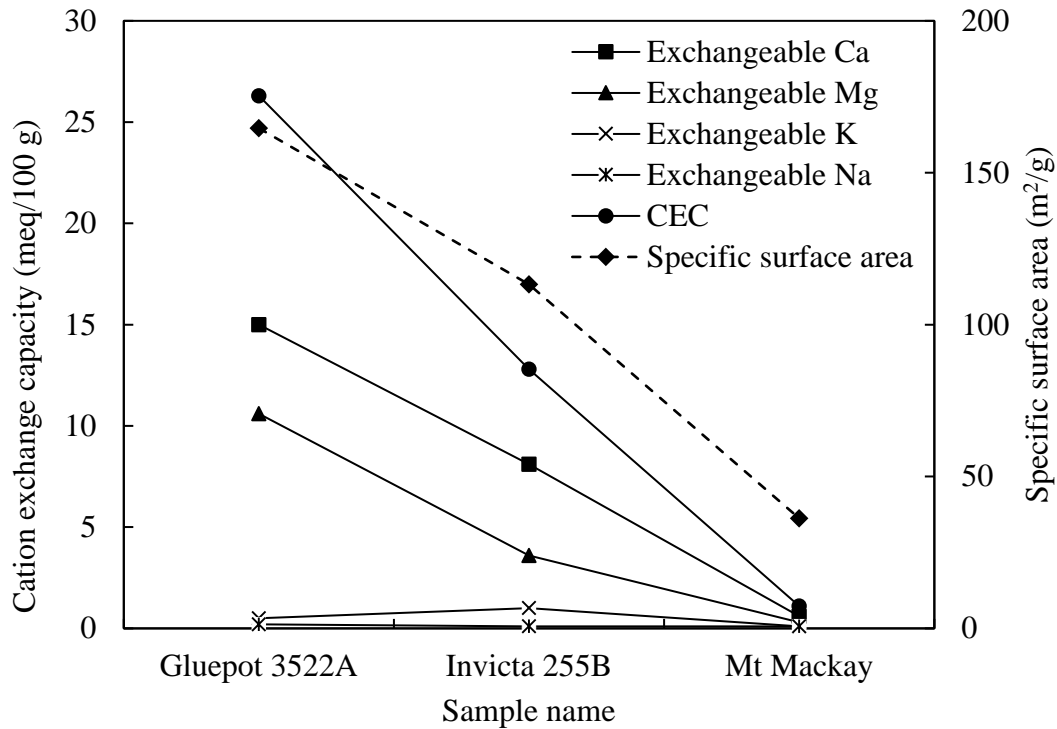


Figure 3.20 Dependence between cation exchange capacity (meq/100 g) and specific surface area (m²/g) in the studied samples

Major exchangeable capacity of the cations of the soil samples was in the following order, $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ (Figure 3.20). It is well documented (van Olphen, 1977) that bivalent sorption complexes help to build larger and stronger aggregates, and so clay soil containing higher proportions of Ca and Mg cations perform better in settling and filtration tests than those with monovalent cations present within the soil sorption complex. A CEC value of 5 meq/100 g, which was obtained for a mixture of 10 wt% of smectite and 90% of kaolinite according to a previous study (Grabowska-Olszewska, 1968), can be considered a threshold value above which settling and filtration characteristics are poor. On this basis, the sample from Mt Mackay is predicted to have superior settling and filtration performance than the samples from Invicta and Gluepot. As the sorption complex contains exchangeable

cations, these cations can be easily displaced and exchanged by other cations delivered from the surface or the ground water environment.

To confirm the results deduced from the Grabowska-Olszewska (1968) rule, settling profiles of the soils in a synthetic juice solution were obtained (Figure 3.21).

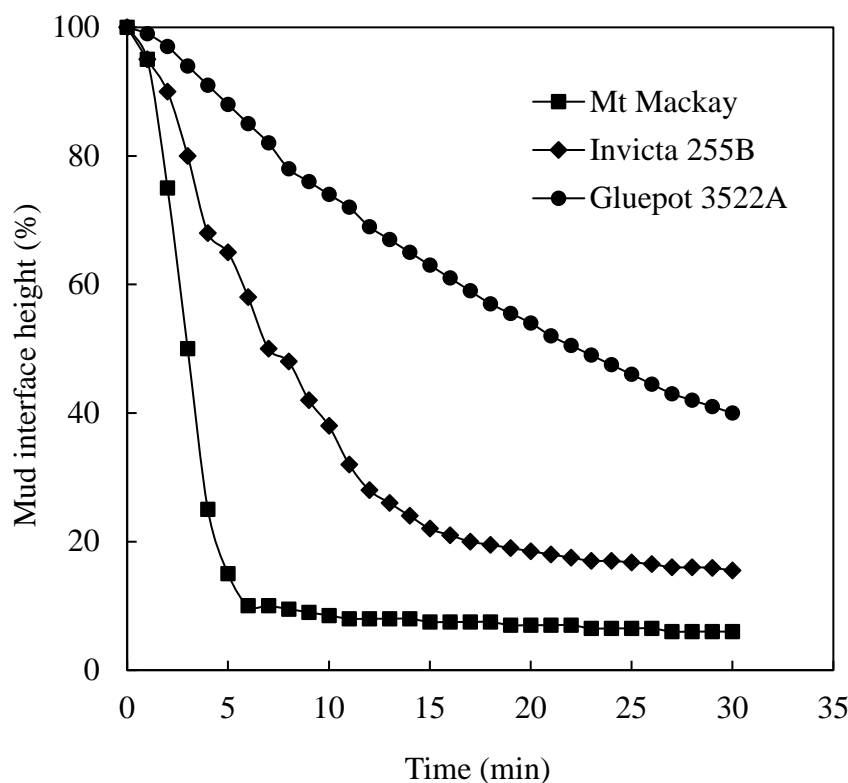


Figure 3.21 Settling profiles of soil (1 wt%) samples

The settling rates were calculated to be 4.9 cm/min, 1.6 cm/min and 0.6 cm/min for Mt Mackay, Invicta, and Gluepot in that order, providing supporting evidence of the results deduced from calculations. The settling rates achieved in this study are from tests using synthetic juice solutions and without the use of flocculants. The settling rate ranges shown in Table 3.9 are typical for real sugarcane juice under factory conditions and include the use of flocculants. The results achieved in this study and the typical ranges experienced at the factory show a significantly higher settling rate for Mt Mackay compared to the other soil samples.

3.3.5.4 Electrokinetic potential and its influence on particle aggregation

Contemporary approaches to describe the behaviour of dilute clay suspensions are based on colloid stability (DLVO) theory (Derjaguin and Landau, 1941; Verwey

and Overbeek, 1948) where competing electrostatic and van der Waals forces generally determine whether particular colloidal clay suspensions will be stabilised (in sol form) or coagulated (in gel form). Chemical changes in the aqueous environment can collapse the clay particle electrical double layer, lower its ζ , and allow particles to approach each other close enough for van der Waals forces to bond them into larger aggregates. This process significantly improves settling rates.

Figure 3.22 shows that the ζ of the soils studied in electrolytes of different concentrations display negative values suggesting particle surfaces were negatively charged in the aqueous solutions. The high values of ζ prevent particles from approaching each other to form larger and more dense flocs or aggregates, so highly dispersed particles (nano-clays) within a suspension are electrostatically stabilised and are resistant to settling. When measured in high purity Milli-Q water, ζ shows more variation due to differences in the soluble salt content in the soil samples. Because measurements were performed on samples with natural sorption complexes some variation may be due to cation exchange processes between soil samples with the background electrolyte.

The influence of mineral composition on ζ of the soils in various environments is presented in Figure 3.22. For all the soils, the ζ increased significantly at very low cation concentrations (<0.03 M) and became steady with further increase in cation concentrations (>0.10 M). There were two distinct inflexions for the Mt Mackay and Gluepot samples, indicating a bimodal distribution of particle sizes. Soils containing smectites show relatively high amorphous content (nano particles) like those from Gluepot and Invicta which show only a slight overall change in the ζ value in the broad ionic strength of NaCl range studied. The sample from Mt. Mackay which contains kaolinite displays a strong correlation between the ζ and increase in ionic strength. In general, for divalent cations, when the ionic strength increases, the ζ trend towards zero. This effect is more significant in the Mt. Mackay sample than the other two soil samples. The soil samples in synthetic juice clearly shows that the Mt Mackay trended a lot closer to zero ζ values with increasing ionic strength, an indication of better coagulation and flocculation properties of the soil, confirming the mineral composition and settling rate data.

The ζ values of smectites, in contrast to kaolinites, are little affected by pH changes because of their thin platelets, and relatively smaller contribution of the edge

areas in the sample surface area. Our samples were investigated within 7-8 pH environments.

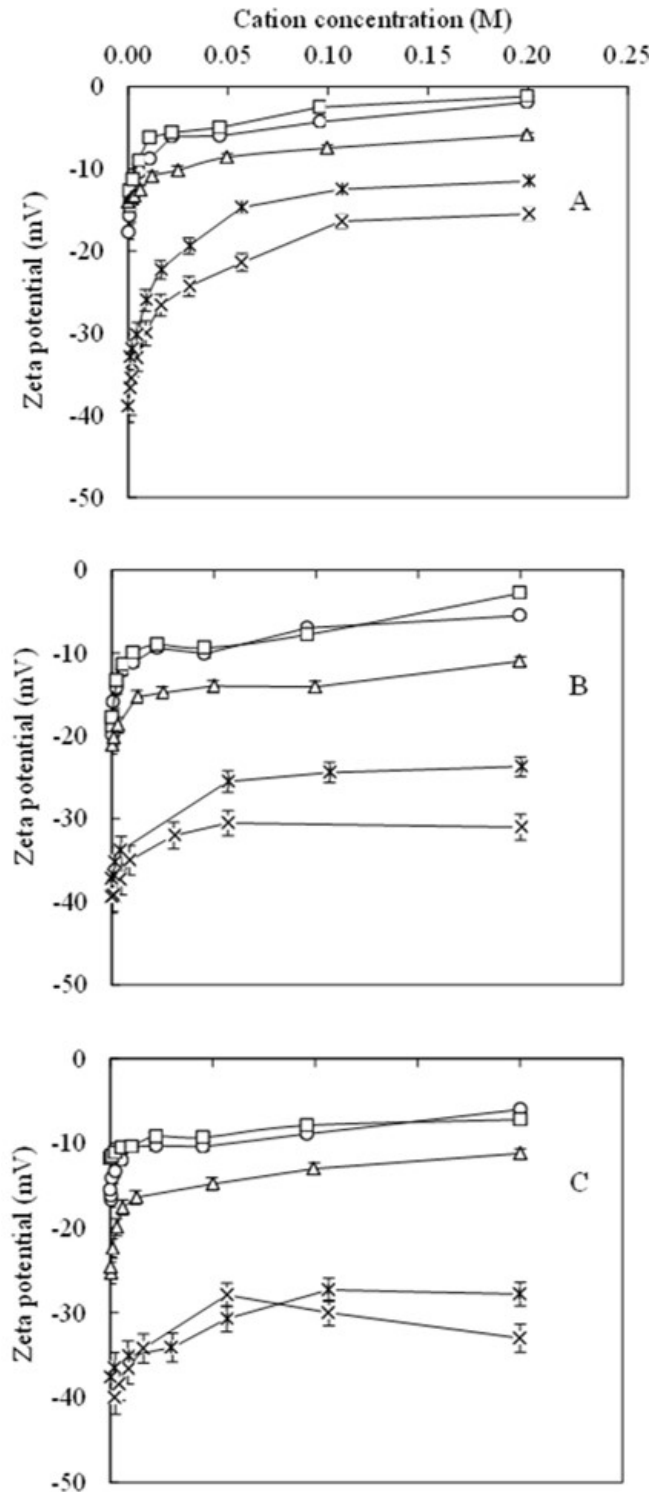


Figure 3.22 Dependence of ζ on electrolyte concentration with Mt Mackay (A), Gluepot (B) and Invicta 255B (C) samples. (-x-) NaCl, (-*-) KCl, (-o-) MgCl₂, (-□-) CaCl₂ and (-Δ-) synthetic juice.

The lack of a significant reduction in the magnitude of the ζ with increases in salt concentration, especially in monovalent salt solutions, is not clearly understood. The ionic strength of bivalent ions is much stronger than monovalent ions and so it has a larger impact in driving ζ towards zero. The lack of significant influence of the ionic strength on the ζ with electrolytes containing monovalent ions may be explained by the presence of strong three-dimensional structure building phenomenon in the suspensions. The TXM micrograph of the clay fraction of the Gluepot sample show kaolinite connected together in a 3-D network (Figure 3.23A). This structural network is better visualized through tomographic reconstruction as shown in Figure 3.23B. The 3-D reconstruction micrograph shows that kaolinite platelets build a voluminous cellular network where particles are connected by bridges to highly dispersed and amorphous particles. Such microstructure building phenomenon in smectite suspension was recently described (Zbik *et al.*, 2014, 2015). With such microstructures, particles are locked into a network and do not behave like individual crystals; rather, they behave like a gel.

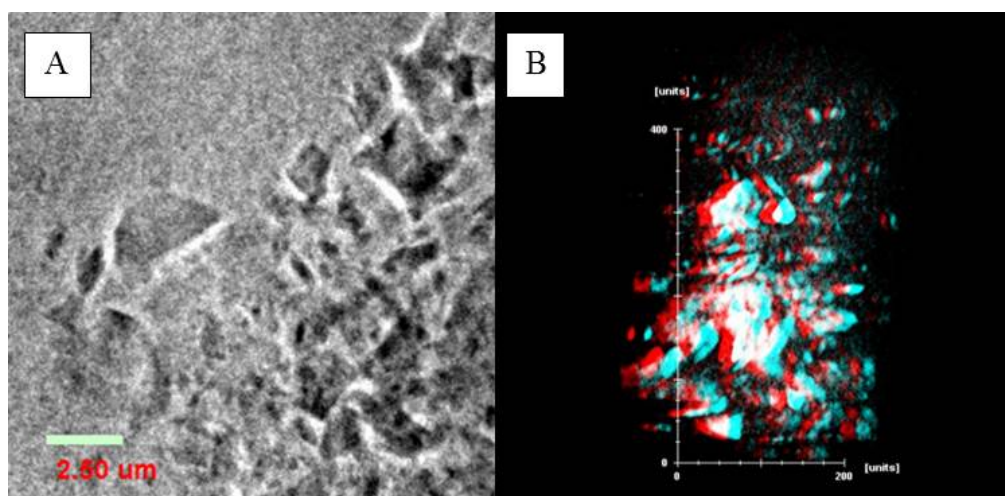


Figure 3.23 TXM micrograph (A) and 3-dimensional anaglyph from the tomography (B) of Gluepot sample

ζ is determined on the principle of electrophoretic phenomenon where clay particles are moving in an electric field. From speed of charged clay particles through an electric field of known strength, the electrophoretic velocity was calculated from which the ζ was obtained using the Smoluchowsky equation. When particles are arrested or just hindered within a gel-like network, their velocity is reduced or hindered by neighbouring particles and flat riding of electrophoretic velocity may occur. This

translates to almost constant ζ . Such unusual effect, virtually unknown in colloid science, was described by (Dukhin, 2007) when observing clear transformation from sol to gel in dilute carbon nanotube suspension. Electrokinetic measurements are quite sensitive to the structure within suspension, and found even to be useful for monitoring the homogeneity of the formed structure. Also, cation exchanges within soil sorption complex and the electrolyte composition may influence the structure of the clay particles.

This structure building phenomenon was found in a previous study (Kotlyar *et al.*, 1996) to be triggered by nano-size particles. The authors found that at a concentration of only 1–1.5 vol.% of nano particles is required to produce a space-filling, gel network. The presence of the extremely small particles (nano-colloids) was found to be associated with smectites and was seen to inhibit flocculation (Kotlyar *et al.*, 1998). TEM (and TXM) revealed that larger particles were arrested within voluminous network of a gelled suspension or flocs. The consequence of this may be the lowering of the ζ of the gel which has a high water holding capacity. Incidentally, it was found that gel formation was effectively instantaneous within the fraction containing particles of diameters less than 200 nm suspended in 0.1 M NaCl solution (Kotlyar *et al.*, 1998). The resulting gel resisted settling in a manner similar to what we observed for the samples from Gluepot and Invicta. In our case, the high content of the fine particles determined in XRD as amorphous and by TEM as nano-clays may cause low solid content aqueous suspension to form a gel which invariably will cause settling problems. It is probable that such structure-building phenomenon will occur if this type of soil is present in sugarcane juice.

3.3.6 Conclusions

High proportions of fine particles (*i.e.*, < 200 nm) were found in soil samples that are difficult to settle. These particles were classified as amorphous by XRD analysis because no diffraction patterns could be obtained and broadening of clay mineral peaks showed high imperfection in their internal structure and high particle dispersion. Electron microscopy confirmed the presence of this highly dispersed phase, and the electron diffraction patterns from films of these particles indicated the crystalline nature of these nano-clays. Erosion of clay particles as observed in TEM micrographs and especially the expandable smectite-like minerals were probably the best candidates for the origin of the nano-clays.

Significant differences in the electrochemical properties of the soils were identified and there was poor dependence between ζ values and electrolyte concentration in mono-valent salt solutions for the difficult to clarify soils. Structure building phenomenon (as shown by TXM) by the nano-clay particles may be responsible for the problems with poor juice clarification by hindering floc aggregates from settling, despite changing environmental chemistry. Further study of nano-clay building structure properties are needed to find the most efficient way of treating such suspensions in sugar juice.

3.3.7 References

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Chapter 4: Settling rate studies on synthetic juices containing soils

4.1 INTRODUCTION

In Chapter 3 the composition and the physico-chemical properties of the three soils were determined using a number of analytical tools. In summary, the soils that are likely to impact on poor coagulation/flocculation processes and those that have slow settling floc characteristics have been shown to have the following features:

- Contain a lower portion of particles that have higher densities.
- Contain a higher portion of organic material.
- Higher amorphous content. These are non-diffracting and hence in nano-scale.
- Higher specific surface area.
- Contain Si:Al ratio of 2:1 typical of montmorillonite type composition.
- Higher cation exchange capacity.
- Higher ζ .

The settling rate data from the sedimentation trials clearly showed that the Mt Mackay flocs had the fastest settling rate and produced the lowest mud height for the same quantity of added soil. On the other hand Gluepot flocs were the slowest to settle and its corresponding mud height was the highest. The results support the anecdotal evidence that the Mt Mackay and Gluepot soils have ‘good’ and ‘bad’ clarification characteristics respectively.

In the free settling zone, intra-aggregate and inter-aggregate water influence floc density as they occupy voids between particles and between microflocs (Figure 4.1). The way particles are arranged in the micro-floc network has a bearing on the void fraction and hence will affect its settling rate. It is probable that the more compact edge to face (E-F) and face to face (F-F) configurations, dominate in the Mt Mackay soils, while the edge to edge (E-E) configuration (a more open structure) dominates in the

Gluepot soil. It is also probable that the differences in settling characteristic are because of a higher amorphous content in the Gluepot sample. The amorphous content as determined by bulk X-ray powder diffraction is non-diffracting, and contains both organic matter and inorganic particles of very small sizes (nano-particles). A higher proportion will be mainly inorganic particles based on the organic content determined by loss on ignition. In addition the proportion of organic matter was noted to be lowest for the Mt Mackay and highest for the Gluepot soil. On a macroscopic level, the proportion of organic matter influences floc structure and the floc density (Suetsugu *et al.*, 2006).

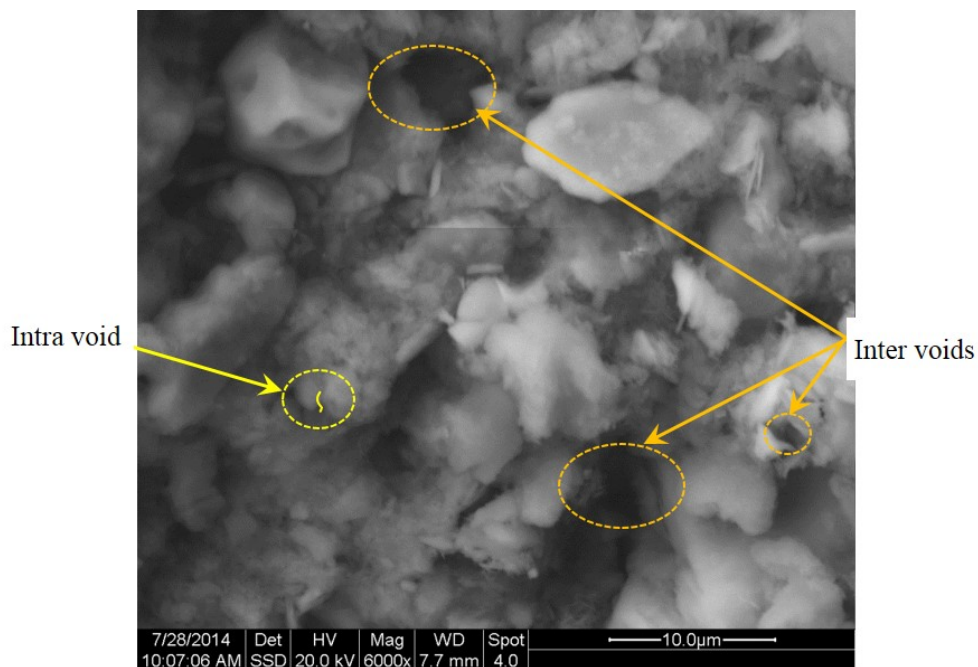


Figure 4.1 Intra- and inter-aggregate water

The results of the work undertaken in Chapter 3 have identified the influencing factors that affect the initial settling rates of flocs in synthetic juice solutions. These influencing factors affect the floc structure which invariably dictates the rate of settling. The influencing factors are:

- Size of flocs
- Density of the flocs
 - Density of individual particles

- Intra/inter voids (Figure 4.2)
- Density of the liquid medium (water/juice)
- Geometry of floc

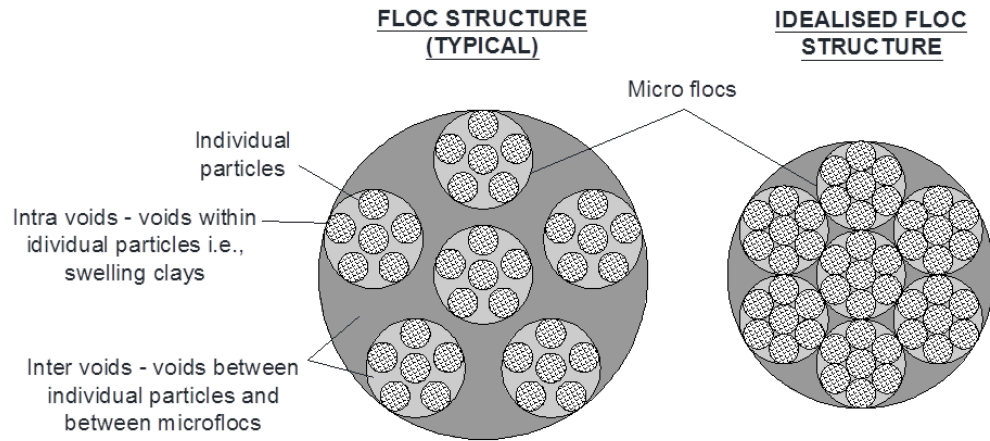


Figure 4.2 Schematics of floc structures (typical and idealised)

Underlying these factors is the surface chemistry of the individual particles, micro-flocs and flocs. The challenge is therefore to develop strategies that should influence or control these factors, and hence floc settling rate. This can be achieved by investigating how to (a) reduce voids or (b) increase floc density.

a) Reduction of voids:

- Intra voids. It is unlikely that the intra voids of the individual particles that enter the juice stream from the milling train (*i.e.*, soil and bagacillo particles) can be changed. However it may be possible to change the structures (and hence the intra void fraction) of those particles that are produced as a result of the chemical and heating reactions that take place during clarification.
- Inter voids
 - Reduce thickness of the electrical double layer by:
 - Using more effective coagulants such as Al^{3+} , Keggin and/or low molecular weight polymers
 - Increase ionic strength

- Reduce exchange capacity – need to reduce the proportion of Na ions on particle surfaces
- Shearing to increase particle to particle collisions
- Branched high molecular weight polymers
- Compounds that cause dehydration
 - Calcium sulphate (gypsum), silica gel
 - Two-stage flocculation. This will involve the following steps:
 - (a) add flocculant, (b) shear, (c) add flocculant to reform flocs

b) Increase floc density:

- Add high density particles to act as ballasting agents in the floc structure
 - Micro-sands
 - Metal oxides
 - Bagasse fly ash
- Reduce bagacillo content in juice by using finer aperture rotary juice screens. However, bagacillo is an effective filter aid for mud filtration and is readily available in the sugar mill. Hence an alternative bagacillo collection and delivery system to the filter station would be required as opposed to obtaining the bagacillo with the juice stream.

In this chapter the impact of bagacillo (fibre), gypsum, bagasse fly ash, stirring speed and stirring time and, flocculant type and dose rate on the settling rate of flocs are investigated using synthetic juices with added flocculant.

4.2 MATERIALS

Bagacillo fibres (size range ~0.2 to 0.4 mm) were sourced from Rocky Point Mill. Bagacillo is the term used to describe the fine portion of bagasse (see section 2.2.2 for further details). In the sugar mill bagacillo is used as a filter aid at the rotary vacuum filters to assist with mud filtration. It is typically sourced and delivered to the filter station either with the mixed juice passing through the rotary juice screens or from the final mill bagasse using pneumatic systems.

Laboratory grade gypsum in the form of calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was supplied by Sigma-Aldrich (Sydney, Australia).

Ash samples were received from Isis Central Mill (Bundaberg Region of Queensland, Australia). Ash is the remaining product after bagasse is combusted in the boiler.

The flocculants used in the tests are described in Table 4.1. The Sucrafloc 2310 and 2320 were supplied by TD Chemicals Pty Ltd (Gold Coast, Queensland, Australia). They have the lowest degrees of hydrolysis and molecular weight compared to the other flocculants.

Magnafloc LT27 is supplied by Ciba. It is in the mid-range in terms of degree of hydrolysis and molecular weight.

The Superfloc flocculants were supplied by Kermira (Albury, New South Wales, Australia). These flocculants all have a molecular weight of 23×10^6 but the degree of hydrolysis varied between 26 to 39 mol%.

The use of all of these flocculants in food manufacturing processes is approved by the United States Food and Drug Administration (USFDA).

Table 4.1 Properties of flocculants

| Flocculant name | Degree of hydrolysis (mol%) | Molecular weight |
|------------------------|------------------------------------|-------------------------|
| Sucrafloc 2310 | 23 - 25 | $7 - 10 \times 10^6$ |
| Sucrafloc 2320 | 23 - 25 | $12 - 15 \times 10^6$ |
| Magnafloc LT27 | 27 | 18×10^6 |
| Superfloc A2115 | 26 | 23×10^6 |
| Superfloc A2120 | 30 | 23×10^6 |
| Superfloc A2125 | 32 | 23×10^6 |
| Superfloc A2130 | 39 | 23×10^6 |

4.2.1 Preparation of flocculant solution

A 100 mL stock flocculant solution at 0.2 wt% was prepared by dispersing and dissolving flocculant powder (0.2 g) in Milli-Q water using a stirrer with a 45° pitch four blade turbine impeller of 50 mm diameter running at 50 r/min for approximately 4 h. The powder was added slowly and carefully during mixing to ensure that each

flocculant granule is wetted to prevent agglomeration and the formation of ‘oysters’. The stock solution was stored in the fridge at ~4 °C. The effective life of a 0.2 wt% stock solution stored at ~4 °C is approximately two weeks. On the day of the tests the stock flocculant solution was used to prepare a 100 mL flocculant solution at either 0.01 wt% or 0.04 wt%.

4.2.2 Stock synthetic juice solution (Electrolyte)

Chemicals, CaCl₂.2H₂O (Chem Supply, Gillman, Australia), MgCl₂.6H₂O (Merck, Kilsyth, Australia), NaCl and KCl (Sigma- Aldrich, Sydney, Australia), were analytical grade.

The stock synthetic juice solution was prepared by dissolving 1.91 g of NaCl, 47.67 g of KCl, 18.34 g of CaCl₂.2H₂O and 31.37 g of MgCl₂.6H₂O in 1000 mL of Milli-Q water.

During the tests a 4 mL aliquot of the stock solution was added to the soil/Milli-Q water suspensions to produce a synthetic juice with an electrolyte composition as detailed in Table 4.2. Potassium is the main cation followed by Ca and Mg ions. No organic acid was added in the solution. The pH of the solutions ranged between 4.67 to 5.93 and the value depended on the soil type.

Table 4.2 Electrolyte concentration in 1 wt% soil

| Parameter | Value |
|--|--------------|
| Na (as NaCl), ppm | 30 |
| K (as KCl), ppm | 1000 |
| Ca (CaCl ₂ .2H ₂ O), ppm | 200 |
| Mg (MgCl ₂ .6H ₂ O), ppm | 150 |
| Molarity, M | 0.038 |
| Ionic strength, M | 0.0604 |

4.3 EXPERIMENTAL

4.3.1 Batch settling tests using electrolyte with flocculants

The mass of soil samples required to produce a soil concentration of 0.2 w/v%, 0.5 w/v% and 1.0 w/v% in 100 mL solutions were determined. The required mass of soil was weighed into 20 mL jar which were then filled with Milli-Q water and

sonicated in a water bath for 5 min to completely break down aggregates. After sonication, the mixture transferred into a glass beaker pre-filled with 76 mL of Milli-Q water. The mixture was stirred using a magnetic stirrer ($\sim 300 \text{ r.min}^{-1}$) and a 5 cm stirrer bar for 1 min. Approximately 4 mL aliquot of the stock synthetic juice solution was added to the mixture to give a volume of 100 mL and the whole stirred for 1 min. At the end, a 0.04 wt% of flocculant (LT27) was added to the mixture in a single dose and stirred for a further 1 min. The flocculated suspension was then transferred into a 100 mL glass cylinder, inverted 10 times and left standing for sedimentation to occur. The mud interface heights were recorded over a 30 min period. The height of glass cylinder at the 100 mL graduation ($\sim 195 \text{ mm}$) was used to determine the settling rates over the first 5 min of sedimentation. The average error in the measurements is $\pm 0.25\%$.

The settling data for the 0.2 w/v% and 0.5 w/v% solutions were difficult to obtain because the mud interfaces were not clearly visible for most of the samples. However for the 1.0 w/v% solution the mud flocs were larger and the mud interfaces were distinct.

The turbidity of the supernatant was determined by measuring its light absorbance at a wavelength of 900 nm and multiplying by 100 for convenience.

4.4 RESULTS AND DISCUSSION

4.4.1 Effect of sonication on settling speed

To test the effect of ultrasonic pre-treatment of the soil (as described in the experimental section) on the particle settling speed two tests were carried out using Invicta 255B (Table 4.3). In test 1 the soil solution was sonicated for 5 min in a water bath, and in test 2 the soil solution was not sonicated. Flocculant LT27 was used at a rate of 0.5 ppm in both tests. The initial settling rates could not be calculated because the interface could not be identified easily. Instead the time taken for the interface to reach the compression zone was measured.

The results show that the particles in the soils that were not sonicated reached the compression zone in $\sim 20\text{-}30 \text{ s}$ compared to the sonicated soil which took at least 5 times longer at 120 s. This means that with ultra-sonication the aggregates disintegrate to finer particles, and it is these particles that contribute to the slower settling rate. In practice the disintegration of soil aggregates can also occur in wet soils (*i.e.*, after rain).

So, in certain situations, a soil with good clarification properties can become a soil with poor clarification properties after a rainfall. This partly explains why issues of slow settling of mud are prevalent during periods of rainfall. There is also the contribution of more soil coming in with the cane supply during rainfall, and so enhances the problem.

Table 4.3 Effect of sonication on settling speed of Invicta 255B

| Test | Ultrasonic pre-treatment of soil | Flocculant (0.5 ppm) | Time to reach compression zone (s) |
|------|----------------------------------|----------------------|------------------------------------|
| 1 | None | LT27 | 20 -30 |
| 2 | 5 min in ultrasonic bath | LT27 | 120 |

4.4.2 Effect of flocculant type and addition rate on clarification performance

The effect of flocculant type and dose rate was evaluated on the clarification performance of Gluepot and Mt Mackay soils. A total of seven flocculants (described in Table 4.1) with varying degrees of hydrolysis (mol%) and molecular weight were tested at three dose rates (0.125 ppm, 0.5 ppm and 1.0 ppm) for each soil. The flocculant dosing rates used for clarification of sugarcane juice in raw sugar manufacturing typically vary between ~3 and 5 ppm (Rein, 2007). The flocculant dosing rates tested in this work are lower compared to what is typically used for real factory juices because the main aim here was to achieve settling rates that are easily distinguishable between the two soils and identify the flocculant type that produces the best clarification performance. The initial settling rate, turbidity of the supernatant and the final mud heights are presented in Table 4.4, Table 4.5 and Figure 4.3 to Figure 4.5.

The results show that the initial settling rates increase and the turbidity of the supernatant decrease as the flocculant dosing rate is increased. The magnitude of the variations in the initial settling rates for the different flocculants are higher as the dosing rate is increased. Also, the final mud heights for the Gluepot soil generally decrease as the flocculant dosing rate is increased however there was little variation for the Mt Mackay soil which were typically in 3-4 % range. These trends (apart from the final mud height for the Mt Mackay soil) are also observed when clarifying real sugarcane juices (Doherty *et al.*, 2003; Mohammed *et al.*, 2016).

Table 4.4 Clarification test results for different flocculant types and dosing rates for Gluepot soil

| Test | Flocculant | | Initial settling rate (cm/min) | Turbidity of supernatant | Final mud height (%) |
|------|------------|-----------------|--------------------------------|--------------------------|----------------------|
| | Name | Dose rate (ppm) | | | |
| 1 | 2310 | 0.125 | 2.0 | 10.5 | 10.0 |
| 2 | 2320 | 0.125 | 2.0 | 15.0 | 8.0 |
| 3 | LT27 | 0.125 | 1.4 | 15.0 | 15.0 |
| 4 | 2115 | 0.125 | 1.8 | 13.0 | 9.5 |
| 5 | 2120 | 0.125 | 2.5 | 17.0 | 6.0 |
| 6 | 2125 | 0.125 | 1.6 | 13.0 | 11.0 |
| 7 | 2130 | 0.125 | 1.8 | 13.0 | 7.0 |
| 8 | 2310 | 0.500 | 10.9 | 6.5 | 5.0 |
| 9 | 2320 | 0.500 | 3.2 | 16.5 | 8.0 |
| 10 | LT27 | 0.500 | - | 2.0 | 6.0 |
| 11 | 2115 | 0.500 | 6.7 | 10.5 | 6.0 |
| 12 | 2120 | 0.500 | 30.9 | 4.7 | 8.0 |
| 13 | 2125 | 0.500 | 2.5 | 12.7 | 8.5 |
| 14 | 2130 | 0.500 | 3.3 | 17.2 | 8.0 |
| 15 | 2310 | 1.000 | 11.2 | 6.2 | 8.0 |
| 16 | 2320 | 1.000 | 53.2 | 3.5 | 8.0 |
| 17 | LT27 | 1.000 | 44.9 | 5.3 | 7.0 |
| 18 | 2115 | 1.000 | 18.3 | 7.2 | 8.0 |
| 19 | 2120 | 1.000 | 48.7 | 4.5 | 8.0 |
| 20 | 2125 | 1.000 | 34.3 | 5.1 | 8.0 |
| 21 | 2130 | 1.000 | 50.9 | 2.4 | 8.0 |

Table 4.5 Clarification test results for different flocculant types and dosing rates for Mt Mackay soil

| Test number | Flocculant | | Initial settling rate (cm/min) | Turbidity of supernatant | Final mud height (%) |
|-------------|------------|-----------------|--------------------------------|--------------------------|----------------------|
| | Name | Dose rate (ppm) | | | |
| 22 | 2310 | 0.125 | 6.1 | 26.0 | 3.0 |
| 23 | 2320 | 0.125 | 6.6 | 23.0 | 3.0 |
| 24 | LT27 | 0.125 | 7.5 | 24.0 | 3.0 |
| 25 | 2115 | 0.125 | 6.6 | 24.0 | 3.0 |
| 26 | 2120 | 0.125 | 6.6 | 22.5 | 3.0 |
| 27 | 2125 | 0.125 | 6.6 | 25.7 | 3.0 |
| 28 | 2130 | 0.125 | 7.0 | 24.0 | 3.0 |
| 29 | 2310 | 0.500 | 35.9 | 7.0 | 4.0 |
| 30 | 2320 | 0.500 | 63.7 | 5.2 | 3.0 |
| 31 | LT27 | 0.500 | 39.7 | 7.5 | 4.0 |
| 32 | 2115 | 0.500 | 59.9 | 6.2 | 4.0 |
| 33 | 2120 | 0.500 | 52.4 | 2.7 | 4.0 |
| 34 | 2125 | 0.500 | 50.2 | 4.0 | 4.0 |
| 35 | 2130 | 0.500 | 39.7 | 4.0 | 4.0 |
| 36 | 2310 | 1.000 | 123.6 | 4.0 | 4.0 |
| 37 | 2320 | 1.000 | 123.6 | 2.7 | 4.0 |
| 38 | LT27 | 1.000 | 78.6 | 5.8 | 4.0 |
| 39 | 2115 | 1.000 | 78.6 | 4.0 | 4.0 |
| 40 | 2120 | 1.000 | 123.6 | 3.8 | 4.0 |
| 41 | 2125 | 1.000 | 101.1 | 3.5 | 4.0 |
| 42 | 2130 | 1.000 | 123.6 | 3.0 | 4.0 |

The initial settling rates of the flocs produced from the Gluepot and Mt Mackay soils are shown graphically in Figure 4.3, Figure 4.4 and Figure 4.5 for flocculant dosing rates of 0.125 pp, 0.500 ppm and 1.000 ppm respectively. The results show that the Mt Mackay flocs always settle faster than the Gluepot flocs at each of the three flocculant dosing rates. These trends confirm the anecdotal evidence that the Mt Mackay soils have better clarification properties compared to Gluepot. The settling rate of the Mt Mackay flocs were also higher when no flocculants were used in the clarification tests carried out in Chapter 3.

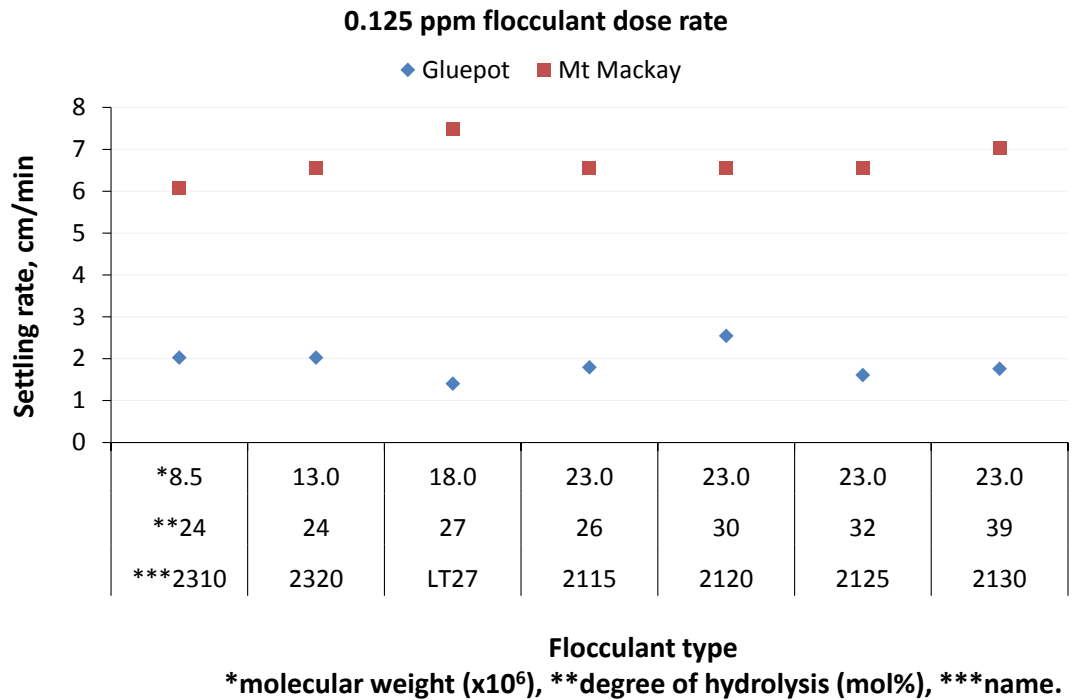


Figure 4.3 Comparison of initial settling rate for Gluepot and Mt Mackay flocs produced from different flocculants at a dosing rate of 0.125 ppm

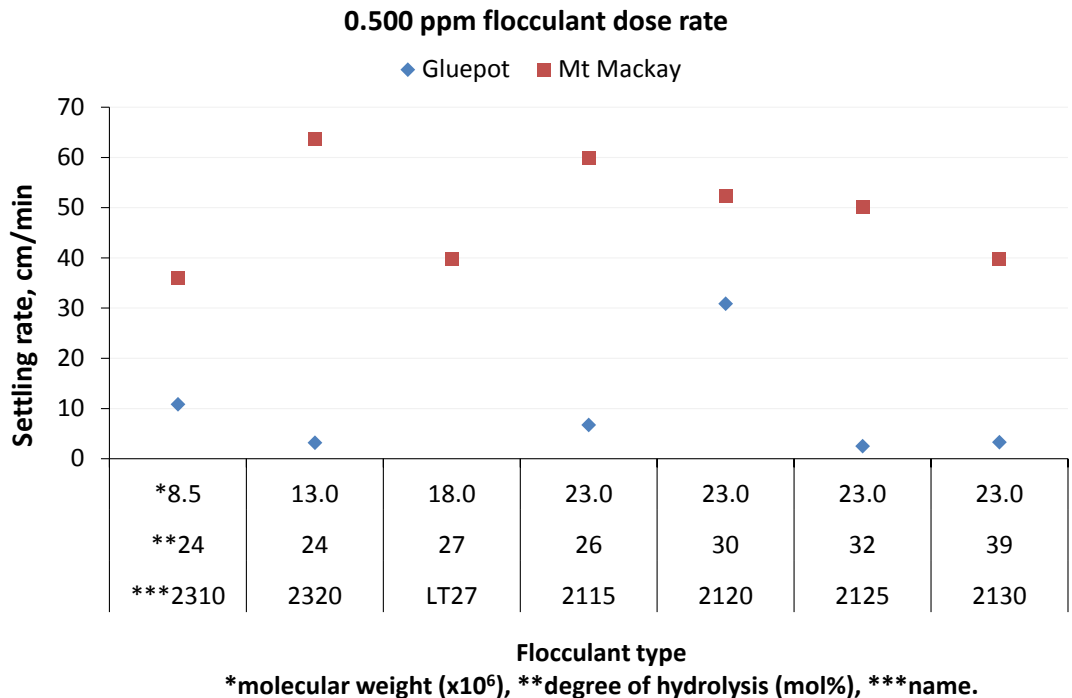


Figure 4.4 Comparison of initial settling rate for Gluepot and Mt Mackay flocs produced from different flocculants at a dosing rate of 0.500 ppm

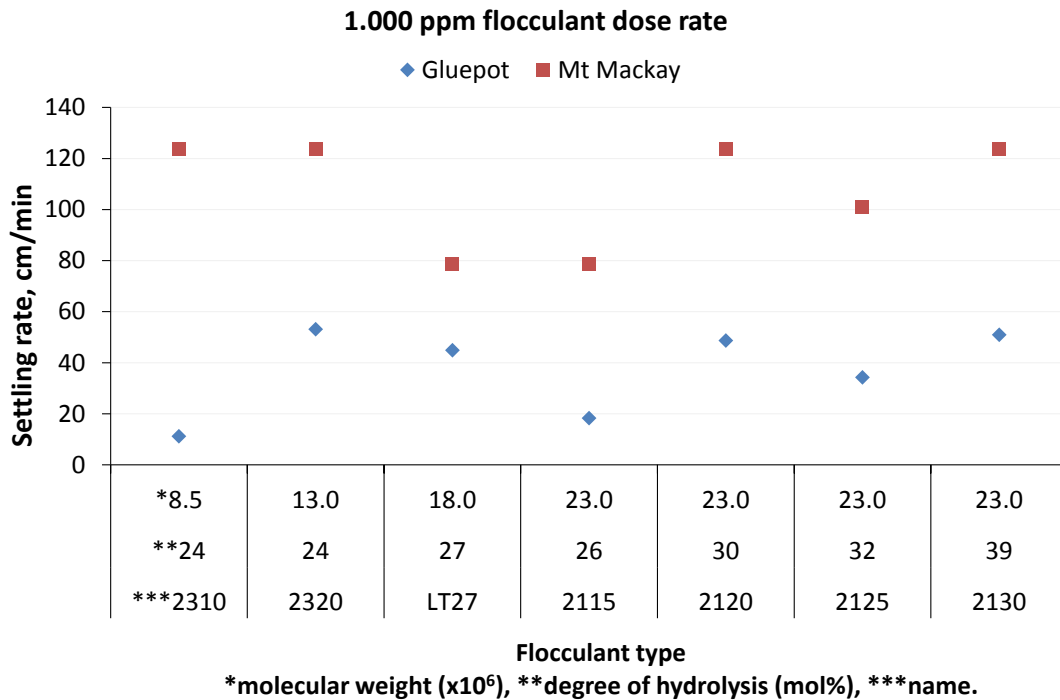


Figure 4.5 Comparison of initial settling rate for Gluepot and Mt Mackay floes produced from different flocculants at a dosing rate of 1.000 ppm

There was no single flocculant that consistently performed better than the other flocculants at all three dosing rates. A similar trend was observed by other researchers (Orfori *et al.*, 2011; Shi *et al.*, 2017; Saritha *et al.*, 2017). For example Orfori *et al.*, (2011) found that the initial settling rate of floes formed by different coal samples did not consistently increase with increases in the flocculant dosing rate for the same mixing speeds. The increases in initial settling rate of the floes from each coal sample appeared to be dependent on the mixing speed. Hence, because the mixing speeds for all tests in this study were maintained at the same rate, the floes formed may not have the optimum bulk density due to the different packing arrangements during flocculation based on the shear rate provided by the mixing speed.

Table 4.6 shows the mean and differences in the initial settling rate, turbidity and final mud heights for the two soils at each of the three flocculant dosing rates. The results show that the largest difference (409 %) in the mean initial settling rates between Gluepot and Mt Mackay soils is largest for the 0.5 ppm dosing rate. It is possible that the magnitude of the increase in settling rate for each unit increase in flocculant dosing rate above a certain dosing rate may tend to decrease due to reverse effect of dispersion (Kanungo, 2005; Shi *et al.*, 2017).

Table 4.6 Differences in the mean initial settling rate and turbidity for Gluepot and Mt Mackay soils

| Flocculant dosing rate (ppm) | Soil | Value | |
|------------------------------|-----------|-------|----------|
| | | mean | diff (%) |
| Settling rate, cm/min | | | |
| 0.125 | Gluepot | 1.9 | 255 |
| | Mt Mackay | 6.7 | |
| 0.500 | Gluepot | 9.6 | 409 |
| | Mt Mackay | 48.8 | |
| 1.000 | Gluepot | 37.4 | 188 |
| | Mt Mackay | 107.5 | |
| Turbidity of supernatant | | | |
| 0.125 | Gluepot | 13.8 | 75 |
| | Mt Mackay | 24.2 | |
| 0.500 | Gluepot | 10.0 | -48 |
| | Mt Mackay | 5.2 | |
| 1.000 | Gluepot | 4.9 | -22 |
| | Mt Mackay | 3.8 | |
| Final mud heights, % | | | |
| 0.125 | Gluepot | 9.5 | -68 |
| | Mt Mackay | 3.0 | |
| 0.500 | Gluepot | 7.1 | -45 |
| | Mt Mackay | 3.9 | |
| 1.000 | Gluepot | 7.1 | -43 |
| | Mt Mackay | 4.0 | |

The turbidity of the supernatant at a flocculant dosage rate of 0.125 ppm is lower for Gluepot but at the higher dosage rates is lower for Mt Mackay. The results show that the optimum flocculant dosing rate for Gluepot is likely to be ~1.0 ppm whereas for Mt Mackay it is likely to be around 0.5 ppm. As per the observations of Kanungo (2005) the flocculant dosing rate beyond 0.5 ppm for Mt Mackay appears to be having a greater reverse effect due to dispersion compared to Gluepot.

The final mud heights for the Mt Mackay soil is consistently lower (by between 43 and 68 %) at all three flocculant dosing rates. Based on the results of some researchers (Kim and Pipes, 1999; Cytawa *et al.*, 2007; Yan *et al.*, 2016; Yu *et al.*, 2016) the final mud height of a suspension after a settling test is lower when the floc settling rate is higher. It is surprising therefore that the final mud height for Mt Mackay increases as the settling rate increases. It should also be noted that the final mud height after a batch settling test does not represent the insoluble solids concentration as juice is between layers of mud.

4.4.3 Effect of adding pre-flocculated bagasse fly ash on settling rate of flocs

The practice of incorporating high density particles into gravity settling clarification systems to improve the bulk density and hence the settling rate of flocs is a relatively new technology and commonly referred to as ballasted flocculation (Young and Edwards, 2003; Lombard *et al.*, 2013; Kumar *et al.*, 2016). In raw sugar manufacturing, bagasse fly ash is a readily available and potentially suitable ballasting agent (*cf* section 2.4.1). The particle density of bagasse fly ash is $\sim 1390 \text{ kg/m}^3$ (Lima *et al.*, 2012).

Preliminary tests using bagasse fly ash (*i.e.*, without pre-flocculating) showed that a reasonable amount of fine ash particles was present in the supernatant with little or no improvement on settling speed. In the sugar factory process, the bagasse fly ash is typically removed from the boiler in a slurry form using water. The slurry undergoes a clarification process using a flocculant to aggregate the ash particles and to aid in the separation process and produce low turbidity water so that it can be recycled back to the boiler ash system. Hence it was decided to pre-flocculate the ash particles prior to use in the clarification tests with the soils.

In these tests the effect of adding pre-flocculated bagasse fly ash at different ratios to the soil content on settling speeds were trialled. Prior to addition the bagasse fly ash were flocculated to form ash aggregates. The flocculated ash aggregates were drained to remove excess flocculant. The aggregated ash particles were then added to the soil solution after it was sonicated in the water bath. The total mass of soil/ash mixture was maintained at 1.000 g. Flocculant LT27 was used for pre-flocculating the ash particles and for the clarification tests.

Table 4.7 summarises the final settling times for the different soil to ash ratios. The final settling times rather than the standard interface height measurements at certain intervals were measured due to difficulties in reading the interface during the initial settling period. The final settling times of soil only (*i.e.*, no ash) solutions are also included.

The results show that there are benefits in adding flocculated ash to the soil solution prior to clarification. The addition of flocculated ash has a more significant impact on the soils that have poor settling rates (*i.e.*, Gluepot and Invicta). For soil to ash ratios of 3:1 the final settling times are at least 63 % and 47 % lower when compared no ash addition for the Gluepot and Invicta 255B soils respectively. The results for Mt Mackay indicate there is only a slight benefit when the total ash content is at least 50 % (*i.e.*, 1:1 ratio).

Table 4.7 Effect of adding flocculated bagasse fly ash on settling time

| Mass of each component | Soil:Ash ratio | Final settling time (min) | | |
|---------------------------|----------------|---------------------------|--------------|-----------|
| | | Gluepot | Invicta 255B | Mt Mackay |
| 1.000 g soil | 1:0 | >30.0 | >10.0 | >4.0 |
| 0.750 g soil, 0.250 g ash | 3:1 | 11.0 | 5.0 to 5.5 | 4.0 - 4.5 |
| 0.666 g soil, 0.333 g ash | 2:1 | 10.0 – 15.0 | 4.75 - 5.25 | 4.0 - 4.5 |
| 0.500 g soil, 0.500 g ash | 1:1 | 4.5 | 4.5 - 5.0 | 2.3 - 2.6 |
| 0.333 g soil, 0.666 g ash | 1:2 | 9.0 | 4.0 | 3.0 - 3.5 |
| 0.250 g soil, 0.750 g ash | 1:3 | 7.0 | 1.75 - 2.00 | 2.5 |

The results are also shown graphically in Figure 4.6. Although the results show higher reductions to the final settling times when higher quantities of flocculated ash is added, it may not provide overall benefits in factory juice clarification processes. This is due to the fact that any ash added to the juice in a raw sugar factory ends up in the filter feed which increases the production of mud cake. Unless the addition of ash also improves filtration efficiency it is likely that higher sugar losses to the mud cake will result. In practice therefore the amount of pre-flocculated ash added to the juice will also need to be assessed in terms of its effect on mud filtration efficiency and pol losses in the mud cake.

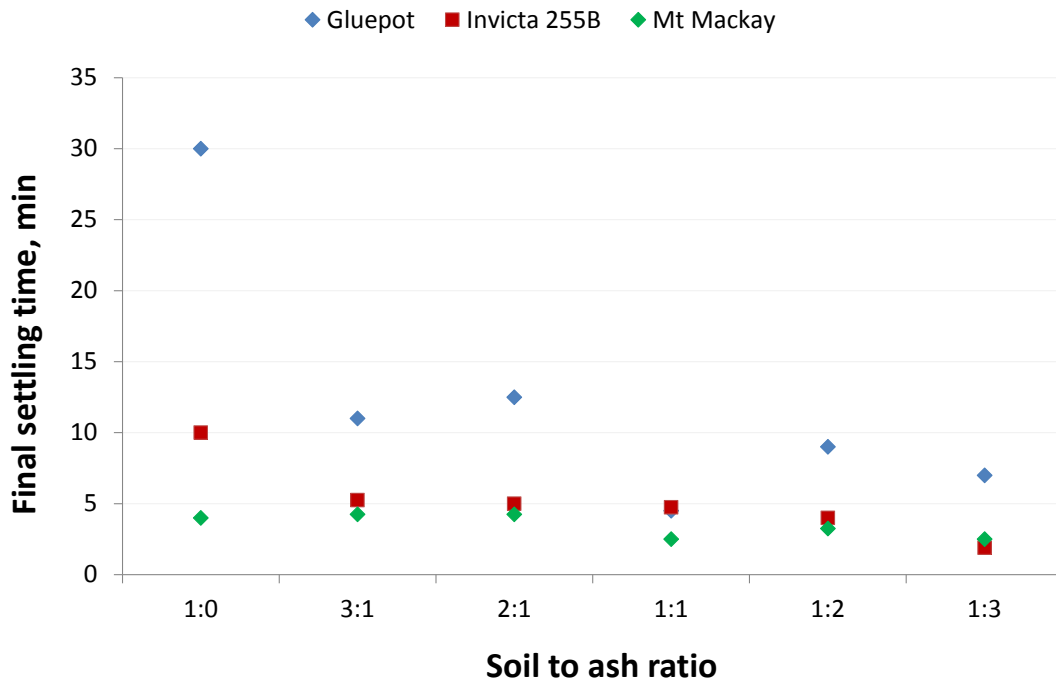


Figure 4.6 Variation in final settling time for various soil:ash ratios (flocculant LT27, dose rate of 0.125 ppm)

4.4.4 Effect of adding gypsum to mixtures of soil and pre-flocculated ash on settling rate of flocs

Akai (1994) found that gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) applied to the puddled water of paddy fields decreased the suspended solid concentration. Although, gypsum is sparingly soluble in water it is always used for calcium addition to sodic soils in aggregation and improvement of permeability without changing pH value (Nettleton *et al.*, 1982; Verhaye and Boyadgiev, 1997; Sinolungan *et al.*, 2009). One of the limitations of using lime only as a coagulant for sugarcane juice clarification is that it delivers excessive free calcium ions and also raises the juice pH at the same time. Hence, using gypsum in combination with lime provides an opportunity to improve flocculation without raising the pH of sugarcane juice above the target set point.

Gypsum is also an effective de-hydrant, as it has tendency to absorb water. One of the characteristics of some bad soils like Gluepot is that they contain clays (*i.e.*, smectites) that tend to absorb water and swell. Swelling causes aggregates that are formed to have reduced bulk density. For example, Kondo and Torrance (2005) demonstrated that, the presence of high-swelling smectite to low activity-mineral-dominated Leda clay increased the salinity and water content ranges above levels

which consolidation settling and zone settling could occur. They attributed the increase in the amount of water that it is strongly adsorbed to the surface and in the space between smectite particles on its swelling nature. Furthermore, Sinolungan *et al.*, (2009) showed that when gypsum was added to various Tondano Lake (Indonesia) clay soils, dispersive free settling patterns did not occur and the turbidity of the supernatant reduced with increasing gypsum concentration. Based on these findings the addition of gypsum into the soil suspensions may improve flocculation and hence increase the floc settling rate and reduce the turbidity of the supernatant.

In the present study the soil/pre-flocculated ash mixtures were sonicated prior to the addition of gypsum. The total mass of the insoluble solids was maintained at 1.000 g. Also, in all mixtures there were equal portions of soil and pre-flocculated ash (*i.e.*, the soil:ash ratio was maintained at 1.0). The soil:ash ratio of 1.0 was selected as it gave the best results (see Figure 4.6). Flocculant LT27 was used for pre-flocculating the ash particles and in all the clarification tests.

Table 4.8 summarises the final settling times for the different soil/ash to gypsum ratios. It was difficult to identify the interface between the supernatant and settling flocs so only the final settling times were recorded. The final settling times of soil/ash only (*i.e.*, no gypsum) solutions from Table 4.7 are also included. The results are also shown graphically in Figure 4.7. They show that as the portion of gypsum is increased the final settling time steadily reduces for Mt Mackay. A similar trend occurs for the Invicta 255B. For Gluepot, when a small portion of gypsum is added (*i.e.*, at a ratio of 19:1) the final settling time increases by ~90 %. As the gypsum portion is increased the trend is similar to Invicta 255B in that there is a slight decrease with increasing gypsum addition. The results clearly show some benefits with Gluepot.

Table 4.8 Clarification results for adding gypsum to mixtures of pre-flocculated bagasse fly ash and soil on settling time

| Mass of each component | Soil/Ash: Gypsum ratio | Flocculant dosing rate (ppm) | Final settling time (min) | | |
|---|------------------------|------------------------------|---------------------------|--------------|--------------|
| | | | Gluepot | Invicta 255B | Mt Mackay |
| 0.500 g soil, 0.500 g ash | 1:0 | 0.125 | 4:30 | 4:45 | 2:30 |
| 0.475 g soil, 0.475 g ash, 0.050 g gypsum | 19:1 | 0.125 | 4:30 | 4:30 to 5:00 | 2:30 |
| 0.450 g soil, 0.450 g ash, 0.100 g gypsum | 9:1 | 0.125 | 8:00 to 9:00 | 3:30 to 4:30 | 2:30 |
| 0.400 g soil, 0.400 g ash, 0.200 g gypsum | 4:1 | 0.125 | 6:30 to 8:30 | 2:45 to 3:45 | 2:00 to 2:30 |

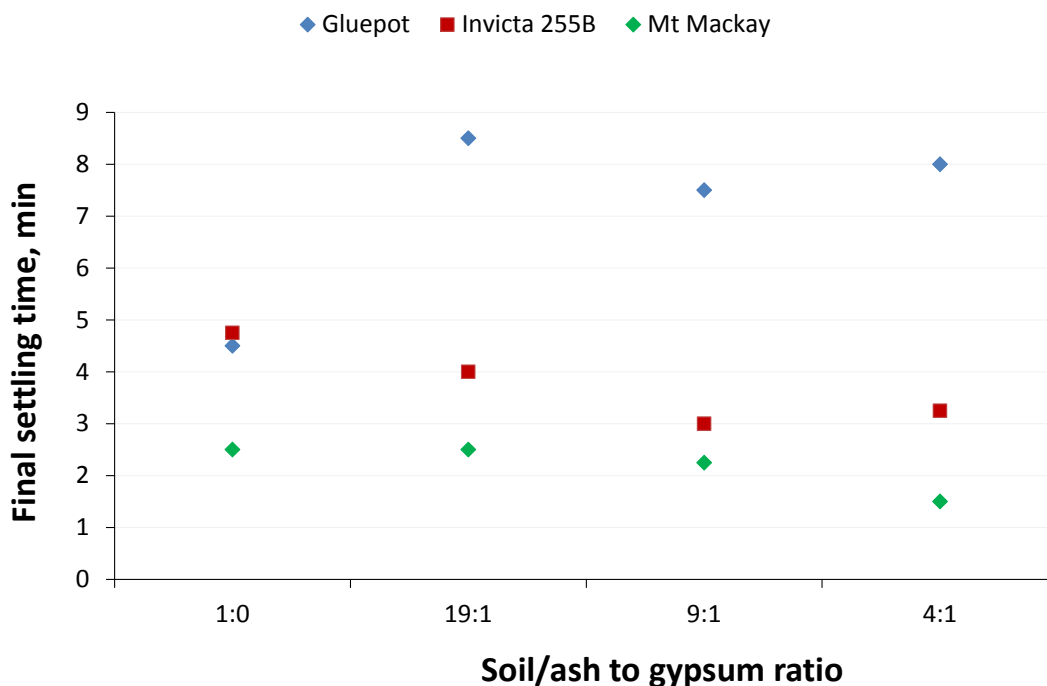


Figure 4.7 Variation in final settling time for different soil/ash to gypsum ratios

4.4.5 Effect of stirrer speed and mixing time on settling rate of Gluepot flocs

Mixing is an important step in coagulation-flocculation processes and many researchers have studied the effect of different mixing conditions on separation efficiency of solid particles from liquid suspensions (Gregory, 1991; Chen *et al.*, 1998; Bouyer *et al.*, 2004; Serra *et al.*, 2008; Ramphal and Sibiya, 2014; Vadasarukkai and Gagnon, 2017). Dosing and mixing conditions affect the average floc size distribution through several rate processes associated with polymer adsorption and particle collision (Gregory, 1991).

High shear mixing assists with the dispersion of the additive as well as increasing the collision rate of the suspended particles, resulting in floc aggregation, provided the suspension is destabilised. As coagulation continues the aggregates grow and become more tenuous after which with more mixing they become structurally fragile and are susceptible to breakup by fluid shear (Serra *et al.*, 2008). During the flocculant (or polymer) addition phase, flocs grow to even larger sizes, so it becomes particularly important to limit rapid mixing to only a few seconds to achieve both flocculant dispersion and adsorption (Gregory, 1991).

In the present study an overhead stirrer with a custom made impeller (Figure 4.8) was used. The impeller has two paddles with rounded outer edges of 5 mm and an effective mixing diameter of 30 mm. The effect of three stirrer speeds (500, 750 and 1000 r/min with tip speeds of ~0.8, 1.2 and 1.6 m/s respectively) and three mixing times (1, 5 and 20 min) on the settling rate of flocs produced from the Gluepot soil were assessed. Mt Mackay and Invicta 255B soils were not assessed in these tests. Flocculant Superfloc A2120 (0.01 % w/v) at a dosing rate of 0.5 ppm was used in all the tests as it was the best performing flocculant for Gluepot (Figure 4.4) . After flocculation gentle mixing at 50 rpm was applied for one minute in all tests.

Table 4.9 summarises the clarification test results. Overall the initial settling rates vary between 2.0 and 8.3 cm/min and for all three stirrer speeds they increased with increasing mixing time. As the initial settling rates increased the supernatant turbidities increased slightly and the final mud heights decreased slightly. Both of these trends are common in most clarification test results including those with real factory juices. At slower settling rates the flocs have more opportunities to adsorb more suspended solids due to increased settling times. Flocs that settle faster also

result in a higher degree of compression when all flocs have settled. This is likely to do with the faster settling flocs having higher bulk densities.

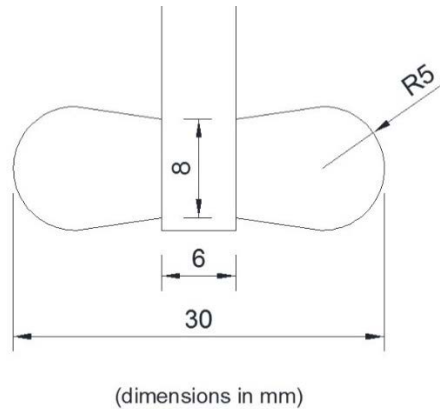


Figure 4.8 **Dimensions of stirrer shaft and impeller**

Table 4.9 **Clarification test results for the stirrer speed and mixing time tests**

| Mixing speed (r/min) | Tip speed of impeller (m/s) | Mixing time (min) | Initial settling rate (cm/min) | Turbidity of supernatant | Final mud height (%) |
|----------------------|-----------------------------|-------------------|--------------------------------|--------------------------|----------------------|
| 500 | 0.8 | 1 | 2.0 | 8.2 | 10.8 |
| | | 5 | 4.0 | 8.3 | 8.3 |
| | | 20 | 6.4 | 8.3 | 7.5 |
| 750 | 1.2 | 1 | 2.9 | 8.6 | 8.5 |
| | | 5 | 4.1 | 8.5 | 8.0 |
| | | 20 | 8.3 | 10.7 | 7.0 |
| 1000 | 1.6 | 1 | 2.3 | 8.2 | 9.5 |
| | | 5 | 2.8 | 8.8 | 9.0 |
| | | 20 | 5.2 | 11.9 | 8.0 |

Figure 4.9 shows the variation in the initial settling speeds with mixing time for the three stirrer speeds. There is less scatter in the results for the 1 min mixing times. For the 500 r/min stirrer speed the results indicate that there is a more significant increase in the settling speed when going from 1 to 5 min (*i.e.*, ~100 % increase) compared to going from 5 to 20 min of mixing (*i.e.*, ~62 % increase). There is a

consistent rise in settling speed for the 750 r/min stirrer speed from 1 to 20 min of mixing. The settling speeds at each mixing time was consistently higher for the 750 r/min stirrer speed. At 5 and 20 mixing times the initial settling speeds were lowest for 1000 r/min stirrer speed. It is likely that at faster stirrer speeds there is the potential for the impeller to damage the aggregates and hence reduce their size due to higher shearing rates.

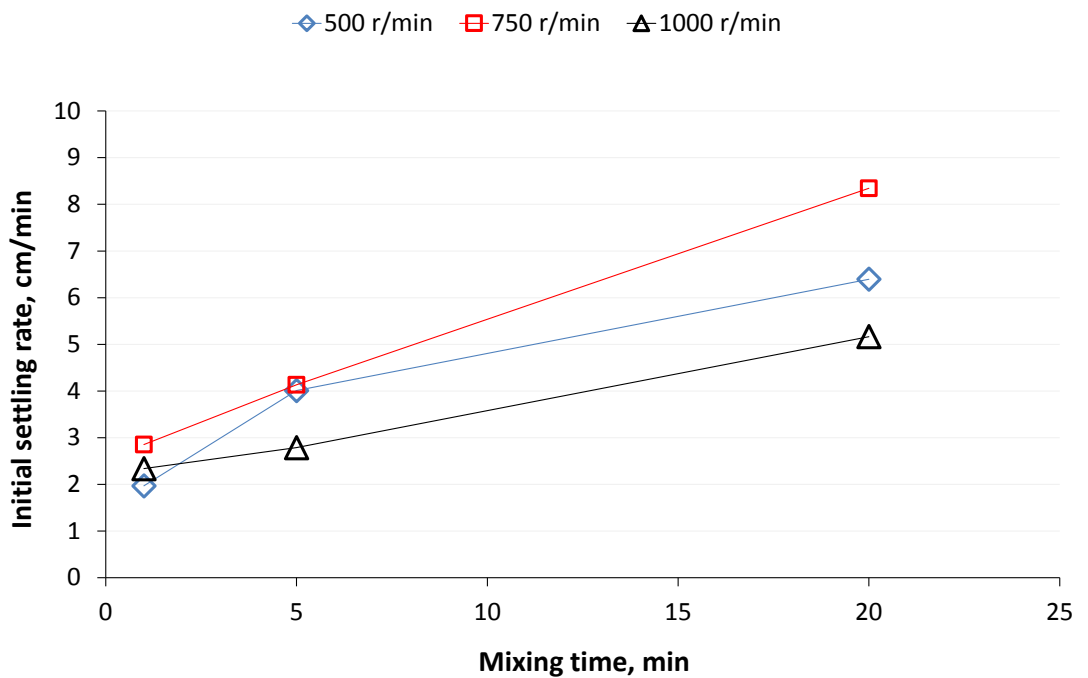


Figure 4.9 Variation in initial settling rate of Gluepot flocs at different mixing times

Figure 4.10 shows the variation in the initial settling speeds with stirrer speeds for the three mixing times. For each of the three mixing times the initial settling speed is higher for the faster stirrer speeds. The results indicate that the optimum stirrer speed for the system tested lies between 500 and 1000 r/min.

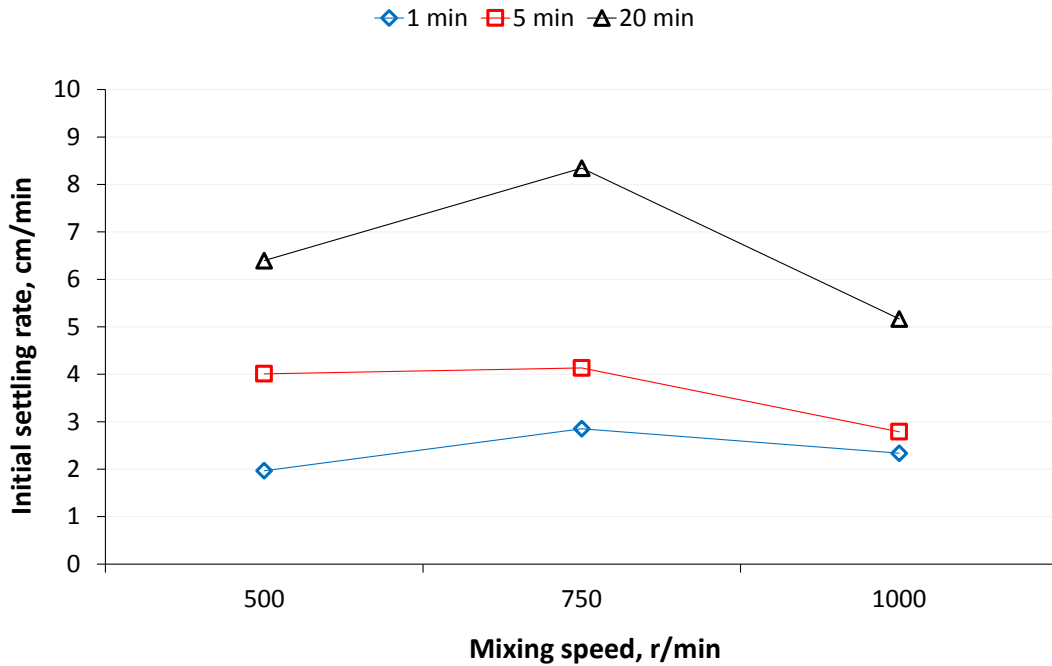


Figure 4.10 Variation in initial settling rate of Gluepot flocs at various stirrer speeds

4.5 CONCLUSIONS

Batch settling tests using soil electrolyte suspensions showed that flocs produced from Gluepot soils consistently performed poorly compared to flocs produced from Mt MacKay soils regardless of the type and dosing rate of the flocculant used. This provides evidence of what was reported anecdotally that Gluepot soils have inherently poor flocculation properties.

The addition of pre-flocculated bagasse fly ash improved the settling rate of all three soils. However, the improvements were only significant for the Gluepot and Invicta 255B soils. At the minimum ash addition rate, *i.e.*, a soil to ash ratio of 3:1 the final settling times of the flocs were 63 % and 47 % lower for the Gluepot and Invicta 255B soils when compared to no added ash. The benefits of pre-flocculated ash for the Mt Mackay soil was only significant when the soil to ash ratio was greater than 1:1. It is remarked that adding insoluble solids such as ash will eventually end up in the mud streams thereby increasing the amount of mud cake produced and potentially poll losses at the filter station. It is important therefore to evaluate the benefits of added

ash not only in terms of improving the settling rate of the flocs but also in terms of mud filtration efficiencies as well.

The addition of gypsum to a mixture of soil and pre-flocculated ash slightly reduced the final settling times for Mt Mackay and Invicta 255B flocs. For Gluepot on the other hand when a small portion of gypsum is added (*i.e.*, at a ratio of 19:1) the final settling time increased by ~90 %.

The evaluation of mixing time and speed was assessed only for the Gluepot soil. The results showed that increasing the mixing time significantly improved the initial settling rate of the flocs. Increasing the mixing speed from 500 to 750 r/min at each of the three mixing times improved the initial settling rate as well. However, when the mixing speed was increased further to 1000 r/min the initial settling rates generally reduced.

4.5.1 References

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Chapter 5: Settling rate studies on factory juice containing soils

5.1 INTRODUCTION

In this chapter, incubated factory juice (with the fibres and other insoluble solids removed) was used to assess to the addition of soil, gypsum, fibre and bagasse fly ash on the settling rate and turbidity of the juices. Ideally, these studies could be undertaken on real factory juices that have inherently poor flocculation properties. In practice, however it is very difficult to obtain such juices as the clarification performance is observed after the incoming juice has passed through the clarifier. The juice residence times in sugar mill clarifiers typically range between ~20 to 45 min for short retention time clarifiers such as the SRI NG clarifier mainly used in Australia. Also, during clarification the juice streams in pipes and the incubation tank are reasonably plug flow so any mixed juice expressed from a given rake will generally pass through the clarification process before its flocculation behaviour is known. As a consequence, factory juice collected randomly from Rocky Point Mill was used to explore the impact of fibre, gypsum and bagasse fly ash on the settling rate of flocs.

5.2 MATERIALS

Factory incubated juice and bagacillo were both sourced from Rocky Point Mill.

Laboratory grade gypsum in the form of calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was used in the tests.

The flocculant used at Rocky Point Mill was Sucrafloc 2522 supplied by TD Chemicals Pty Ltd (Gold Coast, Queensland, Australia). The molecular weight and degree of hydrolysis is 16×10^6 and 25 % respectively. The factory stock flocculant solution has a concentration of 0.26 wt%. On each day of the tests a sample of the factory stock flocculant solution was collected and diluted down to 0.052 wt% using distilled water.

5.3 EXPERIMENTAL

5.3.1 Centrifugation of juice

The incubated factory juice was centrifuged in a laboratory scale centrifuge to remove as much insoluble solids as possible. The juice was centrifuged at 3750 r/min for 10 min.

5.3.2 Sieving of juice

Approximately 10 L of Rocky Point Mill factory incubated juice was passed through a 212 μm sieve. The fibres retained on the sieve were squeezed by hand to remove as much of the juice as possible from the fibres. The squeezed fibres were then transferred from the sieve into a 150 μm filter sock and washed with tap water to remove as much of the non-fibrous components as possible. The filter sock was then squeezed by hand to help dewater the fibres.

Portions of this fibre (88.6 % moisture) was added back to the factory juice samples in which batch settling tests were performed to assess its effect on settling behaviour.

5.3.3 Batch settling tests

Batch settling tests were undertaken using standard settling tubes that are 60 mm in internal diameter and 460 mm in height (each tube has been calibrated 0-400 mm with a 400 mm settling depth and a volume of ~1000 mL) in a SRI designed heated illuminated batch settling test kit (SRI, 1999). Figure 5.1 shows the SRI batch settling kit that was used during the laboratory trials at Rocky Point Mill.

Soil and additives (*i.e.*, fibre, ash or gypsum) were added to the juice and stirred for 1 min. The juice was then heated using an immersion heater to raise its temperature to 76 °C. Milk of lime was then added drop wise to raise the pH of the juice from ~5.7 to the desired set point of 7.8.

The limed juice was then flashed by heating and maintaining its temperature at the boiling point for approximately 30 s. The flashed juice was then transferred to a beaker containing the flocculant solution and gently stirred using a spatula. The flocculated juice was then transferred to the 1000 mL glass batch settling tube in the heated cabinet (shown in Figure 5.1) and left standing for sedimentation to occur. The mud interface heights were recorded over a 30 min period. The height of glass cylinder

at the 1000 mL graduation (400 mm) was used to determine the initial settling rates over the first 0.5 to 1.0 min of sedimentation. The average error in the measurements is $\pm 1.25\%$.

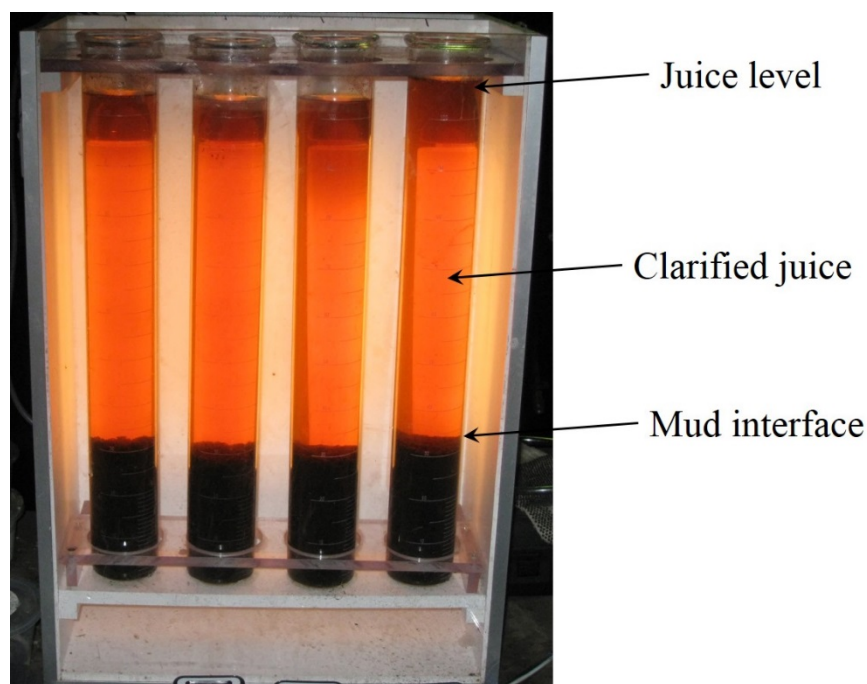


Figure 5.1 SRI batch settling test kit

5.4 RESULTS

5.4.1 Centrifuged juice with added soil

In these batch settling tests, 2.5 g of soil was added to 1000 mL of the centrifuged factory incubated juice. No fibre was added to the soil juice suspensions. The flocculant dosing rate in all tests was 0.52 ppm. To get a greater understanding of the settling behaviour of the flocs formed additional mud interface height measurements were made during the initial settling period, *i.e.*, at 15, 30, 45 and 60 s.

Figure 5.2 shows the settling profiles of the three soil suspensions. Table 5.1 summarises the batch settling test results. The results show very little differences in the settling speeds of the flocs produced from the three different soil types at the different settling time intervals. Also, there is very little difference in the final mud heights. This trend is different to the trends observed for the soil and electrolyte suspensions which consistently showed that the settling rates of the three soils were in the order (from highest to lowest) of Mt Mackay, Invicta 255B and Gluepot. It is not

clear why the same trend was not repeated when the soils were mixed in centrifuged incubated juices. A possible reason could be that the colloidal suspended matter was not removed during centrifugation. The colloidal matter remaining in the centrifuged juice may have had a dominating effect on the clarification properties of the juice.

The reason for the lack of difference in the settling behaviour of the soils mixed in factory juice is not known. It was decided to only use the Gluepot soil in the remaining tests.

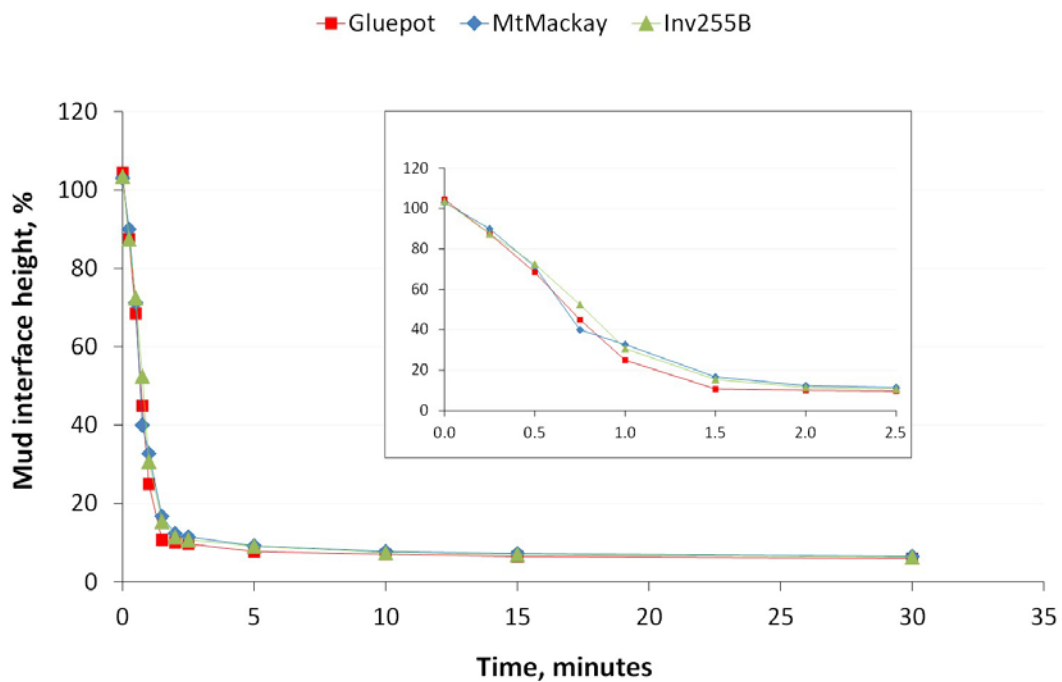


Figure 5.2 Settling data for the three soils flocculated in centrifuged factory incubated juice (inset graph shows first 2.5 minutes of settling)

Table 5.1 Batch settling test results for the three soils flocculated in centrifuged factory incubated juice

| Parameter | Test run | Soil name | | |
|--------------------------------|----------|-----------|-----------|--------------|
| | | Gluepot | Mt Mackay | Invicta 255B |
| Initial settling rate (cm/min) | 1 | 28.0 | 20.0 | 19.2 |
| | 2 | 29.6 | 30.8 | 30.4 |
| | Average | 28.8 | 25.4 | 24.8 |
| Final mud height (%) | 1 | 6.0 | 6.0 | 6.5 |
| | 2 | 6.0 | 7.0 | 6.3 |
| | Average | 6.0 | 6.5 | 6.4 |

5.4.2 Effect of fibre on floc settling speeds

In section 3.2.3.4, the proportion of organic matter was noted to be high with soil samples that are noted to be ‘bad’ or exhibit poor settling and clarification behaviour. On a macroscopic level, it is expected that the proportion of organic matter will influence floc structure and the floc density (Suetsugu *et al.*, 2006). On the basis of earlier results, it was decided to provide further evidence on the impact of organic matter by conducting batch settling tests in which fibre was added.

The effect of fibre on settling rate was tested in two ways. In the first case, soil and fibre solids were removed from the juice using a centrifuge and a fixed quantity of soil and various quantities of fibre added back to the juice. In the second case a sieve was used to remove only the fibre (and not the soil) from the juice.

5.4.2.1 Centrifuged factory juice

Table 5.2 shows the results in which various amounts of fibre were added to the centrifuged incubated juice containing 2.5 g/L of the Gluepot soil prior to clarification. In practice the fibre ratio in factory mixed juice streams are typically ~0.2 %. However, much higher fibre ratios were tested to understand the effect of fibre on the initial settling rate of the flocs.

The results show that as the amount of added fibre is increased the initial settling rate of the flocs decrease and final mud height increases. It is usual for slow settling flocs to also have higher final mud heights.

Table 5.2 The effect of fibre on settling speed of flocs produced from soil and centrifuged factory juice

| Fibre:soil ratio | | 0 | 0.5 | 1.0 | 1.5 | 2.0 |
|-------------------------|---------------------------------------|-----|-----|------|------|------|
| Gluepot | Initial settling rate (cm/min) | 75 | 74 | 54 | 48 | 47 |
| | Final mud height (%) | 4.9 | 7.6 | 10.0 | 13.3 | 16.5 |

5.4.2.2 Sieved factory juice to remove fibres only

In these tests 10 L of incubated factory juice (prior to liming) from Rocky Point Mill was collected and stored frozen at QUT. After thawing the juice was sieved through a 212 μm sieve to remove as much of the fibre component as possible. The separated fibres were then placed inside a 150 μm filter sock and washed using tap water to remove as much of the non-fibre components as possible. After washing, the fibres in the filter sock were squeezed by hand to remove as much of the water as possible. The washing were discharged to the drain. Approximately one tenth of the total washed and dewatered fibres were added back to the 1 L juice aliquots that were used in the tests which included fibre. A total of six batch settling tests were carried out using one litre aliquots of the factory incubated juice. In three of the tests fibre was not added and in the other three tests fibre was added which resulted in a fibre content of 0.28 w/v%.

Figure 5.3 shows the settling profile of the three juice samples with added fibre and the three juice samples without any added fibre. The juice samples without the added fibre settled more rapidly and the final mud heights were lower compared to the three juice samples with the added fibre.

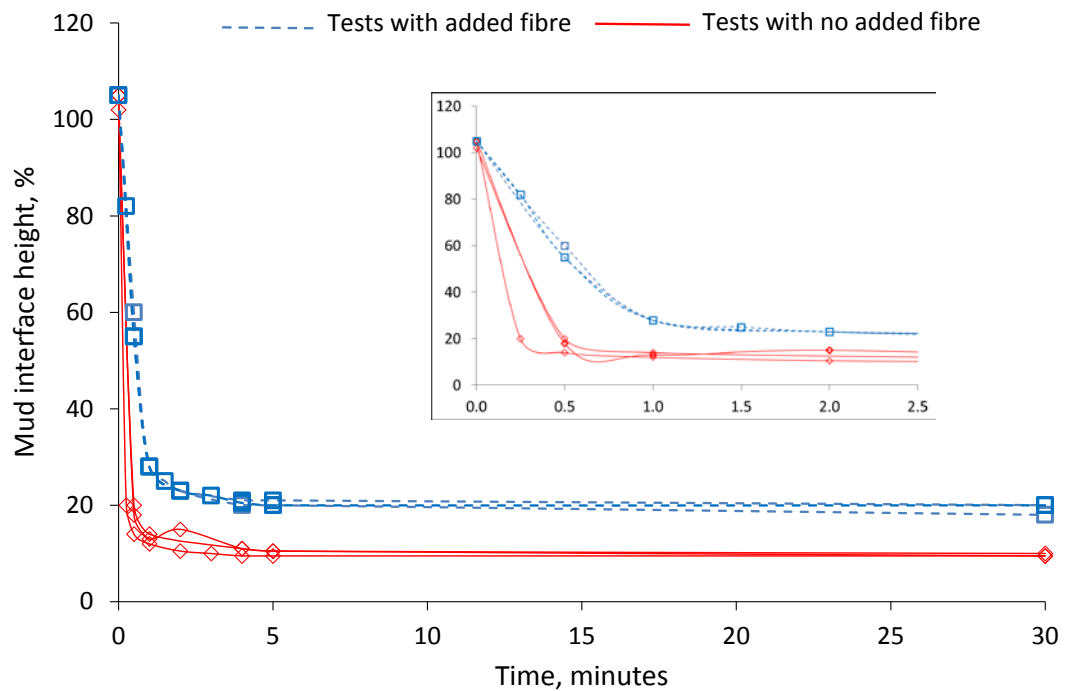


Figure 5.3 Settling profile of sieved factory incubated juice with and without added fibre (inset graph shows first 2.5 minutes of settling)

Table 5.3 summarises the batch clarification test results in terms of initial settling rate, turbidity and final mud heights. The results show that the average initial settling rates are ~69 cm/min and ~39 cm/min for the tests without and with fibre respectively. This shows that by removing fibres from the juice the initial settling rate increases by ~80 %. Only in four of the tests the supernatant turbidity was measured. The average turbidity for tests with fibre was lower at 37.3 compared to the tests without fibre at 46.3.

Table 5.3 Batch clarification test results with and without fibre

| Test # | Juice fibre content, (%) | Initial settling rate, cm/min | | Turbidity | | Final mud height, % | |
|--------|--------------------------|-------------------------------|------|-----------|------|---------------------|------|
| | | Value | Ave. | Value | Ave. | Value | Ave. |
| 1 | trace | 65.6 | 69.3 | - | 46.3 | 9.5 | 9.7 |
| 2 | trace | 69.6 | | 50.2 | | 10.0 | |
| 3 | trace | 72.8 | | 42.5 | | 9.5 | |
| 4 | ~0.28 | 36.0 | 38.7 | - | 37.3 | 18.0 | 19.3 |
| 5 | ~0.28 | 40.0 | | 30.5 | | 20.0 | |
| 6 | ~0.28 | 40.0 | | 44.1 | | 20.0 | |

A common trend in clarification performance is that when settling rates are lower the turbidity of the supernatant is generally lower as well. A possible explanation for this could be that with slower settling flocs there is more opportunities for colloidal particles to adhere to the surfaces of the flocs and hence remove more turbidity. The final mud height in the tests without fibre are ~50 % lower compared to the tests in which fibre was not removed.

The increase in settling rates with the removal of fibres is a significant result and has major implications to the throughput of clarifiers. The settling rate is one of the main variables used to determine the cross sectional area and hence the size of an industrial clarifier for a given juice feed flowrate (Rein, 2007). In practice the higher the long term average settling rate of the floc is the smaller the cross sectional area of a clarifier needs to be and vice versa. Higher settling rates are also desirable as it increases the portion of the incoming juice to be sent forward whilst minimising the portion of underflow produced thereby reducing the hydraulic load on the filter station. The latter also has the potential to reduce the mud cake pol loss and improve the retention of mud solids on the filter screen surfaces and therefore reduce the undesirable recirculation of mud solids back to the clarification station with the filtrate.

5.4.3 Effect of gypsum on floc settling speeds

In these tests various quantities of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was added to the centrifuged factory incubated juice containing 2.5 g/L of the soil. Three ratios of gypsum:soil was trialled, viz., 0:2.5, 0.5:1.0 and 1.0:1.0. No fibre was added in these tests. Factory flocculant (Sucrafloc 2522) was used at a rate of 0.52 ppm on juice volume.

Figure 5.4 shows the settling profile of the Gluepot flocs produced from various quantities of added gypsum. The tests were undertaken for the full 30 min but the chart only shows up to the first 2.5 min to show the slight variation in the profiles.

Table 5.4 summarises the settling test results for the Gluepot flocs at the various gypsum:soil ratios. The results show there is a slight increase when 1.25 g of gypsum is added but then there is a relatively large drop when a 2.5 g of gypsum was added. There is a slight increase in the final mud height. Typically, as settling rate increases the mud height decreases but in these tests the final mud height increased with increasing settling rate except when 2.5 g of gypsum was added.

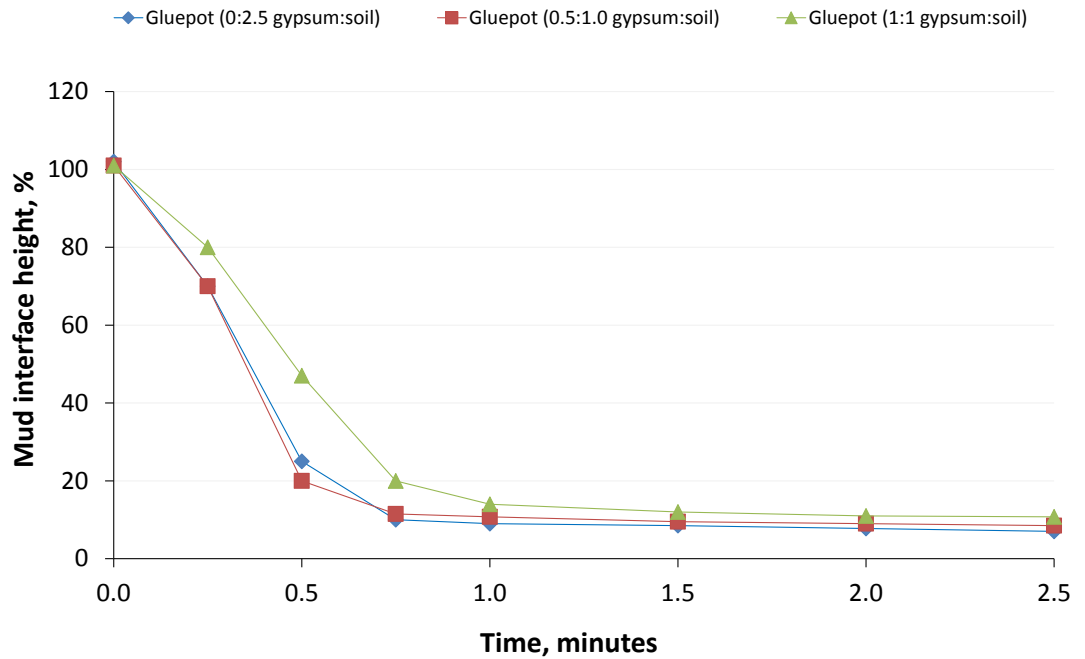


Figure 5.4 Settling profile of Gluepot flocs clarified with various quantities of gypsum in centrifuged factory incubated juice

Table 5.4 Summary of settling test results with added gypsum

| Soil | Gluepot | | |
|-------------------------------|---------|---------|---------|
| | 0.00 | 1.25 | 2.00 |
| Gypsum (g) | 0.00 | 1.25 | 2.00 |
| Gypsum:soil ratio | 0:2.5 | 0.5:1.0 | 1.0:1.0 |
| Initial settling rate, cm/min | 61.6 | 64.8 | 43.2 |
| Final mud height (%) | 5.6 | 6.7 | 7.9 |

5.5 CONCLUSION AND DISCUSSION

The method of comparing the settling behaviour of flocs produced from flocculating the soils in centrifuged factory incubated juices did not prove to be successful. All three soils behaved similarly in contrast to the results achieved in the previous sections where all three soils behaved differently with Gluepot consistently being slowest settling soil and Mt MacKay being the fastest settling soil. It was not possible to come up with a new method that could be used to compare the settling behaviour of the soils in factory juice. The lack of any significant differences between the soil settling rates indicate that the composition of the soils do not affect the

flocculation mechanisms. It is possible that the colloidal particles that remain in the factory incubated juices after centrifugation dominated the flocculation mechanisms.

Tests with and without fibre showed that the flocs which did not contain fibre settled at up to 100 % faster and produce half the volume of mud. This is a significant result as it means that the capacity of an existing clarifier can potentially be doubled if the fibres are removed from the mixed juice at the rotary juice screens. In addition it provides the option for factories to reduce the amount of fibre in the mixed juice prior to clarification when there is an indication that the incoming cane is from an area/farm containing bad soil. The main reason for allowing fibre to enter the mixed juice stream via the perforations in the rotary juice screens is because they are used as a filter aid during mud filtration at the filter station. However there are alternative processes that can collect and deliver the fibres directly to the filter station without it passing through with the juice.

The addition of gypsum produced slight increases in settling rate but these were not significant.

5.5.1 References

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Chapter 6: Summary and conclusions

6.1 KEY FINDINGS AND CONCLUSIONS

6.1.1 Studies on the Physico-Chemical Properties of Soils

In chapter 3 the composition and the physico-chemical properties of the Mt Mackay, Gluepot and Invicta 255B soils were determined using a number of analytical tools. The results supports the anecdotal evidence that Mt Mackay is a ‘good’ soil exhibiting good settling and clarification properties and Gluepot is a ‘bad’ soil exhibiting poor settling and clarification properties. Gluepot had the lowest true particle density, the highest proportion of fine particles (*i.e.*, <1 µm size range), lowest proportion of particles in the >100 µm size range, highest clay fraction and highest organic fraction for both the hydrogen peroxide and loss on ignition methods. Furthermore, the Si:Al ratio for the Gluepot and Invicta 255B soils indicate a mixture of the 1:1 and 2:1 mineral types. The 2:1 mineral is of the montmorillonite type, a known expandable clay. Expandable clays have the ability to absorb more water which reduces its bulk density and hence their settling rates.

Mt Mackay on the other hand had the lowest proportion of fine particles in the <1 µm size range, highest proportion of particles in the >100 µm size range and lowest proportion of clay fraction and lowest proportion of carbonates based on the loss on ignition method (*i.e.*, at 950 °C). The true particle density of Mt Mackay soil was similar to Invicta 255B and both were higher than Gluepot. The organic fraction in both the peroxide and loss on ignition method were lowest for the Invicta 255B soil.

TOF-SIMS analyses showed large differences between the wet and dry soil samples. The largest change between the surface chemistry of the dry and the wet soils appeared to be the dominance of NH₄ and relatively higher proportion of hydrocarbon species in the wet samples. The NH₄ specie is likely to be associated with proteins/amino acids. The wet samples contain a higher proportion of total organics than the dry samples.

The inorganic elemental species responses were intense, and so are expected to play an appreciable role on the surface chemistry of the soils. The wet samples contain higher proportions of Na ions. Here, the adsorbed cations on the surface of the

particles exchange with Na ions in the aqueous environment, thereby increasing the proportion of Na ions on particle surfaces. Sodium ions are effective in particle stabilisation, and hence will not encourage coagulation/flocculation. The results from the TOF-SIMS study also showed that the relative proportions of these ions are far less in the good soils compared with the bad soils. For example, the proportion of Na ions in Gluepot 3552A (the bad soil) is 4 times that of Mt Mackay.

In summarising the findings soils that are likely to impact on poor coagulation/flocculation processes and those that have slow settling floc characteristics are likely to have the following features:

- Contain a lower portion of particles that have higher densities.
- Contain a higher portion of organic material.
- Higher amorphous content. These are non-diffracting and hence in the nano-scale range.
- Higher specific surface area.
- Contain Si:Al ratio of 2:1 typical of montmorillonite type composition.
- Higher cation exchange capacity.
- Higher ζ .

6.1.2 Understanding flocculation properties of soil impurities present in the factory sugarcane supply

Further analysis of the soils were undertaken in chapter 3. High proportions of fine particles (*i.e.*, < 200 nm) were found in soil samples that are difficult to settle. These particles were classified as amorphous by XRD analysis because no diffraction patterns could be obtained and broadening of clay mineral peaks showed high imperfection in their internal structure and high particle dispersion. Electron microscopy confirmed the presence of this highly dispersed phase, and the electron diffraction patterns from films of these particles indicated the crystalline nature of these nano-clays. Erosion of clay particles as observed in TEM micrographs and especially the expandable smectite-like minerals were probably the best candidates for the origin of the nano-clays.

Significant differences in the electrochemical properties of the soils were identified and there was poor dependence between ζ values and electrolyte

concentration in mono-valent salt solutions for the difficult to clarify soils. Structure building phenomenon (as shown by TXM) by the nano-clay particles may be responsible for the problems with poor juice clarification by hindering floc aggregates from settling, despite changing environmental chemistry. Further study of nano-clay building structure properties are needed to find the most efficient way of treating such suspensions in sugar juice.

6.1.3 Studies on synthetic juices with added flocculant

Batch settling tests using soil electrolyte suspensions showed that flocs produced from Gluepot soils consistently performed poorly compared to flocs produced from Mt MacKay soils regardless of the type and dosing rate of the flocculant used. This provides further evidence of the anecdotal evidence that Gluepot soils have inherently poor flocculation properties.

The addition of pre-flocculated bagasse fly ash improved the settling rate of all three soils. However the improvements were only significant for the Gluepot and Invicta 255B soils. At the minimum ash addition rate, *i.e.*, a soil to ash ratio of 3:1 the final settling times of the flocs were 63 % and 47 % lower for the Gluepot and Invicta 255B soils when compared to no added ash. The benefits of pre-flocculated ash for the Mt Mackay soil was only significant when the soil to ash ratio was greater than 1:1. However adding insoluble solids such as ash will eventually end up in the mud streams thereby increasing the amount of mud cake produced and potentially pol losses at the filter station. It will be important therefore to evaluate the benefits of added ash not only in terms of improving the settling rate of the flocs but also in terms of mud filtration efficiencies as well.

The addition of gypsum to a mixture of soil and pre-flocculated ash slightly reduced the final settling times for Mt Mackay and Invicta 255B flocs. For Gluepot on the other hand when a small portion of gypsum is added (*i.e.*, at a ratio of 19:1) the final settling time increased by ~90 %.

The evaluation of mixing time and speed was assessed only for the Gluepot soil. The results showed that increasing the mixing time significantly improved the initial settling rate of the flocs. Increasing the mixing speed from 500 to 750 r/min at each of the three mixing times improved the initial settling rate as well. However, when the

mixing speed was increased further to 1000 r/min the initial settling rates generally reduced.

6.1.4 Studies on factory juice

A very important finding in the present study was the significant effect of fibre on floc settling rate. Juices that did not contain fibres produced flocs that settle up to 100 % faster and produce half the volume of mud compared to juice containing fibre. This is a significant result as it means that the capacity of an existing clarifier can potentially be doubled if the fibres are removed from the mixed juice at the rotary juice screens. In addition it provides the option for factories to reduce the amount of fibre in the mixed juice prior to clarification when there is an indication that the incoming cane is from an area/farm containing bad soil. The main reason for allowing fibre to enter the mixed juice stream via the perforations in the rotary juice screens is because they are used as a filter aid during mud filtration at the filter station. However there are alternative processes that can collect and deliver the fibres directly to the filter station without it passing through with the juice.

The method of comparing the settling behaviour of flocs produced from flocculating the soils in centrifuged factory incubated juices did not prove to be successful. All three soils behaved similarly in contrast to the results achieved in the previous sections where all three soils behaved differently with Gluepot consistently being slowest settling soil and Mt MacKay being the fastest settling soil.

The addition of gypsum produced slight increases in settling rate of the Gluepot flocs but these were not significant.

6.2 FUTURE WORK

One of the important findings in this study was that the settling behaviour of the flocs did not change significantly when a 'bad' soil such as Gluepot for example was added to centrifuged factory juice. As a consequence most of the work was carried out using synthetic based solutions. Although a number of techniques that have the potential to improve the settling rate of flocs in sugarcane juice clarification have been identified, a detailed assessment of the three soils in factory juices was not able to be made. The removal of insoluble solids from factory juice and then adding back the soils did not prove to be successful. One possible solution to overcome this would be for factory staff to collect factory juice samples when cane supplies from the relevant

regions are crushed. This would require the collected juice to be frozen and delivered to the researcher. To factor in the effect of freezing on settling behaviour a series of preliminary tests would need to be undertaken between samples of the same bulk juice being tested before and after freezing.

The current practice of holding rakes of cane from regions that are known to have 'bad' soils aside and blend them in with rakes of cane received regions that do not have clarification issues is labour intensive and not very practical. A potentially applicable and practical solution to overcoming the effects of processing juices extracted from regions that have 'bad' soils is to measure the ζ and hence assess the coagulation-flocculation properties of the mixed juice before it reaches the clarifier. This system would also require the installation a second mixed juice tank that could temporarily hold juices that are deemed to have poor clarification properties. As new rakes of cane are processed and juices with more desirable clarification properties are received the juice with poor clarification properties can be slowly mixed with the incoming juice. Using ζ measurements as an indicator for assessing the clarification properties of raw water is currently used as a guide in some water treatment processes to determine the dosage rates of clarification aids such as coagulants and flocculants. Future work should include the use of ζ measurements for determining the clarification properties of the incoming juices and take appropriate action.

One of the key limitations in studies such as this one is the lack of suitable technologies that can help analyse the internal structure of flocs without the removal of the flocs from suspension. Flocs are inherently very fragile which makes it very challenging to remove from suspension and study their structure without significantly changing its original structure. Due to these limitations researchers tend to focus on settling rate of the flocs as an indication of its bulk density which is an important variable affecting settling rate. Several light scattering techniques have been used by various researchers but many focus on the entire settling phase rather than individual flocs. Ideally individual flocs can be removed from solution, its settling rate measured individually and its structure analysed. One possible solution to achieve this would be to use a gelling agent to set flocs in a fixed position and hence allow it to be analysed in various microscopy devices. This approach would allow a more positive link to be made between various clarification conditions and the structure of the floc.

There are many variables other than the ones tested in this present study that are likely to have an effect on the settling behaviour of the soils. Some examples of other variables which could be assessed include:

- Addition of coagulants other than milk of lime/lime saccharate,
- Further shearing tests that also include fast and slow mixing speeds and mixing times during the coagulation and flocculation phases,
- The use of branched flocculants,
- The addition of flocculant in two-stages. This will involve the following steps: (a) add flocculant, (b) shear, (c) add flocculant to reform flocs

Appendices

Appendix A

Raw data for tests carried out for Chapter 3

Table A. 1 Soil moisture results

| Parameter | Mt Mackay | Invicta 255B | Gluepot 3522A |
|------------------------------|------------------|---------------------|----------------------|
| Petri dish weight, g | 19.6301 | 18.2574 | 19.5554 |
| Sample weight, g | 5.0014 | 5.0066 | 5.0114 |
| Total weight, g | 24.6315 | 23.264 | 24.5668 |
| Total weight (dried), g | 24.1093 | 23.129 | 24.1712 |
| Weight of water, g | 0.5222 | 0.135 | 0.3956 |
| Moisture content, wt% | 10.4411 | 2.6964 | 7.8940 |

Table A. 2 Pycnometer raw data – input parameters (Mt Mackay soil)

| | |
|-------------------|-------------------------|
| Analysis gas: | Helium |
| Reported | 13/05/2014 2:29:25PM |
| Sample mass: | 5.4588 g |
| Temperature: | 18.96 °C |
| Number of purges: | 10 |
| Analysis start: | 13/05/2014 11:33:50AM |
| Analysis end: | 13/05/2014 11:47:52AM |
| Equilibrium rate: | 0.010 psig/min |
| Expansion volume: | 74.1990 cm ³ |
| Cell volume: | 15.7720 cm ³ |

Table A. 3 Pycnometer raw data – input parameters (Gluepot 3522A soil)

| | |
|-------------------|-------------------------|
| Analysis gas: | Helium |
| Reported | 13/05/2014 2:29:26PM |
| Sample mass: | 6.0688 g |
| Temperature: | 18.52 °C |
| Number of purges: | 10 |
| Analysis start: | 13/05/2014 10:44:44AM |
| Analysis end: | 13/05/2014 10:59:11AM |
| Equilibrium rate: | 0.010 psig/min |
| Expansion volume: | 74.1990 cm ³ |
| Cell volume: | 15.7720 cm ³ |

Table A. 4 Pycnometer raw data – true particle density measurement for Mt Mackay soil

| Cycle# | Volume, cm ³ | Volume Deviation, cm ³ | Pressure (P1), psig | Pressure (P2), psig | Elapsed, mm:ss | Temperature, °C | Total Pore Volume, cm ³ | Total Solids Concentration, wt% | Density, g/cm ³ | Density deviation, g/cm ³ |
|---------------------------------|-------------------------|-----------------------------------|---------------------|---------------------|----------------|-----------------|------------------------------------|---------------------------------|----------------------------|--------------------------------------|
| 1 | 2.18 | -0.0003 | 20.234 | 3.133 | 4:27 | 18.91 | 0.6014 | 63.3 | 2.5086 | 0.0004 |
| 2 | 2.1742 | -0.0022 | 20.165 | 3.123 | 5:32 | 18.96 | 0.6017 | 63.34 | 2.5107 | 0.0025 |
| 3 | 2.1759 | -0.0005 | 20.362 | 3.153 | 6:33 | 18.97 | 0.6014 | 63.31 | 2.5088 | 0.0006 |
| 4 | 2.1791 | 0.0027 | 20.263 | 3.137 | 7:35 | 18.94 | 0.6008 | 63.24 | 2.5051 | -0.0031 |
| 5 | 2.1805 | 0.0041 | 20.417 | 3.161 | 8:34 | 18.99 | 0.6006 | 63.22 | 2.5035 | -0.0047 |
| 6 | 2.1744 | -0.0019 | 20.429 | 3.164 | 9:35 | 18.94 | 0.6017 | 63.33 | 2.5105 | 0.0022 |
| 7 | 2.1766 | 0.0002 | 20.17 | 3.123 | 10:40 | 18.95 | 0.6013 | 63.29 | 2.508 | -0.0003 |
| 8 | 2.1745 | -0.0019 | 20.326 | 3.148 | 11:40 | 18.97 | 0.6017 | 63.33 | 2.5104 | 0.0022 |
| 9 | 2.1782 | 0.0018 | 20.247 | 3.135 | 12:40 | 19 | 0.601 | 63.26 | 2.5061 | -0.0021 |
| 10 | 2.1743 | -0.002 | 20.235 | 3.134 | 13:40 | 19 | 0.6017 | 63.34 | 2.5106 | 0.0024 |
| Average | 2.1764 | | 20.285 | 3.141 | | | 0.6013 | 63.30 | 2.5082 | |
| Standard Deviation | 0.00211 | | 0.08968 | 0.01391 | | | 0.00038 | 0.04079 | 0.00242 | |
| Coefficient of Variation | 0.001 | | 0.004 | 0.004 | | | 0.001 | 0.001 | 0.001 | |

Table A. 5 Pycnometer raw data – true particle density measurement for Gluepot 3522A soil

| Cycle# | Volume, cm ³ | Volume Deviation, cm ³ | Pressure (P1), psig | Pressure (P2), psig | Elapsed, mm:ss | Temperature, °C | Total Pore Volume, cm ³ | Total Solids Concentration, wt% | Density, g/cm ³ | Density deviation, g/cm ³ |
|---------------------------------|-------------------------|-----------------------------------|---------------------|---------------------|----------------|-----------------|------------------------------------|---------------------------------|----------------------------|--------------------------------------|
| 1 | 2.612 | 0.0008 | 20.366 | 3.068 | 4:28 | 18.5 | 0.5696 | 59.96 | 2.3234 | -0.0007 |
| 2 | 2.6146 | 0.0034 | 20.279 | 3.054 | 5:30 | 18.51 | 0.5692 | 59.91 | 2.3211 | -0.003 |
| 3 | 2.6137 | 0.0025 | 20.229 | 3.047 | 6:32 | 18.53 | 0.5693 | 59.93 | 2.3219 | -0.0022 |
| 4 | 2.6074 | -0.0038 | 20.426 | 3.078 | 7:39 | 18.5 | 0.5704 | 60.04 | 2.3276 | 0.0034 |
| 5 | 2.6092 | -0.002 | 20.268 | 3.054 | 8:46 | 18.52 | 0.5701 | 60.01 | 2.3259 | 0.0018 |
| 6 | 2.6101 | -0.0011 | 20.46 | 3.083 | 9:52 | 18.52 | 0.5699 | 59.99 | 2.3251 | 0.001 |
| 7 | 2.6101 | -0.0011 | 20.327 | 3.062 | 10:56 | 18.53 | 0.5699 | 59.99 | 2.3251 | 0.001 |
| 8 | 2.6145 | 0.0033 | 20.459 | 3.082 | 11:59 | 18.53 | 0.5692 | 59.92 | 2.3212 | -0.0029 |
| 9 | 2.6118 | 0.0006 | 20.407 | 3.074 | 13:03 | 18.53 | 0.5696 | 59.96 | 2.3236 | -0.0006 |
| 10 | 2.6087 | -0.0025 | 20.308 | 3.06 | 14:03 | 18.55 | 0.5702 | 60.02 | 2.3264 | 0.0023 |
| Average | 2.6112 | | 20.353 | 3.066 | | | 0.5697 | 59.97 | 2.3241 | |
| Standard Deviation | 0.00238 | | 0.07866 | 0.01207 | | | 0.00041 | 0.04196 | 0.00214 | |
| Coefficient of Variation | 0.001 | | 0.004 | 0.004 | | | 0.001 | 0.001 | 0.001 | |

Table A. 6 Mastersizer size Particle size

| Parameter | Mt Mackay | Gluepot 3522A | Invicta 255B |
|---|------------------|----------------------|---------------------|
| Operator Name | choua | choua | choua |
| SOP File Name | HydroLV.cfg | HydroLV.cfg | HydroLV.cfg |
| Measurement Date Time | 9/05/2014 13:41 | 9/05/2014 13:24 | 9/05/2014 10:36 |
| Analysis Date Time | 9/05/2014 13:41 | 9/05/2014 13:24 | 9/05/2014 10:36 |
| Result Source | Averaged | Averaged | Averaged |
| Particle Name | Soil | Soil | Soil |
| Dispersant Name | Water | Water | Water |
| Particle Absorption Index | 0.1 | 0.1 | 0.1 |
| Weighted Residual, % | 2.10 | 2.51 | 2.35 |
| Analysis Model | General Purpose | General Purpose | General Purpose |
| Particle Refractive Index | 1.4 | 1.4 | 1.4 |
| Dispersant Refractive Index | 1.33 | 1.33 | 1.33 |
| Laser Obscuration, % | 8.65 | 9.16 | 9.14 |
| Scattering Model | Mie | Mie | Mie |
| Analysis Sensitivity | Normal | Normal | Normal |
| Concentration, % | 0.01 | 0.00 | 0.01 |
| Uniformity | 2.896 | 12.643 | 12.858 |
| Specific Surface Area, m ² /kg | 2221 | 2645 | 2293 |
| D [3,2], µm | 2.70 | 2.27 | 2.62 |
| D [4,3], µm | 20.6 | 54.7 | 106 |
| Span | 10.207 | 12.746 | 39.785 |
| Dx (10), µm | 0.875 | 0.819 | 0.840 |
| Dx (50), µm | 6.30 | 4.19 | 8.04 |
| Dx (90), µm | 65.2 | 54.3 | 321 |

Table A. 7 Particle size distribution data for the three soils

| Size Classes, µm | Volume Density, % | | |
|-------------------------------|--------------------------|----------------------|---------------------|
| | Mt Mackay | Gluepot 3522A | Invicta 255B |
| 0.010659095 to 0.334671486 | 0 | 0 | 0 |
| 0.380241393 | 0.000115514 | 0.000151773 | 3.73E-05 |
| 0.43201624 | 0.015403151 | 0.019871971 | 0.020952413 |
| 0.490840911 | 0.232229347 | 0.294033144 | 0.311871935 |
| 0.557675331 | 1.114227796 | 1.371022251 | 1.309981223 |
| 0.633610133 | 2.45344697 | 3.007690187 | 2.774599744 |
| 0.719884454 | 3.695678245 | 4.549560703 | 4.129379767 |
| 0.817906153 | 4.355310066 | 5.415772141 | 4.869154034 |
| 0.929274791 | 4.266497771 | 5.394898916 | 4.819346928 |
| 1.055807727 | 3.636186146 | 4.712065738 | 4.186127147 |
| 1.199569781 | 2.887869342 | 3.851952435 | 3.398116486 |
| 1.362906921 | 2.400769703 | 3.256950698 | 2.840870829 |
| 1.548484553 | 2.315438718 | 3.097480027 | 2.657760545 |
| 1.759331011 | 2.531460781 | 3.26244923 | 2.745705524 |
| 1.998886977 | 2.852684514 | 3.523873887 | 2.903729711 |
| 2.271061625 | 3.120286112 | 3.694240654 | 2.973129609 |

| | | | |
|-------------|-------------|-------------|-------------|
| 2.580296417 | 3.264433332 | 3.692464022 | 2.89369633 |
| 2.931637577 | 3.303540877 | 3.545862102 | 2.7002149 |
| 3.330818439 | 3.285475792 | 3.322279766 | 2.457869377 |
| 3.784353005 | 3.242648194 | 3.076754926 | 2.215149143 |
| 4.299642243 | 3.194439398 | 2.84956132 | 2.005475529 |
| 4.885094862 | 3.15436563 | 2.668942292 | 1.85236572 |
| 5.550264524 | 3.124680081 | 2.542964169 | 1.762976436 |
| 6.30600575 | 3.099336808 | 2.464090933 | 1.727575895 |
| 7.164651044 | 3.069401853 | 2.416888564 | 1.723508808 |
| 8.140212144 | 3.02730918 | 2.386147458 | 1.726120959 |
| 9.248608668 | 2.97088346 | 2.364463657 | 1.718634468 |
| 10.5079279 | 2.903663579 | 2.353498305 | 1.697302986 |
| 11.93871994 | 2.831026232 | 2.359006886 | 1.667891465 |
| 13.56433306 | 2.755209754 | 2.382991959 | 1.636645633 |
| 15.41129471 | 2.67638031 | 2.422740919 | 1.607297932 |
| 17.50974438 | 2.594527733 | 2.470589727 | 1.580843946 |
| 19.89392546 | 2.511761782 | 2.514913265 | 1.5565046 |
| 22.60274403 | 2.433771054 | 2.541963261 | 1.532639584 |
| 25.68040374 | 2.369046748 | 2.537482966 | 1.507738242 |
| 29.17712713 | 2.327721623 | 2.490093686 | 1.481972495 |
| 33.14997522 | 2.318035177 | 2.393218045 | 1.456997168 |
| 37.66377863 | 2.341503869 | 2.245587212 | 1.43545621 |
| 42.7921955 | 2.38963697 | 2.051344024 | 1.421251933 |
| 48.61891352 | 2.443691214 | 1.820059241 | 1.419379948 |
| 55.23901552 | 2.477536472 | 1.566497089 | 1.434309699 |
| 62.76053114 | 2.464218267 | 1.310505174 | 1.46880218 |
| 71.30619965 | 2.383228678 | 1.075347477 | 1.524335002 |
| 81.01547288 | 2.224792848 | 0.882684847 | 1.601452711 |
| 92.04679085 | 1.990207251 | 0.744328292 | 1.697316663 |
| 104.5801673 | 1.687401511 | 0.652917574 | 1.79976995 |
| 118.8201271 | 1.32557249 | 0.578211075 | 1.88368111 |
| 134.999044 | 0.938785946 | 0.50329226 | 1.939113749 |
| 153.3809324 | 0.577088282 | 0.425321362 | 1.967622032 |
| 174.2657557 | 0.284781744 | 0.347988791 | 1.972190468 |
| 197.9943213 | 0.077776687 | 0.275959533 | 1.953244096 |
| 224.953842 | 0.006438293 | 0.213585435 | 1.910080811 |
| 255.5842545 | 9.95E-05 | 0.164953113 | 1.844210714 |
| 290.3853991 | 0 | 0.1327337 | 1.760740278 |
| 329.9251753 | 0 | 0.116413718 | 1.665729382 |
| 374.8488101 | 0 | 0.113301065 | 1.562829844 |
| 425.8893863 | 0 | 0.120226565 | 1.451648756 |
| 483.8798056 | 0 | 0.134272218 | 1.329595224 |
| 549.7663801 | 0 | 0.153277422 | 1.195295519 |
| 624.624275 | 0 | 0.175855681 | 1.050522044 |
| 709.6750529 | 0 | 0.201080608 | 0.900127042 |
| 806.3066084 | 0 | 0.227874312 | 0.751413913 |
| 916.0958161 | 0 | 0.254392301 | 0.612742213 |
| 1040.834263 | 0 | 0.277391229 | 0.490605223 |

| | | | |
|-------------|----------|-------------|-------------|
| 1182.557483 | 0 | 0.293212405 | 0.387754386 |
| 1343.578176 | 0 | 0.299529847 | 0.304490147 |
| 1526.523947 | 0 | 0.295163764 | 0.237452979 |
| 1734.38018 | 0 | 0.279696753 | 0.176745511 |
| 1970.538763 | 0 | 0.253455167 | 0.140380476 |
| 2238.85343 | 0 | 0.217093478 | 0.106970341 |
| 2543.702655 | 0 | 0.171409311 | 0.060606376 |
| 2890.061095 | 0 | 0.111743827 | 0.036010495 |
| 3283.580774 | 1.42E-14 | 0.012140719 | 0.003882639 |

Table A. 8 Clay fraction results

| Parameter | Mt Mackay | | Invicta 255B | | Gluepot 3522A | |
|--|-------------|--------|--------------|--------|---------------|--------|
| Sample weight (dried), g | 2.4883 | | 2.8998 | | 2.6377 | |
| Run number | 1 | 2 | 1 | 2 | 1 | 2 |
| Settling time, min | 6 | 23 | 6 | 23 | 6 | 23 |
| Settled distance, mm | 79.2 | 303.6 | 79.2 | 303.6 | 79.2 | 303.6 |
| Available suspension volume containing clay fraction, mL | 223.9 | 858.4 | 223.9 | 858.4 | 223.9 | 858.4 |
| Clay weight (weighed), g | 0.0012 | 0.0022 | 0.00225 | 0.0035 | 0.0025 | 0.0032 |
| Clay content in 1000 mL solution, g | 0.12 | 0.22 | 0.225 | 0.35 | 0.25 | 0.32 |
| Clay content in soil sample, wt% | 4.82 | 8.84 | 7.76 | 12.07 | 9.48 | 12.13 |
| Average clay content, wt% | 6.83 | | 9.91 | | 10.80 | |

Table A. 9 Organic fraction results

| Sample name | Mt Mackay | Invicta 255B | Gluepot 3522A |
|---|-------------|--------------|---------------|
| Weight of cold empty (250 ml) beaker, g | 102.7962 | 117.8624 | 117.4836 |
| Sample weight (dried), g | 2.012 | 2.0045 | 2.0109 |
| Total weight (sample+beaker), g | 104.8082 | 119.8669 | 119.4945 |
| Total weight after drying (cold), g | 104.7954 | 119.8636 | 119.4466 |
| Weight of organics, g | 0.0128 | 0.0033 | 0.0479 |
| Organic fraction, wt% | 0.64 | 0.16 | 2.38 |

Table A. 10 Loss on ignition results

| Parameter | Mt Mackay | Invicta 255B | Gluepot 3522A |
|-----------------------------|-----------|--------------|---------------|
| Crucible, g | 22.6276 | 21.0440 | 20.2918 |
| Soil (wet), g | 2.9431 | 2.9497 | 2.9914 |
| Total weight, g | 25.5707 | 23.9937 | 23.2832 |
| Crucible + soil (105 °C), g | 25.5135 | 23.9162 | 23.0741 |
| Soil (105 °C), g | 2.8859 | 2.8722 | 2.7823 |

| | | | |
|------------------------------------|-------------|-------------|--------------|
| Furnace at 550 °C for 2 hrs | | | |
| Crucible + soil (550 °C), g | 25.2820 | 23.7902 | 22.7144 |
| Soil (550 °C), g | 2.6544 | 2.7462 | 2.4226 |
| Difference in weight, g | 0.2315 | 0.1260 | 0.3597 |
| Organic fraction, wt% | 8.02 | 4.39 | 12.93 |
| Furnace at 950 °C for 2 hrs | | | |
| Crucible + soil (950 °C), g | 25.2697 | 23.7741 | 22.6912 |
| Soil (950 °C), g | 2.6421 | 2.7301 | 2.3994 |
| Difference in weight, g | 0.0123 | 0.0161 | 0.0232 |
| Organic carbonate, wt% | 0.43 | 0.56 | 0.83 |
| Total Loss On Ignition, g | 0.2438 | 0.1421 | 0.3829 |
| Total organic C, wt% | 8.45 | 4.95 | 13.76 |

Table A. 11 Cation exchange capacity data

| Parameter | LOR | Mt Mackay | Invicta 255B | Gluepot |
|------------------------------------|-----|-----------|--------------|---------|
| Exchangeable Calcium, meq/100g | 0.1 | 0.6 | 8.1 | 15 |
| Exchangeable Magnesium, meq/100g | 0.1 | 0.3 | 3.6 | 10.6 |
| Exchangeable Potassium, meq/100g | 0.1 | 0.1 | 1 | 0.5 |
| Exchangeable Sodium, meq/100g | 0.1 | 0.1 | 0.1 | 0.2 |
| Cation Exchange Capacity, meq/100g | 0.1 | 1.1 | 12.8 | 26.3 |

Table A. 12 Specific surface area results

| Parameter | Mt Mackay | Invicta 255B | Gluepot |
|--|-------------|--------------|-------------|
| Diameter, cm | 0.000025 | 0.000008 | 0.0000055 |
| Radius, cm | 0.0000125 | 0.000004 | 0.00000275 |
| Area, cm ² | 4.90625E-10 | 5.024E-11 | 2.37463E-11 |
| Volume, cm ³ | 1.22656E-15 | 4.0192E-17 | 1.30604E-17 |
| Mass, g | 3.25039E-15 | 1.06509E-16 | 3.46102E-17 |
| Surface area, cm ² | 1.1775E-09 | 1.20576E-10 | 5.6991E-11 |
| Number of particles in cm ² | 8.15287E+14 | 2.48806E+16 | 7.65671E+16 |
| Specific surface area, m ² /g | 36.22641509 | 113.2075472 | 164.6655232 |

Table A. 13 TOF-SIMS data – PCA loadings

| Number | Chemical species | PC1 | |
|--------|------------------|-----------|-----------|
| | | Gluepot | Mt Mackay |
| 12 | C | 0.000876 | -0.001376 |
| 13 | CH | 0.000576 | -0.001150 |
| 14 | CH2 | 0.000642 | -0.000815 |
| 15 | CH3 | -0.001182 | 0.002412 |
| 18 | NH4 | -0.014172 | 0.027521 |
| 19 | H3O | -0.000383 | 0.001410 |
| 26 | C2H2 | 0.000946 | -0.000573 |
| 28 | C2H4 | 0.002655 | -0.009729 |
| 29 | CHO | -0.000622 | 0.001560 |
| 29 | CH3N | 0.003905 | -0.004437 |
| 29 | C2H5 | -0.001162 | 0.006024 |
| 30 | CH2O | 0.000829 | -0.000343 |
| 30 | CH4N | 0.000996 | 0.004801 |
| 30 | C2H6 | 0.000503 | -0.001631 |
| 31 | CH3O | -0.002181 | 0.005272 |
| 31 | CH5N | 0.000081 | -0.000227 |
| 32 | CH4O | -0.000018 | 0.000060 |
| 37 | C3H | 0.000054 | -0.000169 |
| 38 | C3H2 | -0.000046 | -0.000266 |
| 39 | C3H3 | -0.001754 | -0.011060 |
| 40 | C3H4 | 0.000885 | 0.000041 |
| 41 | C3H5 | -0.010389 | 0.014218 |
| 42 | C2H2O | -0.000338 | 0.000796 |
| 42 | C2H4N | -0.001791 | 0.001740 |
| 42 | C3H6 | -0.001229 | 0.001511 |
| 43 | C2H3O | -0.002739 | 0.004734 |
| 43 | C2H5N | 0.000750 | -0.000785 |
| 43 | C3H7 | -0.008853 | 0.014274 |
| 44 | C2H4O | 0.001708 | -0.000574 |
| 44 | C2H6N | -0.001150 | 0.002389 |
| 44 | C3H8 | 0.000037 | -0.000830 |
| 45 | C2H5O | 0.000166 | 0.000935 |
| 45 | C2H7N | 0.000146 | -0.000463 |
| 46 | C2H6O | -0.000004 | -0.000077 |
| 47 | CH3O2 | 0.000036 | 0.000142 |
| 50 | C4H2 | -0.000302 | -0.000251 |
| 51 | C4H3 | -0.000414 | -0.000247 |
| 52 | C4H4 | -0.000125 | -0.000091 |
| 53 | C4H5 | -0.001011 | 0.001169 |
| 54 | C3H4N | -0.000069 | -0.000081 |
| 54 | C4H6 | -0.000719 | 0.000440 |
| 55 | C3H3O | -0.000897 | 0.001006 |
| 55 | C4H7 | -0.006013 | 0.006633 |
| 56 | C3H4O | 0.003264 | -0.001494 |
| 56 | C3H6N | -0.000521 | 0.000239 |
| 56 | C4H8 | -0.000484 | 0.000489 |
| 57 | C3H5O | 0.000046 | 0.001727 |
| 57 | C4H9 | -0.003310 | 0.001401 |
| 58 | C3H6O | -0.000135 | 0.000408 |
| 58 | C3H8N | -0.001253 | 0.002535 |
| 58 | C4H10 | 0.000013 | -0.000082 |
| 59 | C2H3O2 | -0.000078 | 0.000267 |
| 59 | C3H7O | -0.000247 | 0.000194 |
| 59 | C3H9N | -0.000146 | 0.000106 |
| 61 | C2H5O2 | -0.000111 | 0.000774 |
| 63 | C5H3 | -0.000071 | -0.000500 |
| 64 | C5H4 | -0.000017 | -0.000152 |
| 65 | C5H5 | -0.000196 | -0.000160 |
| 66 | C5H6 | -0.000097 | -0.000105 |
| 67 | C5H7 | -0.001153 | 0.000697 |

| | | | |
|-----|--------|-----------|-----------|
| 68 | C4H4O | 0.000001 | -0.000107 |
| 68 | C4H6N | -0.000118 | -0.000173 |
| 68 | C5H8 | -0.000116 | -0.000181 |
| 69 | C4H5O | -0.000121 | 0.000743 |
| 69 | C5H9 | -0.001872 | 0.001524 |
| 70 | C4H6O | 0.000079 | -0.000030 |
| 70 | C4H8N | -0.000505 | -0.000180 |
| 70 | C5H10 | -0.000100 | -0.000523 |
| 71 | C3H3O2 | -0.000085 | 0.000797 |
| 71 | C4H7O | -0.000583 | 0.001207 |
| 71 | C5H11 | -0.000629 | 0.000431 |
| 72 | C3H4O2 | 0.000177 | -0.000006 |
| 72 | C4H8O | -0.000125 | 0.000311 |
| 72 | C4H10N | -0.000369 | 0.000598 |
| 73 | C3H5O2 | -0.000008 | 0.001819 |
| 73 | C4H9O | -0.000178 | 0.000293 |
| 75 | C6H3 | -0.000681 | 0.000182 |
| 75 | C3H7O2 | -0.000022 | 0.000180 |
| 76 | C6H4 | -0.000287 | -0.000008 |
| 77 | C6H5 | -0.000841 | -0.000486 |
| 78 | C5H4N | -0.000069 | -0.000107 |
| 78 | C6H6 | -0.000127 | -0.000083 |
| 79 | C6H7 | -0.000321 | -0.000240 |
| 80 | C5H6N | -0.000163 | 0.000059 |
| 80 | C6H8 | -0.000018 | -0.000104 |
| 81 | C5H5O | -0.000065 | 0.000066 |
| 81 | C6H9 | -0.000388 | -0.000172 |
| 82 | C5H6O | 0.000019 | -0.000197 |
| 82 | C5H8N | 0.000071 | -0.000099 |
| 82 | C6H10 | 0.000082 | -0.000123 |
| 83 | C5H7O | -0.000075 | -0.000048 |
| 83 | C6H11 | -0.000367 | 0.000401 |
| 84 | C4H4O2 | 0.000033 | -0.000050 |
| 84 | C5H8O | 0.000073 | -0.000107 |
| 84 | C5H10N | -0.000007 | 0.000127 |
| 84 | C6H12 | 0.000220 | -0.000208 |
| 85 | C4H5O2 | -0.000118 | 0.000393 |
| 85 | C5H9O | -0.000073 | -0.000053 |
| 85 | C6H13 | -0.000071 | 0.000041 |
| 86 | C4H6O2 | -0.000108 | 0.000020 |
| 86 | C5H10O | 0.000176 | -0.000130 |
| 86 | C5H12N | 0.000643 | 0.000402 |
| 87 | C4H7O2 | -0.000128 | 0.000460 |
| 88 | C4H8O2 | 0.000016 | -0.000008 |
| 89 | C3H5O3 | -0.000022 | -0.000064 |
| 90 | C6H4N | -0.000075 | -0.000002 |
| 90 | C3H6O3 | -0.000157 | -0.000009 |
| 91 | C7H7 | -0.000282 | -0.000271 |
| 92 | C7H8 | -0.000021 | -0.000084 |
| 93 | C7H9 | -0.000026 | -0.000195 |
| 94 | C6H6O | -0.000169 | -0.000126 |
| 94 | C6H8N | -0.000448 | 0.000137 |
| 94 | C7H10 | -0.000059 | -0.000047 |
| 95 | C6H7O | -0.000032 | -0.000286 |
| 95 | C7H11 | -0.000135 | -0.000137 |
| 96 | C6H8O | 0.000074 | -0.000137 |
| 96 | C7H12 | 0.000144 | -0.000128 |
| 97 | C5H5O2 | -0.000107 | 0.000332 |
| 97 | C6H9O | -0.000031 | -0.000145 |
| 97 | C7H13 | -0.000023 | -0.000060 |
| 98 | C6H10O | -0.000052 | -0.000030 |
| 99 | C5H7O2 | -0.000511 | 0.000020 |
| 99 | C6H11O | -0.000170 | -0.000137 |
| 100 | C5H8O2 | -0.000120 | 0.000005 |

Table A. 14 TOF-SIMS – Raw spectral data for selected inorganics on dry Gluepot 3522A samples

| Sample | Element | | | | | | | Total spectra |
|--------|---------|-------|--------|--------|-------|-------|-------|---------------|
| | Na | Mg | Al | Si | K | Ca | Fe | |
| 1 | 15190 | 15484 | 201369 | 149342 | 8372 | 24733 | 38497 | 1072948 |
| 2 | 12514 | 11232 | 136282 | 96125 | 4476 | 17846 | 25843 | 883392 |
| 3 | 15420 | 15069 | 185964 | 139901 | 4947 | 21668 | 35055 | 1031749 |
| 4 | 10164 | 10571 | 136978 | 100387 | 5156 | 15164 | 26202 | 904021 |
| 5 | 9456 | 11441 | 149228 | 119328 | 4319 | 17291 | 28792 | 868754 |
| 6 | 17452 | 18753 | 227648 | 166209 | 12939 | 29484 | 44090 | 1186168 |
| 7 | 15540 | 22989 | 274290 | 207550 | 11688 | 36199 | 64236 | 1330904 |
| 8 | 15574 | 24780 | 292313 | 222310 | 12845 | 39357 | 66980 | 1388227 |

Table A. 15 TOF-SIMS – Normalised spectral data for selected inorganics on dry Gluepot 3522A samples

| Sample | Element | | | | | | |
|---------|----------|----------|----------|----------|----------|----------|----------|
| | Na | Mg | Al | Si | K | Ca | Fe |
| 1 | 0.014157 | 0.014431 | 0.187678 | 0.139188 | 0.007803 | 0.023051 | 0.03588 |
| 2 | 0.014166 | 0.012715 | 0.154271 | 0.108814 | 0.005067 | 0.020202 | 0.029254 |
| 3 | 0.014945 | 0.014605 | 0.180242 | 0.135596 | 0.004795 | 0.021001 | 0.033976 |
| 4 | 0.011243 | 0.011693 | 0.151521 | 0.111045 | 0.005703 | 0.016774 | 0.028984 |
| 5 | 0.010885 | 0.013169 | 0.171772 | 0.137355 | 0.004971 | 0.019903 | 0.033142 |
| 6 | 0.014713 | 0.01581 | 0.191919 | 0.140123 | 0.010908 | 0.024857 | 0.03717 |
| 7 | 0.011676 | 0.017273 | 0.206093 | 0.155947 | 0.008782 | 0.027199 | 0.048265 |
| 8 | 0.011219 | 0.01785 | 0.210566 | 0.16014 | 0.009253 | 0.028351 | 0.048249 |
| Average | 0.012876 | 0.014693 | 0.181758 | 0.136026 | 0.00716 | 0.022667 | 0.036865 |
| Std Dev | 0.001764 | 0.002177 | 0.021818 | 0.018407 | 0.002341 | 0.003946 | 0.007586 |
| 95% C.I | 0.001222 | 0.001509 | 0.015119 | 0.012755 | 0.001622 | 0.002734 | 0.005257 |

Table A. 16 TOF-SIMS – Raw spectral data for selected inorganics on wet Gluepot 3522A samples

| Sample | Element | | | | | | | Total spectra |
|--------|---------|-------|--------|--------|-------|-------|-------|---------------|
| | Na | Mg | Al | Si | K | Ca | Fe | |
| 1 | 383496 | 27774 | 312282 | 273999 | 15979 | 43308 | 67121 | 2363942 |
| 2 | 296516 | 22522 | 238477 | 192954 | 13312 | 37081 | 50615 | 1782925 |
| 3 | 261381 | 23363 | 258858 | 276452 | 14326 | 38132 | 54913 | 2197690 |
| 4 | 264353 | 22044 | 241678 | 279566 | 13795 | 35538 | 51645 | 2098426 |
| 5 | 353046 | 28152 | 310196 | 261671 | 16694 | 44457 | 64557 | 2354630 |
| 6 | 484268 | 29749 | 342418 | 267025 | 16648 | 43622 | 71001 | 2704252 |
| 7 | 438346 | 29078 | 334606 | 256571 | 17074 | 44000 | 68490 | 2621999 |
| 8 | 455734 | 28308 | 322370 | 249144 | 17457 | 42352 | 65493 | 2561424 |
| 9 | 502654 | 29012 | 331761 | 264114 | 19742 | 43005 | 70767 | 2564223 |
| 10 | 274174 | 30180 | 323704 | 251475 | 16485 | 49097 | 69702 | 2267698 |

Table A. 17 TOF-SIMS – Normalised spectral data for selected inorganics on wet Gluepot 3522A samples

| Sample | Element | | | | | | |
|---------|----------|----------|----------|----------|----------|----------|----------|
| | Na | Mg | Al | Si | K | Ca | Fe |
| 1 | 0.162227 | 0.011749 | 0.132102 | 0.115908 | 0.006759 | 0.01832 | 0.028394 |
| 2 | 0.166309 | 0.012632 | 0.133756 | 0.108223 | 0.007466 | 0.020798 | 0.028389 |
| 3 | 0.118934 | 0.010631 | 0.117786 | 0.125792 | 0.006519 | 0.017351 | 0.024987 |
| 4 | 0.125977 | 0.010505 | 0.115171 | 0.133227 | 0.006574 | 0.016936 | 0.024611 |
| 5 | 0.149937 | 0.011956 | 0.131739 | 0.11113 | 0.00709 | 0.018881 | 0.027417 |
| 6 | 0.179077 | 0.011001 | 0.126622 | 0.098743 | 0.006156 | 0.016131 | 0.026255 |
| 7 | 0.16718 | 0.01109 | 0.127615 | 0.097853 | 0.006512 | 0.016781 | 0.026121 |
| 8 | 0.177922 | 0.011052 | 0.125856 | 0.097268 | 0.006815 | 0.016535 | 0.025569 |
| 9 | 0.196026 | 0.011314 | 0.129381 | 0.103 | 0.007699 | 0.016771 | 0.027598 |
| 10 | 0.120904 | 0.013309 | 0.142746 | 0.110894 | 0.007269 | 0.021651 | 0.030737 |
| Average | 0.156449 | 0.011524 | 0.128277 | 0.110204 | 0.006886 | 0.018015 | 0.027008 |
| Std Dev | 0.026723 | 0.000895 | 0.007874 | 0.012083 | 0.000484 | 0.001892 | 0.001871 |
| 95% C.I | 0.016563 | 0.000555 | 0.004881 | 0.007489 | 0.0003 | 0.001173 | 0.00116 |

Table A. 18 TOF-SIMS – Raw spectral data for selected inorganics on dry Mt Mackay samples

| Sample | Element | | | | | | | Total spectra: |
|--------|---------|------|--------|-------|-------|------|------|----------------|
| | Na | Mg | Al | Si | K | Ca | Fe | |
| 1 | 3940 | 2835 | 145414 | 56904 | 41637 | 4439 | 5170 | 776921 |
| 2 | 4096 | 2406 | 135258 | 56204 | 80291 | 3591 | 5630 | 861790 |
| 3 | 6473 | 5067 | 208628 | 97227 | 86141 | 5776 | 9525 | 1059856 |
| 4 | 5364 | 4211 | 204896 | 88619 | 66610 | 6512 | 8524 | 1148758 |
| 5 | 7721 | 2868 | 139663 | 58375 | 39648 | 4490 | 5680 | 867912 |
| 6 | 3676 | 2671 | 130555 | 56520 | 40723 | 3951 | 6768 | 812693 |
| 7 | 4727 | 3054 | 157290 | 64297 | 46945 | 4549 | 6810 | 1106158 |
| 8 | 3192 | 2283 | 118385 | 50590 | 37340 | 3291 | 4695 | 764767 |

Table A. 19 TOF-SIMS – Normalised spectral data for selected inorganics on dry Mt Mackay samples

| Sample | Element | | | | | | |
|---------|----------|----------|----------|----------|----------|----------|----------|
| | Na | Mg | Al | Si | K | Ca | Fe |
| 1 | 0.005071 | 0.003649 | 0.187167 | 0.073243 | 0.053592 | 0.005714 | 0.006654 |
| 2 | 0.004753 | 0.002792 | 0.15695 | 0.065218 | 0.093168 | 0.004167 | 0.006533 |
| 3 | 0.006107 | 0.004781 | 0.196846 | 0.091736 | 0.081276 | 0.00545 | 0.008987 |
| 4 | 0.004669 | 0.003666 | 0.178363 | 0.077143 | 0.057984 | 0.005669 | 0.00742 |
| 5 | 0.008896 | 0.003304 | 0.160918 | 0.067259 | 0.045682 | 0.005173 | 0.006544 |
| 6 | 0.004523 | 0.003287 | 0.160645 | 0.069547 | 0.050109 | 0.004862 | 0.008328 |
| 7 | 0.004273 | 0.002761 | 0.142195 | 0.058126 | 0.04244 | 0.004112 | 0.006156 |
| 8 | 0.004174 | 0.002985 | 0.154799 | 0.066151 | 0.048825 | 0.004303 | 0.006139 |
| Average | 0.005308 | 0.003403 | 0.167235 | 0.071053 | 0.059135 | 0.004931 | 0.007095 |
| Std Dev | 0.00157 | 0.000656 | 0.018395 | 0.010082 | 0.018236 | 0.000669 | 0.001056 |
| 95% C.I | 0.001088 | 0.000455 | 0.012747 | 0.006986 | 0.012637 | 0.000464 | 0.000732 |

Table A. 20 TOF-SIMS – Raw spectral data for selected inorganics on wet Mt Mackay samples

| Sample | Element | | | | | | | Total spectra: |
|--------|---------|------|--------|--------|-------|-------|-------|----------------|
| | Na | Mg | Al | Si | K | Ca | Fe | |
| 1 | 83040 | 8472 | 265568 | 132943 | 2E+05 | 11840 | 12610 | 2013236 |
| 2 | 86455 | 8484 | 263813 | 139432 | 2E+05 | 11400 | 13094 | 2012068 |
| 3 | 89514 | 8734 | 281722 | 142859 | 2E+05 | 12070 | 13742 | 2043258 |
| 4 | 81362 | 8520 | 277835 | 137395 | 2E+05 | 12148 | 13818 | 2000505 |
| 5 | 98734 | 8385 | 280409 | 140553 | 2E+05 | 11515 | 15095 | 2064087 |
| 6 | 102649 | 8155 | 280989 | 149549 | 2E+05 | 11738 | 13803 | 2083622 |
| 7 | 91002 | 7774 | 272550 | 143240 | 2E+05 | 10895 | 13395 | 2053127 |
| 8 | 94967 | 7713 | 283306 | 149946 | 2E+05 | 11054 | 13846 | 2108999 |

Table A. 21 TOF-SIMS – Normalised spectral data for selected inorganics on wet Mt Mackay samples

| Sample | Element | | | | | | |
|---------|----------|----------|----------|----------|----------|----------|----------|
| | Na | Mg | Al | Si | K | Ca | Fe |
| 1 | 0.041247 | 0.004208 | 0.131911 | 0.066034 | 0.091669 | 0.005881 | 0.006264 |
| 2 | 0.042968 | 0.004217 | 0.131115 | 0.069298 | 0.089476 | 0.005666 | 0.006508 |
| 3 | 0.043809 | 0.004275 | 0.137879 | 0.069917 | 0.087125 | 0.005907 | 0.006726 |
| 4 | 0.040671 | 0.004259 | 0.138882 | 0.06868 | 0.086932 | 0.006072 | 0.006907 |
| 5 | 0.047834 | 0.004062 | 0.135851 | 0.068095 | 0.086859 | 0.005579 | 0.007313 |
| 6 | 0.049265 | 0.003914 | 0.134856 | 0.071774 | 0.08655 | 0.005633 | 0.006625 |
| 7 | 0.044324 | 0.003786 | 0.132749 | 0.069767 | 0.08566 | 0.005307 | 0.006524 |
| 8 | 0.045029 | 0.003657 | 0.134332 | 0.071098 | 0.085537 | 0.005241 | 0.006565 |
| Average | 0.044393 | 0.004047 | 0.134697 | 0.069333 | 0.087476 | 0.005661 | 0.006679 |
| Std Dev | 0.002979 | 0.000236 | 0.002765 | 0.001791 | 0.00208 | 0.00029 | 0.000316 |
| 95% C.I | 0.002064 | 0.000163 | 0.001916 | 0.001241 | 0.001442 | 0.000201 | 0.000219 |

Table A. 22 Settling test results for soils in synthetic juice with no added flocculant

| Settling time | Mud interface height | | | | | |
|---------------|----------------------|-------|---------------|-------|--------------|-------|
| | Mt Mackay | | Gluepot 3522A | | Invicta 255B | |
| min | ml | mm | ml | mm | ml | mm |
| 0 | 100.0 | 195.0 | 100.0 | 195.0 | 100.0 | 195.0 |
| 1 | 95.0 | 185.3 | 99.0 | 193.1 | 95.0 | 185.3 |
| 2 | 75.0 | 146.3 | 97.0 | 189.2 | 90.0 | 175.5 |
| 3 | 50.0 | 97.5 | 94.0 | 183.3 | 80.0 | 156.0 |
| 4 | 25.0 | 48.8 | 91.0 | 177.5 | 68.0 | 132.6 |
| 5 | 15.0 | 29.3 | 88.0 | 171.6 | 65.0 | 126.8 |
| 6 | 10.0 | 19.5 | 85.0 | 165.8 | 58.0 | 113.1 |
| 7 | 10.0 | 19.5 | 82.0 | 159.9 | 50.0 | 97.5 |
| 8 | 9.5 | 18.5 | 78.0 | 152.1 | 48.0 | 93.6 |
| 9 | 9.0 | 17.6 | 76.0 | 148.2 | 42.0 | 81.9 |
| 10 | 8.5 | 16.6 | 74.0 | 144.3 | 38.0 | 74.1 |
| 11 | 8.0 | 15.6 | 72.0 | 140.4 | 32.0 | 62.4 |
| 12 | 8.0 | 15.6 | 69.0 | 134.6 | 28.0 | 54.6 |
| 13 | 8.0 | 15.6 | 67.0 | 130.7 | 26.0 | 50.7 |
| 14 | 8.0 | 15.6 | 65.0 | 126.8 | 24.0 | 46.8 |
| 15 | 7.5 | 14.6 | 63.0 | 122.9 | 22.0 | 42.9 |
| 16 | 7.5 | 14.6 | 61.0 | 119.0 | 21.0 | 41.0 |
| 17 | 7.5 | 14.6 | 59.0 | 115.1 | 20.0 | 39.0 |
| 18 | 7.5 | 14.6 | 57.0 | 111.2 | 19.5 | 38.0 |
| 19 | 7.0 | 13.7 | 55.5 | 108.2 | 19.0 | 37.1 |
| 20 | 7.0 | 13.7 | 54.0 | 105.3 | 18.5 | 36.1 |
| 21 | 7.0 | 13.7 | 52.0 | 101.4 | 18.0 | 35.1 |
| 22 | 7.0 | 13.7 | 50.5 | 98.5 | 17.5 | 34.1 |
| 23 | 6.5 | 12.7 | 49.0 | 95.6 | 17.0 | 33.2 |
| 24 | 6.5 | 12.7 | 47.5 | 92.6 | 17.0 | 33.2 |
| 25 | 6.5 | 12.7 | 46.0 | 89.7 | 16.8 | 32.7 |
| 26 | 6.5 | 12.7 | 44.5 | 86.8 | 16.5 | 32.2 |
| 27 | 6.0 | 11.7 | 43.0 | 83.9 | 16.0 | 31.2 |
| 28 | 6.0 | 11.7 | 42.0 | 81.9 | 16.0 | 31.2 |
| 29 | 6.0 | 11.7 | 41.0 | 80.0 | 15.9 | 31.0 |
| 30 | 6.0 | 11.7 | 40.0 | 78.0 | 15.5 | 30.2 |

Table A. 23 Summary of settling test results with soils in synthetic juice with no added flocculant

| Parameter | Mt Mackay | Gluepot | Invicta 255B |
|--|-----------|---------|--------------|
| Turbidity (100 x Absorbance at 900 nm) | 22.2 | 5.9 | 6.6 |
| pH @ room temp (~21 °C) | 4.42 | 4.79 | 5.84 |
| Final mud height, % | 6.0 | 40.0 | 15.5 |
| Maximum settling rate over first 5 min, cm/min | 4.9 | 0.6 | 1.6 |

Table A. 24 ζ measurements for soils in various electrolytes

| Molarity (M) | 3.NaCl | | | 3.33 M KCl | | | 1.11 M MgCl ₂ .2H ₂ O | | | 1.11 M CaCl ₂ .2H ₂ O | | | 1.67 M Synthetic juice | | |
|-----------------|---------|-----------------|--------------|------------|-----------------|--------------|---|-----------------|--------------|---|-----------------|--------------|------------------------|-----------------|--------------|
| | Gluepot | Invicta 255B | Mt Mackay | Gluepot | Invicta 255B | Mt Mackay | Gluepot | Invicta 255B | Mt Mackay | Gluepot | Invicta 255B | Mt Mackay | Gluepot | Invicta 255B | Mt Mackay |
| 0.000000 | -39.4 | -38.7 | -38.90 | -37.2 | -37.6 | -38.90 | -19.9 | -16.7 | -17.1 | -18.8 | -11.4 | -14.60 | -21.1 | -25.3 | -14.00 |
| 0.000373 | -39.2 | -38.0 | -36.70 | -36.8 | -35.7 | -32.90 | -18.0 | -16.2 | -17.7 | -17.8 | -11.5 | -13.60 | -21.1 | -24.6 | -14.00 |
| 0.001312 | -40.3 | -38.0 | -35.50 | -35.2 | -37.7 | -33.90 | -17.5 | -15.5 | -15.0 | -17.6 | -11.8 | -14.50 | -20.2 | -22.4 | -13.10 |
| 0.002459 | -39.5 | -40.0 | -33.60 | -33.5 | -36.5 | -31.90 | -15.9 | -14.1 | -15.7 | -16.5 | -11.5 | -12.70 | -20.4 | -22.6 | -13.50 |
| 0.004609 | -37.3 | -38.4 | -33.00 | -33.8 | -37.1 | -30.20 | -14.2 | -13.3 | -13.7 | -13.3 | -11.1 | -11.30 | -18.7 | -19.9 | -13.30 |
| 0.008641 | -35.0 | -36.6 | -30.00 | -24.9 | -35.1 | -26.00 | -12.1 | -12.0 | -10.4 | -11.4 | -10.5 | -9.00 | -18.5 | -17.6 | -12.60 |
| 0.016200 | -34.6 | -34.2 | -26.60 | -33.8 | -37.5 | -22.30 | -11.2 | -10.4 | -8.8 | -10.0 | -10.4 | -6.20 | -15.3 | -16.4 | -10.90 |
| 0.030360 | -32.0 | -35.2 | -24.30 | -31.1 | -34.1 | -19.40 | -9.4 | -10.3 | -6.1 | -9.0 | -9.0 | -5.60 | -14.8 | -10.5 | -10.20 |
| 0.056920 | -30.5 | -27.9 | -21.40 | -25.5 | -30.7 | -14.70 | -10.1 | -10.4 | -6.0 | -9.4 | -9.3 | -5.00 | -14.0 | -14.8 | -8.60 |
| 0.106700 | -25.7 | -30.0 | -16.40 | -24.4 | -27.3 | -12.50 | -7.0 | -8.9 | -4.3 | -7.8 | -7.9 | -2.50 | -14.1 | -13.0 | -7.50 |
| 0.200000 | -31.0 | -33.0 | -15.50 | -23.7 | -27.8 | -11.50 | -5.5 | -6.0 | -1.9 | -2.8 | -7.2 | -1.20 | -11.0 | -11.2 | -5.90 |

Appendix B

Batch settling test data for soils in synthetic juice and added flocculant (Chapter 4 tests)

Table B. 1 Settling test data for 1.0 wt% Gluepot synthetic solution for various flocculants added at 0.125 ppm dosing rate

| Test ID | 2.01 | 2.02 | 2.03 | 2.04 | 2.05 | 2.06 | 2.07 |
|--|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Flocculant name | 2310 | 2320 | LT27 | 2115 | 2120 | 2125 | 2130 |
| Flocculant concentration, wt % | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Flocculant dosage, ppm | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 |
| Flocculant volume, µm | 125 | 125 | 125 | 125 | 125 | 125 | 125 |
| Mixer (magnetic bar) speed, % | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Mix time, min | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Settling time, sec | Interface height, cm | | | | | | |
| 0 | 18.7 | 18.7 | 18.7 | 18.7 | 18.7 | 18.3 | 18.2 |
| 30 | 17.8 | 18.0 | 18.0 | 18.0 | 17.8 | 18.0 | 18.0 |
| 60 | 16.9 | 17.4 | 17.4 | 17.2 | 17.2 | 17.2 | 17.6 |
| 120 | 14.6 | 14.0 | 15.9 | 15.0 | 14.0 | 15.5 | 15.9 |
| 180 | 12.2 | 12.2 | 14.0 | 13.1 | 11.2 | 13.7 | 13.1 |
| 240 | 10.3 | 10.3 | 12.9 | 11.2 | 8.2 | 12.0 | 10.9 |
| 300 | 8.4 | 8.4 | 11.6 | 9.7 | 6.0 | 10.3 | 9.4 |
| 360 | 6.6 | 6.6 | 10.3 | | 3.7 | | |
| 420 | 4.7 | 4.7 | 8.8 | | | | |
| 480 | 2.8 | 2.8 | 7.7 | | | | |
| 540 | 2.8 | | 6.6 | | | | |
| 600 | 2.6 | | 5.2 | | 1.5 | 3.7 | |
| 900 | | | | | 1.3 | 2.8 | 1.7 |
| 1200 | | | | | 1.2 | 2.5 | 1.6 |
| 1800 | 1.9 | 1.5 | 2.8 | 1.8 | 1.1 | 2.1 | 1.3 |
| Final mud height, % | 10.0 | 8.0 | 15.0 | 9.5 | 6.0 | 11.0 | 7.0 |
| Settling rate, cm/min | 2.0 | 2.0 | 1.4 | 1.8 | 2.5 | 1.6 | 1.8 |
| Supernatant turbidity, (100 x Absorbance) | 10.5 | 15.0 | 15.0 | 13.0 | 17.0 | 13.0 | 13.0 |

Table B. 2 Settling test data for 1.0 wt% Gluepot synthetic solution for various flocculants added at 0.5 ppm dosing rate

| Test ID | 3.01 | 3.02 | 3.03 | 3.04 | 3.05 | 3.06 | 3.07 |
|---|----------------------|-------|-------|-------|-------|-------|-------|
| Flocculant name | 2310 | 2320 | LT27 | 2115 | 2120 | 2125 | 2130 |
| Flocculant concentration, wt % | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Flocculant dosage, ppm | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 |
| Flocculant volume, μm | 500 | 500 | 500 | 500 | 500 | 500 | 500 |
| Mixer (magnetic bar) speed, % | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Mix time, min | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Settling time, sec | Interface height, cm | | | | | | |
| 0 | 17.4 | 18.3 | 17.8 | 18.3 | 17.8 | 18.2 | 18.3 |
| 10 | | | 4.7 | | 13.1 | 18.2 | 18.2 |
| 15 | | | 1.9 | | 10.3 | 18.0 | 18.0 |
| 20 | | | | | 7.5 | | 17.8 |
| 30 | 12.2 | 17.2 | 1.7 | 15.9 | 3.0 | 17.6 | 17.4 |
| 60 | 6.6 | 15.5 | 1.5 | 11.6 | 2.2 | 16.5 | 15.9 |
| 120 | | 12.2 | | 3.7 | | 14.0 | 12.5 |
| 180 | | 8.8 | | | | 11.6 | 9.2 |
| 240 | | 5.6 | | | | 9.0 | 6.0 |
| 300 | 1.5 | 3.0 | 1.1 | 1.6 | 1.5 | 6.6 | 2.6 |
| 360 | | | | | | 4.3 | |
| 600 | 1.3 | 2.1 | 1.1 | 1.1 | | 2.6 | 2.1 |
| 900 | | 1.8 | 1.1 | 1.1 | 1.5 | 2.1 | 1.7 |
| 1200 | 1.1 | 1.6 | 1.1 | 1.1 | 1.5 | 1.9 | 1.6 |
| 1800 | 0.9 | 1.5 | 1.1 | 1.1 | 1.5 | 1.6 | 1.5 |
| Final mud height, % | 5.0 | 8.0 | 6.0 | 6.0 | 8.0 | 8.5 | 8.0 |
| Settling rate, cm/min | 10.9 | 3.2 | | 6.7 | 30.9 | 2.5 | 3.3 |
| Supernatant turbidity, (100 x Absorbance) | 6.5 | 16.5 | 2.0 | 10.5 | 4.7 | 12.7 | 17.2 |

Table B. 3 Settling test data for 1.0 wt% Gluepot synthetic solution for various flocculants added at 1.0 ppm dosing rate

| Test ID | 4.01 | 4.02 | 4.03 | 4.04 | 4.05 | 4.06 | 4.07 |
|--|-----------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Flocculant name | 2310 | 2320 | LT27 | 2115 | 2120 | 2125 | 2130 |
| Flocculant concentration, wt % | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Flocculant dosage, ppm | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Flocculant volume, µm | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |
| Mixer (magnetic bar) speed, % | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Mix time, min | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Settling time, sec | Interface height, cm | | | | | | |
| 0 | 17.6 | 18.0 | 17.8 | 18.0 | 14.4 | 17.4 | 17.4 |
| 5 | | | | | | | |
| 10 | 16.5 | 10.3 | 11.0 | 15.7 | 6.6 | 12.2 | 9.2 |
| 15 | 15.9 | 4.7 | 6.6 | 13.7 | 2.2 | 9.4 | 4.7 |
| 20 | 14.6 | 2.4 | 2.2 | 11.8 | 2.1 | 6.0 | 2.2 |
| 30 | 12.7 | 2.1 | 1.9 | 8.8 | 1.9 | 2.4 | 2.1 |
| 60 | 7.5 | 1.8 | 1.6 | 3.0 | 1.7 | 1.9 | 1.7 |
| 120 | 3.0 | | | | | | |
| 300 | 2.1 | 1.5 | 1.3 | 1.7 | 1.5 | 1.5 | 1.5 |
| 600 | 1.7 | 1.5 | 1.3 | | | 1.5 | 1.5 |
| 900 | | | 1.3 | 1.5 | 1.5 | 1.5 | |
| 1200 | 1.5 | 1.5 | 1.3 | 1.5 | 1.5 | 1.5 | 1.5 |
| 1800 | 1.5 | 1.5 | 1.3 | 1.5 | 1.5 | 1.5 | 1.5 |
| Final mud height, % | 5.0 | 8.0 | 6.0 | 6.0 | 8.0 | 8.5 | 8.0 |
| Settling rate, cm/min | 10.9 | 3.2 | | 6.7 | 30.9 | 2.5 | 3.3 |
| Supernatant turbidity, (100 x Absorbance) | 6.5 | 16.5 | 2.0 | 10.5 | 4.7 | 12.7 | 17.2 |

Table B. 4 Settling test data for 1.0 wt% Mt Mackay synthetic solution for various flocculants added at 0.125 ppm dosing rate

| Test ID | 6.01 | 6.02 | 6.03 | 6.04 | 6.05 | 6.06 | 6.07 |
|--|----------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Flocculant name | 2310 | 2320 | LT27 | 2115 | 2120 | 2125 | 2130 |
| Flocculant concentration, wt % | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Flocculant dosage, ppm | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 | 0.125 |
| Flocculant volume, µm | 125 | 125 | 125 | 125 | 125 | 125 | 125 |
| Mixer (magnetic bar) speed, % | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Mix time, min | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Settling time, sec | Interface height, cm | | | | | | |
| 0 | 18.2 | 17.8 | 18.2 | 17.8 | 17.8 | 17.8 | 17.8 |
| 30 | 17.6 | 17.0 | 17.8 | 17.4 | 17.0 | 17.6 | 16.9 |
| 60 | 15.0 | 15.0 | 16.9 | 15.0 | 15.0 | 15.0 | 15.9 |
| 120 | 8.4 | 7.5 | 8.4 | 7.5 | 7.5 | 7.5 | 7.5 |
| 180 | 2.8 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 |
| 240 | 1.3 | 0.9 | 0.9 | 0.9 | 0.7 | | |
| 300 | 1.3 | 0.9 | 0.9 | 0.9 | 0.7 | 0.7 | 0.7 |
| 600 | | 0.7 | 0.7 | 0.7 | 0.7 | 0.6 | 0.7 |
| 900 | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| 1200 | 0.7 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| 1800 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Final mud height, % | 8.0 | 8.0 | 7.0 | 8.0 | 8.0 | 8.0 | 8.0 |
| Settling rate, cm/min | 11.2 | 53.2 | 44.9 | 18.3 | 48.7 | 34.3 | 50.9 |
| Supernatant turbidity, (100 x Absorbance) | 6.2 | 3.5 | 5.3 | 7.2 | 4.5 | 5.1 | 2.4 |

Table B. 5 Settling test data for 1.0 wt% Mt Mackay synthetic solution for various flocculants added at 0.5 ppm dosing rate

| Test ID | 7.01 | 7.02 | 7.03 | 7.04 | 7.05 | 7.06 | 7.07 |
|---|----------------------|-------|-------|-------|-------|-------|-------|
| Flocculant name | 2310 | 2320 | LT27 | 2115 | 2120 | 2125 | 2130 |
| Flocculant concentration, wt % | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Flocculant dosage, ppm | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 | 0.500 |
| Flocculant volume, μm | 500 | 500 | 500 | 500 | 500 | 500 | 500 |
| Mixer (magnetic bar) speed, % | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Mix time, min | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Settling time, sec | Interface height, cm | | | | | | |
| 0 | 17.4 | 17.2 | 17.4 | 16.9 | 16.9 | 17.2 | 16.5 |
| 10 | 11.2 | 7.5 | 11.2 | 7.5 | 8.4 | 9.4 | 9.4 |
| 15 | 8.4 | 1.3 | 7.5 | 1.9 | 3.7 | 4.7 | 6.6 |
| 20 | 4.7 | 1.1 | 4.7 | 1.1 | 1.5 | 1.3 | 1.3 |
| 30 | 1.3 | 0.9 | 0.9 | 0.9 | 1.3 | 1.1 | 1.1 |
| 60 | 1.1 | 0.7 | 0.9 | 0.7 | 1.1 | 0.9 | 0.9 |
| 300 | 0.7 | 0.7 | 0.7 | 0.7 | 0.9 | 0.9 | 0.7 |
| 1800 | 0.7 | 0.6 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| Final mud height, % | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Settling rate, cm/min | 6.1 | 6.6 | 7.5 | 6.6 | 6.6 | 6.6 | 7.0 |
| Supernatant turbidity, (100 x Absorbance) | 26.0 | 23.0 | 24.0 | 24.0 | 22.5 | 25.7 | 24.0 |

Table B. 6 Settling test data for 1.0 wt% Mt Mackay synthetic solution for various flocculants added at 1.0 ppm dosing rate

| Test ID | 8.01 | 8.02 | 8.03 | 8.04 | 8.05 | 8.06 | 8.07 |
|--|----------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Flocculant name | 2310 | 2320 | LT27 | 2115 | 2120 | 2125 | 2130 |
| Flocculant concentration, wt % | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Flocculant dosage, ppm | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 | 1.000 |
| Flocculant volume, µm | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 | 1000 |
| Mixer (magnetic bar) speed, % | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Mix time, min | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Settling time, sec | Interface height, cm | | | | | | |
| 0 | 15.9 | 14.0 | 15.9 | 16.9 | 14.0 | 16.9 | 15.9 |
| 5 | 5.6 | 3.7 | 9.4 | 10.3 | 3.7 | 8.4 | 5.6 |
| 10 | 1.3 | | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| 15 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| 20 | 1.1 | | 1.1 | | | | |
| 30 | 1.1 | | | | | | |
| 60 | 0.9 | 0.9 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| 300 | 0.9 | 0.9 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| 600 | 0.9 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | |
| 900 | 0.7 | 0.7 | 0.7 | 0.7 | | | 0.7 |
| 1200 | 0.7 | 0.7 | 0.7 | 0.7 | | 0.7 | |
| 1800 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| Final mud height, % | 4.0 | 3.0 | 4.0 | 4.0 | 4.0 | 4.0 | 4.0 |
| Settling rate, cm/min | 35.9 | 63.7 | 39.7 | 59.9 | 52.4 | 50.2 | 39.7 |
| Supernatant turbidity, (100 x Absorbance) | 7.0 | 5.2 | 7.5 | 6.2 | 2.7 | 4.0 | 4.0 |

Table B. 7 Batch settling test data for 1.0 wt % Gluepot synthetic solution at various mixer speeds and mixing times using 2120 flocculant at 0.5 ppm

| Test ID | 9.01 | 9.03 | 10.02 | 9.05 | 10.04 | 11.05 | 11.02 | 11.06 | 9.02 | 9.07 | 9.06 |
|---|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Mixer speed, r/min | 500 | 500 | 500 | 500 | 500 | 750 | 750 | 750 | 1000 | 1000 | 1000 |
| Mixing time, min | 1 | 5 | 5 | 20 | 20 | 1 | 5 | 20 | 1 | 5 | 20 |
| Settling time, min | | | | | | | | | | | |
| 0.0 | 100.0 | 95.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| 0.5 | 97.5 | 82.5 | 92.5 | 82.5 | 90.0 | 94.0 | 92.0 | 80.0 | 95.0 | 92.5 | 87.5 |
| 1.0 | 91.0 | 72.5 | 84.0 | 60.0 | 76.0 | 87.5 | 80.0 | 55.0 | 90.0 | 87.5 | 75.0 |
| 2.0 | 80.0 | 50.0 | 64.0 | 20.0 | 50.0 | 71.0 | 58.0 | 15.2 | 77.5 | 72.5 | 47.5 |
| 3.0 | 70.0 | 27.5 | 46.0 | 14.0 | 25.0 | 55.0 | 37.5 | 12.1 | 63.0 | 57.5 | 25.0 |
| 4.0 | 60.0 | 16.0 | 27.0 | | 17.5 | 37.5 | 20.0 | | 52.5 | 45.0 | 18.0 |
| 5.0 | 50.0 | 14.0 | 20.0 | 11.0 | 15.2 | 23.0 | 16.5 | 9.9 | 42.5 | 30.0 | 15.5 |
| 6.0 | 42.5 | | 17.5 | | | 18.0 | 14.7 | | | 22.0 | |
| 7.0 | | 11.5 | | | | 15.9 | | 8.8 | | | |
| 8.0 | | | | | | | | | 20.0 | 17.0 | 12.0 |
| 9.0 | | | | | | | | | | | |
| 10.0 | 18.5 | 9.8 | 13.0 | 8.5 | 11.0 | 12.9 | 11.5 | 8.0 | 16.0 | 15.0 | 11.0 |
| 15.0 | | 8.5 | 11.0 | 8.0 | 9.5 | 10.5 | 9.7 | 7.7 | 12.2 | 12.0 | 9.5 |
| 20.0 | | 8.0 | 9.8 | 7.5 | 8.5 | 9.5 | 9.0 | 7.5 | 11.0 | 10.5 | 9.0 |
| 30.0 | 10.8 | 8.0 | 8.5 | 7.0 | 8.0 | 8.5 | 8.0 | 7.0 | 9.5 | 9.0 | 8.0 |
| Supernatant turbidity after 30 min (100 x Absorbance) | 8.2 | 8.6 | 8.0 | 8.9 | 7.8 | 8.6 | 8.5 | 10.7 | 8.2 | 8.8 | 11.9 |
| Supernatant pH (~22C) | 5.5 | 5.7 | 5.7 | 5.4 | 5.7 | 5.8 | 5.7 | 5.9 | 5.7 | 5.9 | 5.5 |
| Settling rate, cm/min | 2.0 | 4.4 | 3.6 | 7.9 | 4.9 | 2.9 | 4.1 | 8.3 | 2.3 | 2.8 | 5.2 |

Appendix C

Batch settling test data for soils in factory juice and added flocculant (Chapter 5 tests)

Table C. 1 Batch settling test results - Centrifuged factory juice (Rocky Point Mill) with added soil

| Test run | 1 | | | 2 | | |
|--------------------------------|-------------------------------------|-----------|--------------|---------|-----------|--------------|
| Soil | Gluepot | Mt Mackay | Invicta 255B | Gluepot | Mt Mackay | Invicta 255B |
| Soil mass, g | 2.5 | | | | | |
| pH of juice | 5.65 | 5.65 | 5.65 | 5.65 | 5.65 | 5.67 |
| Adjusted pH | 7.86 | 7.8 | 7.86 | 7.81 | 7.87 | 7.94 |
| M.O.L.* volume (mL) | 4.5 | | | | | |
| Flocculant name | Factory flocculant (Sucrafloc 2522) | | | | | |
| Flocculant conc., % | 0.052 | | | | | |
| Floc vol., mL | 1 | | | | | |
| Flocculant dose rate, ppm | 0.5 | | | | | |
| Settling time, min | Interface height, % | | | | | |
| 0 | 105 | 105 | 104 | 104 | 101 | 103 |
| 0.25 | 85 | 95 | 90 | 90 | 85 | 85 |
| 0.5 | 70 | 80 | 80 | 67 | 62.5 | 65 |
| 0.75 | | | 65 | 45 | 40 | 40 |
| 1 | 20 | 50 | 47.5 | 30 | 15.5 | 14 |
| 1.5 | 10.5 | 20 | 19 | 11 | 13.5 | 12 |
| 2 | 10 | 12.5 | 12 | 10.25 | 12.25 | 11 |
| 2.5 | 9.5 | 11.5 | 11.5 | 10 | 11.5 | 10 |
| 5 | 7.5 | 9 | 9.75 | 8 | 9.5 | 8.5 |
| 10 | 7 | 7.5 | 8 | 7 | 8 | 7 |
| 15 | 6.5 | 7 | 7 | 6.5 | 7.5 | 7 |
| 30 | 6 | 6 | 6.5 | 6 | 7 | 6.25 |
| Final mud height, % | 6.0 | 6.0 | 6.5 | 6.0 | 7.0 | 6.3 |
| Initial settling rate+, cm/min | 28.0 | 20.0 | 19.2 | 29.6 | 30.8 | 30.4 |

*Milk of lime (MOL)

+Initial settling rate => settling rate during period 0 to 0.5 min.

Table C. 2 Batch settling test results for sieved factory juice (Rocky Point) with and without added fibre

| Test # | 1 | 2 | 3 | 4 | 5 | 6 |
|-------------------------------|------------------------|-------|-------|-------|-------|-------|
| Added fibre | No | Yes | No | Yes | No | Yes |
| Initial pH | 5.15 | - | - | - | - | 5.20 |
| Adjusted temperature, °C | 76 | 76 | 76 | 76 | 76 | 76 |
| Liming agent | Milk of lime (M.O.L.) | | | | | |
| Adjusted pH | 8.4 | 8.4 | 7.8 | 7.8 | 7.8 | 7.8 |
| Flocculant name (conc.) | Superfloc A2115 (0.1%) | | | | | |
| Dose, ppm on juice | 4.0 | | | | | |
| Settling time, min | Interface height, % | | | | | |
| 0 | 102.0 | 105.0 | 105.0 | 105.0 | 105.0 | 105.0 |
| 0.25 | | | | | 20.0 | 82.0 |
| 0.5 | 20.0 | 60.0 | 18.0 | 55.0 | 14.0 | 55.0 |
| 1 | 14.0 | 28.0 | 13.0 | 28.0 | 12.0 | 28.0 |
| 1.5 | | | | 25.0 | | |
| 2 | | 23.0 | 15.0 | 23.0 | 10.5 | 23.0 |
| 3 | | | | | 10.0 | 22.0 |
| 4 | 11.0 | 20.0 | 11.0 | 21.0 | 9.5 | 20.5 |
| 5 | 10.5 | 20.0 | 10.5 | 21.0 | 9.5 | 20.0 |
| 30 | 9.5 | 18.0 | 10.0 | 20.0 | 9.5 | 20.0 |
| Final mud height, % | 9.5 | 18.0 | 10.0 | 20.0 | 9.5 | 20.0 |
| Clear Juice Turbidity | - | - | 50.2 | 30.5 | 42.5 | 44.1 |
| Initial settling rate, cm/min | 65.6 | 36.0 | 69.6 | 40.0 | 72.8 | 40.0 |

Table C.3 Batch settling test results - Centrifuged factory juice (Rocky Point Mill) with added Gluepot soil for various fibre ratios

| Test# | 1 | 2 | 3 | 4 | 5 |
|--------------------------------------|-------------------------------------|----------|----------|----------|----------|
| Soil | Gluepot | Gluepot | Gluepot | Gluepot | Gluepot |
| Soil mass, g | 2.5 | | | | |
| Fibre:soil ratio | 0 | 0.5 | 1 | 1.5 | 2 |
| Fibre mass, g | 0 | 1.25 | 2.5 | 3.75 | 5 |
| pH of juice | 5.80 | 5.85 | 5.85 | 5.85 | 5.85 |
| Liming pH | 7.9 | 7.96 | 7.82 | 7.94 | 7.85 |
| M.O.L. volume (mL) | 3.0 | | | | |
| Flocculant name | Factory flocculant (Sucrafloc 2522) | | | | |
| Flocculant conc., % | 0.052 | | | | |
| Floc vol., mL | 1.0 | | | | |
| Flocculant dose rate, ppm | 0.5 | | | | |
| Settling time, min | Interface height, % | | | | |
| 0 | 102 | 105 | 105 | 105 | 100 |
| 0.5 | 10 | 50 | 75 | 75 | 70 |
| 1 | 8.5 | 13 | 37.5 | 45 | 41 |
| 1.5 | 7.5 | 11 | 16 | 21 | 22.5 |
| 2 | 7.0 | 10.5 | 14 | 14.5 | 20 |
| 2.5 | 7.0 | 10 | 13 | - | 19 |
| 5 | 6.0 | 8.5 | 11.5 | 15 | 17 |
| 10 | 5.5 | 8.0 | 10.5 | 14.5 | 16.5 |
| 15 | 5.5 | 8.0 | 10.5 | 14 | 16.5 |
| 30 | 5.0 | 8.0 | 10.5 | 14.0 | 16.5 |
| Final mud height, % | 4.9 | 7.6 | 10.0 | 13.3 | 16.5 |
| Initial settling rate, cm/min | 74.8 | 73.6 | 54 | 48 | 47.2 |

Table C. 4 Batch settling test results for centrifuged factory juice with added Gluepot soil and various gypsum

| Test run | 1 | 2 | 3 |
|--------------------------------------|-------------------------------------|----------|----------|
| Soil | Gluepot | Gluepot | Gluepot |
| Soil mass, g | 2.5 | | |
| Gypsum, g | 0 | 1.25 | 2.50 |
| pH of juice | 5.85 | 5.85 | 4.77 |
| Liming pH | 7.88 | 7.88 | 7.83 |
| M.O.L. volume (mL) | 4.0 | 4.0 | 4.0 |
| Flocculant name | Factory flocculant (Sucrafloc 2522) | | |
| Flocculant conc., % | 0.052 | | |
| Floc vol., mL | 1 | | |
| Flocculant dose rate, ppm | 0.5 | | |
| Settling time, min | Interface height, % | | |
| 0 | 102 | 101 | 101 |
| 0.25 | 70 | 70 | 80 |
| 0.5 | 25 | 20 | 47 |
| 0.75 | 10 | 11.5 | 20 |
| 1 | 9 | 10.75 | 14 |
| 1.5 | 8.5 | 9.5 | 12 |
| 2 | 7.75 | 9 | 11 |
| 2.5 | 7 | 8.5 | 10.75 |
| 5 | 6.75 | 7.75 | 9.25 |
| 10 | 6 | 7 | 8.5 |
| 15 | 6 | 7 | 8 |
| 30 | 5.75 | 6.75 | 8 |
| Final mud height, % | 5.6 | 6.7 | 7.9 |
| Initial settling rate, cm/min | 61.6 | 64.8 | 43.2 |