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

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A B S T R A C T
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.

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1. 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 flocculated 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 50 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% 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 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.

2. Materials and methods

2.1. 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 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 larger soil aggregates were broken down to form fine loose soil using a Retsch BB200 jaw crusher prior to mixing to form composites.

Chemicals, CaCl$_2$·2H$_2$O (Chem Supply, Gillman, Australia), MgCl$_2$·6H$_2$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 CaCl$_2$·2H$_2$O and 31.37 g of MgCl$_2$·6H$_2$O in 1000 mL of Milli-Q water.

2.2. Methods

2.2.1. 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$_\alpha$ 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.

2.2.2. 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 min, 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 × 1012 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.

2.2.3. 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 min 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 min intervals over a 30 min period. A plot of mud interface height versus

| 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 3522A | Mackay  | 7.89                | 1–20 (Poor)                                         |
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 ±0.25%.

### 2.2.4. Measurement of physico-chemical properties of clay constituents

The physico-chemical properties of clay constituents (electrokinetic potential [Zeta potential, 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 Zeta potential 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 electrokinetic potential were conducted in electrolytes of Na, K, Ca, and Mg chlorides and a mixture of these metal ions (the mole ratio of Na⁺, K⁺, Ca²⁺ and Mg²⁺ was 3.4:67.2:13.1:16.2) at different ionic strengths. The average error for the determination of the electrokinetic potential is ±5%.

The specific surface areas of the clay fractions (below 2 μm) 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 calculated by the method of Zbik and Smart (1998). The average error for the measurement of the specific surface areas is ±5%.

### 3. Results and discussion

#### 3.1. 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. Fig. 1 shows the XRD spectra of the three soil samples. Gluepot 3522A 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.

Invicta 255B consists of quartz, potassic and calciumfeldspars, 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 (Fig. 1), the Mt Mackay sample contains quartz, potassic and calciumfeldspars, 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 2).

#### 3.2. Electron microscopy

Figs. 2–4 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 (Fig. 2A) 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 and 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 Fig. 2B. The EDX spectrum (Fig. 2C) 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.

#### Table 2

Composition of soils (wt%) by bulk XRD analysis.

| Mineral type     | Gluepot 3522A | Invicta 255B | Mt Mackay |
|------------------|---------------|--------------|-----------|
| 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       |

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Fig. 2. Results from electron microscope investigation of Gluepot 3522A. A- TEM micrograph shows poorly crystalline kaolinite platelets displaying pseudo-hexagonal symmetry, irregular smectite flakes and film of amorphous extremely dispersed particles are present. B- SEM micrograph showing continuous film of submicron flexible smectite flakes and kaolinite pseudo-hexagonal platelets covered mostly by an amorphous blanket. C- EDX result indicates the presence of Na, Al, Si, Ti, and Fe elements; the Al to Si ratio is typical of 2:1 sheet silicates like smectite and illite.

Fig. 3. Results from electron microscope investigation of Invicta 255B. A, TEM micrograph of poorly crystalline kaolinite platelets displaying pseudo-hexagonal symmetry, and irregular sheets of illite. B, SEM micrograph displays continuous blanket of irregular illite sheets and kaolinite pseudo-hexagonal crystals. C, EDX result indicates the presence of Na, Al, Si, and Fe elements; the Al to Si ratio is typical of 2:1 sheet silicates like illite.
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 (Fig. 2A and B) are most dispersed in comparison to the other two soils.

The TEM micrograph of the Invicta 255B sample (Fig. 3A) 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 of ~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 [Fig. 3A]. Some halloysite in a twisted tube arrangement were observed to form complex aggregates up to 500 nm in diameter. The TEM micrograph for the Invicta sample (Fig. 3B) displays a continuous blanket of irregular shaped illite sheets, kaolinite pseudo-hexagonal crystals and irregular shaped ‘probably’ illite platelets (Fig. 3A). The EDX results presented in Fig. 3C indicate the presence of Na, Al, Si, and Fe elements, the Al to Si ratio is most similar to 2:1 sheet silicates.

The TEM of Mt. Mackay (Fig. 4A) 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. 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 in situ 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 (Fig. 1). 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 to 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 (Fig. 4B) shows a mixture of grains (up to 5 μm in diameter) and a dispersed phase which is composed mostly of kaolinite. C, EDX results show almost equal proportion of Al and Si peak heights which is typical for kaolinite-type 1:1 sheet silicate composition and the presence of Na, Al, Si, K, and Fe elements.

Fig. 4. Results from electron microscope investigation of Mt Mackay. A, TEM micrograph displays kaolinite crystals having pseudo-hexagonal symmetry, larger gibbsite crystal and tubular halloysite which is probably transforming to gibbsite. B, SEM micrograph shows mixture of larger, up to 5 μm in diameter grains and dispersed phase which are composed mostly of kaolinite. C, EDX results show almost equal proportion of Al and Si peak heights which is typical for kaolinite-type 1:1 sheet silicate composition and the presence of Na, Al, Si, K, and Fe elements.
3.3. 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 (Fig. 1) 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 (Fig. 1), 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).

Fig. 5 shows the CEC of the three soil samples. High CEC corresponds with high specific surface area and amorphous content (Table 2). 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.

Major exchangeable capacity of the cations of the soil samples was in the following order, Ca²⁺ > Mg²⁺ > Na⁺ > K⁺ (Fig. 5). 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 rule, settling profiles of the soils in a synthetic juice solution were obtained (Fig. 6). 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 1 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.

3.4. 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 electrokinetic potential, 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.

Fig. 7 shows that the electrokinetic potential 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 electrokinetic potential 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, electrokinetic potential 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 electrokinetic potential of the soils in various environments is presented in Fig. 7. For all the soils, the zeta potential 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 zeta potential value in the broad ionic strength of NaCl range studied. The sample from Mt. Mackay which contains kaolinite displays a strong correlation between the zeta potential and increase in ionic strength. In general, for divalent cations, when the ionic strength increases, the zeta potential 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 zeta potential 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 electrokinetic potential 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. The lack of a significant reduction in the magnitude of the Zeta potential 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 Zeta potential towards zero. The lack of significant influence of the ionic strength on the Zeta potential 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 (Fig. 8A). This structural network is better visualized through tomographic reconstruction as shown in Fig. 8B. 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 (Zhik et al., 2014, 2015). With such micro-structures, particles are locked into a network and do not behave like individual crystals; rather, they behave like a gel.

Zeta potential 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 electrokinetic potential (i.e., Zeta potential) 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 Zeta potential. Such unusual effect, virtually unknown in colloid science, was described by (Dukhin, 2007) when observing clear transition of 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 Zeta potential 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.

4. Conclusion

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 electrokinetic potential 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.

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