SOME ASPECTS OF CALCIUM PHOSPHATE CHEMISTRY IN SUGARCANE CLARIFICATION

By

WOS DOHERTY, DW RACKEMANN
Sugar Research and Innovation,
Queensland University of Technology, Brisbane, Qld
w.doherty@qut.edu.au

KEYWORDS: Clarification Chemistry, Liming, Calcium Phosphate, Colorimetric Method, Absorbance.

Abstract

THIS PAPER reviews some aspects of calcium phosphate chemistry since phosphate in juice is an important parameter in all sugar juice clarification systems. It uses basic concepts to try and explain the observed differences in clarification performance obtained with various liming techniques. The paper also examines the current colorimetric method used for the determination of phosphate in sugar juice. In this method, a phosphomolybdate blue complex formed due to the addition of a dye is measured at 660 nm. Unfortunately, at this wavelength there is interference of the colour arising from within the juice and results in the underestimation of the amount of soluble inorganic phosphate content of juice. It is suggested that phosphate analysis be conducted at the higher wavelength of 875 nm where the interference of the juice colour is minimised.

Introduction

While the basic chemistry of sugar juice clarification is understood, details of some of the interactions between various impurities remain unknown. The main reason stems from the complexity of the interactions between constituents of the juice and inconsistency in juice composition. Juice composition depends on a variety of conditions such as the cane variety, age of the cane, geographical location and growing conditions, as well as on the harvesting and milling processes. The work by Naidoo and Lionnet (2000) on South African sugarcane clearly highlights the effect of cane variety and agricultural factors (e.g. cane age, ratoon number, rainfed and irrigation) on colour, phosphate, silica, calcium, potassium and sulphate contents of juice. Cane variety and geographical location were found to be statistically significant (5% level) on colour, gums and inorganic phosphate. Geographical location was also statistically significant (5% level) on calcium and potassium, while cane variety was weakly statistically significant (10% level) with these elements.

The phosphate level in sugar juice is a key parameter in the success of the clarification process by defecation. Juices with insufficient phosphate (<~300 mg/L as P₂O₅) generally clarify poorly and produce hazy clarified juices (Deben, 1976; Steindl, 1998). Factory experience has shown that stale cane normally clarifies better when phosphate is added to juice prior to clarification (Dymond, 1950). However, excessive phosphate in the clarified juice impacts negatively on sugar filterability (Bennett and Regnauth, 1960) and
increases scaling of the evaporators. Conversely, if too much lime is added or the mixed juice contains high levels of residual calcium, the clarified juice becomes dark, increased scaling occurs in the evaporators and pans, ash in sugar increases, and molasses exhaustion is less efficient.

In many situations where the calcium level in mixed juice is adequate and the pH is appropriate for maximum calcium phosphate precipitation, the variable that requires adjustment is the phosphate content of juice. Steindl (1998) found from a phosphate (as P$_2$O$_5$) survey conducted in a factory over a 24-hour period that the level in mixed juice varied between 64 mg/L and 414 mg/L P$_2$O$_5$. The weighted average was 197 mg/L P$_2$O$_5$, implying that extra phosphate should be added to mixed juice for optimum clarification performance. However, it is known that certain juice types may contain far in excess of the normal requirement of inorganic phosphate and yet clarify poorly. The work reported here provides information to the process chemist on some aspects of phosphate chemistry in juice clarification. This paper also provides some preliminary work by Doherty and Rackemann (2008) that suggests that the current colorimetric method used for the determination of soluble inorganic phosphate in sugarcane juice is inadequate.

**Calcium phosphate precipitation**

Sugarcane juice contains soluble inorganic phosphates, which, after the addition of lime/lime saccharate to increase the pH to prevent sucrose inversion, form insoluble calcium phosphate phases. Calcium phosphate particles are involved in the formation of flocs, and hence are pivotal in the clarification process.

In aqueous solution, the main reactions that occur to produce calcium phosphates are:

\[ \text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- \rightarrow \text{Ca} (\text{H}_2\text{PO}_4)_2 \]  
(1) monocalcium phosphate, MCP

\[ \text{Ca}^{2+} + \text{HPO}_4^{2-} \rightarrow \text{CaHPO}_4 \]  
(2) dicalcium phosphate, DCP

DCP can be present as dicalcium phosphate dihydrate (DCPD) or dicalcium phosphate anhydrate, (DCPA).

\[ 3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2 \]  
(3) tricalcium phosphate, TCP

\[ 2\text{CaHPO}_4 + 2\text{Ca}_3(\text{PO}_4)_2 \rightarrow \text{Ca}_8\text{H}_2(\text{PO}_4)_6 \]  
(4) octacalcium phosphate, OCP

\[ \text{Ca}_3(\text{PO}_4)_2 + 2\text{Ca}^{2+} + \text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{OH} + 2\text{H}^+ \]  
(5) hydroxyapatite, HAP

In addition, tetracalcium phosphate [Ca$_4$(PO$_4$)$_2$OH$_2$] is formed.

Because some of these reactions are sequential, i.e. some reaction products participate as reactants in further reactions, the distribution of calcium phosphate products depend on the kinetics of each reaction.

Thermodynamically, HAP is the most stable form of the calcium phosphate phases (Kibabezyc et al., 1988), however, it has been found experimentally that the calcium to phosphate ratio is 1.45, significantly lower than the expected ratio of 1.67 for HAP (Nancollas et al., 1979). This is because of differences in the stoichiometric ratios between calcium and phosphorus lattice ions in the HAP structure.
Figure 1 shows the calcium ion concentration versus pH of an aqueous solution saturated with calcium phosphate. At pH ~7.8 (the normal pH of limed cane juice in Australian sugar mills), HAP is the most stable followed by TCP. However in limed factory juices amorphous TCP is the predominant phase formed in the clarifier.

The effectiveness of the juice clarification process would be considerably increased if a larger proportion of HAP was formed instead of TCP since HAP would remove a significant proportion of proteins and consequently reduce the formation of melanoidins. The challenge is for researchers to develop conditions during clarification conducive for the formation of HAP.

Flocculation

Particles suspended in solution are subject to a number of different forces. These include:

Gravity, the force which separates particles according to density, with the densest suspended solids moving towards the bottom of the vessel in which they are suspended.

Van der Waals forces are short range attractive forces between suspended particles. These forces tend to draw suspended particles towards each other.

Brownian forces, dependent on temperature, impart motion to colloidal particles through collision of particles and molecules of the suspending medium. Electrostatic repulsion between charged particles tends to keep the particles apart, though shearing has an opposite effect.

Coagulation of the suspended particles occurs when the forces of attraction exceed the forces of repulsion. However, the major physical reaction that occurs during clarification is the enhanced flocculation of micro-particles by the addition of an anionic copolymer flocculant. There are three mechanistic pathways possible for the binding of such a polymer to a particle. These are (a) depletion flocculation; (b) charge annihilation/charge patch
flocculation; and (c) bridging flocculation. In bridging flocculation, the high molecular weight polymer acts as long threads connecting particles together. The bridges may form through electrostatic attraction, hydrogen bonding or van der Waals forces. In sugarcane juice, anionic acrylamide-sodium acrylate copolymer is used to achieve flocculation (Fellows and Doherty, 2006). While it should be expected that electrostatic repulsion would prevent flocculation due to the close proximity of negatively charged juice particles, it has been established that cationic bridging through calcium ions bonding with the ionic acrylate group occurs (Crees et al., 1991). Large floc structures are formed by this process.

Muhle and Domacsch (1990) noted that the strength of flocs formed by bridging flocculation depends on the number of bridges formed between mud particles, the free segment/surface adsorption energy and the fraction of polymer segments in the adsorbed state. Therefore, the efficiency of bridging is a function of several physico-chemical parameters, including the molecular weight of the polymer, the charge density of the polymer, the concentration of the polymer, the size and charge of the juice particles, the juice pH, and juice temperature. In addition, the speed of flocculation is directly proportional to the velocity gradient in the solution and it is known that the type, speed and duration of agitation have a marked effect on floc structure (Peng and Williams, 1993).

Effect of liming technique on calcium phosphate flocs

As reported by Doherty et al. (2002), and illustrated in Table 1, lower turbidity is achieved with lime saccharate rather than with milk of lime. The mean value of turbidity (per 100 brix) for liming with saccharate is 27.9 and 62.3 for liming with milk of lime, and from the (two tailed) t-test on paired samples the difference is highly significant although greater variability was observed for the milk of lime results.

The mean value for phosphate (as P₂O₅ mg/L on brix) with saccharate is 16.1 and 35.6 with liming with milk of lime, and from the (two tailed) t-test on paired samples the difference is highly significant. This implies that lime saccharate reduces the amount of suspended solids in clarified juice and also reduces the phosphate content. Why?

The process chemist is aware that the ratio of syrup to lime in lime saccharate has a strong bearing on clarified juice turbidity – as turbidity decreases with increase in syrup to lime ratio. The question is, how can we account for these occurrences? Why does syrup added to lime to form saccharate influence the nature of calcium phosphate, the material primarily responsible for the removal of suspended solids?

These observed differences can be explained by considering the nature of the calcium phosphate formed and the physico-chemical interactions that occur during clarification. When lime/milk of lime is mixed with syrup, the calcium in the lime interacts with sucrose to form mono-, di- and tri-calcium saccharate.

The predominant phase is dependent on the reaction conditions. Of the three, mono-calcium saccharate is the most soluble form hence providing a higher proportion of calcium ions readily available for interaction with inorganic phosphate ions. In order to have the mono-calcium saccharate as the predominant phase, a sucrose to calcium molar ratio of 7:1 is recommended.

So, any ratio less than this would have a mixture of saccharates with varying degrees of available calcium ions. As lime saccharate provides more available calcium ions than milk of lime due to enhanced solubility, more calcium phosphate would be precipitated, resulting in reduced amounts of phosphate in clarified juice.
The suspended particles in juice generally carry a negative charge. For coagulation of the particles to take place the overall charge on the particles has to be neutralised to near zero charge. Calcium phosphate forms when milk of lime/lime saccharate is added to the juice. The particles are positively charged and form flocs which entrapped suspended solids. When lime saccharate (with high syrup to lime ratios) is added to juice, spontaneous precipitation of fine calcium phosphate particles occurs because of the readily available calcium ions from the highly soluble mono-calcium saccharate. With milk of lime or with lime saccharate mixtures with low syrup to lime ratios, the proportion of readily available calcium ions is relatively small, resulting in the formation of bigger calcium phosphate particles. The calcium phosphate particles formed with lime saccharate would therefore have higher charge to mass ratio than the particles obtained with milk of lime (or lime saccharate mixtures with low syrup to lime ratios). As such, they are more effective in neutralising the negatively charged suspended particles in juice. This would invariably increase the rate of collision between the small sized juice particles, thereby forming larger floc aggregates that can more readily trap more particles. This will then lead to reduced juice turbidity.

**Table 1**—Results for clarified juices (Doherty et al., 2002).

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Type of lime solution</th>
<th>Turbidity @900 nm</th>
<th>Turbidity per 100 brix</th>
<th>Phosphate (as P₂O₅), mg/L on brix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Intermediate* liming with saccharate</td>
<td>6.3</td>
<td>33.0</td>
<td>31.9</td>
</tr>
<tr>
<td>1</td>
<td>Intermediate liming with milk of lime</td>
<td>20.8</td>
<td>112.1</td>
<td>69.0</td>
</tr>
<tr>
<td>1</td>
<td>Hot** liming with saccharate</td>
<td>5.5</td>
<td>28.4</td>
<td>7.2</td>
</tr>
<tr>
<td>1</td>
<td>Hot liming with milk of lime</td>
<td>5.1</td>
<td>27.1</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>Intermediate liming saccharate</td>
<td>7.3</td>
<td>39.6</td>
<td>10.9</td>
</tr>
<tr>
<td>2</td>
<td>Intermediate liming with milk of lime</td>
<td>11.4</td>
<td>60.4</td>
<td>28.6</td>
</tr>
<tr>
<td>2</td>
<td>Hot liming with saccharate</td>
<td>4.4</td>
<td>22.0</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>Hot liming with milk of lime</td>
<td>4.0</td>
<td>20.0</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>Intermediate liming with milk of lime</td>
<td>11.2</td>
<td>59.8</td>
<td>50.7</td>
</tr>
<tr>
<td>3</td>
<td>Intermediate liming with saccharate</td>
<td>4.9</td>
<td>26.1</td>
<td>17.1</td>
</tr>
<tr>
<td>3</td>
<td>Hot liming with milk of lime</td>
<td>14.3</td>
<td>71.3</td>
<td>24.9</td>
</tr>
<tr>
<td>3</td>
<td>Hot liming with saccharate</td>
<td>5.5</td>
<td>26.6</td>
<td>9.2</td>
</tr>
<tr>
<td>4</td>
<td>Hot liming with milk of lime</td>
<td>15.6</td>
<td>85.6</td>
<td>67.5</td>
</tr>
<tr>
<td>4</td>
<td>Hot liming with saccharate</td>
<td>3.5</td>
<td>19.3</td>
<td>34.2</td>
</tr>
</tbody>
</table>

* Primary juice (at 76°C), lime saccharate/milk of lime to pH = 7.8, heat to 100°C flocculate and clarify in settling tube. **Primary juice (at 76°C), heat to 100°C, add lime saccharate/milk of lime to pH = 7.8, flocculate and clarify in settling tube.

Studies on calcium phosphate flocs indicated that liming with saccharate gave larger and looser flocs than liming with milk of lime (Doherty et al., 2002), and therefore is expected to be better for removing impurities through physical entrapment and adsorption. In addition, the reduced settling rate obtained with saccharate aids the ‘sweeping’ of suspended solids. A probable explanation for these effects is that the calcium phosphate particles within the floc aggregate formed with lime saccharate are relatively small in size and are more likely to form a loose floc structure due to electrostatic repulsion forces.

**Turbidity versus clarified juice phosphate**

As has been stated and is generally accepted, clarified juice with low turbidity is achieved when sufficient phosphate is present in the mixed juice. Some sugar mills link their
turbidity output to a phosphate pump so that phosphoric acid is added to mixed juice when the turbidity outputs reach unacceptably high levels.

Recently, studies were conducted in a mill, where an on-line phosphate device was used to monitor the level of phosphate in clarified juice, so that comparisons could be made with turbidity outputs. Figure 2 presents the turbidity and phosphate results.

There is no correlation between turbidity and the phosphate content of the clarified juice. For this set of results, the addition of phosphoric acid did not reduce the turbidity of the clarified juice. In fact, its addition increased the level of phosphate in clarified juice which impacts on filterability and scale formation in the evaporators.

In this instance, it is more than likely that the mixed juice contained sufficient inorganic phosphate to achieve satisfactory clarification.

So, it would be beneficial for the process chemist to have at his disposal an on-line device to monitor phosphate level (as well as calcium) in mixed juices.

In situations where there is excessive phosphate in juice but poor clarification, the option open to the process chemist is either to increase the liming pH or to add, if available, soluble calcium salts i.e. calcium chloride.

**Phosphomolybdate method for the determination of inorganic phosphate in juice**

Taylor and Miller (1914) introduced a method for the colorimetric determination of inorganic phosphate. This method has been modified over the years and is the primary method used for the determination of phosphate in aqueous solutions.
The principle of the method involves the condensation of orthophosphate and molybdic acid to form phosphomolydic acid, which on reduction produces a blue colour complex. The intensity of the blue colour is proportional to the amount of phosphate in a sample.

The Australian sugar industry uses the method for the determination of total (i.e. acid-soluble inorganic phosphate) and soluble (i.e. water-soluble inorganic phosphate) phosphate (BSES, 2001).

If the amount of soluble inorganic phosphate is being determined, no pH adjustment of the juice prior to analysis is required.

However, if the total amount of phosphate is being determined, the pH of the juice is adjusted to 4.0 by adding sulphuric acid. In the current method, the juice is then filtered under vacuum with acid-washed Supercel.

Known amounts of acid, molybdate, amidol (2, 4-diaminophenol dihydrochloride) and sodium metabisulphite are added to the filtered solution and the absorbance is measured at 660 nm after about 10 min to allow full development of the blue-coloured complex.

Berenblum and Chain (1938) reported on the class of substances which interfere with the colorimetric determination of phosphates. These include:
- Compounds which alter the acidity of the solution. These are acids, alkalis and buffering salts.
- Compounds which form molybdenum complexes which are difficult to reduce and therefore reduce the amount of molybdic acid available for reduction. These compounds include oxalates, fluorides, and citrates.
- Compounds which reduce the concentration of the reducing agent e.g. nitrites.

It is reported in the modified method used by the Australian sugar industry that the presence of low concentrations of organo-phosphorus compounds and cations and anions found in cane juice do not interfere to a significant extent with the phosphate determination (BSES, 2001).

As the determination of phosphate is a colorimetric method, it would suggest that the colour of the cane juice could add to the error of the absolute phosphate value obtained.

As the colour of the cane juice varies with cane variety and location, it was necessary to re-examine whether the measurement of the blue complex at 660 nm was the most suitable wavelength for the determination of phosphate in cane juice, particularly with clarified juices.

**Absorbance of colour in juice**

A UV scan of a clarified juice solution treated for phosphate determination (i.e. colour reagents added to juice) was carried out over the range 400 to 900 nm.

The absorbance of the molybdate blue complex is shown in Figure 3. The absorption reaches a maximum at around 725 nm (not at 660 nm) and thereafter plateaus. Similar results were obtained with a standard phosphate solution.

The absorption curve of untreated clarified juice (Figure 4) shows that absorption decreases with wavelength. Comparing Figures 3 and 4 shows that interference of colour is more significant at 660 nm than at 800–900 nm.

Based on this, it was decided to conduct tests using sensors with 660 nm and 875 nm wavelengths.
Fig. 3—The absorbance of the phosphomolybdate colour complex in clarified juice.

Fig. 4—Absorption curve of untreated clarified sugar juice.

Analysis of phosphate in mixed and clarified juices

Samples of mixed juices and clarified juices were collected from a number of Australian sugar mills and examined with the two sensors. The results are shown in Table 2 and indicate differences in the phosphate level between the two sensors. The differences in
the measured phosphate levels varied between 8% and 15% for mixed juice samples and between 10% and 30% for clarified juice samples. While the tests were not exhaustive, these results suggest that the current BSES method for phosphate determination using a 660 nm wavelength underestimates the phosphate level in cane juice. Using the current BSES method for phosphate determination, results would become increasingly important if measurements are used for factory processing control, which is not the case at present in most Australian factories.

The results of Table 2 also show a wide variation in phosphate levels in cane juice over the various milling districts. A number of sugar factories clearly had phosphate levels far below the recommended P$_2$O$_5$ value of 300 mg/L.

### Table 2—Variation of soluble phosphate concentrations (as P$_2$O$_5$, mg/L) of cane juices.

<table>
<thead>
<tr>
<th>Factory</th>
<th>Mixed juice</th>
<th>Clarified juice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>660 nm</td>
<td>875 nm</td>
</tr>
<tr>
<td>A</td>
<td>233</td>
<td>264</td>
</tr>
<tr>
<td>B</td>
<td>129</td>
<td>152</td>
</tr>
<tr>
<td>C</td>
<td>538</td>
<td>593</td>
</tr>
<tr>
<td>D</td>
<td>204</td>
<td>222</td>
</tr>
<tr>
<td>F</td>
<td>135</td>
<td>156</td>
</tr>
<tr>
<td>G</td>
<td>189</td>
<td>207</td>
</tr>
<tr>
<td>H</td>
<td>430</td>
<td>485</td>
</tr>
<tr>
<td>I</td>
<td>170</td>
<td>191</td>
</tr>
<tr>
<td>J</td>
<td>491</td>
<td>528</td>
</tr>
<tr>
<td>K</td>
<td>141</td>
<td>150</td>
</tr>
</tbody>
</table>

### Conclusion

The success of a clarification process depends on a fundamental understanding of the influential role played by soluble inorganic phosphate.

Although the role of soluble inorganic phosphate is very important in the understanding of the mechanisms of clarification, the disregard of the role of the physico-chemical nature of juice, the chemical and physical reactions during clarification (including the reactions of organic salts and proteins, degradation of sucrose and reducing and polymerisation reactions), and the role of calcium would result in the process chemist being unable to maintain and improve productivity and produce sugar with increased compliance with premium grade criteria.

The use of turbidity alone to monitor juice quality completely disregards the role of soluble impurities in sugar manufacture.

### Acknowledgements

The financial support of the Sugar Research Development Corporation and a syndicate of Australian mills are acknowledged. The authors wish to thank James Whyte of MEP instruments for evaluating both sensors.

### REFERENCES


