

Improved Sugar Cane Juice Clarification by Understanding Calcium Oxide-Phosphate-Sucrose Systems

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S Supporting Information

ABSTRACT: It is accepted that the efficiency of sugar cane clarification is closely linked with sugar juice composition (including suspended or insoluble impurities), the inorganic phosphate content, the liming condition and type, and the interactions between the juice components. These interactions are not well understood, particularly those between calcium, phosphate, and sucrose in sugar cane juice. Studies have been conducted on calcium oxide (CaO)/phosphate/sucrose systems in both synthetic and factory juices to provide further information on the defecation process (i.e., simple liming to effect impurity removal) and to identify an effective clarification process that would result in reduced scaling of sugar factory evaporators, pans, and centrifugals. Results have shown that a two-stage process involving the addition of lime saccharate to a set juice pH followed by the addition of sodium hydroxide to a final juice pH or a similar two-stage process where the order of addition of the alkalis is reversed prior to clarification reduces the impurity loading of the clarified juice compared to that of the clarified juice obtained by the conventional defecation process. The treatment process showed reductions in CaO (27% to 50%) and MgO (up to 20%) in clarified juices with no apparent loss in juice clarity or increase in residence time of the mud particles compared to those in the conventional process. There was also a reduction in the SiO₂ content. However, the disadvantage of this process is the significant increase in the Na₂O content.

KEYWORDS: Calcium phosphate, sugar cane, clarification, clarified juice, defecation

INTRODUCTION

Raw cane juice and its subsequent form (mixed juice, MJ) are stable suspensions that contain large numbers of suspended particles. The soluble components of juice include sucrose, glucose, fructose, proteins, oligosaccharides, polysaccharides, organic acids, amino acids, and salts. The suspended material largely consists of bagacillo (a lignocellulosic byproduct), soil, sand, clay, starch, waxes, fats, and gums. The relative amounts of the components in both phases depend on the variety, maturity, and condition of the cane plant, soil type, and the harvesting method and conditions. In general, the composition of the dispersed phase is not critically important in terms of clarification behavior. Rather, it is the nature or state of the surface of the suspended particles in the juice that determines the overall behavior of the juice. The aims of the clarification process are to remove suspended and colloidal particles, remove nonsucrose impurities (e.g., proteins, polysaccharides and inorganic materials), and raise the juice pH to minimize inversion of sucrose during subsequent processing. Clarification affects juice filterability, heat transfer coefficients of evaporators, sucrose crystallization, and the quality and quantity of raw sugar produced. It affects the color, crystal morphology, crystal content, ash, and polysaccharide content of raw sugar. In the raw sugar refinery, poor filtration and reduced refined sugar yields can be traced back to the poor clarification of mixed juice in sugar mills. Clarifier performance and clarified juice quality affect factory throughput, molasses purity, and raw sugar quality.

From the 1960s to early 1980s research in Australia on the utilization of flocculants and optimization of clarifier design led to considerable improvements in settling rates of the juice

particles and the clarified juice quality.¹ The design improvements have led to significant increases in the capacity to size ratio of Australia's Sugar Research Institute (SRI) clarifiers as compared to multitray clarifiers. The decrease in juice residence times has been remarkable; up to 3.5 h residence time for multitray clarifiers has been reduced to as low as 20 min for the SRI clarifier.¹ However, the effectiveness of the conventional clarification process depends, to a certain extent, on the nature and type of the calcium phosphate precipitated.² The formation of calcium phosphate from supersaturated solutions has been widely studied and is readily accessible in the literature.^{3–12} The nature of the calcium phosphate phases formed in sugar juice depends on (a) calcium and phosphate ion concentrations, (b) magnesium ions, (c) the pH of the solution, and (d) the presence of impurities such as organic acids, and carbonates.^{4,5,13–17} Thus, the efficiency of sugar juice clarification is closely linked with the juice composition (including suspended or insoluble impurities), the inorganic phosphate content in the mixed juice, the liming conditions, and interactions between juice components at high pH and temperatures. The addition of lime to the juice, with heating, precipitates both inorganic (mainly calcium phosphate) and organic calcium salts.

The mode of clarification in many sugar cane factories around the world is simple defecation. Lime addition may occur as milk of lime or lime saccharate (lime dissolved in juice or syrup). In Australia, the process is based on the addition of lime as lime

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saccharate, after primary heating of the juice to 72–76 °C, to raise the pH of the juice to approximately 7.8–8.0. The juice is then heated further to about 102 to 105 °C and is flashed to the atmosphere before entering the clarifier. Polyacrylamide flocculant is added to the juice in the feed launder of the clarifier, and the combined action of the flocculant and precipitating calcium phosphates form large flocs that settle out in the clarifier. Because the phosphate level in the juice is particularly important, phosphate can be added to the mixed juice, prior to heating, in the form of superphosphate fertilizer or phosphoric acid. The major disadvantage of using lime or lime saccharate to raise juice pH for calcium phosphate precipitation is the very high levels of CaO in clarified juices arising not only from the added lime but also from the endogenous calcium in raw juice. Excessive CaO levels in clarified juices affects clarified juice quality which in turn affects scaling of the evaporators, pans and fugals, and molasses exhaustion. In order to address this issue and get a better and improved understanding of calcium phosphate chemistry in sugar solutions, laboratory studies have been carried out on the formation of calcium phosphate in synthetic and factory juices in the presence of different bases.

MATERIALS AND METHODS

Materials. Concentrated solutions of sodium hydroxide, ammonium hydroxide, phosphoric acid, aconitic acid, and hydrochloric acid were prepared with analytical reagent chemicals (Merck, Victoria, Australia) and Millipore deionized water. Lime saccharate was prepared by mixing 100 g of 200 g/kg solution of analytical grade calcium oxide (APS Specialty Chemicals, Brisbane, Australia) and 100 g of 65 mass% sucrose. Sucrose was an analytical grade reagent (Sigma-Aldrich, Sydney, Australia).

Factory primary juice (i.e., MJ after the primary heaters) that had been previously stored frozen was defrosted and filtered through 0.45 μm filter prior to use. Samples of primary juices were obtained from five Australian sugar factories located in different sugar cane growing districts. The pH of both the synthetic and factory juices was measured on a Hanna Model HI 9025 m with the high temperature probe Uteck EC-FG-7350401B.

The inorganic ions were analyzed using a Varian Vista-MPX CCD simultaneous inductively coupled argon plasma optical emission spectrometer (ICP-OES). To reduce the interference of the sugar organic matrix, it was necessary to dilute the samples to a sucrose concentration of ~1 mass%.

Methods. The experimental procedure has been divided into three stages in order to build a better understanding of calcium oxide/phosphate/sucrose systems that would impact on scale-forming ions in clarified sugar cane juice. The first stage of the laboratory investigation was to determine in some detail the amounts of residual CaO and P₂O₅ remaining after treating different juices, at selected temperatures, with different alkalis. This stage of the work was also to provide insights on the solution chemistry of calcium phosphate under various processing conditions. The second stage of the investigation on filtered primary juice built on the information obtained in the first stage and was aimed at establishing whether a two-stage alkali treatment would result in reduced amounts CaO and P₂O₅ in the treated juices. The third stage of the investigation was a practical demonstration of the two-stage treatment process in factory juice clarification.

Investigations with Synthetic Juices. To examine the effect of different alkalis on calcium phosphate precipitation, experiments were conducted on synthetic juices using lime saccharate, sodium hydroxide and ammonium hydroxide at different temperatures and pH values. The compositions of the juices labeled A, B, C, D, and E are shown in Table 1.

Table 1. Composition of Synthetic Juices

constituents	juice A	juice B	juice C	juice D	juice E
	pH 5.7	pH 4.4	pH 4.4	pH 3.0	pH 5.8
CaO (mg/L)	393	257	257	60	399
P ₂ O ₅ (mg/L)	318	319	193	319	319
aconitic acid (mg/L)	1000	1000	1000	1000	1000
sucrose (mass%)	12	12	12	12	0

As aconitic acid is by far the most predominant organic acid in juice and constitutes about two-thirds of the organic acid content, it was used in the study to model the total organic acids present in juice. Juice A is regarded as an ideal juice since it contains not only sufficient amounts of CaO and P₂O₅ to form Ca₃(PO₄)₂, but contains sufficient amount of inorganic phosphate necessary for good clarification.^{11,18}

The experimental form was a 5 × 3 × 3 × 3 × 2 design with 5 synthetic juices, 3 bases (lime saccharate, sodium hydroxide, and ammonium hydroxide), 3 pH values (7.0, 7.5, and 8.0), and 3 temperatures (50, 76, and 90 °C). The experiments were performed in duplicate. The treated synthetic juices were filtered through a 0.45 μm filter and the filtrate acidified with HCl and stored frozen prior to analysis by ICP-OES for Ca and P. The experimental error involved in the precipitation studies was less than 5%. The error was determined by estimating the confidence interval of the standard deviation based on pooled duplicate measurements.¹⁹ The precipitates obtained with juice A at pH 8 were washed with water and dried in a vacuum oven to a constant weight and the weight noted. The proportions of Ca and P in the precipitates were also determined by ICP-OES after dissolution in dilute HNO₃. This was to establish the composition of the primary precipitate in juice A.

Investigations with Filtered Primary Juice. Similar calcium phosphate precipitation experiments as those outlined for the synthetic juices were carried out with a filtered factory primary juice. The factory juice had been previously stored frozen. To remove the effect of suspended and coagulated particles (which will vary from one aliquot to the other) on the amount of precipitate formed, the juice was filtered through a Whatman No. 52 filter paper. The alkalis examined were lime saccharate, sodium hydroxide solution, and ammonium hydroxide solution, a two-stage process involving adding lime saccharate to a heated juice to a set pH and then adding sodium hydroxide solution/ammonium hydroxide solution to the final pH. The precipitates were washed with distilled water and dried in a vacuum oven to a constant weight. The experiments were performed in duplicate and the results recorded as average values.

The amounts of free calcium ions in the filtrate after the removal of the precipitated residue were determined with a calcium electrode (a Radiometer ion-selective membrane electrode type ISE25Ca) and 1 M KCl calomel reference electrode.

Investigations with Factory Primary Juices. For these series of experiments, samples of factory primary juices were clarified with the two-stage addition process of lime saccharate followed by sodium hydroxide and sodium hydroxide followed by lime saccharate at 3 pH values (7.5, 7.8, and 8.0) and two liming temperatures (76 and 90 °C), boiled and settled in standard settling tubes [each tube of 1 L capacity with dimension of 460 mm (h) × 55 mm (i.d.)] in a SRI-designed heated illuminated clarification box. A dose equivalent to 3 mg/kg of superfloc (a polyacrylamide-co-sodium acrylate flocculant; Cytac, Australia) was applied before settling. As the mud was unstirred, the mud heights were not indicative of values obtained in commercial clarifiers. Control experiments were also conducted with lime saccharate at pH 7.8 and 76 °C, typical conditions used by Australian sugar factories. The clarification experiments were conducted in triplicate. Samples of clarified juices were siphoned off for storage and subsequent analysis.

The settling rate of the flocculated mud particles were determined by measuring the level of the mud interface at 0.5, 1.0, 2.0, and 3.0 min.

The initial settling rate (mL/min) was obtained from the graphical analysis of the initial linear slope.

Turbidity of the clarified juices was determined by measuring the absorbance (*A*) at 900 nm in 1 cm cells against distilled water.²⁰ The turbidity of the clarified juice was defined as 100*A*. The percentage error for turbidity determination was $\pm 0.3\%$.

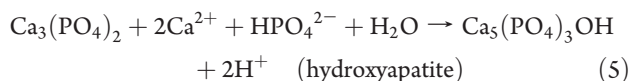
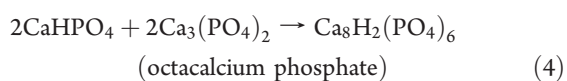
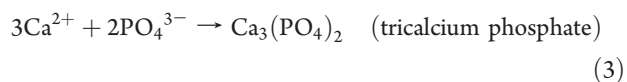
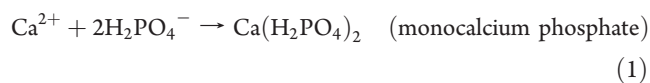
Color was determined at pH 7 by measuring the absorbance at 420 nm in 1 cm cells.²¹ For syrup color determinations in the range of 34000 to 42000 ICU, the reported 95% repeatability is $\sim 5\%$ of the mean color value.²¹ This repeatability value has been assumed to be the case in the present study. Dry substance was measured using an air oven at 98 °C.²²

Sucrose contents of the factory juices were determined by high performance liquid chromatography analysis. Samples were diluted to give $\sim 1\%$ sucrose concentration and filtered through a 0.45 μm filter for analysis. The column used was a 250 \times 7.8 mm i.d., 10–15 μm , 10% Na^+ with a guard column 28 \times 7.8 mm i.d. of the same material (Shodex KS801). Sucrose was separated using this column equilibrated at 65 °C and was detected by a Waters 410 Refractive Index Detector. The eluent was water at a flow rate of 0.5 mL/min. The purity of the clarified juice was calculated as the percentage ratio of sucrose content to dry substance.

The inorganic ion concentrations of the clarified juices were determined by ICP-OES. The experimental error for the clarification experiments for the inorganic ions was $\sim 5\%$.¹⁹

RESULTS AND DISCUSSION

Solution Chemistry. The main reactions that occur in limed juice to produce calcium phosphate phases^{10–12} are as follows:



In addition, tetracalcium phosphate [$\text{Ca}_4(\text{PO}_4)_2\text{OH}_2$] is also formed.

Juices with insufficient phosphate generally clarify poorly and produce clarified juices of high turbidities.^{11,19} Juices with excessive phosphate increases the level of soluble calcium and phosphate in clarified juices, thereby increasing scaling intensity and the amount of scale formed in the evaporators and pans. The increase in the phosphate level in the clarified juices also reduces sugar filterability.³ Excessive calcium ions in clarified juices increase scaling in the evaporators, pans, and centrifugals, increases ash in sugar, and reduces molasses exhaustion. As such, the concentrations of soluble calcium and phosphate both in juice before and after clarification are critical in determining the efficiency of not only the clarification process but also the productivity of the sugar manufacturing process and the quality of the product sugar.

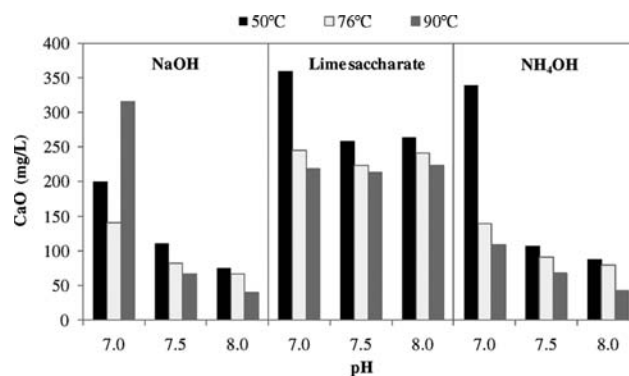


Figure 1. Effect of added caustic soda, lime saccharate, and ammonium hydroxide on the concentration of CaO in synthetic juice A at 50 °C, 76 °C, and 90 °C.

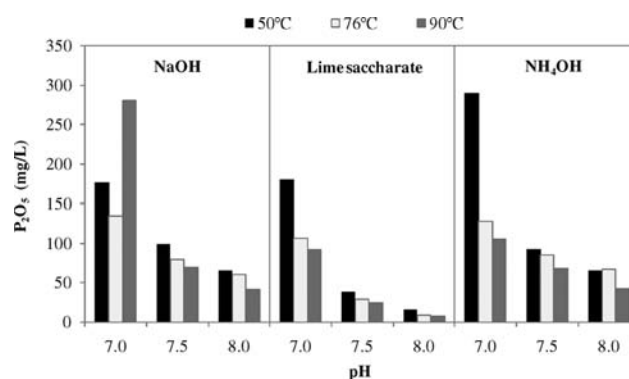


Figure 2. Effect of added caustic soda, lime saccharate, and ammonium hydroxide on the concentration of P_2O_5 in synthetic juice A at 50 °C, 76 °C, and 90 °C.

The results of the calcium phosphate precipitation studies in juice A are presented in Figures 1 and 2, with the changes in residual CaO and P_2O_5 concentrations at different pH values and temperatures. The results show that the amount of untreated CaO and P_2O_5 are highly dependent on the juice's final pH and working temperature. The amount of residual CaO and P_2O_5 were also found to depend on juice type. For a majority of the juices, irrespective of the alkali used, juices limed at 50 °C contained the largest proportions of unreacted CaO and P_2O_5 compared to the juices limed at 76 and 90 °C, respectively. This is due to increased solubility of the calcium phosphate phases at the lower temperature. However, some treated juices do not follow this trend. These are (a) juice A treated with sodium hydroxide at 90 °C and at pH 7, (b) juice B treated with ammonium hydroxide at 76 °C and pH 7, (c) juice C treated with sodium hydroxide at 90 °C and pH 8, and (d) juice E treated at 90 °C and at pH values of 7.0 and 7.5. For these juices, with the unavailability of sufficient calcium ions, it is probable that the type of phosphate phases formed under these conditions is controlled by stoichiometry rather than inverse solubility effect. The dominant phosphate species at pH ~ 7 is H_2PO_4^- followed by HPO_4^{2-} , whereas at higher pH the reverse is true.¹¹ Hence, at a pH of ~ 7 the stoichiometry of calcium phosphate phases is different from the other systems that follow the inverse solubility rule.

As the highest levels of CaO and P_2O_5 contents were obtained with juices treated at pH 7 and at 50 °C, only the data obtained for synthetic juices heated at 76 and 90 °C, with pH values of

7.5 and 8.0, respectively, have been critically examined. As shown in Figures 1 and 2, where lime saccharate is the base, all the juices have precipitated the majority of their P_2O_5 though significant proportions of CaO remain in solution. Where the initial levels of P_2O_5 contents in the juices are the same (i.e., juices A, B, D and E), the average level of CaO remaining after precipitation (at pH 7.5 and 8.0) is about 235 mg/L for juices limed at 76 °C and 220 mg/L for juices limed at 90 °C. In the case of juice C (where there is insufficient phosphate ions available for interaction with calcium ions), once calcium phosphate precipitation is complete, any extra added lime saccharate adds proportionately to the CaO content remaining in the juice. These results highlight the critical role played by the initial concentration of P_2O_5 in juice in determining the CaO content of treated juices. The results also raise the issue of high levels of unreacted CaO in juice when lime saccharate is used. Aconitic acid in its dissociated forms contains the species $H_2C_6H_3O_6^-$, $HC_6H_3O_6^{2-}$, and $C_6H_3O_6^{3-}$. The first dissociation constant (K_1) of aconitic acid (4.8×10^{-3} at 25 °C) is weaker than that of phosphoric acid (7.52×10^{-3} at 25 °C).²³ However, the second dissociation constant ($K_2 = 4.6 \times 10^{-5}$ at 25 °C) is well over 500 times that of phosphoric acid (6.23×10^{-8} at 25 °C). As the K_2 values occur predominantly at the pH range between 4 and 7, it is expected that $HC_6H_3O_6^{2-}$ would readily form complexes with calcium ions in solution, making the calcium ions inaccessible for interaction with phosphate ions in situ. Therefore, in situations where free calcium ions are available, such as with lime saccharate addition, the calcium phosphate precipitation process preferentially occurs with these ions instead of the calcium present in the juice which is predominantly present as a complex.

As shown in Figures 1 and 2 where sodium hydroxide or ammonium hydroxide are the alkalis, all the juices have surrendered large proportions of the initial CaO and P_2O_5 contents to calcium phosphate formation. Similar results were obtained with juices B and C. With juice D, practically all the initial CaO content was used up in calcium phosphate precipitation, while the majority of the initial P_2O_5 content of the juice remained unreacted (Figures 3 and 4). A plausible explanation for these effects is that during precipitation a fixed amount of soluble CaO and P_2O_5 is removed from solution and that once one of the lattice forming ions has been depleted (in this case calcium), precipitation stops, and the other ion is left in excess. The ratio of the concentration (in mg/L) of CaO to P_2O_5 that was withdrawn from solution was found to be about 1.3 for all treated juices with the exception of juice D (treated with sodium hydroxide), which had a ratio of 2.2.

When the results of juice A were compared to those of juice E (where the reaction was carried out in the absence of sucrose), there were no noticeable differences between the precipitation path of calcium phosphate carried out in the presence and absence of sucrose. This is not to say that the physical nature of the calcium phosphate is not different between the two systems.

From the foregoing, the major disadvantage of using of lime saccharate in calcium phosphate precipitation is the high levels of residual CaO in the juice at high pH. However, the use of lime saccharate results in significant low levels of P_2O_5 , relative to the other alkalis. As no one alkali can be used to achieve both maximum calcium and phosphate removal, a combination between lime saccharate and sodium hydroxide or between lime saccharate and ammonium hydroxide should reduce the concentrations of these ions in clarified juices.

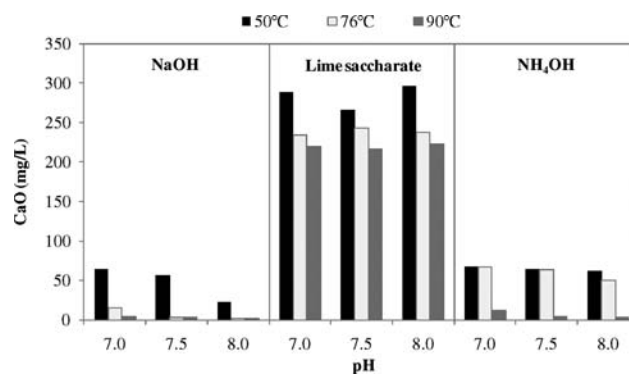


Figure 3. Effect of added caustic soda, lime saccharate, and ammonium hydroxide on the concentration of CaO in synthetic juice D at 50 °C, 76 °C, and 90 °C.

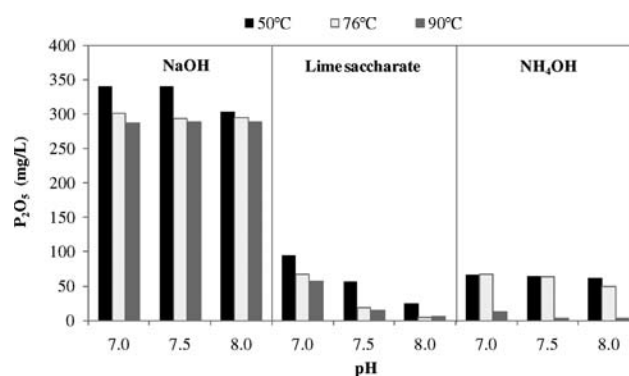


Figure 4. Effect of added caustic soda, lime saccharate, and ammonium hydroxide on the concentration of P_2O_5 in synthetic juice D at 50 °C, 76 °C, and 90 °C.

Composition of Solid Phases. The results of the composition of the precipitates formed with juice A at a pH of 8.0 are given in Table 2. No analysis was carried out on the solids obtained with other juices. The results show that increasing amounts of calcium (as CaO) is precipitated as the juice temperature is increased from 50 to 90 °C and that the precipitates obtained with lime saccharate contain the highest proportions of CaO to P_2O_5 at a given temperature. The actual calcium phosphate phases are not known. The molar ratio of CaO to P_2O_5 in juice A is 1.04, implying that there are enough lattice ions to form $Ca_3(PO_4)_2$, which has a molar ratio of 1. None of the precipitates formed with the various bases attained the ratio of 1 (except ammonium hydroxide at 50 °C). The precipitates formed with lime saccharate and ammonium hydroxide have slightly higher ratios, while those of sodium hydroxide have slightly lower values. This probably implies that the precipitates formed with lime saccharate and ammonium hydroxide contain the highest proportions of $Ca_3(PO_4)_2$ relative to the other precipitates prepared with sodium hydroxide. It is worth mentioning that $Ca_3(PO_4)_2$ is the precursor for hydroxyapatite formation, which is an effective adsorbent for protein removal;¹ therefore, it is beneficial to include lime saccharate in raising juice pH for clarification.

Calcium Phosphate Precipitation in Filtered Primary Juice. In order to provide additional information on the solution chemistry of calcium phosphate in the presence of juice constituents, some selected experiments were conducted with a filtered factory primary juice using a combination of alkalis.

Table 2. Composition of Calcium Phosphate Precipitate for Trials Using Juice A at a pH of 8

type of base	juice temp. (°C)	CaO (mmol/L)	P ₂ O ₅ (mmol/L)	CaO/3P ₂ O ₅
NaOH	50	22.95 ± 0.51	7.92 ± 0.05	0.97
	76	23.79 ± 1.61	8.27 ± 0.55	0.96
	90	25.23 ± 0.41	8.49 ± 0.51	0.99
lime saccharate	50	26.28 ± 2.20	8.08 ± 0.07	1.08
	76	27.40 ± 1.20	8.46 ± 0.22	1.08
	90	29.09 ± 0.64	8.54 ± 0.31	1.14
NH ₄ OH	50	21.16 ± 0.41	7.04 ± 0.11	1.00
	76	21.96 ± 0.71	7.16 ± 0.51	1.02
	90	21.98 ± 0.51	7.40 ± 0.11	1.04

Table 3. Effects of Added Lime Saccharate, Sodium Hydroxide, and Ammonium Hydroxide on the Concentrations of CaO, MgO, and P₂O₅ in Filtered Primary Juice

type of base	pH of juice	temp of juice (°C)	composition of treated juice					wt of precipitate (mg)
			CaO (mg/L)	P ₂ O ₅ (mg/L)	MgO (mg/L)	free Ca as CaO (mg/L)		
none	5.1	40	301	338	318	nd	nd	
lime saccharate	7.0	76	339	210	321	55	120	
		90	359	191	336	58	90	
	8.0	76	299	91	294	55	230	
		90	358	82	303	44	260	
NaOH	7.0	76	202	231	322	66	50	
		90	182	228	313	40	70	
	8.0	76	126	142	279	51	90	
		90	131	138	279	44	140	
NH ₄ OH	7.0	76	210	273	354	53	20	
		90	173	207	320	50	70	
	8.0	76	173	197	323	52	80	
		90	112	122	276	41	140	
lime sacch/NaOH	6.0/8.0 ^a	76	149	122	285	39	130	
		90	149	122	274	46	190	
	6.5/8.0	76	162	90	270	44	240	
		90	175	90	269	40	260	
	7.0/8.0	76	195	91	311	44	190	
		90	221	91	279	43	210	
lime sacch/NH ₄ OH	6.0/8.0	76	144	98	278	37	180	
		90	178	119	273	38	180	
	6.5/8.0	76	171	82	291	39	240	
		90	177	67	293	36	260	
	7.0/8.0	76	207	86	296	37	190	
		90	182	72	269	35	200	

^a The first number is the initial pH of liming, and the second number is the final juice pH.

Table 3 shows the results of added lime saccharate, sodium hydroxide, and ammonium hydroxide on the concentrations of CaO, MgO, and P₂O₅ in filtered primary juice, at different liming temperatures and at different juice pH values. It also shows the results of the two-stage processes involving adding lime saccharate to a heated juice to a set pH and then adding sodium hydroxide solution/ammonium hydroxide solution to the final pH. The magnesium ion (as MgO) concentrations in the juices were monitored because of their influence on calcium phosphate precipitation.⁵ As expected, samples that were treated first with lime saccharate and then with either sodium hydroxide or ammonium hydroxide gave significant lower CaO values compared with the samples treated with only lime saccharate.

The P₂O₅ values of juices treated with a two-stage alkali addition process were similar to the lime saccharate system. Table 3 also shows the levels of unreacted MgO and the weight of precipitates formed after the addition of alkali. The two-stage alkali process reduced the MgO content of the treated juice relative to the MgO content in juice obtained with lime saccharate treatment. This may be because some of the Mg²⁺ ions have occupied vacant Ca²⁺ sites in the crystal lattice of calcium phosphate based on the concept of structural substitution in the crystal lattices of ions of similar sizes.¹¹

The weight of the precipitate gives an indication of the total amount of impurities removed from solution. An adequate quantity of precipitate must be formed in the juice to enhance

sweep flocculation (i.e., the ability of the flocs to adsorb impurities as the flocs settle) and increase the settling rates of the juice particles. In order to be able to ascertain the best treatment option, the levels of unreacted CaO, P₂O₅, and MgO together with the corresponding weights of precipitate formed were examined as an entity. On the basis of this, the procedure which involved first adding lime saccharate to juice to a pH of 6.5 and then adding sodium hydroxide to a pH 8 at a juice temperature of either 76 or 90 °C was identified as the best option for further investigation. However, it should be noted that the largest quantity of precipitate was formed with the juice limed at 90 °C than the juice limed at 76 °C, although the level of unreacted CaO was higher at the higher temperature. Similar results were obtained for the two-stage processes involving lime saccharate and ammonium hydroxide addition. One advantage of using ammonium hydroxide over sodium hydroxide is that ammonium ions are readily volatilized by heat and so do not have the melassigenic action associated with sodium ions on sucrose. However, the use of ammonium hydroxide is compromised by the release of corrosive ammonia to the atmosphere.

The levels of free calcium ions (reported as CaO) in the treated samples are shown in Table 4. These values are 6 times lower than the values obtained by ICP-OES. This means that most of the Ca²⁺ ions in juice are bound and are not readily available for chemical interaction because of the formation of complexes with the organic acids in the juice as has been deduced from the synthetic juice study. As such, during the clarification of juice with lime saccharate, the inorganic phosphate ions preferentially react first with the available free endogenous calcium ions in juice before reacting with the calcium ions from the added lime saccharate, leaving the calcium complex in solution. This results in high residual calcium in clarified juice. It is presumed that the degree of association between calcium and saccharate is far less than that between calcium and organic acids. In situations where sodium hydroxide or ammonium hydroxide is used, after the initial reaction between phosphate ions and the free endogenous calcium ions, further reactions will inevitably proceed with the calcium complex in solution.

Clarification Experiments with Factory Primary Juice.

Calcium phosphate precipitation studies on filtered primary juice indicated significant reduction in the levels of CaO and to a lesser extent MgO in samples treated with the two-stage process, with initial liming to pH 6.5, compared to samples treated with only lime saccharate (i.e., control). In light of this, clarification experiments using this two-stage process were carried out on factory juices on-site at three sugar mills. In one set of experiments for the two-stage process, lime saccharate was added first to raise the juice pH to 6.5, followed by the addition of sodium hydroxide to raise the juice pH to the desired value. In another set of experiments, the order of addition of lime saccharate and sodium hydroxide was reversed. Juices 1 and 2 were from different factories, while juices 3, 4, and 5 were from the same factory (Table 4). As shown in Table 4, the turbidity, color, and phosphate levels of the control samples were marginally lower than the samples which had been treated with the two-stage process. The differences in the settling rate and mud volume between the control and the two-stage process were not significant. The apparent purity of the clarified samples was similar (except the control of juice 3).

The two-stage processes give lower levels of CaO and P₂O₅ in clarified juices, compared to the conventional clarification process (Table 4). As shown in Table 4, significant CaO reductions

(27% to 50%) were obtained with samples clarified with the lime saccharate and sodium hydroxide solution mixtures compared to the clarified juice obtained by the normal process (i.e., control). The correlation equation between the amount of CaO and Na₂O content is given by:

$$Y = 2 \times 10^{-4}x + 89.7810^{-2}; R^2 = 0.60 \quad (6)$$

where *Y* is the ratio of the CaO content for the two-stage process to the conventional process, and *x* is the amount of sodium hydroxide added as Na₂O in mg/L.

As such, the amount of CaO in clarified juice can be regulated on the basis of the amount of sodium hydroxide added during the clarification process. The clarification results of Table 4 also show a reduction in the MgO contents of up to 20% for clarified juices obtained with mixed alkalis, though this is variable. For these juices, some reductions in SiO₂ values (juice 4, Table 4) were also obtained.

Although these studies focused on the use of lime saccharate in the two-stage process, it is envisaged that similar results would be obtained with milk of lime. It should be noted that clarified juices obtained with lime saccharate alone have higher CaO levels but lower P₂O₅ contents than clarified juices obtained with milk of lime.² Thus, if milk of lime was used to replace lime saccharate there would be lower CaO levels in the clarified juices for these systems.

Typically, during sugar cane juice processing, the heating surface area of evaporators becomes increasingly scaled as a result of fouling. With increasing scale deposition, the rate of heat transfer across the evaporator heating surface area is diminished, and the net effect is a reduction in the capacity that juice can be processed to concentrated juice. To maintain a nominated sugar cane processing rate, the first effect calandria pressure will increase so as to provide a larger temperature difference across the evaporator set. However, once the low pressure steam valve to the first effect is fully opened, the evaporation rate for the set will decline with increasing scaling. There are three main options that can be employed to maintain the crushing rate at the target value. These are as follows:

- (1) Reduce the addition of water to the mills and filters. However, a reduction in the amount of added water to the milling train and the filter station generally reduces the amount of sucrose recovered from bagasse (i.e., sugar cane fiber) and the residue from clarification (i.e., mud). Consequently, during the period when the amount of added water is reduced, the effect of scale deposition is to reduce sugar recovery and hence reduce the revenue to the mill.
- (2) Allow the syrup concentration to reduce and increase the evaporation load on the pan stage. The impact of reduced syrup concentration on the factory depends on many factors including the capacity of the pan stage (where sucrose crystallization is carried out), the sucrose content of the cane supply, and the pressure of the vapor/steam supplied to the pans.
- (3) A combination of options 1 and 2.

In practice, sugar factories generally adopt option 3 in order to maintain the crushing rate at a target value. Despite this practice, sugar factories record sugar and molasses losses. Therefore, by adopting a strategy of using a clarification procedure involving a combination of calcium and sodium alkalis will reduce scale formation and deposition and thus limit the extent option 3 is

Table 4. Results of Clarification Experiments on Factory Primary Juices

liming type ^a	settling rate (cm/min)	mud vol. (%)	turbidity Per 100 Bx	apparent purity (%)	color at pH 7	CaO mg/kg on dry solids	MgO mg/kg on dry solids	P ₂ O ₅ mg/kg on dry solids	SiO ₂ mg/kg on dry solids
juice 1					10300	883	1749	745	453
L-76-7.8	37	27	52.7	87.1	9200	2322	1701	15.8	396
LC-76-7.5	60	17	62.5	86.8	10700	1119	1786	52.1	390
LC-76-7.8	48	22	67.3	87.0	11300	1425	1688	46.5	330
LC-76-8.0	37	29	67.3	87.1	11000	1440	1683	62.1	409
juice 2					13200	999	1709	749	483
L-76-7.8	38	27	52.9	88.5	11400	2359	1650	21.2	418
LC-90-7.5	43	30	68.0	88.7	11900	1355	1675	36.6	377
LC-90-7.8	51	23	67.8	88.5	12000	1335	1580	41.7	375
LC-90-8.0	54	21	78.8	88.4	12000	1145	1429	31.5	383
juice 3						1422	1730	908	432
L-76-7.8	48	22	72.9	86.8	12300	2354	1563	20.8	401
CL-76-7.5	48	24	93.2	88.4	14400	1471	1367	46.6	377
CL 76-7.8	42	28	83.8	88.3	13700	1518	1277	31.4	375
CL-76-8.0	55	20	83.7	88.2	12300	1565	1240	20.9	383
juice 4						1214	1556	1041	526
L-76-7.8	48	23	47.1	89.1	10700	2261	1533	15.7	460
CL-90-7.5	47	24	52.2	89.0	11200	1648	1403	31.3	136
CL-90-7.8		27	56.9	89.1	11000	1619	1107	20.7	264
CL-90-8.0	32	33	57.3	88.9	11000	1515	942	20.8	255
juice 5 ^b						1323	1894	653	495
L-76-7.8	38	28	7	87.7	8400	2499	1794	15.7	424
LC-76-7.8	46	24	8	87.9	9800	1463	1668	26.3	337
LC-76-7.8	46	26	7	87.8	9000	1479	1688	31.3	381

^a L is lime saccharate clarification; LC is the two-stage process with lime saccharate added to juice to raise the juice pH to 6.5, followed by the addition of sodium hydroxide solution to raise the juice pH to the desired value prior to clarification; CL is the two-stage process with sodium hydroxide solution added to juice to raise the pH to 6.5, followed by the addition of lime saccharate to raise the juice pH to the desired value, prior to clarification. The first number is the temperature of liming, and the second number is the final pH, e.g., L-76-7.8 represents liming juice to pH 7.8 at 76 °C. ^b Clarification carried out with the P₂O₅ level in the juice increased to 300 mg/L. The P₂O₅ level in the juice prior to clarification was 120 mg/L.

used. The down side of using this clarification procedure is the possible melassigenic property (i.e., a substance that binds to water and sucrose) associated with sodium ions, reducing sucrose crystallization. Previous laboratory and limited factory experiments by Saska and Cuddihy,²⁴ indicated that soda ash (i.e., sodium carbonate) may be used to replace lime in juice clarification with a different type of flocculant. The sugar produced in the laboratory using the process was of quality similar to that of commercial raw sugar, in terms of color and ash contents.²⁴ As the experiments were limited, the impact of the process of scale formation was not accessed, including on the effect of sucrose crystallization.

In summary, the results from the study of CaO/phosphate/sucrose systems have provided further insights on the chemistry of calcium phosphate formation in sugar solutions and have clearly shown that no single alkali can be used alone to achieve maximum calcium phosphate precipitation with reduced amounts of CaO and P₂O₅ in treated juices. Excessive CaO in clarified juice can be minimized by using a combination of alkalis, at a particular initial pH set-point, during juice clarification as has been demonstrated with factory primary juices. The present study has also shown that the two-stage clarification process can operate under similar operating conditions (e.g., same final lime pH and liming temperature) and use the same type of flocculant as the conventional process. This, therefore, makes it easier to be adopted by sugar mill process engineers. The two-stage process

has the potential benefits of reducing fouling of sugar mill evaporators, pans, and centrifugals, hence extending the times between evaporator cleaning. The use of such a clarification process may minimize options employed to maintain target crushing rate as a consequence of evaporator fouling.

■ ASSOCIATED CONTENT

Supporting Information. Information on the concentrations of residual CaO and P₂O₅ of juice A after calcium phosphate precipitation at 76 °C; information on the compositions of treated synthetic juices B, C, and E, heated at various temperatures and pH values; graphical plots showing the effects of added NaOH on CaO and MgO levels in clarified juices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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