



# Understanding the causes of calcium carbonate crystal growth and inhibition during the carbonatation refining of raw sugars

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## ABSTRACT

The inhibitory activity of soluble and insoluble starch (0–550 ppm/Brix) in factory raw sugars were investigated using simulated refinery carbonatation clarification reactions to underpin what causes the undesirable formation of CaCO<sub>3</sub> crystal fines ( $\leq 5 \mu\text{m}$ ). It was found that CaCO<sub>3</sub> crystal growth was inhibited mostly by soluble starch by forming starch-Ca<sup>2+</sup> metal complexes. Insoluble (granular) starch, however, had a greater affinity for inhibiting CaCO<sub>3</sub> crystallization because it retained the carbonatation clarification reactants, i.e., Ca<sup>2+</sup> and OH<sup>-</sup>, in the granule interior which caused granule gelatinization and increased viscosity of the melt liquor. Causes for poor press filterability and CaCO<sub>3</sub> fines using raw sugar melts were found to be complex and attributed to the combinatorial roles that both soluble and insoluble starch have, among other impurities. More studies are now warranted at the carbonatation refinery to correlate processing characteristics with raw sugars quality attributes to underpin how each impurity impedes carbonatation.

## 1. Introduction

Raw sugar filterability is an important quality parameter that impacts the throughput of a cane refinery. This is because the physico-chemical properties of raw sugar melts and their impurities can adversely affect two of the major processing stages used in a carbonatation refinery, i.e., carbonatation clarification and press filtration. Carbonatation clarification and press filtration are chemical and mechanical processes, respectively, that are based on the reaction of slaked milk of lime (MOL, or Ca(OH)<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>) to produce the precipitate calcium carbonate (CaCO<sub>3</sub>), as shown in Scheme 1. The CaCO<sub>3</sub> precipitate serves as an *in situ* filter aid that removes sugar impurities from melt (raw sugar) liquor and helps to maintain refining efficiency.

Raw sugar quality attributes, such as moisture, reducing sugars, and colorants, are not considered to be major contributors to inefficient carbonatation clarification and press filtration compared to their negative effect on refined sugar quality. Compared to polysaccharides, mono- and disaccharides have a small effect on CaCO<sub>3</sub> precipitation (Duchstein, Kniep, & Zahn, 2013). The concentration, molecular weight size, and physical forms (insoluble/amorphous/soluble) of other raw sugar impurities, however, have been found to reduce the efficiency of

carbonatation clarification reactions and subsequent press filtration units. Examples of these impurities are ash, the presence of microbial bodies and extraneous artifacts, turbid insoluble and amorphous particles, some large molecular weight colorants, and polysaccharides (Chou, 1983).

Soluble polysaccharides, such as starch, cellulose, and charged dextrans, have been reported to affect CaCO<sub>3</sub> formation by modifying the size, shape, and composition of the CaCO<sub>3</sub> crystals (Amjad, Pugh, & Reddy, 2002; Kontrec, Kralj, Brečević, & Falini, 2008; Shtukenberg, Ward, & Kahr, 2017). Dextran is an impurity arising from deteriorated sugarcane. Charged dextrans interfere with carbonatation reaction kinetics and slow crystal growth whereas uncharged dextrans only reduce the CaCO<sub>3</sub> crystal size when their molecular weight is increased. In contrast, starch polysaccharides are natural cane impurities contained in insoluble granules, which can impact carbonatation refining despite the use of amylases beforehand at the sugarcane factory. Until 2013, it was considered that all of the sugarcane starch extracted into crusher juices were completely solubilized by the end of the factory evaporation process and, therefore, the derived raw sugars only contained solubilized starch. Since then it has been unequivocally shown that this is not always true (Cole et al., 2013). In fact, three different starch forms, i.e., (i) 1–6  $\mu\text{m}$  insoluble rigid granule, (ii) 6–10  $\mu\text{m}$  swollen, amorphous

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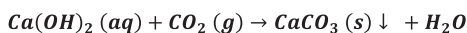
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Scheme 1.

granule, and (iii) solubilized starch comprised of ~17.5% amylose and ~81.5% amylopectin, can be contained in raw sugars at different concentrations and ratios to one another (Cole et al., 2016a, 2016b). Considering the new information that starch can exist in raw sugars in different concentrations and physical forms and even transform from one form to the other (Cole et al., 2013), it became critical to revisit how starch affected carbonatation sugar refining. This is especially the case if technical solutions to processing problems are to be found. Moreover, this is even more important since current efforts to minimize the impact of starch and/or other soluble impurities on liquor clarification reactions at refineries and their subsequent downstream units are limited to (i) predicting sugar filterability using analytical methods, (ii) blending multiple raw sugars to prevent major delays in sugar refining, and/or (iii) making impromptu modifications to the process to avert long delays in throughput (Maria Diamond, ASR refinery, personal communication; Demone & Burchell, 2013; Lee & Donovan, 1995; Lionnet, 2002; Nenadkevich, 1984).

In the first two parts of this study, Cole et al. (2016a, 2016b) identified how each physical starch form and concentration uniquely affected each stage in carbonatation clarification, which encompassed much more than just investigating the production of unwanted CaCO<sub>3</sub> fines (< 5 μm). It was observed that starch either hindered CaCO<sub>3</sub> precipitation, limited crystal growth, or completely prevented the MOL and CO<sub>2</sub> chemical reactions. Press filtration was adversely affected by insoluble starch because the intermediate swollen starch form increased liquor viscosity and coated press filter membranes (Cole et al., 2016a, 2016b). Although insoluble starch did not contribute to the majority production of CaCO<sub>3</sub> fines (< 5 μm), the carbonatation clarification reaction required more MOL for the reactions to proceed. Excluding its effects on viscosity, insoluble starch minimally affected the formation of CaCO<sub>3</sub>. Carbonatation clarification reactions, on the other hand, were predominantly influenced by the soluble starch form, even at concentrations below the 250 ppm/Brix total starch penalty threshold, and almost solely produced CaCO<sub>3</sub> fines with inefficient liquor clarification and press filtration (Cole et al., 2016b). Soluble starch also slightly decreased the viscosity of the carbonatated liquor and facilitated flowability, an indication that the water structure and/or water interactions within the carbonatated melt liquor had been disrupted (Cole et al., 2016a; Eggleston, Vercellotti, Edye, & Clarke, 1995).

In consideration of the chemistry involved in the production of CaCO<sub>3</sub> crystals and previous results by Cole et al. (2016a, 2016b), it was apparent that the production of CaCO<sub>3</sub> fines was traceable to the nucleation and induction stages of the reaction. In this final study, the involvement of starch in limiting CaCO<sub>3</sub> nucleation and crystal growth was investigated using potentiometry and binding studies. The effects of starch concentration and physical form as well as other raw sugar impurities on the carbonatation refining processes are also discussed.

## 2. Materials and methods

### 2.1. Chemicals and sugar samples

Stock solutions of calcium chloride (CaCl<sub>2</sub>), sodium bicarbonate (NaHCO<sub>3</sub>), and 67.0 Brix sucrose (99.95%) were prepared daily from analytical grade chemicals. Each physical starch form and corresponding concentration (0–1000 ppm) used in this study were from commercial materials and their stock solutions were also prepared on a ppm basis. The starch forms evaluated included insoluble and swollen corn starch (Cole et al., 2013) and soluble potato starch. All chemicals were purchased from Sigma Aldrich Company (St. Louis, MO, USA).

### 2.2. Simulated carbonatation clarification

Simulated carbonatation clarification experiments were conducted using 67.0 Brix sucrose solutions with < 1000 ppm insoluble, swollen, or soluble starch as previously reported by Cole et al. (2016b). After the carbonatation reaction was completed, the carbonatated liquor was diluted with water or 67.0 Brix sucrose, respective to the appropriate medium, to < 1.5% suspended solids. The diluted carbonatated liquor was clarified with a plate-frame filter press (Model 177, Avery Filters, Westwood, NJ, USA) equipped with a polyester cloth filter that was supplied by Domino Sugar Refinery (ASR, Arabi, LA, USA). The filter cake was rinsed once with deionized water (50 °C) to remove trace sucrose and then collected from the filter press, dried overnight at 100 °C in an oven, and then weighed to determine per cent yield of CaCO<sub>3</sub> mud as compared to the non-starch and/or non-sucrose control. The filtered liquor was also analyzed for unreacted calcium content.

### 2.3. Growth inhibition of CaCO<sub>3</sub> by starch form

The growth inhibition of CaCO<sub>3</sub> by starch form was evaluated during the simulated carbonatation clarification reaction. Because Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> ions are consumed during CaCO<sub>3</sub> growth and H<sup>+</sup> is released producing a more acidic solution (Scheme 2), 1 M NaOH was added to counter the increasing acidity using pH stat control.

The injected volume of 1 M NaOH per unit time was recorded and proportional to CaCO<sub>3</sub> nucleation and growth rate (Nielsen et al., 2012). The fractional inhibition of CaCO<sub>3</sub> precipitation (Θ), was quantified by observing the change in growth rate using the relationship:

$$\Theta = \frac{r_0 - r_i}{r_0} \quad (1)$$

where a Θ of 0 and 1 indicates no or complete inhibition, respectively, r<sub>0</sub> represents the initial growth rate in the pure non-starch system, and r<sub>i</sub> represents CaCO<sub>3</sub> growth rate in the presence of starch. More details regarding the interaction between starch and the CaCO<sub>3</sub> crystal, or reactants, were obtained by comparing the r<sub>0</sub> and r<sub>i</sub> values. If r<sub>i</sub> returned to r<sub>0</sub>, for example, than this indicated that the starch became embedded in the growing CaCO<sub>3</sub> crystal, and once all of the starch was completely internalized by the growing CaCO<sub>3</sub>, then the growth rate resumed at the rate of the system without starch.

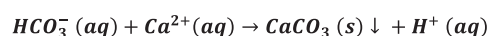
The binding affinity (α) and maximum fractional inhibition value at infinite concentration of starch (A) were determined by plotting the starch concentration [S] and Θ and fitting the data with an L-type Langmuir isotherm described by Eq. (2).

$$\Theta = A \frac{\alpha [S]}{1 + \alpha [S]} \quad (2)$$

This functional form indicates that inhibition is caused by starch adsorption on the active growth sites of CaCO<sub>3</sub> during the induction and nucleation periods of carbonatation.

### 2.4. Potentiometric evaluation of starch complexation of calcium ions

An aqueous solution of calcium ions (Ca<sup>2+</sup>) was prepared by dissolving 2 g CaCl<sub>2</sub> in 1 l of distilled water. In 100 ml, 250 ppm starch suspension (insoluble or swollen starch) or solution (soluble starch) was prepared and allowed to stir for 30 min at room temperature (~25 °C) to allow time for the starch to complex with the calcium ions. Then the starch-calcium complex underwent titration with 1 M NaOH using a Dosino 803 and Titrando 836 autotitration system (Metrohm, Riverview, FL, USA), in which the uptake of 1 M NaOH was recorded by



Scheme 2.

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