



Modeling the co-precipitation of silica and calcium oxalate in sugar solutions



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ABSTRACT

Solution chemistry plays a significant role in the rate and type of foulant formed on heated industrial surfaces. This paper describes the effect of sucrose, silica (SiO₂), Ca²⁺ and Mg²⁺ ions, and trans-aconitic acid on the kinetics and solubility of SiO₂ and calcium oxalate monohydrate (COM) in mixed salt solutions containing sucrose and refines models previously proposed. The developed SiO₂ models show that sucrose and SiO₂ concentrations are the main parameters that determine apparent order (*n*) and apparent rate of reaction (*k*) and SiO₂ solubility over a 24 h period. The calcium oxalate solubility model shows that while increasing [Mg²⁺] increases COM solubility, the reverse is so with increasing sucrose concentrations. The role of solution species on COM crystal habit is discussed and the appearance of the uncommon (001) face is explained.

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1. Introduction

The processing of natural aqueous feedstocks (e.g., sugar cane juice, beer and ground water) inevitably leads to the fouling of plant equipment and loss of heat transfer capacity in heat exchangers. The role of silica (SiO₂) fouling in the chemical industry is well documented and its deposition on surfaces poses some significant challenges in the efficient operation of plant equipment (Muller-Steinhagen, 2000; Neofotistou and Demadis, 2004; Ning, 2003; Sheikholeslami and Tan, 1999). Co-precipitation with other salts increases the complexity of the problem as these salts, e.g., calcium salts, are able to strengthen (through intergrowth) the SiO₂ deposits or cover the deposits (layering). This makes chemical cleaning more expensive and time consuming as more than one type of cleaning agent is required (East et al., 2011a, b).

Recently East et al. (2013) studied the effect of solution composition on the kinetics and thermodynamics of the co-precipitation of calcium oxalate (monohydrate, COM) and SiO₂ in sugar solutions, commonly found in the evaporators of Australian sugar factories. Table 1 shows the conditions for the laboratory tests (at two SiO₂ supersaturation ratios (SS)) used in that study. Eqs. (1)–(4) show the preliminary models that were generated for SiO₂ apparent order (*n*) and apparent rate (*k*) of reaction and solubility after 24 h ([SiO₂]₂₄) as well as the solubility of Ca²⁺ ([Ca²⁺]_{eq}). Eq. (5)

was fitted to the SiO₂ concentration time series to generate values for *n* and *k*.

$$n = -13.2 + 65.7 \times 10^{-3}[\text{Suc}] + 56.4 \times 10^{-3}[\text{SiO}_2] + 36.7 \times 10^{-3}[\text{Mg}^{2+}] - 53.0 \times 10^{-6}[\text{SiO}_2]^2 - 99.9 \times 10^{-6}[\text{SiO}_2][\text{Mg}^{2+}] \quad (1)$$

$$k = -6.01 \times 10^{-3} - 5.28 \times 10^{-6}[\text{Ca}^{2+}] + 41.1 \times 10^{-6}[\text{Suc}] + 17.2 \times 10^{-6}[\text{SiO}_2] - 0.166 \times 10^{-6}[\text{tAC}] + 0.148 \times 10^{-6}[\text{Ca}^{2+}][\text{Suc}] + 1.87 \times 10^{-9}[\text{Ca}^{2+}][\text{tAC}] \quad (2)$$

$$[\text{SiO}_2]_{24} = 1090 - 72.3 \times 10^{-3}[\text{Ca}^{2+}] - 4.08[\text{Suc}] - 3.93[\text{SiO}_2] - 1.19[\text{Mg}^{2+}] + 4.70 \times 10^{-3}[\text{SiO}_2]^2 + 3.22 \times 10^{-3}[\text{SiO}_2][\text{Mg}^{2+}] \quad (3)$$

$$[\text{Ca}^{2+}]_{\text{eq}} = -28.3 + 0.949[\text{Ca}^{2+}] - 0.101[\text{Suc}] + 0.116[\text{Mg}^{2+}] + 5.92 \times 10^{-3}[\text{tAC}] - 3.36 \times 10^{-3}[\text{Ca}^{2+}][\text{Suc}] - 0.668 \times 10^{-3}[\text{Ca}^{2+}][\text{Mg}^{2+}] - 48.3 \times 10^{-6}[\text{Ca}^{2+}][\text{tAC}]$$

The equations showed that tAC had little effect on the system given how much it is expected to vary in the process ([Ca²⁺]_{eq} ± 1.5 mg L⁻¹, *k* ± 7%) (East et al., 2013). Also, values for [Mg²⁺] used by East et al. (2013) only represented the minimum [Mg²⁺] found in sugar cane juices (East et al., 2012; Thai and Doherty, 2011).

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Table 1
Test scheme for the generation of the preliminary model.

Component	Concentrations
Sucrose ([Suc])	25 and 40 wt/v%
Silica ([SiO ₂])	[Suc] = 25 wt/v%: 320 and 400 mg L ⁻¹ (SS = 1.8 and 2.3) [Suc] = 40 wt/v%: 250 and 320 mg L ⁻¹ (SS = 1.8 and 2.3)
Calcium ([Ca ²⁺])	41 and 200 mg L ⁻¹
Magnesium ([Mg ²⁺])	0 and 84 mg L ⁻¹
<i>trans</i> -Aconitic acid ([tAC])	0 and 1300 mg L ⁻¹
Oxalate ([C ₂ O ₄ ²⁻])	90 mg L ⁻¹

The present study is an advancement of the present knowledge on the co-precipitation of silica and calcium oxalate by: (a) developing a three-point non-linear and robust model, instead of the two-point linear model developed by East et al. (2013), to effectively describe and predict the co-precipitation of silica and calcium oxalate in synthetic sugar juice solutions; (b) using realistic [Mg²⁺] and [tAC] and including intermediate [Suc], [SiO₂] and [Ca²⁺] values to mimic different types of sugar cane juice, (c) verifying the models with experimental data, and (d) studying COM crystal habits and growth in more complex synthetic juice solutions.

2. Experimental

2.1. Materials

Concentrated stock solutions of CaCl₂·2H₂O (Chem Supply, Gillman, Australia), Na₂C₂O₄ (Sigma–Aldrich, Sydney, Australia), Na₂SiO₃ (Sigma–Aldrich, Sydney, Australia), MgCl₂·6H₂O (Merck, Kilsyth, Australia), HCl and NaOH were prepared from analytical reagent grade chemicals (Merck, Kilsyth, Australia) dissolved in CO₂-free distilled water. *trans*-Aconitic acid, *tAC* (Sigma–Aldrich, Sydney, Australia) and sucrose (Merck, Kilsyth, Australia) used in this study was analytical grade and the sucrose did not contain any measurable amounts of oxalic acid or other organic acids.

2.2. Test scheme

A face-centred central composite design (CCD) was used to investigate the effect of change in concentration of four solution components (Table 2) on the formation of calcium oxalate and SiO₂. The lower and upper concentrations selected for sucrose are similar to the concentrations of sucrose entering the 3rd and 4th effects of an Australian sugar factory with a quintuple evaporator set, respectively. The concentration of silica ([SiO₂]), oxalate

Table 2
Values for the independent variables of the central composite design.^a

Component (mg L ⁻¹)	-1	0	1
[Suc]	25 wt/v%	32.5 wt/v%	40 wt/v%
Silica SS ^b	SS = 1.8	SS = 2.05	SS = 2.3
[SiO ₂] in 25 wt/v% sucrose	320	360	400
[SiO ₂] in 32.5 wt/v% sucrose	270	310	350
[SiO ₂] in 40 wt/v% sucrose	250	290	320
[Ca ²⁺] mg L ⁻¹	41	125	200
[Mg ²⁺] mg L ⁻¹	0	126	252
[tAC] mg L ⁻¹	1300	1300	1300
[C ₂ O ₄ ²⁻] mg L ⁻¹	90	90	90

^a Tests conducted at 60 °C and pH = 6.

^b Values of SiO₂ in mg L⁻¹ were used for the modeling. SiO₂ solubility changes with [Suc] (Yu et al., 2003).

([C₂O₄²⁻]) and *trans*-aconitic acid ([tAC]) cover the general concentration range found in juices entering the 3rd and 4th effects of the same evaporator set. SiO₂ SS was used as a test parameter instead of concentration due to the significant reduction in solubility of SiO₂ caused by the high concentrations of sucrose (Yu et al., 2003). This is intended to keep the “driving force” for silicic acid polymerization constant over the test series so the effects of other components can be seen. The calcium concentration limits were selected to give a molar ratio of 1:1 and 5:1 [Ca²⁺] to [C₂O₄²⁻]. The Ca²⁺ and Mg²⁺ ion concentrations selected cover the levels found in syrups in Australian sugar factories (East et al., 2012; Thai and Doherty, 2011). The design consisted of a 2^p factorial augmented by 2p axial points and a centre point, where p is the number of varied solution constituents (p = 4). For this study, a total of 27 experiments were conducted with 16 factorial points, 8 axial points and 1 centre point replicated 3 times for experimental error calculation.

SiO₂ n, k and solubility after 24 h were determined for each test along with the [Ca²⁺] at equilibrium and were used as the responses for the CCD.

2.3. Methodology

Sucrose, Ca²⁺ and Mg²⁺ ions and *trans*-aconitic acid were mixed in CO₂-free water (~350 mL) at 60 °C and the pH was adjusted to 6.0 using a portable pH meter (Hach H160, Loveland, Co, USA) with an Ionode PBFC single junction Ag/AgCl pH probe with saturated KCl reference solution, which was calibrated before each test using Isolab pH 4.01 ± 0.02 at 25 °C and 7.00 ± 0.02 at 25 °C buffer solutions. Sodium oxalate (90 mg L⁻¹ C₂O₄²⁻ in the final solution) and SiO₂ solutions (at 60 °C) were placed in separate beakers, their pHs were adjusted to 6.0 and added at the same time to the sucrose solution containing the other compounds. The solution was quickly made up to 500 mL and transferred to capped 15 mL plastic tubes. The tubes were then placed in a water bath at 60 °C. Samples were taken after 20, 40 and 60 min, followed by one sample every hour, and analyzed. The use of a water bath does not represent the fouling environment in sugar factory evaporators, which have a temperature gradient at the tube walls. However, Yu (2003) found no significant difference using a water bath and a single heated tube on the co-precipitation of silica and calcium oxalate. Tests were stopped after 24 h because of the hydrolysis of sucrose. It was found in a separate experiment that 40 wt/v% sucrose solution degraded by 2%, 16% and 34% after 10 h, 24 h and 120 h respectively in solutions containing Ca, C₂O₄²⁻, SiO₂ and *tAC* (East et al., 2013).

Samples were analyzed for reactive [SiO₂], [Ca²⁺] and [C₂O₄²⁻] as described by Yu et al. (2002, 2003). Reactive silica was analyzed with a Cintra 40 double-beam UV-Visible spectrometer (GBC Scientific Equipment Pty. Ltd., Braside, VIC, Australia) using the silica-molybdate complex colorimetric method (APHA, 1996). The samples were filtered through 0.2 μm membrane filters and [Ca²⁺] and [C₂O₄²⁻] were determined from the filtrate. Oxalate ion concentration was determined by UV-Vis using a colorimetric method (Burriel-Martí et al., 1953). However, it could not be accurately determined because of significant interferences when *tAC* and Mg²⁺ ions were present, and so the data obtained was not used in this work. Ca²⁺ ion concentrations were determined using inductively coupled plasma – optical emission spectroscopy (ICP-OES Vista MPX, Varian Inc., Mulgrave, VIC, Australia).

2.4. Analysis of calcium oxalate crystals

After 24 h, samples were centrifuged and washed with Millipore water, then with ethanol (96%, Merck, Kilsyth, Australia) and oven dried at 40 °C. X-ray powder diffraction (XRD) was conducted using PANalytical X'Pert MPD XRD equipment emitting

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