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FORMATION OF THERMODYNAMICALLY UNSTABLE CALCIUM OXALATE DIHYDRATE IN SUGAR MILL EVAPORATORS

By

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Abstract

CALCIUM OXALATE (CaOX) is the most intractable scale component to remove in sugar mill evaporators by either mechanical or chemical means. The operating conditions of sugar mill evaporators should preferentially favour the formation of the thermodynamically stable calcium oxalate monohydrate (COM), yet analysis of scale deposit from different sugar factories have shown that calcium oxalate dihydrate (COD) is usually the predominant phase, and in some cases is the only hydrate formed. The effects of *trans*-aconitic, succinic and acetic acids, all of which are present in sugarcane juice, and ethylenediamine tetraacetic acid disodium salt (EDTA) on the growth of CaOX crystals have been examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD) and thermogravimetric analysis (TGA). *trans*-Aconitic acid, which constitutes two-thirds of the organic acid component in sugarcane juice, in the presence of sugar resulted in the formation of COD and COM in a 3:1 ratio. EDTA was the most effective acid to promote the formation of COD followed by *trans*-aconitic acid, then acetic acid and lastly succinic acid.

Introduction

Calcium oxalates (CaOXs) are a group of crystalline compounds present in plant leaves, kidney and bladder 'stones', beverage processing plants and calandria tubes in sugar mill evaporators.

CaOX and silica are the main components of composite scales formed in the later stages of the evaporation process of sugar mill evaporators. The CaOX component of the scale is responsible for the ineffectiveness of the common cleaning agents such as caustic soda and sulphamic acid. Expensive chelating agents such as ethylenediamine tetraacetic acid disodium salt (EDTA) in high concentration are therefore used for its removal.

CaOX exists in three phases: calcium oxalate monohydrate (COM), dihydrate (COD) and trihydrate (COT). It is sparingly soluble in water and its solubility increases with increasing temperature and ionic strength (i.e. soluble ash), but is little affected at pH > 4 (Walford and Walthew, 1996). Of the three CaOX phases COT is the most soluble followed by COD and COM is the least soluble phase (Nancollas, 1982, Streit *et al.*, 1998).

The least soluble, COM, is thermodynamically stable at temperatures > 60°C. However, both COD and COT are kinetically favoured in the initial stages of crystallisation due to the Ostwald-Lussac rule, but readily transform to COM via a dissolution-recrystallisation process (Skrtic *et al.*, 1987).

The operating conditions of sugar factories should encourage the formation of COM, yet analysis of scale samples from different Australian sugar factories have shown that COD is the predominant phase (Doherty *et al.*, 1993).

This implies that other factors must be contributing to its preference precipitation. COD formation is most favoured by: high initial $[Ca^{2+}]/[oxalate^{2-}]$ ratios, stirring dynamics, low temperatures, increasing amounts of magnesium and potassium ions, colloidal phosphates and carboxylic acids (Skrtic *et al.*, 1987; Callejas-Fernandez *et al.*, 1993; Cody and Cody, 1994). Yu and co-workers (Yu *et al.*, 2002, 2003) have evaluated the thermodynamics and the kinetics of CaOX crystallisation in sugar and silica solutions in order to improve understanding of composite fouling of silica and CaOX.

The results showed that silica in a supersaturated solution of CaOX inhibited the rate of CaOX crystallisation, while the presence of sugar enhanced the crystallisation process. This was later shown to be due to the preferential precipitation of COT or COD (Yu *et al.*, 2005).

For the binary CaOX and silica systems, the co-precipitation of CaOX and silica in the presence of sucrose led to the stabilisation of either COD or COT, depending on the initial concentration of CaOX (Yu *et al.*, 2006). From the foregoing, it is evident that the composition of the sugarcane juice plays a significant role in the type of CaOX phase that is precipitated.

As sugarcane juice contains significant amounts of organic acids (5000 ppm) (Walford, 1996), this paper examined the effects of *trans*-aconitic acid (which comprises two-thirds of the organic acids in juice), succinic acid and acetic acid in the presence and absence of sucrose on the crystallography and morphology of CaOX. EDTA was included in the investigation to assess the impact that the number of carboxyl groups per organic acid has on CaOX crystallisation process, and because EDTA is the cleaning agent of choice for CaOX removal in sugar mill evaporators.

Experimental details

Reagents

Calcium chloride, potassium chloride, acetic acid, sodium oxalate, *trans*-aconitic acid, sucrose, EDTA, sodium hydroxide, hydrochloric acid, ethanol and acetone were analytical grade materials purchased from Sigma Aldrich or Fluka. Deionised water with a conductivity of 0.3 $\mu\text{S}/\text{cm}$ was used in solution preparation.

Preparation methods

The CaOX systems studied were made to contain similar acid concentrations to those present in a typical Australian sugarcane juice.

A sucrose concentration of 46% w/v and a working temperature of 80°C were chosen to approximately match the conditions present in a No. 4 vessel of a quintuple evaporator set of an Australian sugar factory.

Calcium oxalate precipitate formed in an aqueous solution (Control)

100 mL solution (adjusted to pH 7.2) containing 0.3738 g of calcium chloride, and 0.6721 g of potassium chloride was prepared with deionised water. 25 mL of sodium oxalate solution (1.34 mg/mL) pH adjusted to 7.2, was slowly added to the 100 mL solution in a 'rocking' water bath maintained at 80°C \pm 0.1°C.

The mixture was stirred for 30 min and the crystals removed, washed with deionised water followed by acetone. The crystals were dried in a vacuum oven at 40°C.

Calcium oxalate precipitate formed in the presence of sucrose

The solution composition was similar to the control except that the 100 mL solution also contained 57.5% w/v sucrose.

Calcium oxalate precipitate formed in the presence of an organic acid

Aqueous solutions and 57.5% w/v sucrose solutions were prepared as above, containing in addition either acetic acid (79.3 mg, 1380 ppm on dry solids), succinic acid (156 mg, 2710 ppm on dry solids), *trans*-aconitic acid (230 mg, 4000 ppm on dry solids) or disodium EDTA (362 mg, 4410 ppm on dry solids).

Scanning and transmission electron microscopy

Each sample was mounted on an SEM stub by placing a suspension of the sample in acetone on the stub and the acetone allowed to evaporate.

The sample was gold coated and SEM images were obtained using a FEI Quanta 200 Environmental SEM at an accelerating voltage of 15 kV.

The samples for TEM examination were prepared by placing a drop of each sample (suspended in a 50:50 mixture of water and ethanol) in a copper grid and removing the solvent with a filter paper. The samples were examined on a Philips CM 200 analytical TEM operating at 200 kV.

X-ray powder diffraction

Phase characterisation was carried out using a PANalytical X'Pert MPD XRD equipment emitting a Cu_α (1.5418 Å) radiation. The x-ray powder patterns were

indexed based on parameters obtained from the International Centre for Diffraction Data powder XRD card index.

Thermogravimetry analysis

Thermal decomposition of the samples was carried out in a TA ® Instruments incorporated high-resolution thermogravimetric analyser (series Q500) in a flowing nitrogen atmosphere (80 mL/min).

Approximately 5–10 mg of sample was heated in an open platinum crucible at a rate of 5.0 °C/min up to 1000°C.

Results

Morphologies of calcium oxalate

Figure 1 shows the SEM micrographs of CaOX crystals grown in aqueous solution and organic acid. The control samples (Figure 1A and Figure 1B) consist of ‘X’ shaped serrated crystals of 70 µm to 80 µm in length which look like stellates. There are cruciform crystals (~ 40 µm) sparsely dispersed in the stellates.

A similar morphology was obtained with the crystals grown in acetic acid (Figure 1C) and in acetic acid and sucrose (Figure 1D), though these crystals are not regular, showing twining. Cruciforms of larger proportions were also formed.

The crystal sizes of the CaOX crystals grown in solutions containing acetic acid and sucrose were 20% smaller in length than those grown in solutions containing only acetic acid.

The shape of the CaOX crystals grown in the presence of succinic acid appears like four intertwined crescent moons (Figure 1E).

A small number of these crystals are serrated. The crystal sizes range from ~ 30 µm to 60 µm. In both tests there is a lower percentage of the crystals that are cruciforms when compared to the acetic acid tests.

The SEM of CaOX grown in both succinic acid and sucrose (Figure 1F) indicated similar but smaller sized crystals (<40 µm), with most crystals having two joined crescents instead of four.

The outside edges of the crescents were serrated with a feathery appearance.

For the CaOX prepared with *trans*-aconitic acid and EDTA (Figure 1G-Figure 1J), there are two morphologies: one is the cruciform shape that is also present in the other CaOX systems, and the other is distorted spheroids (~5 µm to 10 µm) which are highly twinned.

The crystals prepared with sucrose were similar except that the cruciforms were slightly bigger in size.

The cruciform population was highest in the CaOX systems grown from the solution containing EDTA and sucrose.

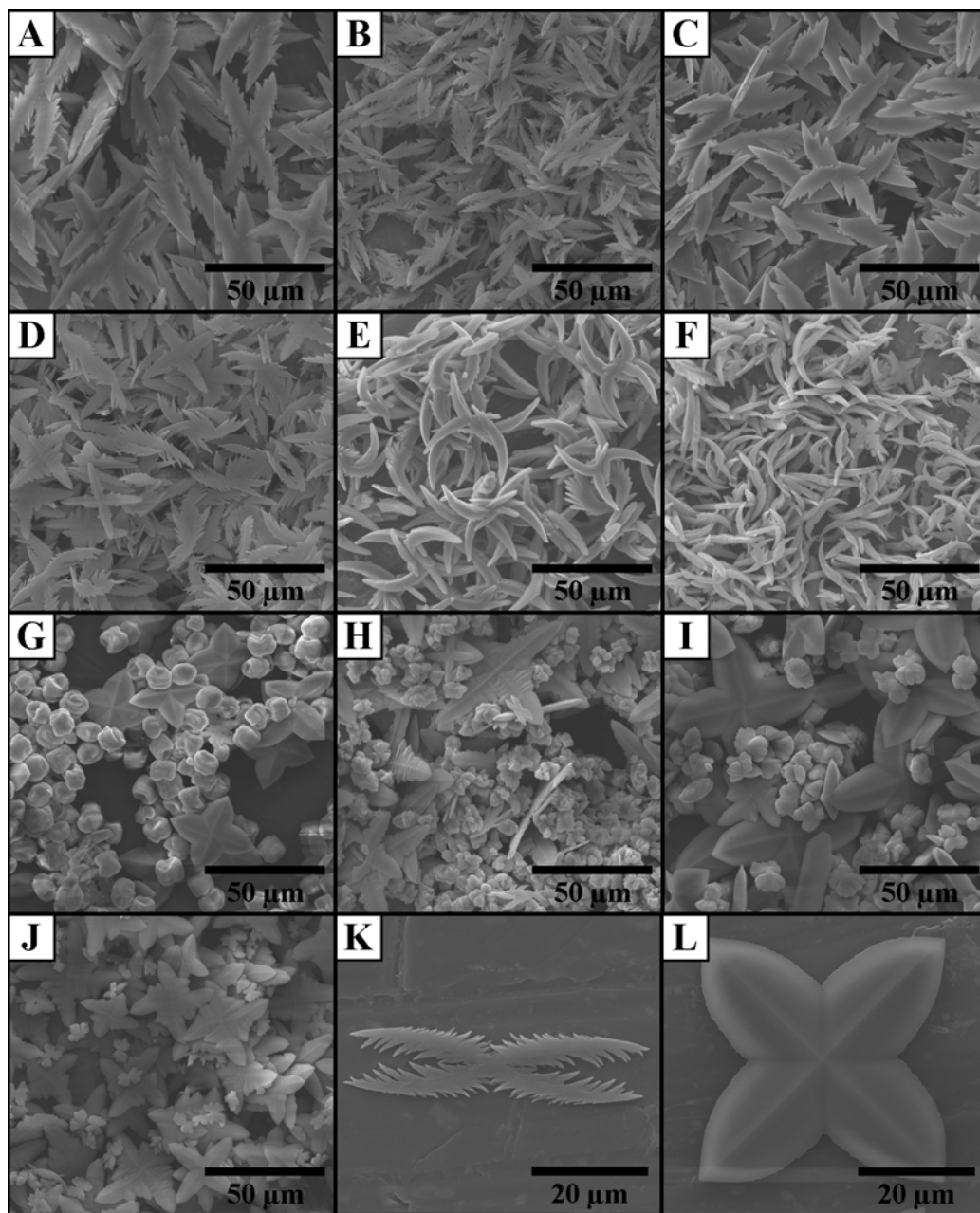


Fig. 1—Scanning electron micrographs of CaOX crystals grown in aqueous solution at pH 7.2 and 80 °C. (A) no additive; (B) sucrose only; (C) in the presence of acetic acid; (D) in the presence of acetic acid and sucrose; (E) in the presence of succinic acid; (F) in the presence of succinic acid and sucrose; (G) in the presence of *trans*-aconitic acid; (H) in the presence of *trans*-aconitic acid and sucrose; (I) in the presence of EDTA; (J) in the presence of EDTA and sucrose; (K) stellate shaped crystal and (L) cruciform shaped crystal.

A further evaluation of the CaOX crystals grown in the various solutions by TEM showed that the crystals formed in layers as illustrated in Figure 2. These layers were made up of nano-sized crystals exhibiting sizes of a few nanometers (Figure

2B). The existence of the nano-sized crystals was more evident with *trans*-aconitic acid and EDTA, an additive with a greater chelating power than acetic acid and succinic acid.

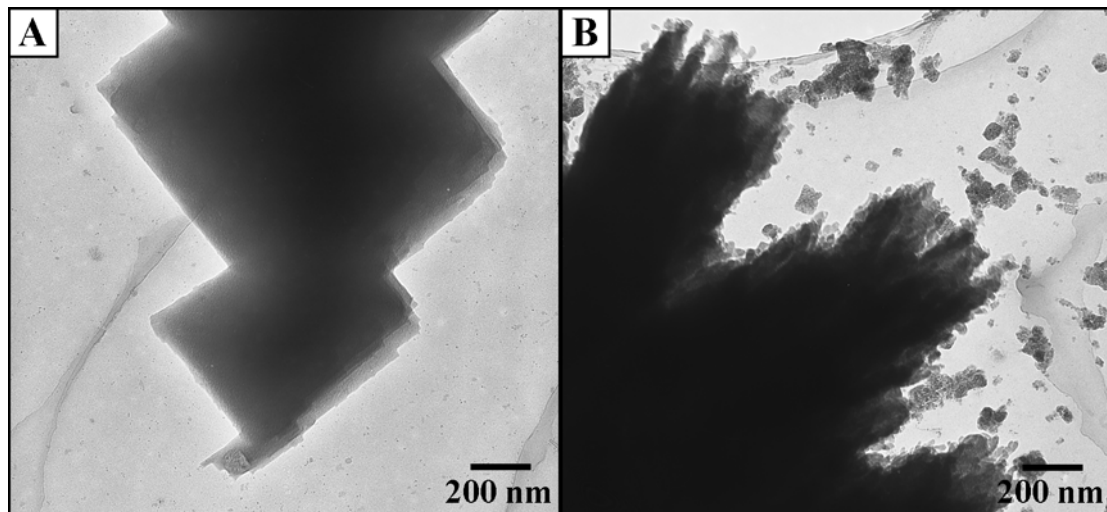


Fig. 2—TEM images of CaOX crystals grown (A) in the presence of succinic acid and (B) in the presence of EDTA.

As shown in Figure 1, there are significant differences in morphology between CaOX crystals grown in *trans*-aconitic acid, EDTA or succinic acid and crystals grown in aqueous solution. These results indicate that *trans*-aconitic acid, EDTA and, to a lesser extent, succinic acid have stronger inhibitory effects for COM formation than acetic acid. The ionisation constant (pK) at 25°C for acetic acid is 4.75, succinic acid is 5.61, *trans*-aconitic acid is 4.46 and EDTA is 10.2. As the working pH for these CaOX systems is 7.2, it is expected that these acids have the ability to form complexes with calcium ions and it has been suggested that the inhibitory effect shown by these acids is a result of competition between the carboxylate groups of the acids and the oxalate ions for calcium ions and/or their preferential adsorption onto CaOX crystal surfaces (Cody and Cody, 1994; Doherty *et al.*, 1994).

It may well be that proportion of the cruciform crystals that forms in the CaOX system is dependent on the complexing ability of the organic acid. EDTA has a stronger ability to form complexes with calcium ions than the other acids (Doremus *et al.*, 1978) and, as shown in Figure 1E, has the largest proportion of the cruciform crystals. Doherty *et al.* (1994) have shown that apart from the characteristic tetragonal and bipyramidal forms, CaOX can also exist in cruciform, stellate and spheroidal forms. As such, the stellates and spheroids formed in the present study are likely to be COM and the cruciforms probably COD, with EDTA having the greatest potential to form this phase.

Crystallographic forms of calcium oxalate

Table 1 gives the phases formed from the different CaOx systems as determined by XRD. The results indicate that the crystallisation of CaOX in an organic acid solution is different from that in aqueous solution. COM is still the major phase, apart from the case where the crystals were grown in EDTA. COD formation is in the following order EDTA > *trans*-aconitic acid > acetic acid > succinic acid.

Table 1—Effect of organic acids on calcium oxalate crystallographic forms.

Organic acid	Calcium oxalate composition (%)		
	COM	COD	COT
Control (no acid)	97.8	0.2	2.0
Control and sugar (no acid)	96.8	0.5	2.7
Acetic acid	96.5	–	3.5
Acetic acid and sugar	81.4	18.6	–
Succinic acid	97.5	2.5	–
Succinic acid and sugar	95.5	4.5	–
<i>trans</i> -Aconitic acid	60.8	39.2	–
<i>trans</i> -Aconitic acid and sugar	25.9	74.1	–
EDTA	9.4	90.6	–
EDTA and sugar	6.8	93.2	–

The main XRD diffraction peaks for COM obtained in the absence of acid were located at the interatomic distances 5.93 Å, 3.65 Å, 2.36 Å and 1.82 Å suggesting preferential growth of the (–101), (020), (130) and (040) planes.

Apart from the CaOX crystals grown in acetic acid, new characteristic COD peaks were obtained for the other systems. The main diffraction peaks for COD of 3.69 Å, 2.41 Å and 2.24 Å suggests a preferential growth on the (002), (103) and (213) planes.

Thermal decomposition of CaOX crystals

The thermal decomposition of the CaOX crystals grown in organic acids and aqueous solution was carried out in order to confirm the XRD data. Figure 3 shows a typical thermal decomposition profile of CaOX. The decomposition occurs in three stages: the first peak at 101°C is due to the loss of water molecules from the crystal lattice, the second peak at 419°C results from the formation of calcium carbonate, and the third peak at 560°C is formation of calcium oxide (Kloprogge *et al.*, 2004).

The results of Figure 3 indicate that the dehydration process is complete by 110°C. The percent weight losses associated with pure COM (i.e. CaC₂O₄.H₂O) and pure COD (CaC₂O₄.2H₂O) dehydration are 12.3% and 22% respectively. As such the percentage weight loss of the CaOX obtained from a particular system should give a qualitative indication as to whether the crystals are predominantly COM or COD.

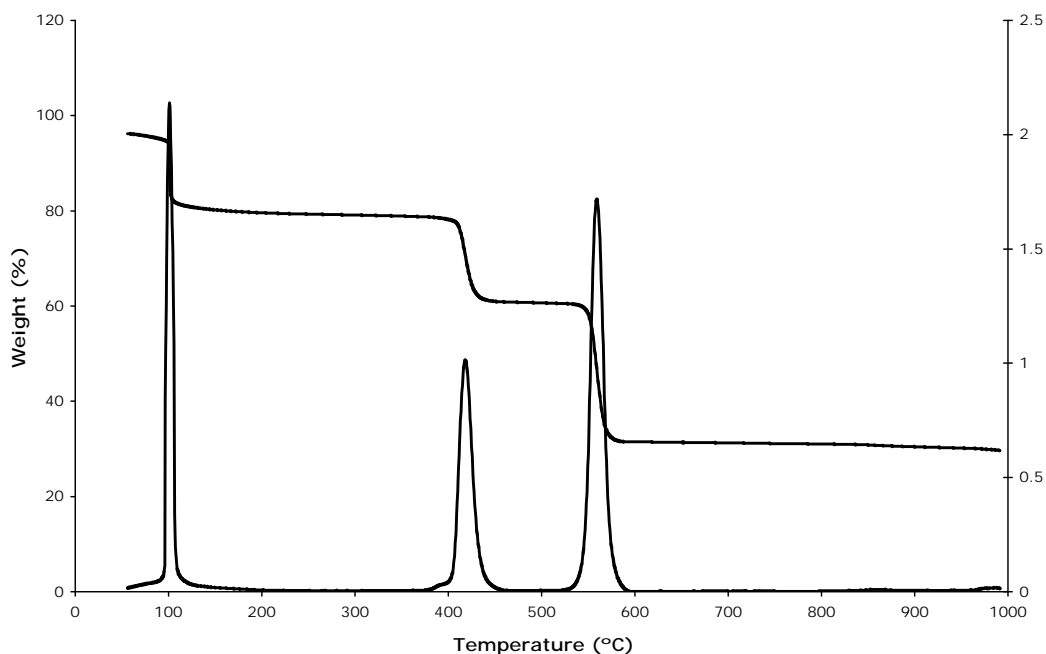


Fig. 3—Thermal decomposition of CaOX crystals grown in *trans*-aconitic acid.

In Table 2, the weight loss determined by TGA for CaOX crystals grown in various systems is listed.

The values obtained are higher than the theoretical value for pure COM implying that COT or COD are present in these samples. Also, higher values are obtained for crystals grown in an organic acid and sugar than in the same system without sugar.

The percentage weight loss for the crystals grown in EDTA and sugar is 22.21% which approximates to that of pure COD. These TGA data are consistent with the data obtained by XRD and SEM.

Table 2—Dehydration of CaOX grown in different systems.

Organic acid	Weight loss (%)
Control (no acid)	12.9
Control and sugar (no acid)	13.8
Acetic acid	12.6
Acetic acid and sugar	16.5
Succinic acid	13.0
Succinic acid and sugar	15.2
<i>trans</i> -Aconitic acid	19.1
<i>trans</i> -Aconitic acid and sugar	19.9
EDTA	21.2
EDTA and sugar	22.2
Pure COM	12.3
Pure COD	22.0

Discussion

Previous work (Nancollas, 1983; Manne *et al.*, 1990; Doherty *et al.*, 1994; Sikiric *et al.*, 1999) has shown that the more soluble and thermodynamically unstable COT and COD usually form as precursors to COM formation. They appear at the initial stages of the reaction and undergo a phase transition through a dissolution-crystallisation process. However, the transition process may be inhibited by the presence of additives (organic and/or inorganic), presumably through adsorption of these additives on specific crystal planes (Manne *et al.*, 1990; Cody and Cody, 1994).

In the present study COT is the initial phase formed in the control and in the CaOX systems with acetic acid (Table 1), before undergoing phase transition. For CaOX systems with other organic acids, COD appears to be the initial phase formed.

The results have shown that acetic acid and succinic acid are poor inhibitors of COM formation, while EDTA and, to a lesser extent, *trans*-aconitic acid are effective inhibitors. Acetic acid contains one carboxylate group, while succinic acid contains two. It appears that, under our experimental conditions, greater than two carboxylate groups (*trans*-aconitic acid has three and EDTA has four) are necessary to suppress COM formation and strongly adsorb on the (002), (103) and (213) planes of COD. This is contrary to Cody and Cody (1994) who reported that at least two carboxylate groups were necessary to suppress COM formation.

The binding ability of these organic acids may be due to their ability to adopt conformations in which two or more carboxylate groups can interact with the surfaces of the CaOX (Fleming *et al.*, 2001) inhibiting COM growth.

This process will also result in structural matching on certain CaOX crystal planes (Gilbert, 1990). In fact Cody and Cody (1994) were of the view that only linear molecules with carboxyl group spacing of approximately three C-C bond lengths could fit into the COM crystal lattice.

Doherty and Wright (2004) and Yu *et al.* (2006) studied the effect of sucrose molecules on COM inhibition. Yu *et al.* (2006) were of the view that the enhanced formation of COD with increase in sucrose concentration was related to the adsorption capacities of the CaOX hydrates. COM adsorbed polymeric molecules 3× more than COT and 10–15× more than COD (Tomazic and Nancollas, 1980).

Thus, at high sucrose concentration, COD would be able to adsorb sucrose molecules and preferentially form. The formation of COD in sucrose solution may also be related to the changes in the initial CaOX supersaturation due to reduced solubility of CaOX in sucrose solution (Yu *et al.*, 2006).

In the COD crystal structure, the calcium located in the polyhedron has six of the eight oxygen atoms belonging to four oxalate groups, one less oxalate group than COM (Tazzoli and Domeneghetti, 1980). As such, a high calcium/oxalate ratio favours the formation of COD (Grases *et al.*, 1990).

Carboxylic acids with their higher electronegativity would electrostatically repulse the oxalate ions within the vicinity of the growing nuclei, increasing the calcium/oxalate ratio, and hence stabilise COD formation (Doherty *et al.*, 1994).

The morphologies (with growth in certain planes) of COM and COD formed in the various systems examined may also be related to lattice matching and the ionic characters of the different planes (Yu *et al.*, 2006).

The reduction in crystal size (from SEM micrographs) for COM crystals grown from acetic and succinic acids solutions in the presence of sugar may be related to increased supersaturation due to reduced water activity.

The increase in crystal size for the CaOX systems with either *trans*-aconitic acid or EDTA in the presence of sugar where COD is formed, is probably because crystal growth occurs in a reduced number of nucleation sites due to complex formation between *trans*-aconitic acid/EDTA with calcium ions.

From the present study and previous studies it is concluded that the thermodynamically unstable COD is preferentially formed in sugar mills because of the following:

Organic acids. Sugarcane juice contains carboxylate-bearing acids *trans*-aconitic, succinic, acetic, citric, malic etc., which are known to suppress the formation of COM. The formation of mixed COM-COD scale could probably, in part, be related to the proportion of COM-forming additives (e.g. succinic acid) relative to the other organic acids.

Sucrose. The presence of sucrose in CaOX systems shifts the phase composition from COM to COD.

Silica. Previous work by Yu *et al.* (2006) have reported that the presence of silica enhanced COD formation due to preferential adsorption of silica molecules on crystal planes based on electrostatic interactions as well as structural and stereochemical relationships.

Calcium. High calcium to oxalate ratios favour COD formation. Sugarcane juice generally has a high calcium/oxalate ratio and this ratio will be higher in situations of over liming during clarification and the recirculation of unclarified mud filtrate which has substantial quantities of calcium.

Cody and Cody (1994) used molecular modelling (i.e. computers to simulate chemical compounds and processes) to establish the structural compatibility between carboxylate groups and CaOX.

This probably led to the development of scale inhibitors, such as poly(maleic acid) and poly(acrylic acid), currently used for scale control. These inhibitors were developed for aqueous systems where the roles of sucrose and silica were not considered. In designing scale inhibitors for the sugar industry, the influence these and other macromolecules (polysaccharides, surface-active compounds, and proteins) have on CaOX inhibition should be taken into account as well as carboxylate-based inhibitors containing more than two carboxylate groups per molecule. Because COD contains fewer adsorption sites than COM and is poorly adsorbing (Cody and Cody, 1994), the new scale inhibitor should be used in relatively high concentrations and must meet 'Generally Recognised as Safe' (GRAS) and Food and Drug Administration guidelines.

Conclusion

The effect of organic acids and sugar on the crystallisation of CaOX was investigated. COM inhibition and COD formation was in the order EDTA > *trans*-aconitic acid > acetic acid > succinic acid. The presence of sugar enhanced the formation of COD. To design effective scale inhibitors for CaOX the role of organic acids, sugar and silica must be considered.

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