

PRELIMINARY MODEL FOR OXALATE FORMATION IN EVAPORATOR SCALE

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Abstract

The study of the organic acid composition of scale from evaporators indicates that oxalic acid is the major organic acid constituent in the later effects. A model of oxalate solubility in sucrose solution leads to the conclusion that oxalate precipitation in scale arises from degradation of juice components.

Keywords: model, evaporator scale, calcium oxalate

Introduction

The composition and analysis of scale samples from local mills has received much attention in recent years due to the effect of scale formation on evaporator fouling. Methods of analysis include X-ray fluorescence (XRF) and X-ray diffraction (XRD) (Walthew and Turner, 1995). Although these procedures identify the type of crystal structure and give the inorganic composition of the scale, they do not give quantitative values, especially for the precipitated salts of organic compounds. These compounds include organic acids extracted from cane and those produced in the factory by chemical and microbial degradation of sugar. Oxalic acid is the most common organic acid found in scale (Carruthers *et al.*, 1956; Walthew and Turner, 1995), normally as the calcium oxalate salt in either of its two crystalline forms, *viz.* calcium oxalate monohydrate or calcium oxalate dihydrate. XRD has shown that calcium oxalate will generally be found in the later effects of the evaporator station. Precipitated oxalate in scale is either due to oxalic acid present in the cane or decomposition of cane constituents during processing. Little information is available on the thermodynamics and kinetics of calcium oxalate formation in the presence of sucrose. Research on oxalate formation has been undertaken in the beet industry under different processing conditions (Carruthers *et al.*, 1956). A local study was therefore undertaken with the following objectives:

- to develop a method of analysis for determining the organic acid composition of scale
- to determine the thermodynamic properties of calcium oxalate formation
- to define a preliminary model for calcium oxalate formation in the evaporator station
- to use this model to determine whether oxalate in evaporator scale originates from cane juice or chemical decomposition.

Experimental

The organic acid compositions of acid digested scale, clear juice and syrups were measured using ion-exclusion high performance liquid chromatography (HPLC) with a dilute sulphuric acid mobile phase and refractive index detection. The procedure is described in Appendix 1. Oxalate concentrations in synthetic juice and syrup samples were measured spectrophotometrically using a colorimetric method (Burriel-Marti

et al., 1953) based on the change in absorbance at 520 nm of a ferri-salicylate complex on addition of oxalate. Details are described in Appendix 2. Titratable acidity in clear juice (10 g) and syrup (5 g) was measured on a Metrohm E346 Potentiograph using 0,1 N sodium hydroxide and titrated to an end point of pH 8,1.

Results and discussion

Analysis of scale

Chromatographic separation techniques exist for quantitatively analysing the organic acid content of juices and factory products (Oldfield *et al.*, 1973, Reinefeld *et al.*, 1975, de Bruijn *et al.*, 1984, Blake *et al.*, 1987, Celestine-Myrtill and Parfait, 1988). Most of these are tedious in their sample preparation and are not suited to analysing large numbers of scale samples. Attempts at quantifying the organic composition of scale have included isolating oxalate (Schmidt, 1954) using a wet chemical technique and a range of acids using ion exchange and paper chromatography (Crees *et al.*, 1992). Schmidt's (1954) method has the problem of over-estimating the oxalate composition in cane factory scale due to interference with co-precipitated aconitic acid (Walford, 1995), and the paper chromatography technique is semi-quantitative. The acid digestion and HPLC method described in Appendix 1 is both quantitative and rapid. Table 1 summarises reproducibility of the digestion procedure, and linear range and sensitivity of the method for a variety of acids found in scale are summarised in Table 2.

Table 1
Reproducibility of scale digestion (n = 5)

Acid	g/100 g scale	RSD %
Oxalic	4,2	1,6
Phosphoric	0,4	2,4
Citric	0,4	2,0
Malic	0,6	2,5
Aconitic	38,2	0,5

Table 2
Summary of linearity and sensitivity

Acid	Linear Range (ppm)	MDQ* (ppm)
Oxalic	5-500	>2
Phosphoric	5-200	>2
Citric	5-200	>2
Malic	5-500	>2
Aconitic	5-500	>2

* MDQ = minimum detectable quantity

A comparison of a standard and a typical scale chromatogram is shown in Figure 1. The phosphate value by this method may be lower than the true value due to incomplete

dissolution of calcium phosphate in the form of hydroxy apatite. Oxalic acid results of the analysis of a variety of scale samples are shown in Table 3. These results confirm the trend shown by XRD analysis that oxalate formation tends to be found in the later effects of the evaporator station (Walthew and Turner, 1995).

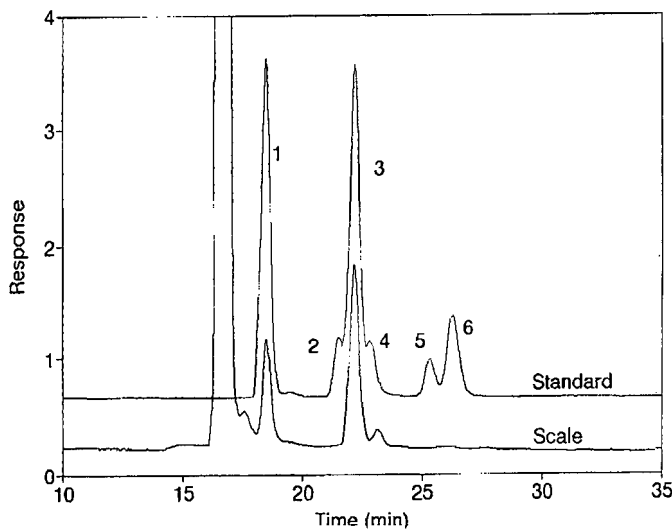


FIGURE 1: Ion exclusion chromatogram showing acids in calibration standard and typical evaporator scale sample (Key: 1 = oxalic, 2 = citric, 3 = phosphoric, 4 = tartaric, 5 = malic, 6 = aconitic)

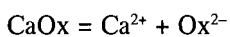
Table 3

Oxalate composition of scale samples (expressed as % free acid in sample)

Mill		Effect				
		1	2	3	4	5
Noodsberg	Normal			7,9	5,1	10,6
	Antiscalant trial			2,9		12,4
Pongola	July 1993	0,7	1,4	3,4	8,0	2,7
Maidstone	August 1995	7,7	10,3	11,5	9,9	
	July 1995	6,2	10,3	9,4	5,9	
	August 1995	10,3	9,9	10,4		
	August 1995	6,2	3,8			
	July 1995	8,4		13,7		
Felixton	July 1995			1,1	0,9	
	August 1995	1,4	1,5	4,1	10,5	11,2
	Composite 1994	0,9	2,0	5,9	9,5	6,5
	August 1995		0,5	0,5	12,1	
Malawi	August 1995	0,7	0,8	1,1	2,6	2,6
Umbombo Ranches, Swaziland				6,0	3,8	
India		0,4	2,3	8,8	11,5	3,5

Thermodynamic properties of calcium oxalate

For a salt such as calcium oxalate, the equilibrium reaction for dissolution in water can be written:



The solubility is defined by the solubility product (K_{sp}):

$$K_{sp} = [Ca^{2+}] \times [Oxalate^{2-}] \quad (1)$$

where $[Ca^{2+}]$ and $[Oxalate^{2-}]$ are the activities of the calcium and oxalate ions, respectively. In dilute solutions the activity can be replaced with the molar concentration (moles/L). Le Châtelier's principle states that the position of chemical equilibrium will shift in a direction that counteracts the applied stress in order to keep K_{sp} constant. Thus addition of lime will reduce oxalate concentration. Calcium oxalate has a K_{sp} of $2,3 \times 10^{-9}$ in water at 20°C (Latimer and Hildebrand, 1965). It should be noted that K_{sp} values reported in the literature are only valid in dilute aqueous solutions and are probably invalid in sucrose solutions.

To investigate the solubility of calcium oxalate in sugar solutions at varying temperatures and brix values requires the determination of oxalate concentration at trace levels in these solutions. In a cane juice solution other ions present (iron, magnesium, phosphate, proteins and organic acids) could form complexes with calcium and oxalate, making calculations of oxalate concentration difficult to interpret. This was overcome by using synthetic sugar solutions and analysing for oxalate as described in Appendix 3. The resulting concentration of oxalate ion as a function of temperature and brix is shown in Table 4.

Table 4

Oxalate concentration in synthetic sucrose solutions (expressed as ppm oxalate)

Brix (°)	Temperature (°C)			
	50	60	70	85
0,0	11,0	12,6	14,9	16,3
10,4	4,7	5,1	3,4	1,3
20,2	2,0	2,2	1,9	0,5
30,4	2,2	2,8	2,0	0,4
41,2	1,5	2,0	1,1	0,5
61,2	1,0	1,0	0,9	0,3

The results show that the solubility of calcium oxalate in aqueous sucrose solution decreases with both increasing sucrose concentration and increasing temperature. An exponential curve of the form:

$$y = b1 * \exp(-b2 * x) + b3 \quad (2)$$

where y = solubility

b1, b2, b3 are temperature related constants

x = sucrose concentration

can be fitted to each set of data, an example of which is shown in Figure 2. Expressing the constants b1, b2, b3 from each curve as a function of temperature (Table 5) and substituting into equation 2 leads to the equilibrium concentration of oxalate in solution being expressed as a function of both temperature and brix:

$$ppm \text{ oxalate} = b1 * \exp(-b2 * Bx) + b3$$

where $b1 = (0,18915 * T) + 0,1121$

$b2 = (0,00504 * T) - 0,1654$

$b3 = (-0,0300 * T) + 3,084$

and T = temperature (°C).

Table 5
Calculated constants b1, b2, b3

Temperature (°C)	Constant			R ²
	b1	b2	b3	
50	9,75	-0,1037	1,262	0,9918
60	10,977	-0,1126	1,620	0,9842
70	13,798	-0,1811	1,114	0,9955
85	15,964	-0,2716	0,336	0,9999

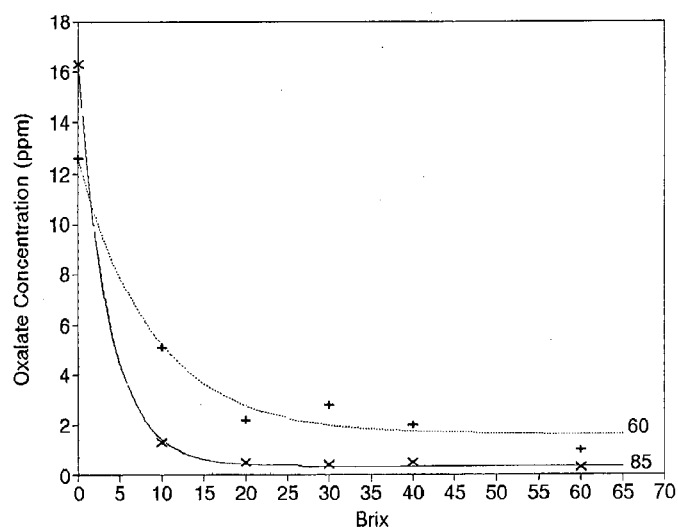


FIGURE 2: Effect of temperature and sucrose on calcium oxalate solubility

A theoretical equilibrium oxalate concentration across a model evaporator station can be calculated using the above equation and average values for temperature and brix (Table 6). Values for oxalate concentrations above 100°C have not been calculated. This was due to experimental problems associated with sampling from pressurised test vessels. The model shows that oxalate concentration decreases between the clarifier and second effect; only in the later effects does the solubility increase slightly. This would indicate that oxalate should precipitate in the earlier stages. Oxalate concentration of scale samples indicate that in practice oxalate precipitates mainly in the later effects. The conclusion to be drawn would be that the oxalate in scale is not coming from the juice.

Table 6
Calculated oxalate concentration in a model evaporator station
(assuming no calcium and 300 ppm calcium in juice)

Stage	Temperature (°C)	Brix (°)	Calcium oxalate (ppm)	
			(0 ppm Ca)	(300 ppm Ca)
Clear juice	90	12	0,9	0,0013
2	105	28	N/A*	N/A*
3	97	34	0,2	0,0000
4	86	42	0,5	0,0006
5	57	65	1,3	0,0013

* N/A = not applicable

The model is based on the equilibrium solubility of calcium oxalate and assumes no calcium present in the solution. This is obviously not the case in process streams. Modifying

the model to account for calcium present in juice can be achieved by calculating the K_{sp} values of calcium oxalate from the previous data by assuming that the molar concentration of oxalate and calcium are equal at equilibrium. This is only valid provided no other calcium or oxalate are present other than from the added calcium oxalate, as is the case for the synthetic test solutions. Equation 1 can be written in the form:

$$K_{sp} = [\text{Oxalate}^2]^{-2}$$

since the calcium concentration must equal the oxalate concentration. The resultant solubility product as a function of temperature and brix can be calculated and substituted into equation 2:

$$K_{sp} = b1 * \exp(-b2 * Bx) + b3$$

where $b1 = (0,5425 * T) - 11,8388$

$$b2 = (0,009767 * T) - 0,3527$$

$$b3 = (-0,00803 * T) + 0,7833 \text{ and}$$

$$T = \text{temperature } (^\circ\text{C})$$

Using the same evaporator conditions as in Table 6, and the oxalate concentration as a function of temperature, brix and calcium concentration can be calculated (Table 6). Calcium concentrations of 200 to 400 ppm in the clear juice are routinely encountered and an average of 300 ppm is used in the model. These results show that little, if any, calcium oxalate should be present in clear juice entering the evaporators. Given the large quantity of calcium in factory streams and the low solubility of calcium oxalate in these streams, it is difficult to explain the presence of relatively large quantities of oxalate in scale as originating from the mixed juice. The evidence here would seem to point either to the degradation of sugar or the partial decomposition of other organic compounds present in the juice under oxidising conditions. Decomposition of some form of acidic precursor to form oxalic acid was proposed in the beet industry (Katz, 1955). Lack of sensitive analytical techniques precluded definitive conclusions. Decomposition of organic compounds is the proposed cause in the cane process streams as evidenced by the results of decolourising experiments.

The use of ozone and sulphite as decolourising agents for juices and syrups has been studied at the Sugar Milling Research Institute (Davis, 1995). Samples from ozonolysis were analysed for organic acids and it was found that aconitic acid concentrations decreased whilst glycolic, malic and oxalic acids increased (Table 7) by up to five-fold with increasing ozone concentration. In the presence of ozone (a strong oxidising agent), aconitic acid is able to undergo oxidation to form an ozonide (Morrison and Boyd, 1973) which can react with water to form malic and glycolic acids, which can react further to form oxalic acid. Although ozone is not normally present in factory streams, oxidising conditions can exist with the added possibility of metallic catalysts (especially copper) and this route could account for the presence of oxalate in scale. Further evidence for the proposed source of oxalic acid is provided by the results of the sulphitation trials. Sulphur dioxide acts as a reducing agent in solution and should therefore eliminate or reduce the quantity of oxalic acid formed. This is clearly shown in Table 7. This trend was also shown in anti-scalant trials at NB using sulphitation (Walthew and Turner, 1995). Monthly composites of clear juice and syrup samples from six mills were analysed for organic acids and titratable acidity. Both the normalised glycolic acid concentration and titratable acidity increased between juice and syrup, lending further support to this proposed model (Table 8). Both clear juice and syrup samples showed no detectable

oxalic acid (<1 ppm) indicating complete precipitation of the calcium oxalate as predicted by the model. Further study is continuing.

Table 7

Acid concentration of syrups subjected to ozonolysis (expressed as ppm free acid in solution)

Acid	Sample						
	Control	O ₃ ppm			SO ₂ ppm		
	Syrup	1 000	2 000	3 000	1 000	2 000	3 000
Oxalic	59	86	104	120	40	47	48
Citric	586	606	596	579	564	570	509
Phosphoric	236	188	167	168	144	167	125
Tartaric	75	76	65	67	56	130	82
Malic	474	565	612	672	472	485	464
Aconitic	2 841	2 697	2 667	2 621	2 639	2 676	2 401
Succinic	34	73	69	70	41	36	47
Glycolic	61	164	218	336	68	67	87
Lactic	211	213	213	201	201	236	223

Table 8

Analysis of monthly composite samples showing average increase in titratable acidity and glycolic acid

Mill [n]*	Titratable acidity (syrup-clear juice) meq/Bx ()**	Glycolic acid (syrup-clear juice) ppm/Bx ()**
Pongola [5]	0,0236 (36)	35 (48)
Felixton [7]	0,0279 (40)	50 (50)
Darnall [9]	0,0253 (37)	26 (56)
Noodsberg [6]	0,0322 (61)	36 (51)
Sezela [6]	0,0157 (16)	105 (150)
Umzimkulu [6]	0,0126 (15)	15 (29)

* [n] = number of composite samples

** () = percentage increase on clear juice average values
meq = milliequivalents

Conclusions

The presence of calcium oxalate in evaporator scale samples cannot be satisfactorily explained by the presence of oxalic acid in mixed juice samples. The proposed model indicates that all the oxalate is removed during normal clarification and there should thus be little oxalate precipitation in the evaporators. It is proposed that most of the calcium oxalate present in scale arises from decomposition of other components of the juice, possibly aconitic acid, under oxidising conditions.

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Appendix 1

The measurement of organic acid salts in scale, clear juice and syrup using ion-exclusion HPLC

Equipment:

Pump	Spectra-Physics Isochrom pump
Column	BioRad HPX-87H (300 mm x 7,8 mm) in series with Phenomenex Resex H* (300 mm x 7,8 mm)
Detector	Erma ERC 7512 Refractive Index detector
Integrator	HP3396 Series II (height mode)

Conditions:

Solvent	0,0075N H ₂ SO ₄ filtered (0,45 µm) and stirred at 65°C on a hotplate
Flowrate	0,5 ml/min
Column temperature	30°C (BioRad); 70°C (Phenomenex)
Sample volume	100 µl
SPE Cartridge	Waters QMA SepPak

Standard preparation:

Stock standard solution was made by dissolving an appropriate amount of either the free acid or its sodium or potassium salt in water and making dilutions as required.

Sample preparation:

Scale. A weighed, ground scale (0,5 g) was leached overnight in 10 ml 1 N HCl at 50°C. This was made up to 200,0 ml volumetrically with water, filtered and injected into the HPLC.

Procedure for isolating acids from a sugar matrix on a QMA SepPak

	Steps	Purpose
1	5 ml 0,5 N KCl	Equilibration
2	5 ml H ₂ O	
3	5 ml air (blow SepPak dry)	
4	2 ml sample	Isolation of acids
5	20 ml H ₂ O	
6	10 ml air (blow dry)	
7	1,5 ml 0,2 N H ₂ SO ₄ (into vial)	Elution of acids
8	2 ml air blow dry (into vial)	

Clear juice and syrup. The pH of a weighed 5 g juice sample or 1 g syrup sample with 5 ml water, was adjusted to 8,5 with 0,1 N NaOH and made up to 10,0 ml volumetrically with water. A 2 ml aliquot was used in the isolation scheme shown above.

Appendix 2

Colorimetric determination of oxalate ion

Equipment:

Spectrophotometer	Phillips PU8620 UV/VIS/NIR Absorbance mode
Wavelength	520 nm
Cell	1 cm

Reagent:

Ferric solution (1)	0,15 g ammonium ferric sulphate dissolved in 250 ml water
Salicylate solution (2)	1% sodium salicylate
Coloured reagent (3)	125 ml of solution 2 is added to solution 1, 1:1 ammonium hydroxide is added dropwise until a yellow col-

our appears, 10 drops are added in excess and made up to 500 ml with glacial acetic acid

Procedure:

Coloured reagent (5 ml) is added to 5 ml of sample or standard, mixed and the absorbance is read. A standard curve is generated between 0 and 20 ppm and the sample concentration is calculated.

Appendix 3

Experimental procedure – synthetic juices

Synthetic juice (10, 20, 30, 40, 60° Bx) was made by dissolving Analar sucrose in an appropriate quantity of water. The sucrose had been shown by HPLC (Appendix 1) to be free of organic acids. Calcium oxalate (50 mg) was added with stirring to the sucrose solution (50 ml), heated to the required temperature and maintained at this temperature for a period of 30 minutes. Duplicate samples (5 ml) were removed by filtration (10 μ polycarbonate filter attached directly to a 5 ml graduated syringe) directly from the juice and diluted immediately with coloured reagent (Appendix 2) for oxalate determination.