

# SOFTENING OF CLEAR JUICE

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## Abstract

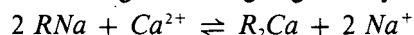
The removal of calcium and magnesium ions (softening) from clear juice can be beneficial to downstream processes. Such benefits include reduced evaporator scaling and the improved potential for the application of ion exclusion chromatography for additional sucrose recovery. The results of experiments in the laboratory and on a pilot plant scale are presented. These show that it is possible to soften clear juice using a strong acid cation exchange resin in the sodium form. A pilot evaporator has shown that softening substantially reduces evaporator scaling in the first effect.

## Introduction

The aim of this investigation was to determine the feasibility of removing calcium from sugarcane clear juice. This would improve processing by reducing evaporator scaling and serve as a pretreatment for the ion exclusion chromatographic desugaring of molasses. Softening is the term used to describe the removal of hardness determining ions which are mainly calcium, magnesium and, to a lesser extent, iron and manganese from solutions. Softening may be accomplished by the addition of chemicals or by ion exchange processes. Softening by ion exchange involves the substitution of an ion in a solution with another ion without any change in ionic concentration. The hardness-determining ions are removed by exchange with sodium ions. The ion exchanger is usually a strong acid cation exchanger and this softening process may also be referred to as sodium cation exchange.

### Mechanism of softening

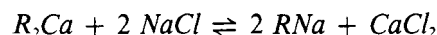
Softening is one of the simplest ion exchange processes (Miyahara, 1968) but Oldfield *et al.*, (1980) point out that the reaction mechanism is not one of straight calcium/sodium exchange as magnesium has the same affinity for the resin as calcium. The calcium and magnesium in cane juice could occur in the bicarbonate, sulphate or chloride forms to give species such as  $NaHCO_3$ ,  $Na_2SO_4$  or  $NaCl$  after ion exchange. In practice the resin cannot remove all the calcium ions from the juice because some of the calcium is present as part of a complex which does not participate in the reaction. Calcium needs to be present as a cationic species to be removed. For most purposes the following reaction mechanism for ion exchange softening is generally accepted:



where R represents the resin polymer which normally consists of polystyrene crosslinked by divinyl benzene (DVB) to form a matrix of insoluble beads. The degree of crosslinking, expressed as a percentage of DVB added to the polymer during manufacture, determines the physical strength (high DVB) and porosity (low DVB). Sulphonic functional groups ( $R_n-SO_3-Na^+$ ) fixed to the resin surface take part in the exchange of ions and hence the term strong acid cation exchange (Shore *et al.*, 1988).

When the resin is entirely in the calcium (and magnesium) form it is said to be exhausted and regeneration with sodium ions is necessary. Regeneration thus serves to remove the calcium and magnesium from the active sites and replace

them with sodium ions. The form of the regenerant waste may be either  $CaCl_2$  or  $MgCl_2$  (Lancrenon and Printemps, 1984). A simplified reaction of the regeneration is shown below.



Industrial resins are normally quoted as having a total exchange capacity in eq/l (about 2.0), i.e. number of equivalents of active sites per litre of resin. However the basic operating capacity is dependent on the amount of regenerant used. The regeneration efficiency depends on the concentration of the regenerant. For strong acid cation exchangers in the sodium form the recommended regenerant strength is 10% NaCl and the amount of NaCl required to regenerate the resin is normally 150 – 200 g/l of resin.

### Benefits of softening with respect to ion exclusion

Ion exclusion chromatography is a technique which is widely used in the beet industry to recover up to 90% of the sucrose lost to final molasses. The process uses a column, or number of columns, packed with porous ion exchange resin beads. Separation occurs as a result of the size and the charge of the constituents in the molasses resulting in two main fractions. One of these is a high purity sucrose fraction and the other a low purity non-sucrose fraction. For this process to work in the cane sugar industry calcium must be eliminated from the molasses to be processed. This may be done at the clear juice, syrup or molasses stages.

To explain why softening is best done on clear juice rather than syrup or molasses consider the following law of mass action at equilibrium (Schneider, 1978).

$$\left( \frac{X_{Ca^{2+}}}{X_{K^+}} \right)_R = K \left( \frac{C_R}{C_S} \right) \left( \frac{X_{Ca^{2+}}}{X_{K^+}} \right)_S$$

where

- $X_{Ca^{2+}}, X_{K^+}$  = The fraction of the total concentration in equivalents per unit volume or unit of weight which is attributable to calcium or potassium.
- $C_R, C_S$  = Total concentration of ions (in equivalents per unit volume or weight) in the resin and solution respectively.  $C_S$  can be measured and  $C_R$  is a function of the particular resin used.
- $K$  = Equilibrium constant which is dependent on the valencies of the ions and the affinity of a particular ion for the resin.
- $R, S$  = Indices for the resin and solution respectively.

The total capacity ( $C_R$ ) of the resin is a constant and the ratio of calcium to potassium ions in solution

$\left[ \left( \frac{X_{Ca^{2+}}}{X_{K^+}} \right)_S \right]$  is essentially the same (except for some cal-

cium removed in scale) from clear juice to molasses.

In order to maximise  $\left[ \left( \frac{X_{Ca^{2+}}}{X_{K^+}} \right)_S \right]$ , which means more

calcium will be exchanged on to the resin, it will be necessary to decrease the total concentration ( $C_s$ ). This trend is shown in Figure 1. The ratio of calcium to potassium is assumed to be constant and  $C_R$  is taken as 2,0 eq/l.  $C_s$  is low for clear juice (0,05 eq/l) and high for molasses (1,05 eq/l). In other words the equation predicts that calcium from the solution will adsorb onto the resin more readily at low  $C_s$  (i.e. when  $\left[\left(\frac{X_{Ca^{2+}}}{X_{K^+}}\right)_s\right]$  is high), but potassium will be the preferred

ion at high  $C_s$ . This observation is important when considering the removal of calcium ions for chromatographic sugar recovery, i.e. it is better to soften clear juice (low  $C_s$ ) for sucrose recovery from molasses than to try to soften molasses (high  $C_s$ ) as the resin is not effective at removing calcium at high  $C_s$  (Zievers and Novotny, 1974).

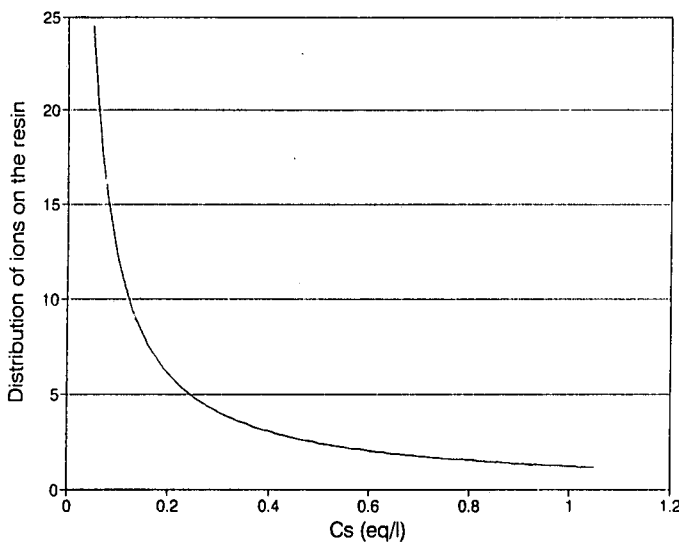


FIGURE 1 Graph showing the relationship between the distribution of ions on the resin  $\left[\left(\frac{X_{Ca^{2+}}}{X_{K^+}}\right)_s\right]$  and the total concentration of ions in the feed liquor (for  $C_R = 2,0$  eq/l).

**Benefits of softening in terms of evaporator scaling**

Many references point out the effect that softening of beet juice has on eliminating the need to clean the evaporators during a crushing season (Gupta *et al.*, 1967; Felber, 1971; Lubenski and Mackay, 1974; Gryllus and Delavier, 1975; Shore *et al.*, 1988; Zanaianis *et al.*, 1990 and Lancrenon, 1991 to name but a few). In fact, in 1951, Dymond reported that ion exchange was the ultimate solution to scale problems in the Natal sugarcane growing areas. Evaporator scale is predominantly  $Ca_3(PO_4)_2$  in the earlier effects and calcium oxalate in the latter effects (Honig, 1963) which suggests that removal of calcium will eliminate this type of scale. The calcium as a percentage of the scale from a number of South African factories for the 1992/93 season analysed at the SMRI (Figure 2) shows that scale in evaporators is indeed mostly calcium. The advantages of not having to clean the evaporators include the saving in down time and in the cost of chemicals and labour used for the cleaning. Clean evaporators will also ensure that evaporation rates remain constant. This will avoid (a) a drop in the syrup brix, (b) lower vapour pressures and (c) extended boiling times in the pans if the crushing rate and juice flow rate are to remain the same.

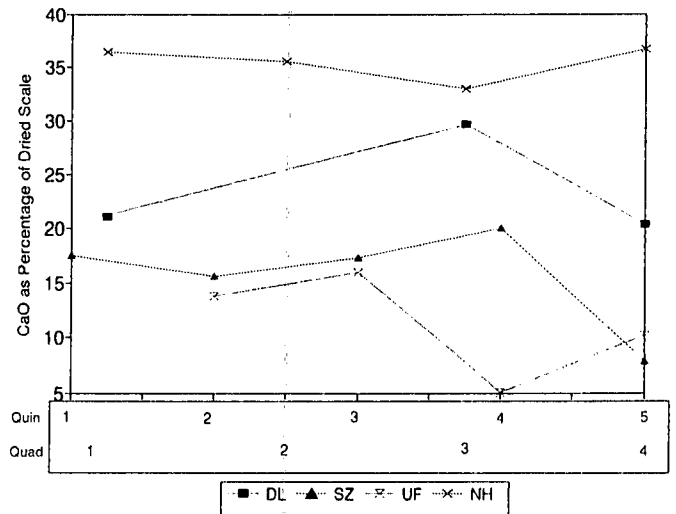


FIGURE 2 Calcium as a percentage of the total scale sample for a number of factories for the 1992/93 season.

**Technical trials carried out at the SMRI**

*Laboratory work*

In order to test if it were technically feasible to soften clear juice, small scale laboratory trials were conducted using ion exchange resins in glass columns. A water jacketed column, run at 80°C, was filled with a polystyrene based strong acid cation exchange resin in the sodium form (Amberjet 1200H, Acix-NCP). Ions of interest are calcium and magnesium (for removal, i.e. softening), potassium (for recovery) and sodium (to determine when the resin is near exhaustion). Calcium and magnesium both adsorb onto the resin so for theoretical capacity calculations these two ions were expressed together on the basis of equivalents rather than on a mass basis. According to the laboratory trials, using a resin volume of one litre with an exchange capacity of 2,0 eq/l, 73 l of clear juice will be softened by one litre of resin (data from Table 1). If the resin were to be used until potassium breakthrough then one litre of resin would soften and remove potassium from 30 l of clear juice.

Ion	ppm	meq/l
Ca <sup>2+</sup>	300	14,97
Mg <sup>2+</sup>	150	12,34
K <sup>+</sup>	1500	38,37
Na <sup>+</sup>	40	1,74

Figure 3 is the profile of the softening cycle. This particular test was not conducted long enough to run the resin to full capacity. The exchange between the divalent ions and sodium can be seen (sodium is liberated into the clear juice stream), showing that it is possible to soften clear juice using strong acid cation exchange resins in the sodium form. Some of the calcium is not removed from the clear juice by this ion exchange treatment (96-97% removal).

*Potassium recovery*

The profile given in Figure 4 shows clearly that calcium, magnesium and potassium displace sodium. When all the exchange sites are occupied by these three ions the divalent

ions displace potassium. The sharp drop in the sodium ions and increase in potassium can be exploited to recover potassium from clear juice by a simple column arrangement.

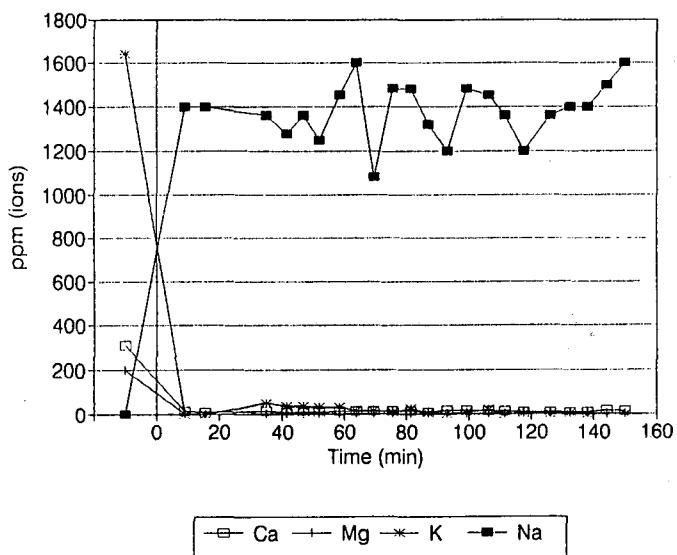


FIGURE 3 Softening profile of clear juice on a laboratory scale.

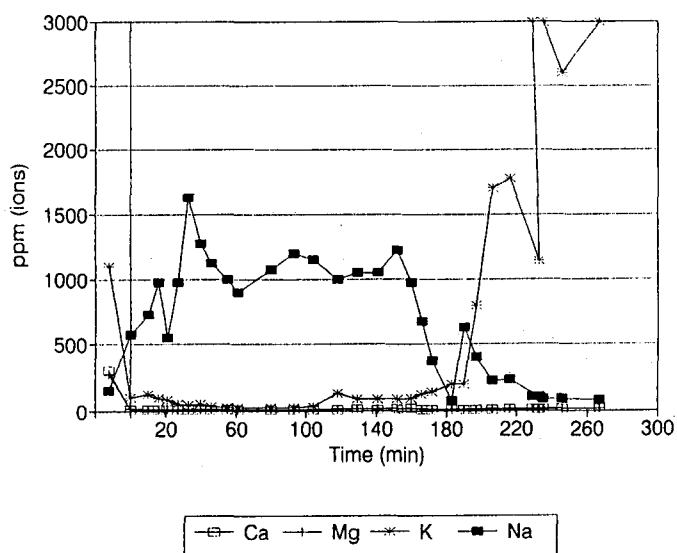


FIGURE 4 Softening profile of clear juice showing the behaviour of potassium.

### Pilot plant trials at Sezela Mill

#### Description of ion exchange equipment

The SMRI resin pilot plant previously used for the assessment of decolourising resins (Getaz, 1990) was modified to treat clear juice. An in-line filter (about 300 µm sieve size) was added to minimise deposition of solids on the columns. The four columns were packed with Amberjet 1200H, one litre each. The plant was erected at Sezela mill where clear juice was easily tapped off the main stream. This removed the need to transport and preserve large quantities (a minimum of 100 l/day) of clear juice that could deteriorate easily. The availability of Vapour One (V1) from the factory was essential for evaporator scaling tests.

A small holding tank (30 l) for clear juice was installed to facilitate clear juice feed to the columns. Air, water, vacuum (from the filtrate receivers) and electricity were connected.

The columns were maintained at 100°C by the juice which passed through a waterbath set at this temperature. The flow rate was set at an average of 5 bed volumes per hour (BV/h) per column. This made it possible to produce 20 l of softened juice per hour with all four columns in operation. For most of the initial pilot plant work the interest was solely in softening (i.e. removal of calcium) and not in investigating the costs, amounts of regenerant required, quantity of rinse water, service cycle breakthrough (calcium and potassium) or potassium recovery. For these tests the resin was regenerated with excess brine (greater than 200 g/l of resin) and the columns were taken off-line well before the calculated breakthrough. For each column running at 5 BV/h, breakthrough (all sodium sites occupied without the effect of potassium displacement) is expected after 4 h of operation (i.e. 20 l). The resin was regenerated after 2,5 h. This was done to ensure minimal calcium or potassium in the soft stream so that the effects of sodium on downstream processes could be evaluated. Some of the data for the softening of clear juice are presented in Table 2.

Table 2  
Clear juice softening pilot plant ion analysis

Ion/ppm	"Unsoftened" juice (Control)	When Bx <sub>in</sub> = Bx <sub>out</sub>	After 2 BV	After 6 BV
Ca <sup>2+</sup>	320	13	11	8
Mg <sup>2+</sup>	160	14	0	2
K <sup>+</sup>	1350	11	0	0
Na <sup>+</sup>	1	1380	1300	1300

#### Parallel boiling tests

Softened and control ("unsoftened") juices were collected, preserved with Busan, transported to the SMRI and frozen overnight. A week of column operation produced enough softened juice for evaporation in the SMRI pilot evaporator and boiling in the SMRI pilot pan. The massecuite was centrifuged in the SMRI basket centrifuge (Lionnet and Reid, 1993). The sugar was washed with a saturated sugar solution, air dried overnight and affinated. The unwashed, unaffinated sugar had a salty taste, absent in the washed and affinated sugars. The colours for both control and softened samples (clear juice, syrup, massecuite, molasses and sugar) were very similar. While boiling the pan the massecuite from the softened syrup appeared much darker than the control massecuite but this had little effect on the sugar colour, in fact the sugar colour from treated sugar appeared to be less.

Conductivity ash in the soft sugar was lower. This is expected as most of the potassium has been replaced by less conductive sodium. The brix of the soft clear juice was slightly lower because of the sweetening on and sweetening off procedures that are necessary.

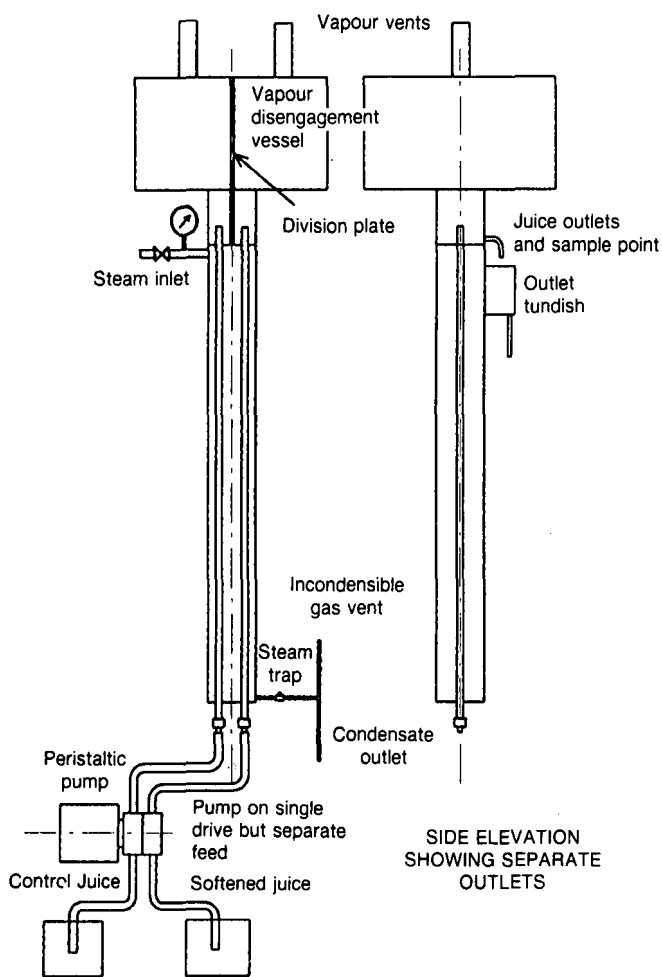
Exhaustion is affected by the softening process. This is because sodium ions are more melassigenic than calcium and magnesium ions, the tendency being in the order:

$$Mg^{2+} < Ca^{2+} < Na^{+} < K^{+}$$

Therefore by exchanging, stoichiometrically, sodium for divalent ions the exhaustion will drop. This is shown in the SMRI pilot plant trials on the A-boiling of two syrup samples which are identical but for the cation composition. Using the SJM formula (and the true purity of the products) the percentage of recoverable sucrose for the control syrup is 63,21, whereas for soft syrup it is 61,45 – a difference of 1,8 units. This represents a considerable loss if conventional recovery techniques are used but not if chromatographic recovery is introduced.

**Evaporator scaling tests**

**Equipment** A small two-tube climbing film evaporator was built to establish the influence of softening clear juice on the scaling of evaporators. A schematic of the evaporator is shown in Figure 5. The two removable tubes, 19 mm in diameter and 1,5 m long, were made from 316 stainless steel. The tubes with separate feed inlets are enclosed by the same heating source, in this case V1, with separate feed inlets. Juice is pumped into each tube at the same rate via peristaltic pump heads attached to a single drive unit. A dividing plate at the top of the evaporator ensures that the evaporated streams remain separate. A large disengagement vessel contains any splashing and an outlet is provided to vent the vapour to atmosphere. Average V1 pressure at SZ was about 50 kPa gauge. This represents a steam temperature of 111°C. With this steam pressure and a flow rate of 17,6 l/h of juice per tube an evaporation rate of 6,3 l/h is possible in a clean (unscaled) tube.



**FIGURE 5** Schematic of a two tube pilot evaporator.

**Initial tests and scale composition**

The evaporator was run for 30 h without cleaning to produce enough scale for analysis and to compare the extent of scaling. During this period the flow rate had to be increased to prevent the "soft" tube from drying out, although on occasions this did happen. The outside of the evaporator had not been lagged at this stage, but was subsequently lagged. After 30 h the tubes were removed and it was obvious that the control tube had scaled far more than the soft one. Weighing the tubes established that 10,1 g of scale had deposited on the control tube and only 0,9 g on the soft tube

(probably due to drying). The scale in the soft tube was only visible on the top 15-20 cm of the tube. Both scale samples were analyzed by X-ray fluorescence (XRF) and the analyses are given in Table 3. The larger amount of calcium in the control scale compared to that in the soft scale is evident. The soft scale appears to be largely silica. During this test the brix of the evaporated soft juice (syrup) was 60° if the flow rate was too low. This suggests that no scale is likely to develop in the first effects (confirmed in the next section) and that later effects may scale, probably at reduced rates.

**Table 3**

Calculated analysis of bulk sample from XRF analysis of raw and soft scale

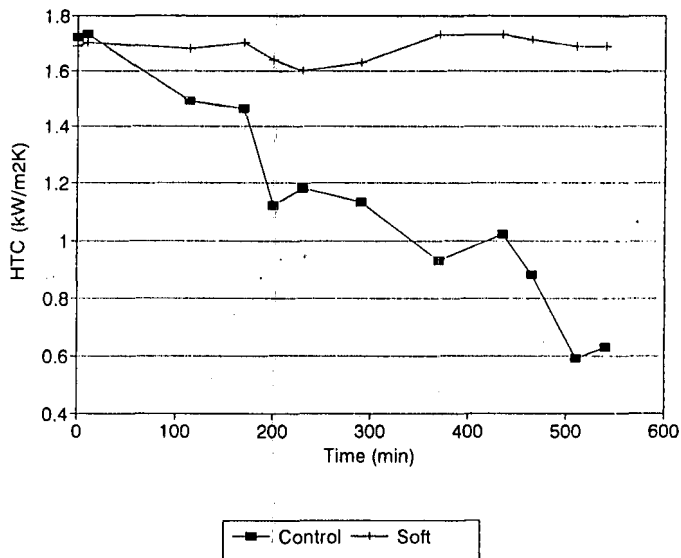
Species	Raw	Soft
SiO <sub>2</sub>	1,2	65,3
Al <sub>2</sub> O <sub>3</sub>	1,3	7,9
Fe <sub>2</sub> O <sub>3</sub>	0,6	0,2
MgO	4,3	0
CaO	21,6	0,6
P <sub>2</sub> O <sub>5</sub>	23,0	0,9
K <sub>2</sub> O	0,2	0
SO <sub>4</sub> <sup>2-</sup>	0,9	1,3
Organics + water	46,9	23,7

**Heat transfer coefficient (HTC) measurements**

Before conducting HTC measurements the evaporator tubes were removed and cleaned with a wire brush and 10% HNO<sub>3</sub>. With the evaporator lagged (to minimise heat loss) and a high flow rate (17,6 l/h) chosen to keep the flow rate constant throughout the test, the heat transfer coefficient (HTC) was measured for each tube over a period of time. The variables recorded were the steam pressure, the brix of the evaporated liquor, the feed temperature and mass flow rate for each tube (see the Appendix for the calculation of the HTC).

The HTCs for each tube over time are shown in Figure 6 where the rapid drop in HTC for the control tube and the steady HTC for the soft tube are noteworthy. On inspection of the tubes the soft tube was completely clean, confirming that first effect evaporator scale would be significantly reduced.

This exercise was repeated after the tubes had been cleaned *in situ* using 20% NaOH which was recirculated and heated



**FIGURE 6** HTCs of soft and control evaporator tubes.

with steam for approximately 20 min. This was followed by a hot water wash. The feed lines to the tubes were then exchanged to ensure that the tube position in the evaporator had no effect on the rate of scaling. The trend shown in Figure 6 is apparent in Figure 7, but the soft tube, although starting with a lower HTC (probably due to inadequate cleaning), maintained the same HTC whereas the control tube (which had been the soft tube in the previous test) started at a higher HTC which then dropped as rapidly as in Figure 6.

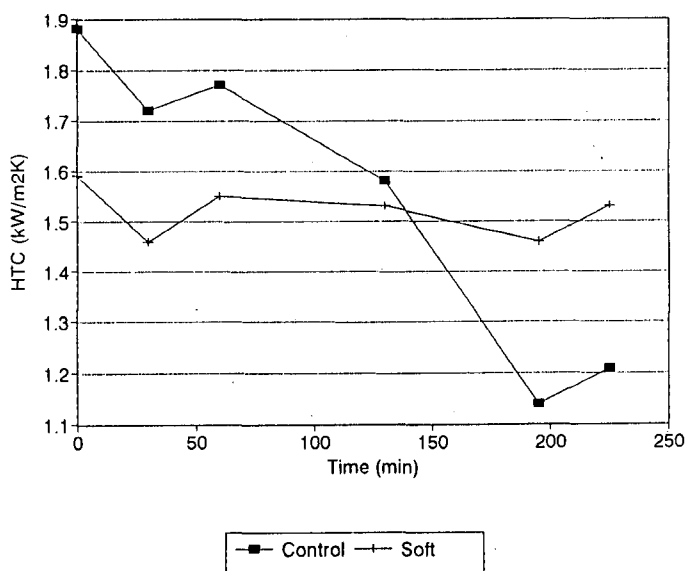


FIGURE 7 HTCs of soft and control evaporator tubes after *in situ* chemical cleaning.

It can therefore be concluded that softening would significantly reduce scale formation in first effect evaporators. This is because the first effect scale is predominantly  $Ca_2(PO_4)_3$ . Any calcium oxalate scale normally found in later effect evaporators would also be eliminated. The effect of silica on scale formation in later effects still needs to be determined.

### Economic considerations

The costs quoted here are applicable to a conventional softening plant of suitable capacity. Variations which solve some of the problems of this conventional system (e.g. high salt requirement) are available in the beet industry. The basic operating costs (water, salt and resin) of the conventional softening process for a 400 m<sup>3</sup>/h clear juice factory with the cation concentrations shown in Table 1 are summarised in Table 4. The budget estimate of capital cost for a plant of this size, including the first charge of resin, is R2,5 to R3 million.

Table 4  
Some operating costs

Unit	Unit cost	Cost/ton cane*	Cost/ton raw sugar**
NaCl	R400,00/ton	R1,69	R16,16
Water	80c/m <sup>3</sup>	15c	R1,40
Resin makeup (5% per year)	R4,80/ℓ	1c	10c

\* Tons cane crushed/season = 1 710 000 tons.

\*\* 9,55 tons cane = one ton raw sugar.

The cost of cleaning evaporators (which is about R0,40/ton of cane) would be significantly reduced. Improved vapour pressures would reduce boiling times and hence increase capacity. Reduced down time (increased capacity) and less damage to tubes (reduced maintenance costs) are also savings that softening of clear juice will ensure. These figures are however difficult to quantify. If potassium could be recovered for sale as fertiliser this would probably ensure the economic viability of the softening process. However, in the absence of desugaring molasses, the increased loss of sugar in molasses would be a severe economic disadvantage.

### Conclusions

It has been shown that softening sugarcane clear juice is technically feasible. Laboratory trials as well as pilot plant work have indicated that as much as 97% of the calcium in clear juice can be removed by strong acid cation exchange resins operating in the sodium form. There is also the potential to recover potassium from the clear juice. Potassium is currently being imported into South Africa at considerable cost. Furthermore, it has been shown that by softening clear juice, evaporator scaling in first effect evaporators is significantly reduced. It is also probable that scaling in later effects would be reduced.

The major costs of a conventional process for softening clear juice are those of the NaCl for regeneration, the amount of waste water that requires treatment and the loss of sucrose to molasses. These aspects will be addressed in the 1994/95 season. Softening of clear juice also provides the additional benefit of producing a soft molasses which is suitable for ion exclusion recovery of sucrose.

### Acknowledgements

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### APPENDIX

#### Calculation of the heat transfer coefficient

$$U = \frac{Q}{A \Delta T}$$

$$Q = Q_c + Q_h$$

$$Q_c = m \left( 1 - \frac{Bx_{in}}{Bx_{out}} \right) L_v$$

$$Q_h = m \times SH \times \Delta t^*$$

$$\Delta T = \frac{\Delta t_1 - \Delta t_2}{\ln \left( \frac{\Delta t_1}{\Delta t_2} \right)}$$

where

U = Heat transfer coefficient (kW/m<sup>2</sup>K)

Q = Total heat (kJ/s)

A = 0,0985 m<sup>2</sup>

Q<sub>c</sub> = Evaporation load (kJ/s)

Q<sub>h</sub> = Heat required to heat juice to boiling (kJ/s)

m = mass flow of juice (l/h)

L<sub>v</sub> = latent heat of steam (kJ/kg)

Δt\* = (temp of juice at boiling + BPE) - feed temp (K)

Δt<sub>1</sub> = steam temp - feed temp (K)

Δt<sub>2</sub> = steam temp - boiling temp of juice (K)

SH = specific heat of juice (1-0,006 × Bx<sub>in</sub>)(4,187) (kJ/kgK)