

SOME FACTORS AFFECTING THE CONCENTRATION OF SILICA IN CANE JUICE EVAPORATORS

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Abstract

Silica remains one of the most common and problematic components in cane sugar juice evaporator scale. The relationship between silica concentration in clear juice and its precipitation in the evaporator train is considered. Methods of reducing silica levels in clear juice through changes in the extraction conditions are investigated through laboratory experimentation, which shows that pH and cane preparation may be important variables. The laboratory findings have been supported by factory experience which found that reduced liming in the diffuser resulted in lower silica concentrations in the evaporator scale.

Introduction

Previous work has shown silica to be a major component of scale in the evaporators and pans of cane sugar mills (Rein, 1990; Walthew and Turner, 1995). Evidence accumulated so far suggests that silica is deposited as a result of reduced solubility as the brix increases across the evaporator train and pans, and this is shown in Figure 1 (Walthew, 1996). This figure demonstrates the sensitivity of the system to the initial silica concentration in clear juice and shows that a higher silica concentration in clear juice will not only lead to more scale being formed but also that scale rich in silica is more likely to be formed in earlier vessels.

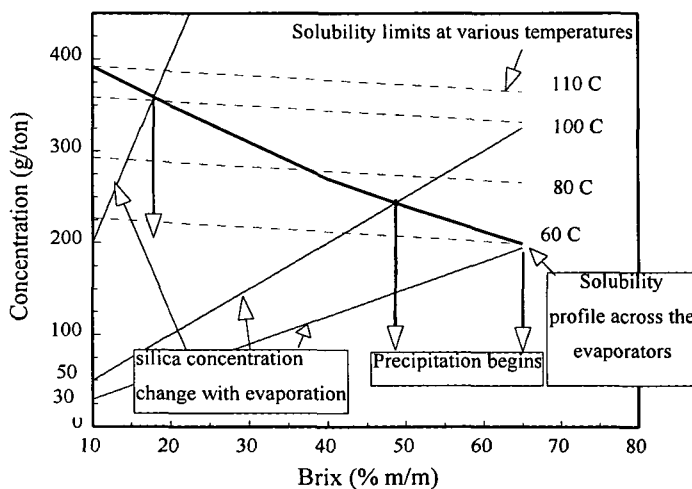


Figure 1. Silica solubility across a typical evaporator train showing the precipitation pathway for silica assuming silica concentrations of 30, 50 and 200 ppm in clear juice.

Silica presents a particularly challenging problem to the industry for the following reasons:

- Softening of clear juice by ion exchange does not appear to remove silica effectively from juice. As a result those vessels in which silica is deposited will still require regular cleaning even if juice softening is instituted (Davis *et al.*, 1997).
- Silica is an essential trace element in the cane plant and is thus not likely to be greatly reduced by varietal changes or geographic location (Clarke, 1974; Matichenkov *et al.*, 1995). While it would be useful to install a process to remove silica, in the short term it is expedient to operate the extraction system in such a way as to minimise silica solubilisation. By comparison, the levels of silica in beet juices are significantly lower than in cane juices and thus are not as great a problem in that industry.
- Silica and silicate rich scales can precipitate in a variety of forms, and the precipitation mechanism and its control are not well understood. Antiscalent chemicals have not yet been shown to reduce the silica concentrations in scale significantly.
- In many cases the silica and silicate scale are physically hard and relatively chemically resistant to attack. Consequently it is difficult to remove by both mechanical and chemical cleaning (Walthew *et al.*, 1997).
- Silica is not appreciably removed during the clarification process (Alexander and Parrish, 1953).
- Soluble silica in juice may be a contributing factor to other process problems such as acid beverage floc (Clarke, 1974).

Clearly it would be of great benefit to develop methods and procedures to reduce the level of silica in juice, through a reduction in the silica extracted with the sucrose. Thus this paper considers some possible methods of minimising silica dissolution during extraction, through both laboratory trials and factory measurements.

Theoretical considerations and experimental design

Silica enters the sugar mill either as part of the sugar cane plant or as extraneous matter. Silica is contained in the plant tissue and cell walls (Alexander and Parrish, 1953), and is thus present in all the plant components, namely the stalk as well as the leaves (trash). The relative rates at which silica

and sucrose are extracted may offer some possibility for control of silica while maintaining acceptable sucrose extraction. Consequently leach tests were conducted on prepared cane, bagasse, tops and trash.

Non-vegetable matter in cane is mainly quartz sand, silt and clays. The probability of this being the source of soluble silica is low, based on solubility data (Chan *et al.*, 1988) and previous work by Alexander and Parrish (1953). Nevertheless the possibility of silica in mud being leached needs to be examined, since recent work has proposed that mud be recycled to the diffusers as a means of eliminating filter stations (Lionnet and Sahadeo, 1997; Meadows *et al.*, 1998). Samples of clarifier mud were thus leached to determine whether this could be a source of soluble silica.

Factors affecting the ease with which silica is solubilised from the potential silica sources are:

The preparation of the cane. Preparation prior to extraction will determine the surface area available for leaching of silica and may have some influence on silica dissolution. Two batches of cane were prepared, one with a high degree of preparation (fine), and another with a lower degree of preparation (coarse).

The pH of the solution in contact with the material. Silica solubility is strongly influenced by pH and shows a rapid increase in solubility above pH 7. To examine this effect leach tests were carried out at 'natural pH' levels (no pH adjustment was made) and at pH 7 and pH 9.

The method of pH adjustment. While sodium hydroxide is easier to use for pH control it may result in differences between the experimental work and the real process (which uses only lime), although there have been some moves to consider the use of sodium hydroxide for pH control in the factory. A slaked lime slurry and sodium hydroxide were both used and the relative rates of leaching were compared.

The brix of the solution. Brix has an effect on the solubility of silica as reported by Poynton and Alexander (1957) and may therefore have some effect on the dissolution of silica in juice.

Experimental method

Feed materials

Cane (variety NCo376) was obtained from the South African Experiment Station (SASEX) nursery at Mount Edgecombe and divided into two batches. The first batch was given a high degree of preparation resulting in a fine material with a preparation index (PI) of about 93, to simulate the typical degree of preparation in the factories. The other half of the cane was less thoroughly shredded resulting in a coarse material with a preparation index of approximately 87. Tops and trash were also obtained from SASEX and were shredded (fine) before leaching. Bagasse was obtained in a single batch from MS. To check the leaching behaviour of 'normal' cane prepared in the factory, several batches of prepared cane were obtained from FX over a period of about a week (one sample per shift). All samples were obtained fresh, prepared and divided into batches, and then frozen until used.

Adjustments of pH were made using NaOH or slaked lime solution. In both cases chemically pure chemicals were used. Distilled water from the laboratory was used in the leach tests was distilled water from the laboratory to ensure no random variation due to silica in the municipal water supply.

Procedure

All leach tests were conducted using a stirred, leach vessel with a volume of about 5 L. The vessel was jacketed and hot water was circulated from a water bath maintained at 70°C. The equipment used has been described in detail by Lionnet (1985). For all trials the procedure was as follows:

The required quantity of material was thawed and weighed. This was added to the leach vessels containing 3,5 L of water preheated to 80°C. Adding the material reduced the temperature to the required 70°C. The pH was maintained by the addition of NaOH or lime slurry where required. Samples were withdrawn through a strainer, and rapidly filtered and stored frozen until analysed for brix and silica. Silica was analysed using the colorimetric method given in Appendix A.

Results

Tests designed to compare lime and sodium hydroxide as neutralising agents suggested that silica may be more rapidly leached when using the NaOH. Thus for all tests intended to simulate the extraction process lime slurry was used. For leach tests involving prepared cane no pH adjustment was made for the lowest pH level tested, but the pH was measured and was found to be about 5,5.

To enable comparison of the leach rates, the silica and brix concentrations were considered, over time. The silica on brix (ppm/percent) is shown graphically in Figures 2 and 3. Figure 2 shows clearly that there is a quantity of silica available which is rapidly taken into solution but that the concentration is not increased with further leaching. Comparison of the graphs in Figure 3 with those in Figure 2 clearly indicates that the fine material released more silica more readily than the coarse material as the pH was raised. The shape of the silica on brix curve can be explained by considering the different leaching rates of the brix and the silica, and this is shown graphically in Figure 4. This figure shows that while the brix rapidly rises at first and then tails off, the silica continues to be leached at higher pH values. Taken together, these results demonstrate that while more brix is extracted by longer residence times in the diffuser, when the pH is raised and the cane PI is high, excessive amounts of silica are also dissolved. Thus careful control of the pH to as low a value as possible in the diffuser is desirable. Even short periods of time at high pH values will result in high soluble silica levels in the resultant juice which will not easily precipitate or be removed during clarification.

The sensitivity of bagasse to pH and brix concentrations is summarised in Figure 5. This shows that again pH is the most crucial factor since brix cannot in effect be controlled. This result indicates quite clearly that excessive residence times at high pH levels should be avoided. Leaching tests on tops and trash are summarised in Figure 6. This shows similar trends to

that for bagasse, although at pH 5 silica is leached more extensively from tops and trash at higher brix levels. Interestingly the brix level did not appear to have a similar effect on the rate of silica leaching from bagasse.

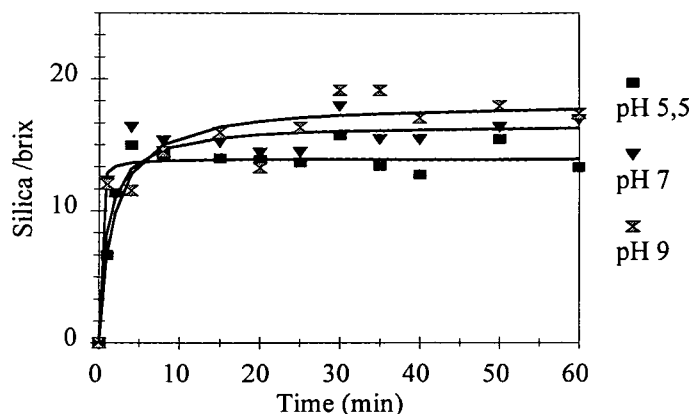


Figure 2. Silica on brix over time for coarse cane leached at pH 5.5, 7 and 9.

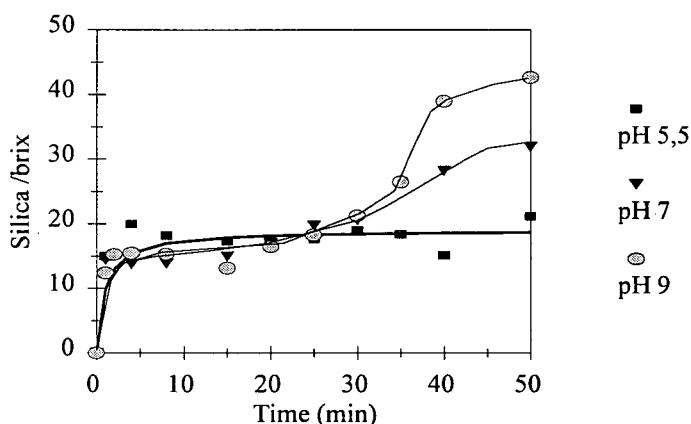


Figure 3. Silica on brix over time for fine cane leached at pH 5.5, 7 and 9.

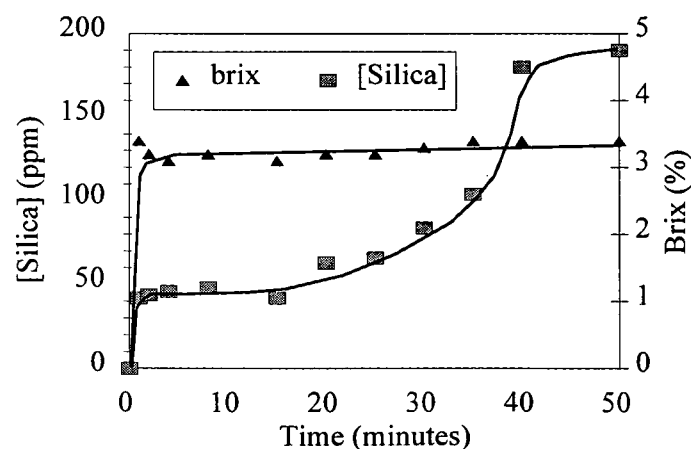


Figure 4. Leach rates for brix and silica at pH 9 using fine cane.

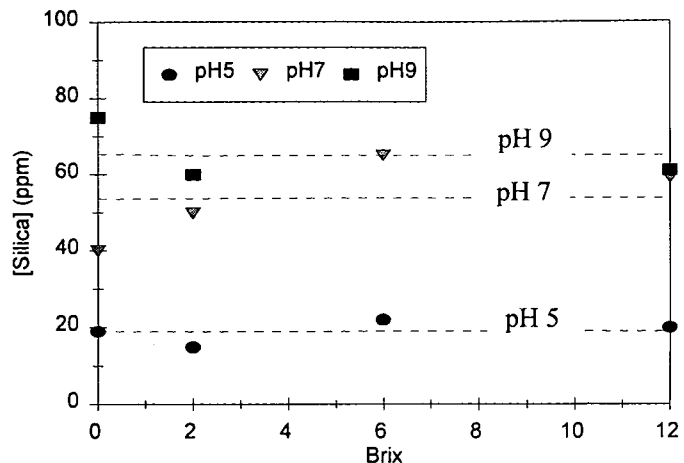


Figure 5. Silica leached from bagasse at different pH and brix levels, in a 60 minute period.

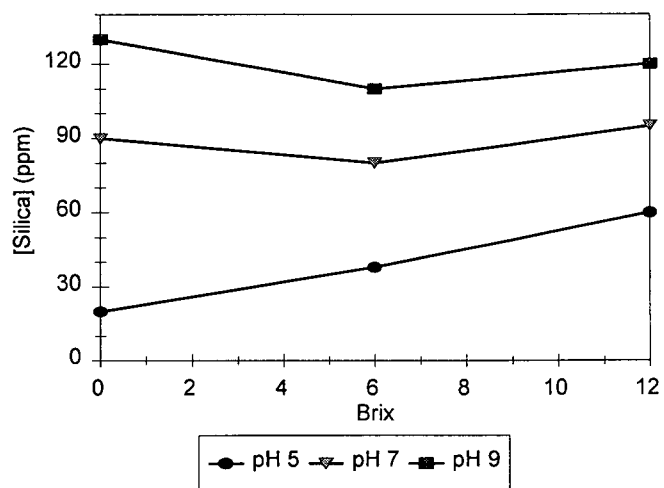


Figure 6. Silica leached from tops and trash at different pH and brix levels, in a 60 minute period.

Trials to test the ability of clarifier mud to produce soluble silica found that no measurable quantity of silica was leached even at pH 9 over a one hour period. This endorses previous findings (Alexander and Parrish, 1953) and shows that there is no danger of raising silica levels in juice by adding mud to the diffuser.

The above results are all based on perfectly cleaned cane prepared at the Sugar Milling Research Institute (SMRI) and may not have represented real prepared cane. Furthermore it is necessary to examine the natural variation in leachable silica in cane. To this end samples of prepared cane from FX were leached at different pH values at 70°C for 40 minutes. The result is shown in Figure 7 and shows the strong effect pH has on the extraction of silica during processing. To check the total amount of silica available compared with that actually leached, two samples of the FX prepared cane were ashed, and the ash was analysed by x-ray fluorescence (XRF). This showed that the amount of silica leached is quite small (250 to 570 mg/kg of cane) compared with the total amount available (awaiting confirmation of XRF results).

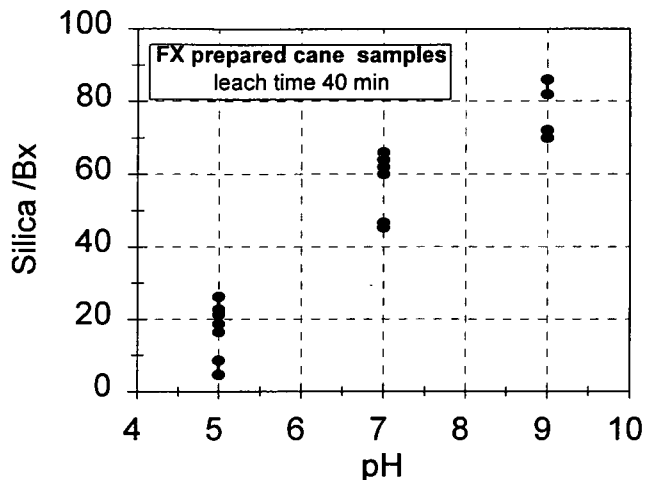


Figure 7. Silica on brix leached from various samples from FX.

Quantitative calculations from the above trials suggest that a silica concentration of about 50-100 ppm may be achievable for a mixed juice of about 13° brix, if the pH is kept low during extraction, and cane is perfectly cleaned free of tops and trash before extraction. This is in agreement with figures calculated by Alexander and Parrish (1953). This compares with silica concentrations of between 200 and 4000 ppm on clear juice actually measured at a number of factories over the last four seasons, and the beet industry where thin juice would have a maximum level of 50 ppm silica on juice.

The silica concentrations shown in Figures 2 to 5 are relative since different quantities of material were leached in each case. To enable a comparison to be made between the different materials, and provide values for further work, it is useful to calculate the amount of leachable silica per kilogram of material under the conditions tested. This is summarised in Figure 8, which clearly shows the relatively high quantities of soluble silica in tops and trash, compared to bagasse. The numbers in Figure 8 are based on fresh material. On a dry mass basis the trends are the same. While processing problems associated with tops and trash are well known (Scott *et al.*, 1978), this set of results demonstrates that such material can also add to problems of evaporator fouling. Figure 8 also suggests that the leach tests on the finely prepared material were similar in behaviour to FX, prepared cane samples, and thus these tests are a reasonable approximation of factory conditions.

Factory trials

In practice the diffuser pH is controlled though the addition of lime, and not all mills practice diffuser liming. The above laboratory work clearly suggests that diffuser liming may lead to high silica levels which in turn may result in scale containing high levels of silica. To test the above theory scale was collected from FX evaporators after periods when the diffuser was limed normally, when it was partially limed, and after it had not been limed at all. Scale samples were taken from all vessels in the 'B' tail and analysed using XRF methods described previously (Walthew, 1996). FX provides a good test of the above laboratory work since it traditionally

produces excessively high silica scale (Walthew and Turner, 1995). The results are shown in Figure 9 and indicate quite clearly that the silica concentrations in scale were effectively reduced by limited liming, especially in the later effects. Interestingly there was no apparent drop in the pH of the mixed juice reported over that time period.

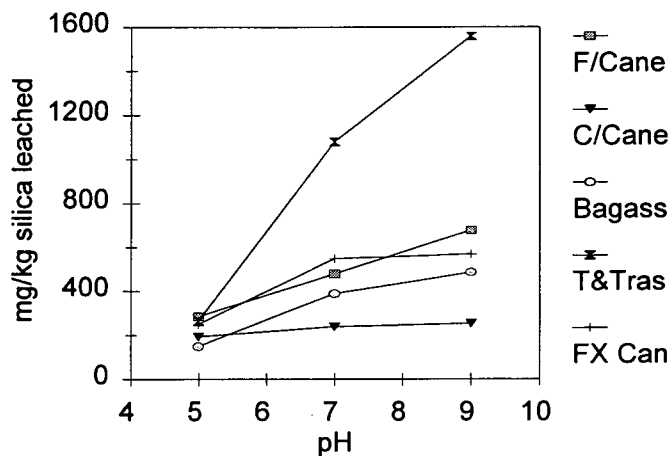


Figure 8. Leachable silica in various materials leached at pH 5, 7 and 9 for 40 minutes.

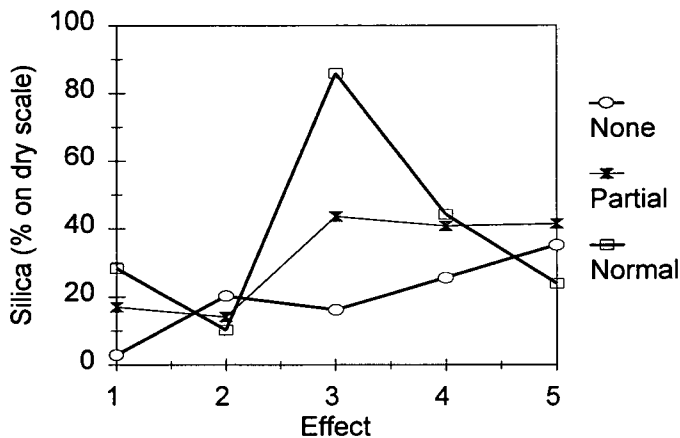


Figure 9. Silica in evaporator scale when no liming, partial liming and normal liming was carried out at FX.

Conclusions

The above work demonstrates that pH control during extraction has the potential to reduce the silica levels in clear juice significantly and hence reduce silica scale in the evaporators. However, it is important to acknowledge that liming of the diffuser is carried out to limit corrosion as well as to reduce inversion, and that diffuser liming is a complex issue in which a number of practical as well as theoretical factors must be considered (Beckett and Graham, 1989; Lionnet, 1985; Schaffler, 1988). The laboratory work also clearly shows that there is a minimum silica level of between 50 and 100 ppm which is the best that can be expected, provided the raw water entering the factory and other feed materials such as lime do not contribute to raising this concentration level. Figure 1 suggests that, at the 50 to 100 ppm level, severe fouling of the final effects could still be a

problem, but that silica scale in the earlier effects can probably be eliminated. While the effect of reduced preparation is interesting its application is limited since it has been well established that a high degree of preparation is necessary to achieve the desired sucrose extraction (Rein, 1972).

Further work is required in the following areas:

- Methods of removing silica from juice in a cost-effective manner using chemical or ion exchange techniques either during extraction or clarification, or as an added unit operation.
- The contribution of raw water sources and excessive recycling of factory water and other feed streams on the silica levels.
- Methods designed to force silica to be precipitated in a softer and more easily cleaned form.

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APPENDIX A Analysis of silica

Apparatus

Spectrophotometer
Pipette (50 cm³)
Pipette graduated (100 cm³)
Volumetric flask (100 cm³)

Reagents

Hydrochloric acid (1:1)
Ammonium molybdate reagent (ca. 9%, pH 7-8)
Oxalic acid solution

Procedure

- Pipette 50 cm³ filtered boiler water into each of two volumetric flasks.
- To the one flask add 1 cm³ HCl and 1,5 cm³ oxalic acid, make to volume with distilled water and use for the blank reading.
- Dilute to ca 85 cm³ with distilled water.
- Add to it in rapid succession 1 cm³ HCl and 2 cm³ ammonium molybdate reagent.
- Mix well and allow the solution to stand for 5-10 minutes.
- Add 1,5 cm³ oxalic acid solution and mix thoroughly.
- Make to volume with distilled water and shake well.
- Read the colour in a 10 mm cell, after two minutes and before 15 minutes, at 410 nm using distilled water as zero reference.
- Read the blank, against distilled water.
- From a calibration graph, read the quantities of silica corresponding to the optical densities obtained.

Example

Optical density of sample	= 0,285
Optical density of blank	= 0,040
mg silica in sample from sample reading, a	= 1,25
mg silica in blank from blank reading, b	= 0,05
Silica content of aliquot taken	= (a - b) mg

⇒ mg/L silica in sample
 = [(a - b) * 1000]/[aliquot taken (cm³)]
 = [(1,25 - 0,05) * 1000]/[50]
 = 24,0 mg/L