

ASPECTS OF THE EFFECTS OF SILICA DURING CANE SUGAR PROCESSING

G R E LIONNET and D C WALTHER

Tongaat Hulett Sugar, Durban, South Africa

Abstract

Silica is a major component of soil and is an essential element for the sugarcane plant. It can exist in juice as a solute, as a colloid and as distinct particles. Its chemistry is complex; it reacts with aluminium, calcium, magnesium, potassium, iron and with organic polyphenols.

Factory streams contain soluble silica, which is present naturally in the cane. There is however, evidence of contamination from soil and clay, entering the mill with the cane. This contamination could add relatively large quantities of silica, of aluminium and of iron to the juice.

Poor quality lime can contain much soluble silica, which is then transferred to the juice.

Silica, aluminium and iron have been found to be major components of the inorganic content of clarifier muds, of the suspended matter in a turbid clear juice and of the suspended matter in a poor filtering raw sugar. These three species can also be major constituents of evaporator scale.

The paper discusses the points mentioned above, and presents available data relevant to the South African industry. It also comments on the impacts of silica during clarification and on sugar quality. The difficulties associated with the determination of silica in sugar products are mentioned.

Keywords: silica, solubility, aluminium, soil, colloids, iron

Introduction

Silica is a major component of the earth's crust and is an essential element for the sugarcane plant; its presence in cane and in cane juices is one of the main differences between cane and beet. Its chemistry is complex, particularly in terms of its solubility in water and of its ability to react with aluminium, calcium, magnesium, potassium and iron. Cane sugar streams always contain silica since it is naturally present in the cane plant; the situation is further complicated by the fact that the contamination of cane by soils containing clay can add large quantities of silica and of aluminium to the juice, since clay is an aluminosilicate.

The relevance of silica to plants in general and to sugarcane in particular, has recently been reviewed by Meyer and Keeping (2000); in 1998, Walthew *et al.* looked at the impact of silica on evaporator scale, and commented on methods to reduce its concentration in juices. These papers highlight silica's complex and multi-functional role in the cane sugar industry and stress the need for more work.

Silica in nature

About 95% of the outermost solid layer of the earth consists of silica and of silicates (Iler, 1979). Soluble silica in nature comes from the weathering of minerals, as little originates from sand; river water contains 5 to 40 mg/L of SiO₂ while the concentrations in seawater range from 2 to 15 mg/L. Colloidal clays and related minerals can dissolve in seawater to give SiO₂ concentrations of about 10 mg/L.

Soluble silica is found in most plants and animals. In hot, tropical regions, aluminosilicates weather to yield soluble silica and residues high in alumina (Ebbing, 1996); in cold regions, alumina is removed and the residue is rich in silica. The difference is believed to be due to the presence and absence respectively, of vegetation; decomposing vegetation in tropical regions produces tannins and other catechol-like organic compounds, which are known to dissolve silica in neutral solutions.

Silicon is often found (Meyer and Keeping, 2000) in high concentrations among the inorganic constituents of plants and grasses; for example, sugarcane and rice accumulate large amounts of silicon as SiO₂·nH₂O, in localised specific cells. Sugarcane can accumulate more silica than any other nutrient from the soil. In Puerto Rico the above-ground parts of a 12-month old cane crop had taken 379 kg of silicon per hectare, compared to 362 kg per hectare of potassium and 140 kg per hectare of nitrogen.

Nitrogen and silica play important roles in the susceptibility and resistance of crops to stalk borer damage. Increasing nitrogen can increase the survival of borer larvae in maize; increasing silica can reduce larval survival. The mandibles of larvae of the rice stem borer are damaged when the silica content of the rice plants is high. Improved silica nutrition caused a marked increase in the resistance of sugarcane to stalk borer. Silica in rice reduced the need for fungicide and enhanced resistance to pests and diseases. Silica in plants may stimulate natural defence reactions, for example the production of metabolites such as flavonoids. Silica is also involved in the water economy of the plant. (Meyer and Keeping, 2000).

The solubility of silica

The dissolution of silica in water is not a simple solubility process like that of sucrose or of NaCl (Iler, 1979); it involves reversible chemical reactions such as its hydrolysis in an excess of water, catalysis by the OH⁻ ion, and various effects due to the presence of traces of impurities. Thus, terms such as 'the solubility of silica' or 'soluble silica' need to be carefully defined; it cannot be assumed that they carry the usual straightforward meanings applicable to sucrose, for example.

The silica/water system is complicated further by the fact that there are many different types of silica; amorphous silica can exist as anhydrous, non-porous SiO₂; quartz is the most important of several crystalline forms of silica, and there are many different hydrated forms of silica. Iler (1979) gives the data shown in Table 1.

Iler also comments on the effect of pH on the solubility of silica in water; at pH values of 8.5 and higher the solubility increase is very pronounced, both at room temperature and at temperatures near boiling. There is also a marked particle size effect; Iler shows that the solubility of particles smaller than 5 nm is about 30 to 40% higher than that of larger particles. The solubility of silica can increase in sugar solutions, relative to water (Walthew *et al.*, 1998). Finally, the equilibria between silica in solution and solid silica are not easily reversible: the precipitate can age thus making it less soluble (Iler, 1979).

Table 1. The solubility of silica in water as affected by its hydration form (Iler, 1979).

Composition	Solubility (mg/L water at 18 to 22°C)
SiO ₂ .2.5H ₂ O	18
SiO ₂ .2.0H ₂ O	44
SiO ₂ .1.5H ₂ O	58
SiO ₂ .1.0H ₂ O	61
SiO ₂ .0.5H ₂ O	120

Chemistry

Silica in aqueous solution often exists as colloidal particles whose surfaces are chemically active (Iler, 1979). The Al³⁺ ion, even in minute concentrations, adsorbs on the silica particles, affecting solubility and other properties; Ca²⁺, Mg²⁺ and phosphoric acid are also relevant. Reactions with organic compounds are generally more complex; catechol, an organic phenol, attacks quartz and dissolves amorphous silica to form complexes. Other phenolics react with silica to form complex ions, which in turn react with atmospheric oxygen to form dark, insoluble residues. Iler also reports that a specific granular magnesia absorbent produced from magnesite has been used for silica removal from water. Betz *et al.* (1940) report on the successful use of active magnesia to remove silica from boiler feed water. In both those cases the pH required for optimum silica removal may be outside that possible with juice and reagents could be expensive; experimental work with juice would be of value. Alexander and Parrish (1953) report that magnesium oxide can be effective in removing silica from juice; again investigations are needed. Venton (1952) made a comprehensive study of the means of producing active magnesia, to be used in juice clarification.

Sugarcane processing

Analytical procedures for the determination of silica

Alexander and Parrish in 1953 had clearly identified the difficulties associated with the determination of silica in sugar products. These workers mention two important points. Firstly the concentrations for both 'total' silica and 'soluble' silica should be determined; they recommend analytical procedures involving straining the juice to remove gross particles of sand and fibre, followed by a gravimetric analytical technique, with an ashing step, to obtain the total silica; another portion of the strained juice is filtered through a retentive filter paper (Whatman No. 42) and the clear filtrate analysed by a colorimetric method for the soluble silica. Secondly, they indicate that the analytical procedures are complicated and time consuming.

Recent work (Walford, 2003) confirms the findings of Alexander and Parrish (1953), in terms of the need to analyse for both the total and soluble forms, and in terms of the complexity of the analytical procedures. In addition, Walford comments on sample preservation; freezing for example can cause severe errors on the determination of soluble silica in clear juice but not in mixed juice. Walford concludes that there are now instrumental methods which can be used to determine both soluble and total silica in sugar products.

Silica in cane

Naidoo and Lionnet (2000) measured the concentrations of soluble silica in sugarcane extracts from the direct analysis of cane (DAC) procedure. In extracts from clean, fresh cane

stalks, that is stalks without trash, tops or roots and free from soil particles, they found soluble SiO₂ levels of 300 to 850 mg/kg brix. The concentration of SiO₂ was affected mostly by the geographical location of the cane; variety did not have a statistically significant effect. Walthew *et al.* (1998) found about 50 mg/kg Brix, which are low compared to the previous results, but high when compared to concentrations in sugar beet.

Juice from clean, fresh stalks was extracted and clarified in the laboratory (Sahadeo *et al.*, 2002; Govender, 2003); the defecation muds were ashed (1000°C) and then analysed for SiO₂, MnO, Fe₂O₃ and Al₂O₃, by X-ray fluorescence (XRF). The process was repeated with juice extracted from clean stalks to which tops and trash had been added, and with juice from a sugar factory. Since the muds were ashed before analysis, the silica results would be representative of the total silica. Averaged results are given in Table 2.

Table 2. X-ray fluorescence analyses of ashed clarification muds.

Element	% ashed muds (m/m) from		
	clean cane	cane + tops + trash	industrial cane
SiO ₂	1	4	11
Al ₂ O ₃	0	0.2	2
Fe ₂ O ₃	0.5	2	1
MnO	0.5	-	1

Silica, aluminium, iron and manganese are all present in soil. Clearly, the industrial cane shows higher concentrations for all these species, particularly silica, in the clarification muds, indicating contamination of the cane with soil.

Walthew *et al.* (1998) show that high pH values result in more silica being released from the cane into the juice during diffusion. These workers also found relatively high concentrations of soluble silica in tops and trash, compared to bagasse.

Mixed and clear juices

Some effects of the defecation process on the levels of silica in juices, as given by Sahadeo *et al.* (2002) and Sang *et al.* (1974) are shown in Table 3.

Table 3. Silica in mixed and clear juices.

Source	Mixed juice	Clear juice	Remarks
Laboratory clarification: Clean cane	600	325	Laboratory clarification. Soluble SiO ₂ in mg/kg brix. Sahadeo <i>et al.</i> (2002).
Clean cane + tops + trash	700	350	
Industrial cane	450 - 850	250 - 425	
Industrial cane	1010	680	Juices from milling. Total SiO ₂ in mg/kg brix. Sang <i>et al.</i> (1974).

Thus, about 40% of the silica can be removed during clarification. This result must however be treated with caution; the removals shown in Table 3 are not consistent, and the analytical difficulties have already been mentioned.

Alexander and Parrish (1953) state that the insoluble or colloidal silica concentration in mixed juice is nearly always greater than that of the soluble silica; this applied to juices

obtained from laboratory milling of normal cane stalks and of cane stalks specially cleaned to remove all soil and sand; the same conclusion was reached with industrial juices. These authors conclude that insoluble silica is a normal constituent of cane juices.

Lime

Van der Poel *et al.* (1998) and Alexander and Parrish (1953) note that lime can add much soluble silica to the juice; Alexander analysed lime samples and found soluble silica contents of 0.5 to 1.2%, m/m, on lime and concluded that this was sufficient to account for about 50% of the soluble silica in clear juice.

Burning limestone in kilns, particularly if salts of sodium or of potassium are present causes any clay or quartz to react in ways that render silica and alumina soluble when the lime is slaked. This will obviously add silica and alumina to the juice; in the beet industry the presence of these two impurities was clearly linked to filtration problems during carbonatation, and to increased scaling in the evaporators. Van der Poel *et al.* (1998) discuss lime quality and state that its SiO₂ content should be less than 2%. Honig (1953) notes that the presence of silica, at about 5% on limestone, is associated with a phenomenon called 'dead burning', which reduces the quality of the lime considerably; his specification for the acceptable, total silica content of lime is less than 1%. Honig states that silica is one of the most objectionable impurities of lime. The solubility of silica is greatly increased at alkaline pH values; the conditions in lime slakers will thus greatly increase the possibility of silica being taken into solution.

Filter cake

Van der Poel *et al.* (1998) give a range of 9 to 20% for the silica content of dry filter cake. This is of practical interest since Meyer and Keeping (2000) suggest that filter cake and fly ash should be considered as sources of silicon for the cane plant.

Evaporator scale

The presence of silica in evaporator scale, and its impact on heat transfer and evaporator cleaning, are well established (Walthew, 1994; Walthew *et al.*, 1998); the conditions during extraction, for example the pH, can strongly affect the levels of silica in the juice. In Southern Africa, evaporator scale has been analysed by XRF and by X-ray diffraction (XRD) since 1997. Published (for example Davis *et al.*, 1997; Walthew *et al.*, 1998) and unpublished results have been used to obtain the data presented here. The analytical approach used for XRF is to ash the scale sample and then analyse this inorganic ash for its constituents; silica is thus expressed as total SiO₂ % ashed scale, on a mass-to-mass basis, while aluminium and iron are given as Al₂O₃ and Fe₂O₃ % ashed scale, respectively.

Juice softening (Davis *et al.*, 1997) resulted in a large, relative increase in the silica content of evaporator scale. The normal, hard juice produced a scale with 1 to 33% SiO₂, while the soft juice produced a scale with a silica content of about 70%; this scale contained mostly silica since Ca²⁺ and Mg²⁺ were removed, but the overall quantity of silica would stay the same. This could well have implications with regards to the ease with which the tubes are cleaned mechanically.

Over the period 1999 to 2002, about 40 evaporator scale samples were analysed by XRF and XRD. The scale samples originated from 1st, 2nd, 3rd, 4th and 5th effects, in raw sugar factories from South Africa, Malawi and Swaziland, where clarification involves liming.

The following averaged results were obtained:

- SiO₂ : Average concentration 33% (m/m) on ashed scale. The lowest concentration was 0 and the highest 82%, representing a very wide range.
- Al₂O₃ : The average concentration was 1.5% (m/m) on ashed scale, with a range of 0 to 5%.
- Fe₂O₃ : The average concentration was 7% (m/m) on ashed scale, with a range of 0 to 52%.

The results were also averaged over the effects, as shown in Table 4. The concentration of silica is highest in the 4th and 5th effects, while that of aluminium decreases steadily from the first to the last effect.

Table 4. Composition of ashed evaporator scale.

Effect	% ashed scale (m/m)				
	1	2	3	4	5
SiO ₂	22	21	20	48	64
Al ₂ O ₃	7	3	2	1	0.5
Fe ₂ O ₃	9	5	7	3	10
Total	38	29	29	52	74

Silica in a turbid clear juice and in a poor filtering VHP sugar

A visually turbid industrial clear juice was catch sampled at a factory and centrifuged in the laboratory to separate the suspended matter. A poor filtering VHP sugar (unrelated to the clear juice sample) was dissolved and the solution also centrifuged in the laboratory. The separated suspended solids were then analysed by XRF, to give the results shown in Table 5 (Lionnet, 2002).

Table 5. Analysis of the suspended solids in a turbid clear juice and in a poorly filtering VHP (% ashed sample, m/m).

Element	Suspended matter from:	
	Turbid CJ	Poor filtering VHP
SiO ₂	20	51
Al ₂ O ₃	12	14
Fe ₂ O ₃	7	8
P ₂ O ₅	10	10
CaO + MgO	50	15
Total	99	98

Silica, aluminium and iron account for large proportions of the inorganic species present in the suspended matter found in these two samples; this conclusion is based on two samples only and it obviously needs much more work to be validated. Alexander and Parrish (1953) state that practically all the silica found in sugar is present as the insoluble form.

Silica in refineries

Godshall *et al.* (1976) give concentrations of silica in refinery products, as shown in Table 6.

These authors state that silica was removed efficiently by treatment with bone char, and by crystallisation; surprisingly, phosphatation did not remove silica. Unfortunately, the use of sweet waters which contained high concentrations of silica (up to 36 mg/kg) often negated

these benefits. The use of silica based filter aids can result in the concentration of soluble silica increasing in the liquors.

Soluble silica has been associated with process problems such as acid beverage floc (Clarke, 1974).

Table 6. Silica (as Si) in refinery streams.

	Raw sugar	Melt	Phosphated liquor	Char liquor	Resin liquor	Jets	Refined sugars
Si (mg/kg)	28	25	28	3	15	16 - 18	2 - 4

Conclusions

Silica is a major component of soils; it is also an essential nutrient for the sugarcane plant; soluble and insoluble silica are thus found in cane and in cane juices. The impact of silica in cane sugar factories is complicated by the fact that cane stalks, tops, trash and root systems can contain varying, and sometimes large, quantities of clay which is an aluminosilicate. It is therefore usual to find silica in juices not only in the soluble form but also as colloidal matter and as suspended matter of varying particle size.

Furthermore, silica can exist as crystalline, amorphous and hydrated forms. Its chemistry is complex; it involves chains and networks of silicon/oxygen bonds, and it interacts with metals such as aluminium, iron, potassium, calcium and magnesium. It also reacts with complex polyphenolics; it is well established that cane contains many phenolic compounds.

Finally, the solubility of silica in water, or in cane juice, is a complex process which involves hydrolysis and surface reactions. pH has a critical role; in water, the solubility of silica shows a pronounced increase at pH values above about 8.5. The particle size of the silica has also been shown to have an important effect on its aqueous solubility.

A number of authors show that lime of poor quality can add soluble silica to the juice. It might be useful to introduce procedures to test lime for silica.

Analysis of many samples of evaporator scale shows that about 40% of the inorganic content of the scale is accounted for by SiO_2 , Al_2O_3 and Fe_2O_3 ; the ranges however, are very wide. In 1st, 2nd and 3rd effects, these three species account for about 30% of the inorganic content but this rises to above 50% in 4th and 5th effects.

The analysis of the suspended matter in a turbid clear juice and in a solution made from a poor filtering VHP sugar showed that 40% and 70% (m/m) respectively, of the inorganic content consisted of SiO_2 , Al_2O_3 and Fe_2O_3 .

This paper indicates that silica in industrial streams can originate from the cane itself, but that the contamination of cane by soil and clay can introduce silica in the factory; this contamination also introduces aluminium into the process. Experimental evidence shows that the presence of soil and clay interferes with clarification and could well result in poor sugar quality.

Many of the above points need further work for confirmation or for greater clarity. The main conclusion of this paper could well be that the impact of silica in cane processing has been somewhat neglected, particularly in terms of sugar quality. There is therefore a need for more work dealing with silica.

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