*Proceedings of The South African Sugar Technologists' Association — June 1994*

# THE POTENTIAL APPLICATION OF ION EXCLUSION CHROMATOGRAPHY FOR ADDITIONAL SUCROSE RECOVERY FROM MOLASSES

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## Abstract

Ion exclusion chromatography presents a technical opportunity to recover up to 90% of the sucrose normally lost to final molasses. In the South African sugar industry this could increase overall recovery by at least three units. The technology is being applied on a commercial scale in two cane factories in Japan and numerous beet factories in Europe and the United States of America. This technology is discussed along with a number of special problems associated with applying it to cane molasses. Some of the initial work and research directions at the Sugar Milling Research Institute are given.

## Introduction

The large amount of sucrose left in beet molasses (50-60%) after crystallisation prompted sugar producers to seek alternative means of increasing sugar recovery. In 1954 the Dow Chemical Company patented (Bauman, 1954) the idea of ion exclusion as a result of the observation by Wheaton and Bauman (1953) that ion exchange resins may be used to separate molecular constituents by size as well as by charge. The Ultra Sucro Process, a batch ion exclusion pilot plant system, demonstrated that about 80% of sucrose could be recovered from cane and beet molasses by ion exclusion chromatography (Anon., 1956). In 1975 the Pfeifer and Langen company started a full scale operation using 55 m$^3$ of resin packed in a batch column 8 m high and 3 m in diameter (Schneider and Mikule, 1975). Separations based on a simulated moving bed concept designed by the Amalgamated Sugar Company have been in operation in the beet industry since 1985 (Chertudi, 1991). Recently a central processing plant was commissioned in Scottsbluff, Nebraska, by Western Sugar Company. This central desugarisation plant is capable of storing 29,6 million litres of molasses supplied by rail from Western's other beet factories (Anon., 1994). As early as 1984 the first cane sugar factory to apply this technology was built in Okinawa, Japan. This installation recovers up to 80% of the sucrose in B-molasses thereby eliminating the need for a C-station and increasing overall recovery by three units (Kakihana, 1989).

### *Beet molasses pretreatment*

Pretreatment of beet molasses usually involves filtration and ion exchange to remove suspended matter and divalent cations, respectively. Some factories are softening thin juice (removing divalent cations) to gain the benefits of reduced evaporator scaling and the necessary ion removal for subsequent desugaring.

### *The principle of ion exclusion chromatography*

Ion exclusion is a chromatographic technique for separating materials of different ionic activity and molecular size by means of ion exchange resins which are strongly acidic cationic resins in the monovalent salt form (e.g. potassium). The resin is made by crosslinking divinyl benzene (DVB) with a polystyrene matrix, which contains sulphonic groups for cation attachment. The resins are manufactured as beads which, when packed in a column, provide interstitial spaces for the passage of large molecules.

Generally, non-ionised smaller molecules such as sucrose, glucose and fructose are able to enter the resin beads whereas ionised and/or large molecules such as colour will not be able to enter the resin matrix. These large molecules will then pass quickly through the interstitial spaces, while the smaller molecules will take the longer route through the resin matrix. This phenomenon is exploited to separate sucrose from all the other molasses constituents which are either of high molecular weight or possess charge. In other words, a sucrose-rich fraction is separated from a non-sucrose fraction. The former is usually about 80-90% pure and is used directly to produce white sugar in the beet industry.

### *Batch ion exclusion chromatography*

Early industrial plants in the beet industry used a discontinuous or batch ion exclusion system where the resin bed remained fixed and feed flowed down the column. The operational steps are similar to bench type or analytical chromatography. At measured intervals a portion of molasses feed is applied to the top of the column and eluted with water. During passage through the resin, the separation of molasses constituents gradually establishes what is termed the mass transfer zone (MTZ) which is formed within the column (see Figure 1).

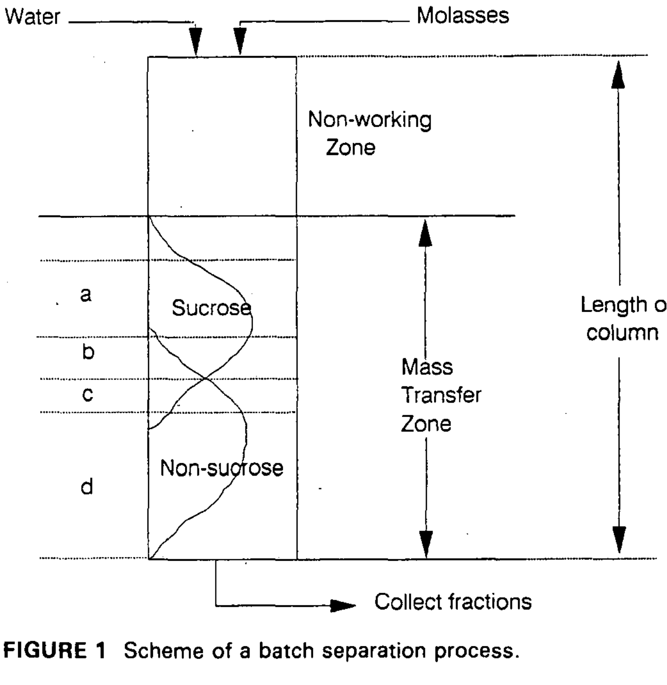

**FIGURE 1** Scheme of a batch separation process.

The separated fractions of the MTZ are collected at the outlet and diverted to the appropriate stream, sucrose recovery or molasses waste. Further additions of molasses are made to the column once enough free resin becomes available at the top, separated by a buffer of water that has been responsible for the removal of sugars from the resin beads at the top of the column. In industrial systems overlapping fractions (b & c in Figure 1) are recycled by re-loading to the top of the column in an order such as to generate a separation profile as close to that in the top of the column as possible.

*Continuous ion exclusion chromatography*

The efficiency of the ion exclusion desugaring process and resin utilisation may be increased by using continuous systems. A separation profile always exists in the continuous process. Figure 2 shows schematically the profile on the column, noting that the MTZ occupies the length of the column, thereby utilising all the available resin. Of the many continuous systems available, the simulated moving bed concept is used in many beet factories for desugaring of molasses (Gadomski, 1991). The simulated moving bed usually consists of eight or more columns with multiport valves which open and close, depending on the location of the separation profile, to feed molasses and water and to withdraw sugar and non-sugar streams. Recycling of fractions is therefore not necessary.

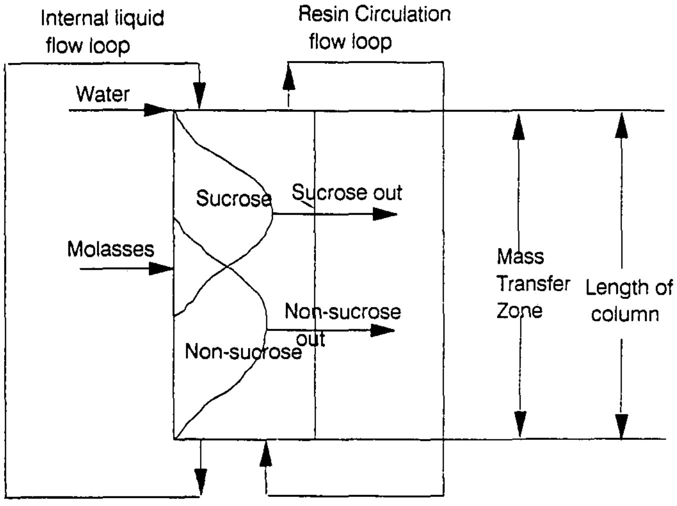

**FIGURE 2** Scheme of a continuous separation process.

*Cane molasses desugarisation*

Based on a recovery of 80% of the sucrose lost to final molasses in the 1990 season (i.e. 8,76 × 0,8) the overall recovery of sucrose may be increased from 86,66% (Lionnet, 1990) to 93,67%, an increase of 7,01 units in overall recovery. However in practice only about 3-4 units of recovery would probably be realised. This is because before this technology can be used to desugarize cane molasses, the molasses needs to be pretreated to remove particles bigger than 20 μm and most of the divalent cations (>0,1% dry substance). In the beet industry dilution, filtration and ion exchange softening are sufficient. The same applies to the cane industry although this technology is more suited to desugaring beet molasses, which contains as much as 60% sucrose (cane 30%) and has less suspended material and less calcium than does cane molasses. This means that for cane there is more cost involved in the pretreatment of molasses per unit of sucrose recovered. The high levels of invert sugars in cane molasses may however partially compensate for the lower sucrose levels because it may be possible to produce a valuable liquid invert sugar end product in addition to crystalline sucrose.

*Cane molasses pretreatment*

*Suspended matter.* Due to the nature of cane molasses (mud, sand etc. brought in with the cane) a physical separation as well as chemical treatment to remove much of the suspended solids is necessary. Several methods have been applied. The addition of $H_3PO_4$ and pH adjustment with NaOH followed by decanter centrifugation was tested by Hongisto and Heikkilä (1977). Two commercial operations in Japan successfully pretreat B-molasses for ion exclusion. The Hokubu Seito Co. Haneji factory at Okinawa uses horizontal decanter centrifuges to remove most of the suspended solids of diluted (50°Bx) and heated (75°C) molasses. The remaining suspended solids are removed by rotary vacuum filtration using a precoat of diatomaceous earth. The Showa Togyo Co Kikai factory applies a chemical treatment using $Na_2CO_3$ and $Ca(OH)_2$. The precipitate of $CaCO_3$ and $Mg(OH)_2$ is then filtered (Kakihana, 1989).

*Removal of divalent ions.* The concentration of calcium needs to be reduced to less than 0,1% dry substance (d.s.) which is normally achieved by the use of ion exchange resins. In beet molasses there is less calcium (beet 0,3% d.s., cane 2,1% d.s.) which is another factor which makes this process more economical for beet molasses desugarisation. The Haneji factory uses a weak acid cation exchange resin while the chemical treatment described above for the Showa Togyo factory is sufficient for divalent ion removal.

## Work carried out at the SMRI

*Initial trials*

It was found that ultrafiltration (UF) using a 40 000 dalton ultrafiltration crossflow (UFCF) membrane unit was sufficient for removing suspended solids from B-molasses (Patel, 1991). Ion exchange using a strong acid cation exchange resin in the sodium form (Duolite C20, supplied by Acix-NCP) was used to remove calcium from B-molasses pretreated with a UFCF membrane. The profile of the ion exchange treatment is shown in Figure 3. This line of investigation was discontinued due to the high cost of ceramic membranes, even though the process is technically feasible.

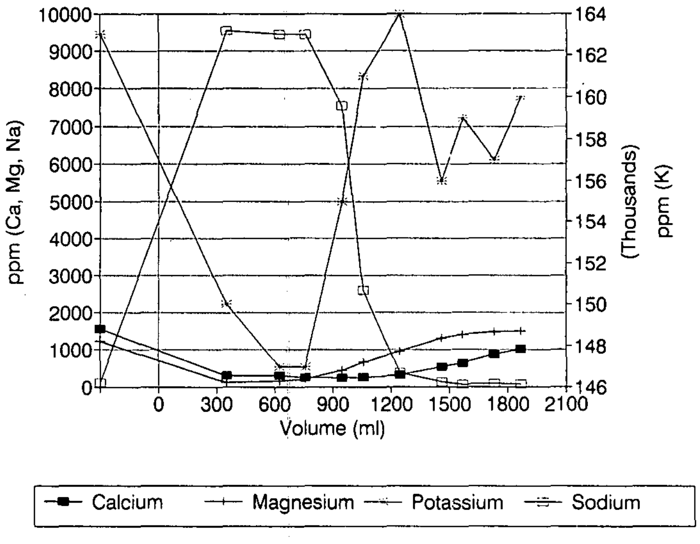

**FIGURE 3** Profile of the softening of 50°Bx B-molasses pretreated by a UFCF membrane unit.

### *Heating and cooling molasses*

Heating final molasses after dilution to 50°Bx produces a sediment mass which may be removed by centrifugation. This was observed by the centrifugation of cold dilute molasses (25°C), heated dilute molasses (80°C) and heated dilute molasses which was cooled before centrifugation. Centrifugation of heated molasses after cooling removed the most suspended matter. The longer the cooling period before centrifugation the more suspended matter was removed. This suggests that heating and cooling molasses that is to have suspended matter removed by disc-stack centrifugation is important.

These observations imply that the measurement of suspended matter in molasses will depend on the heating and/or cooling treatment. Therefore heating (1 h) and cooling (overnight at room temperature) periods were used for the analytical determination of the extent of suspended solids removal during this project. Centrifugation in a batch centrifuge to extinction (i.e. no further sedimentation) was sufficient to ensure an adequate determination of the "sludge" in molasses.

### *Disc-stack centrifugation*

Disc-stack centrifugation was investigated as a means of removing suspended solids using the LAPX 202 supplied by Alpha-Laval (Alpha Engineering, Durban). Final molasses was diluted to 50°Bx and heated to 80°C before centrifuging at varying flow rates without cooling as it was assumed that cooling molasses would not be economically acceptable. This exercise was conducted to determine an acceptable flow rate capacity of diluted molasses to the centrifuge. Flow rates applicable to the range of solids to be removed from dilute molasses were tested. A typical plot of the work carried out is shown in Figure 4. During these tests it was noted that the centrifuge aerated the sample and a scum formed on the clarified sample. This observation was investigated further by testing the effect of the addition of flocculant, added to the clarified molasses as it emerged from the centrifuge, on the removal of solids. This is shown in Figure 4 as a single point at the highest flow rate tested.

The centrifuged molasses was allowed to stand for 20 min after the addition of flocculant and the scum was removed from the surface. It is postulated that apart from removing the larger particles the disc-stack centrifuge sufficiently aerates the sample for adequate flocculant flotation which removes any finer particles the centrifuge is unable to remove.

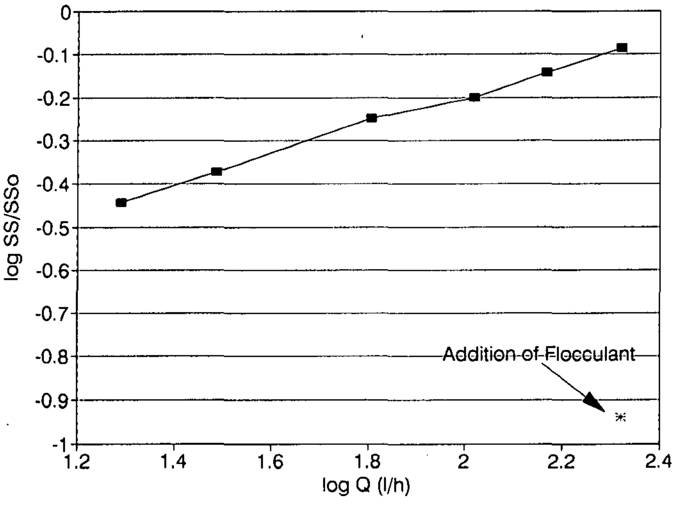

**FIGURE 4** Suspended solids removal by disc-stack centrifugation at varying flow rates with flocculant addition to the clarified liquor. (Q = flow rate (l/h), $SS/SS_0$ = suspended solids in the clarified liquor/suspended solids in the feed).

### *Variations in sludge quantity and composition*

The quantity of sludge separated by the disc-stack centrifuge from molasses obtained from a number of mills varied considerably. This trend is shown in Figure 5. The mills are plotted by geographical location, north to south. The variations in sludge quantity are also seasonal, shown by a weekly survey of sludge quantity on 50°Bx final molasses for each South African mill over the 1993/94 season. Some mills show little variation whereas with others the variation is considerable. As an example the sludge percentage for Sezela Mill is shown in Figure 6.

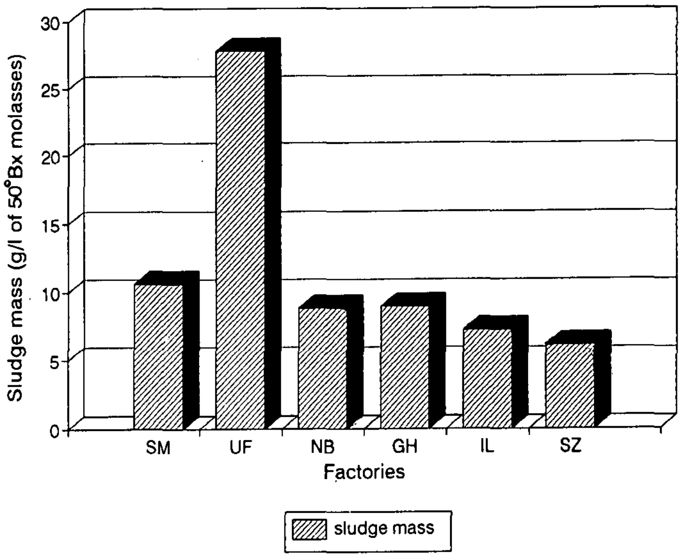

**FIGURE 5** Trends of sludge quantities for a number of South African factories.

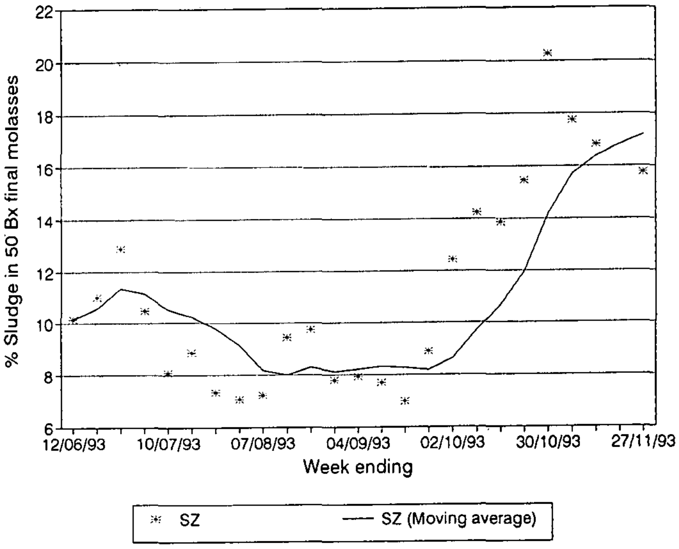

**FIGURE 6** Trend in sludge quantities for SZ during the 1993/94 season with a 25 week moving average.

Table 1 shows the full analysis of sludge samples after disc-stack centrifugation of final molasses from a number of mills. The molasses samples had been diluted to 50°Bx and heated to 80°C before centrifugation. The potassium content in some of the samples was high. For example, UF final molasses sludge had a potassium content of 20% on dry sample. The high amounts of potassium in some of the sludge samples would make this product potentially suitable for application to sugarcane fields. Washing of the sludge to recover sugar may be necessary before this is possible. However, washing the sludge often results in a loss of 40% of the potassium to the wash water. High potassium levels were associated with high $SO_3^{2-}$ levels suggesting that the potassium may have been present as a sparingly soluble $SO_3^{2-}$ salt/complex.

**Table 1**
**Full analysis of the sludge from the centrifugal clarification of a number of molasses samples from different mills**

| Mill | SZ | IL | GH | SM | UF | NB |
|---|---|---|---|---|---|---|
| % Moisture | 42,01 | 31,65 | 31,18 | 35,86 | 37,47 | 27,88 |
| % Ash at 650°C (on dry sample) | 88,1 | 53,5 | 77,8 | 74,47 | 71,11 | 82,37 |
| % Ash at 800°C (on dry sample) | 89,4 | 51,4 | 78,7 | 73,43 | 71,98 | 83,57 |
| % On ash (800°C) | | | | | | |
| $SiO_2$ | 41,42 | 5,8 | 11,03 | 9,31 | 7,83 | 3,64 |
| CaO | 22,98 | 12 | 33,51 | 19,28 | 16,29 | 58,24 |
| MgO | 34,04 | 0,8 | 5,57 | 1,42 | 2,56 | 13,1 |
| $K_2O$ | 9,07 | 21,1 | 16,5 | 38,15 | 28,79 | 4,6 |
| $Na_2O$ | 0,55 | 0,2 | 0,52 | 0,09 | 0,31 | 0,07 |
| $Fe_2O_3$ | 0,53 | 0,1 | 0,25 | 0,36 | 0,12 | 0,35 |
| $SO_3^{2-}$ | 12,36 | 41,2 | 21,62 | 35,4 | 39,19 | 5,96 |
| CuO | 0,03 | 0 | 0,11 | 0,006 | 0,006 | 0,04 |

## Discussion and conclusions

It is necessary to remove both suspended solids and divalent cations before the chromatographic desugaring of molasses. Continuous centrifugation combined with flocculant assisted flotation clarification proved adequate for the former. Sludge quantities and compositions varied widely from mill to mill and quantities varied with time of year. The removal of divalent cations is the subject of a separate paper (Thompson, 1994). The application of the pretreatments and ion exclusion provides an opportunity to recover additional sucrose from South African molasses. Favourable economics are likely to depend on additional benefits such as reduced evaporator scaling and the sale of recovered potassium and invert sugars.

## Acknowledgements

The author wishes to record his thanks to Alpha-Laval Engineering, Durban, for the loan of the disc-stack centrifuge used for the above trials. Thanks are also due to Messrs N Whiting and C Curren for their assistance with regard to the centrifuge. Thanks are also extended to S Wienese for the many molasses sludge analyses that were performed.

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