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RECENT TRENDS IN THE USE OF ION EXCHANGE IN THE SUGAR INDUSTRY

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CONTENTS

I. INTRODUCTION

The purpose of this article is not to explain the principle of ion exchange and recount the history of its application in the sugar industry. An excellent and very comprehensive review of Landi and Mantovani,[1] published in 1975, provides a good basis for understanding the ion exchange principle, as well as a chronology of its use in the beet sugar industry from 1941 to the mid-seventies.

We will discuss here the trends observed in the industry over the last ten years or so.

Our discussion will be limited to the so-called "conventional" sugar industry. We would be remiss, however, if we failed to mention that during this same '75-'85 period a new sugar industry emerged,[2] one with an impressive growth rate in the United States: the manufacture of high fructose corn syrup by the

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corn refiners. This industry presently produces more than 40% of all the sweeteners consumed in the United States, and at the heart of their manufacturing process we find the latest enzymatic and ion exchange technologies. In reading this review one should keep in mind that this young industry of high fructose corn syrups has created a market for ion exchange resins which is now far greater (in terms of resin volume consumption) than the volume of resin presently consumed by the conventional sugar industry.

The sugar industry (and we will henceforth be speaking of the conventional sugar industry) now faces a great challenge--one which will determine its future existence: how to decrease production costs and increase sugar recovery in order to remain competitive with the new high fructose corn syrup industry.

One answer, and to a large degree the most significant, is ion exchange. Ion exchange is now used by most of the world's important sugar producers.

To present ion exchange in the sugar industry as a new technology--pioneered by small, specially-funded groups which experiment with new, unproven technologies--is a gross misrepresentation. The fact is, ion exchange is now the intelligent choice of most progressive companies, who use this unit operation for separation very profitably in their sugar process, when dictated by their particular market and the current economic situation.

When used wisely, ion exchange can significantly improve the profit margin of the sugar manufacturer. Most successful sugar manufacturers in the Western world use it extensively. Increased profits through the use of ion exchange are, however, seldom publicized. This is probably mainly because ion exchange is not used by every sugar manufacturer, and, in a market where competition is keener than ever, the deciding factor between two competing companies could directly relate to the use of ion exchange.

The increased profits enjoyed by those in the sugar industry employing ion exchange processes confirm the progress made in this area in the last decade.

This progress is reflected in

- better resin characteristics,
- better ion exchange engineering,
- better plant control,
- inclusion of waste water treatment in the ion exchange process (when required), and
- optimum integration of the ion exchange system in the general factory process--which generates indirect, supplementary savings to further enhance global factory economics.

The principal industrial applications for ion exchange in the sugar industry today are:

- thin juice deliming (beet sugar industry)

- nonsugar removal from beet thin juice/thick juice/low green syrup/ molasses (beet sugar industry)
- liquid sugar production from thick juice (beet sugar industry)
- Quentin process (beet sugar industry)
- decolorization of fine liquors (cane and beet sugar refineries)

II. PROGRESS MADE IN RECENT YEARS

A. Resin Characteristics

1. Macroreticular* Resins

Developed in early 1960 by Rohm and Haas,[3] the macroreticular resins have, without a doubt, had a profound effect on the progress of ion exchange in the sugar industry. Processes which previously used gel type resins were upgraded by using this new range of products available on the market.

One of the main reasons for the success of these resins is their excellent physical stability, which allows for attrition resistance under conditions of high flow rate and severe osmotic shock. This is particularly important in processes where, during the same cycle, sugar syrups at high Brix and very dilute water solutions are passed successively through a resin bed: Gryllus process, decolorization of fine liquor, Quentin process, etc.

Another reason for their use is that they are particularly efficient in the removal of colloidal and high molecular weight substances (e.g., production of liquid sugars from cane molasses).

More recently, the development of a complete range of macroreticular adsorbent resins opened a new avenue in the decolorization of sugar solutions. These adsorbent resins have been used by the beet sugar industry for several years now in the production of liquid sugar from thick juice.

2. Acrylic Resins

Polystyrene type resins have been used in the sugar industry for years, for all applications.

Special applications have now been developed for the acrylic type resins, significantly improving the economics of the processes involved. For example, we have

(1) the use of acrylic anion exchange resins for the demineralization of thin juice in the beet sugar industry,[1]

(2) the use of acrylic, strong anion exchange resins in the chloride form for the decolorization of fine liquors in the sugar refinery,[4] and

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* The term "macroreticular", introduced by Rohm and Haas Company, characterizes the physical pore structure of this new type of ion exchange resin and polymeric adsorbent. In adsorption terminology, macroreticular refers to pores of a diameter larger than 400 angstroms.

(3) the use of acrylic, weak cation exchange resins[5] for the final affination of liquid sucrose in mixed-bed ion exchangers.

For each of these cases acrylic resin offers a different advantage:

For (1) - High capacity nonsugar removal.

For (2) - High capacity decolorization, and excellent yield in regeneration.

For (3) - Low acidity, avoiding the production of invert sugar.

3. Improvement in Capacity of Polystyrenic Macroreticular Anion Exchangers

For the demineralization of beet sugar products, acrylic weak-base resins, due to their higher nonsugar removal capacity, are often preferred to the polystyrenic weak-base resins.

The resin manufacturers have endeavored to provide new, high-capacity, macroreticular, polystyrenic weak-base resins for the demineralization of sugar products.[6] This has been mainly in response to the demands of the corn refining industry, which has always preferred polystyrenic resins over the acrylic resins. Presently, high-capacity, weak-base acrylic, and high-capacity, weak-base polystyrenic resins give very similar results in terms of nonsugar removal. The choice of acrylic or polystyrenic resin is based more on factors such as regeneration efficiency, physical stability, resin life, the product treated, etc.

4. Efforts to Improve Hydraulic Characteristics of Ion Exchange Resins

Ion exchange resins come in granular and spherical forms. The spherical form is presently the most popular due to its superior hydraulic characteristics. Most ion exchange resins are supplied as spherical beads having a diameter between 0.2 and 1.2 mm, with 90% of the beads within ± 20% of the mean bead size.

Dow Chemical Company[7] recently introduced what they term "monosphere" resins, the resin beads being within ± 10% of the mean bead size. This bead size, they claim, is "tailored" to the customer's requirements. This latest improvement will mainly affect the hydraulic characteristics of the resin.

5. Reproducibility of Resin

In industrial use, different batches of the same brand-name resin sometimes display differences in resin behavior which cannot always be attributed to operating differences in the ion exchange plant.[8] Small differences in the resin manufacturing process itself can in fact affect the properties of the resin. This is extremely difficult to detect early in resin life, since the rinsing properties or physical characteristics (bead moisture, bead breakage, etc.) can only be judged after many cycles. Part of the progress achieved in resin characteristics is, therefore, in the standardization and better control of resin manufacture in order to ensure perfect reproduction from one batch of resin to another.

6. Outlook: New Products for Decolorization or Demineralization of Sugar

(a) Powdered Resins

Although the subject under discussion here is the use of resin beads which can be saturated and regenerated in ion exchange reactors, we must not overlook the recent use in the sugar industry of powdered resins--mainly for decolorization of concentrated syrups[9]--which act in the same way as powdered activated carbon and can be used in conjunction with the filtration process for these syrups.

(b) Mineral Resins

The term "ion exchange resins" is very often considered as calling for organic polymeric compounds, in exactly the same way as the membranes were assimilated in organic compounds. Today, research is being carried on using mineral porous beads[10] as raw material for the production of ion exchange resins. This follows the same trend observed in membrane technology with the recent development of mineral membranes.

Concluding this chapter on the progress made in resin manufacture, it can be stated unequivocally that the commercial resins now available have improved characteristics, compared with those produced ten to fifteen years ago. This means that the processes using resins are now more economical because of improved resin performance and extended resin life. In certain cases, the use in the sugar industry of new types of resin (such as the strong-base acrylic resins) has been a real technological breakthrough.

B. Ion Exchange Process, Engineering and Equipment

As is the case with most technologies, ion exchange is in perpetual evolution as a result of the work being continually carried on for the purpose of improving the process, the engineering, and the equipment.

We will not go into detail here with regard to the different technologies being applied, but rather summarize briefly the recent trends, as well as the guidelines being followed.

1. Process Considerations

(a) Continuous System Versus Fixed-Bed

Between 1960 and 1975 intensive efforts were made by innovative process designers[11,12] to promote the "universal" continuous system, where resins are moved continuously, countercurrent to the different fluids they encounter. While the theory is very attractive, most of these systems have ultimately proven unsuccessful.

Experience shows that for ion exchange technology, as is true for other technologies, there is no universal system. Furthermore, here, the simple solution is the ultimate answer: It is easier to move the different fluid streams through the resin beads.

More than 95% of the industrial-scale ion exchange plants using resin in today's sugar industry are of the so-called fixed-bed type, where the resin is placed in a fixed reactor, where all the operations of a cycle take place (sweetening-on/off, regeneration, rinsing, etc.). The only sequence where resin can sometimes be moved out of the reactor is the backwashing sequence.

It is important to consider the progress made in the design of these fixed-bed systems--which can be any of a variety of designs, depending on the resin used and the type of application involved.

A word about the use of fixed beds as a "discontinuous" process technology: Ion exchange is discontinuous in principle due to its sequential characteristic, the resin being submitted to different operations in a methodical, sequential order. The fixed-bed technology is particularly well adapted to this sequential characteristic. This does not mean, however, that a proper arrangement of fixed-bed reactors cannot fit perfectly into a continuous process. This is especially true today, in light of the progress made in automatic control.

(b) Use of Reagents for Resin Regeneration

In most cases, the use of ion exchange systems in the sugar industry requires reagents for the regeneration of the resins. The cost of these reagents is always an important consideration in the decision to install an ion exchange system. Therefore, the process designer takes into account the reagent consumption in the conception of his ion exchange system design. Based on this consideration, the evolution of the process has tended to concentrate on:

- Minimization of reagent consumption.
- Recovery of reagents for marketing in another form (such as fertilizer).
- Recycling of reagents.
- Complete elimination of reagents.

(i) Minimization of Reagent Consumption

Considerable progress has been made in recent years in minimizing the consumption of reagents. A decisive step in this progress has been the systematic use of countercurrent regeneration in the design of ion exchangers--particularly those using strong cation or strong anion resins. When applied, this allows savings of up to 40% of the normal amount of reagent required in the cocurrent regeneration of these types of resin.[13]

(ii) Recovery of Reagents for Marketing in Another Form

Another way to minimize the cost of reagent consumption is to recover the reagents after regeneration to sell in another form.

For example: In the thin juice demineralization using the H-OH form of the resins, sulfuric acid and ammonia used for the regeneration of the resins can be sold as fertilizer, when combined with potassium extracted from the thin juice.[14]

(iii) Recycling of Reagents

Efforts have been made to design systems which recover reagents through the use of other unit operations, such as distillation. The systems use reagents which are sufficiently volatile to be recovered in this manner, such as ammonium carbonate.[15]

It does not appear that a real industrial breakthrough has been achieved in this area, although an industrial plant has run for several campaigns at the Enns factory (Austria) using this principle.

Recently, laboratory tests and pilot studies, with ammonium bicarbonate as the regenerant, have been conducted using the same principle[16,17] to seek better regeneration techniques.

(iv) Eliminating the Use of External Reagent

Some processes have been developed which eliminate totally the use of external reagents for resin regeneration. The most well-known of these processes is the Gryllus.[18, 19] In this process, thick juice or low green syrup is used for the regeneration of the resins after their exhaustion. The conventional deliming system uses brine, an external reagent, for the same purpose.

The Gryllus process is a clever technique for totally eliminating the use of external regenerant by employing in the process one of the beet sugar factory's internal syrup streams for the purpose of regeneration.

Another example of a process which does not consume reagents is the ion exclusion process, based on the chromatographic separation of sugar and nonsugar. This has been developed on an industrial scale for the purification of beet molasses.[20] It should be noted, however, that before this process is initiated, a complete softening of the molasses must be accomplished. This softening consumes reagents (NaCl or HCl, or NaOH).

Needless to say, in the process design, reagent cost is not the only factor to be considered in the economic evaluation.

In comparing a process using reagents with a process assumed to not use reagents, it is important to consider the entire process, including both pre-treatment and post-treatment. The cost for these auxiliary treatments can be very high, not only in reagents and energy, but also in sugar losses.

It will be interesting to follow the future of two nonsugar removal technologies in the beet sugar industry: ion exclusion for the treatment of beet molasses versus ion exchange for the treatment of thin juices and thick juices.

(c) Problems of Product Intermixture

Efforts have also been made in recent years to decrease product intermixture--which creates recycle problems--through improved process design. When using solutions of different densities in the ion exchange reactors, the idea is to respect the natural order of introduction of products in the reactor.[21] For example: A lower density solution would be introduced in downflow, if it is introduced in the system after a heavy density solution.

Using downflow or upflow systems, depending on the density of the product, is no longer a difficult engineering problem. Designs are now much more flexible in this regard. As a result, the dilution effect, or sweetwater production, is better controlled, thus rendering the ion exchange process more attractive than in the past.

2. Engineering Considerations

(a) Sizing of Reactors

One of the rules in designing fixed-bed columns is to end up with a resin bed which allows enough contact time for the ion exchange reaction, as well as smooth handling of the resin during the run (no excessive pressure drop, space for the resin to swell, etc.), and a smooth regeneration (backwashing possibilities for a resin expansion of up to 50% or more of its compacted volume). There have been no major breakthroughs here.

Usually, the ion exchangers are made of cylindrical reactors containing beds of resin having a bed depth of 0.7 to 2 m. In certain cases, in order to allow the resin to swell, the reactors have a conical shape.

Due to the more extensive use of ion exchange resins, there is now a demand for larger ion exchange reactors than in the past. With a large volume reactor, special engineering features must be incorporated. The construction of pressurized vessels in a workshop is limited by the maximum allowable diameter for transporting the vessel from the workshop to the factory. As the bed depth required for smooth operation in a single bed of resin is also limited, one can see that there are restrictions to consider in the construction of single cell systems. It is the responsibility of the ion exchange specialist to decide if, for the volume of resin considered, a single cell or multiple cell system is required.

The larger the ion exchange reactor, the larger the surface area for the distribution and collection of the fluids passed through the reactor.

Therefore, special care must be taken to assure that there is a homogeneous distribution of fluids through the reactor.

(b) Decompression and Backwashing of the Resins

Special mention should be made of the backwashing possibilities of a resin bed in a reactor, since this is one of the key factors in good regeneration.

Conventionally, backwashing is made at the conclusion of every cycle to verify

(1) the elimination of suspended solids still present in the product and which have been filtered by the resin bed during the running period;
(2) the elimination of resin fines created by resin attrition and which should not be allowed to accumulate in the resin bed; and
(3) the total swelling of the resin, making certain that no part of the bed remains compacted--which could create premature resin attrition and possible channeling, with preferential passages for the fluids.

Depending on the "cleanness" of the product to be treated, the swelling characteristics of the resin in the process, and the required volume of resin for the application, the above three requisites can be accomplished--either together or separately--during the backwashing of the resin. For example: For an upflow process design the resin will rise to the top of the reactor during the run and migrate to the bottom of the reactor during the downflow regeneration. Resin decompaction will automatically occur when advancing from the run to the regeneration, making backwashing at every cycle unnecessary, if the product treated is clean and the resin is in good condition. The backwashing device is designed accordingly.

This particular example shows the type of progress achievable with a good understanding of the true function of the backwashing operation. Fewer backwashings can mean considerable savings in water.

(c) Countercurrent Regeneration

Even without a "revolution" in ion exchange technology, the present extensive use of countercurrent regeneration is certainly one of the most progressive steps made in ion exchange technology. Cocurrent regeneration is no longer justified--along with the building of ion exchange plants using strong anion resins regenerated with NaOH or strong cation resins regenerated with hydrochloric or sulfuric acid.

Even if the countercurrent regeneration requires a slightly higher capital cost investment, this is very quickly recovered through savings in reagent consumption.

When using this technology it is important to make sure that the bed of resin is properly packed. If the regeneration is made in upflow, the resin should never be fluidized. Each engineering group has its method for accomplishing this. Regardless of how this is achieved, proper bed packing will ensure the efficiency of the regeneration.

(d) Upflow Design

In speaking of the progress made in engineering design, a word should be said regarding the choice of upflow design where there are intermixture problems or where the density of the resin is lower than that of the product to be treated. For example: In the treatment of syrups at 60% total solids or more, the resin may float in the syrup. In such cases, the downflow system does not guarantee good packing of the resin bed.

Since the conception of upflow design no longer presents a problem, the engineer now has the choice of upflow or downflow, depending on the process requirement. This lends much more flexibility to ion exchange technology.

The upflow design is now much more visible in industry. The Bayer Company has contributed greatly to this phenomenon.[22,23]

3. Equipment Considerations

(a) Pressurized Vessels

Ion exchange reactors are usually pressurized vessels, especially those for large industrial plants. The current range of pressure varies between 3 and 10 bars, depending on the application. Passing syrups or other viscous products through ion exchange reactors (as is the case with the sugar industry) makes it necessary to apply pressure to these fluids. Care must be taken to control the pressure drop through the resin beds. It is important to avoid a big pressure drop through the resin bed. Depending on the resins, a pressure drop of 0.2 to 2 bars is within the acceptable limit.

(b) Rubber Lining

While discussing the progress made in ion exchange technology, it is important to point out at the same time certain state-of-the-art features which have been improved on, but not radically changed. Rubber lining is one such feature. At this stage of the technology, no better protection against corrosive products and reagents has been found than rubber-lining the reactors. Rubber lining is well adapted to the static shape of the ion exchange plant and the usual range of temperature and products treated. It presently has no economical equivalent, insofar as resistance to corrosion from diluted acids, such as hydrochloric or sulfuric acid, or the organic acids often present in the products being treated. Improvements in rubber linings have been made specifically for the food and sweeteners industries, to meet FDA and USDA requirements.

(c) Distribution System

An important part of the ion exchange reactor is the device for distributing and collecting the different fluids passed through the resin.

There are two main types of equipment presently in use:

(1) Distribution Platforms

These are platforms with numerous perforations. Each hole is equipped with a special nozzle which allows only the fluid to pass through, not the resin. Platforms are used when the resin bed must be supported by them or compacted against them. When using the platform at either extremity of the reactor, the distribution of the fluids is made on the side of the platform where the resin is not present. The uniformity of distribution across the reactor is ensured by the individual nozzles being placed at measured intervals.

(2) Network of Tubular Screens

Another method for distributing and collecting fluids is by the use of a network of special tubular screens placed across the reactor and connected to a central collector. The screens are slotted, allowing the fluid to pass through and leave the resin behind. This system is now widely used in the industry and is particularly well suited to mixed-bed technology, or countercurrent technology, where it is necessary to have the distribution system placed inside the load of resin.

Regardless of the system used, platform or tubular screen, it is very important that the system be supported by the proper mechanical device to withstand the forces exerted within the reactor. These forces are due to

--pressure drop through the resin bed, and

--swelling of the resin, which can result in intense pressure against the distribution system, especially if this system is located inside the resin bed.

Typical materials of construction for the nozzles and screens are polypropylene or stainless steel. The stainless steel is more suitable for the screens due to its mechanical characteristics, but special care must be taken due to possible corrosion problems.

(d) Valves

Valves are an intrinsic part of ion exchange technology, since this technology uses so many different types of fluids which must be introduced into the system and collected from it, one after the other.

Each fluid is controlled by one or several valves at the inlet and outlet of the reactor--particularly when using automatic systems, which is now generally the case. Depending on its complexity and the process in use, an ion exchange plant in the sugar industry may include anywhere from thirty to three hundred automatic valves.

The reliability of these valves is essential to the successful operation of the ion exchange plant. Needless to say, their proper maintenance is an important factor.

Until recently, the most popular valve in use in an ion exchange plant was the diaphragm type valve, rubber lined or not, depending on the fluids. Recent improvements in the "tightness" of the butterfly valve make it an interesting alternative to the diaphragm valve, particularly for diameters over 150 mm.

C. Ion Exchange Plant Control

In the development of ion exchange in the sugar industry, one very obvious advancement is in plant control.

Most plants installed before the seventies were manual plants. These had limited instrumentation and were controlled only by the skill of the operator. These operators could not be employed in other jobs in the factory and, too, each operator had his own individual method of operation. This limited the ion exchange possibilities to relatively simple processes, such as deliming of thin juice, for example, where the number of valves and fluids to be controlled was not excessive.

The limits for the manually controlled ion exchange plant in the sugar industry were probably reached with the demineralization of thin juice, where the short cycle means that at least three sets of cation and anion exchangers must be used for continuous operation--two in regeneration while the third is in operation. The success of such a plant was entirely dependent upon the operator's skill. The possibilities for human error were such that the manually-operated plant could not be considered absolutely reliable.

One recent industrial application of ion exchange technology in the sugar industry is the production of high quality liquid sucrose from thick juice, without using crystallization.[24] This most essential progress for the sucrose industry would not have been possible without automatic plant control and reliable instrumentation.

1. Control Instruments

In the past, the ion exchange plant was often controlled by the factory's laboratory, whose duty it was to determine the end of the cycles, or give the operators the main parameters for the regeneration.

This control still exists today, but only as a check for the automatic controls. For example: The cycle of a demineralization train is fixed to a certain volume of product being treated. This is controlled by measurement of the feed flow of the incoming product, by means of an electromagnetic flowmeter, and calculating therefrom the exact volume passed through the system, until a certain preselected amount is reached. When this preselected volume is reached, the plant automatically starts the next sequence.

In order not to rely solely on a volume controller, there are additional controls to check the quality of the product emerging. In the case of a demineralization train, the continual measurement of pH and conductivity of the outgoing product will trigger an alarm if there is a quality problem, calling this to the operator's attention--and, if necessary, stop the plant.

Progress such as this in instrument control has made the ion exchange process much more reliable and easier to operate.

One principle applied in today's ion exchange unit is that of relying on the actual volume passed through the system during each sequence, rather than the time elapsed, as was done in the past. The control panels of these plants, therefore, include a number of volume counters, whereas before there were timer controls.

Summarizing the different levels of control in the modern ion exchange unit, the general rule would be:

Level 1	Control through preselected volume.
Level 2	On-line quality control by specific sensors (pH, conductivity, color, etc.).
Level 3	Laboratory control.

(Level 1 is the routine control, Level 2 the alarm control, and Level 3 the optimization control.)

In certain cases, there are no existing, or at least no reliable, on-line controls. For example: For the control of calcium removal in a deliming plant there is at present no on-line sensor. In this case, only Level 1 and Level 3 apply. The setting for Level 1 is determined by the analysis made at Level 3.

2. Automatic Sequence Control

The instrumentation allows the operator to control the flow, volume and characteristics of the product passed through the ion exchange system in one sequence and to stop that sequence when desired. Passing from one sequence to the next (opening/closing of specific valves, and starting/stopping of specific pumps, etc.) is controlled by an automated device. In early ion exchange technology this was done manually.

There were several stages of improvement in sequence control between the sixties and eighties. The beginning of automation was in the use of pneumatic systems for opening and closing the pneumatic valves individually from a control panel. This relieved the operator of the responsibility of doing this manually. Further improvement came about in the form of a "combined" valve control for a simultaneous opening and closing of the appropriate valves for a sequence. This was accomplished by means of pre-engineered mechanical devices which allowed air distribution to the valves in a predefined order. It, however, had the disadvantage of being a very rigid arrangement which did not make allowance for changes in the established sequence. Then, in the seventies, came the use of electrically activated solenoid valves for the control of the pneumatic valves. Sequence programming could be arranged by means of a diode matrix, assigning to each sequence the necessary valves and pumps. This had the advantage of flexibility, since the sequence programming could be easily changed by simply removing and resetting the removable diodes.

Next to arrive on the scene, at the end of the seventies, were the programmable controllers, using microprocessors. This is the latest stage in the development of this technology, and it represents total control of the sequential operations of an ion exchange plant. The programmable controller system offers the required flexibility, with absolute reliability, and it can be connected to computers which monitor the overall operation of the factory.

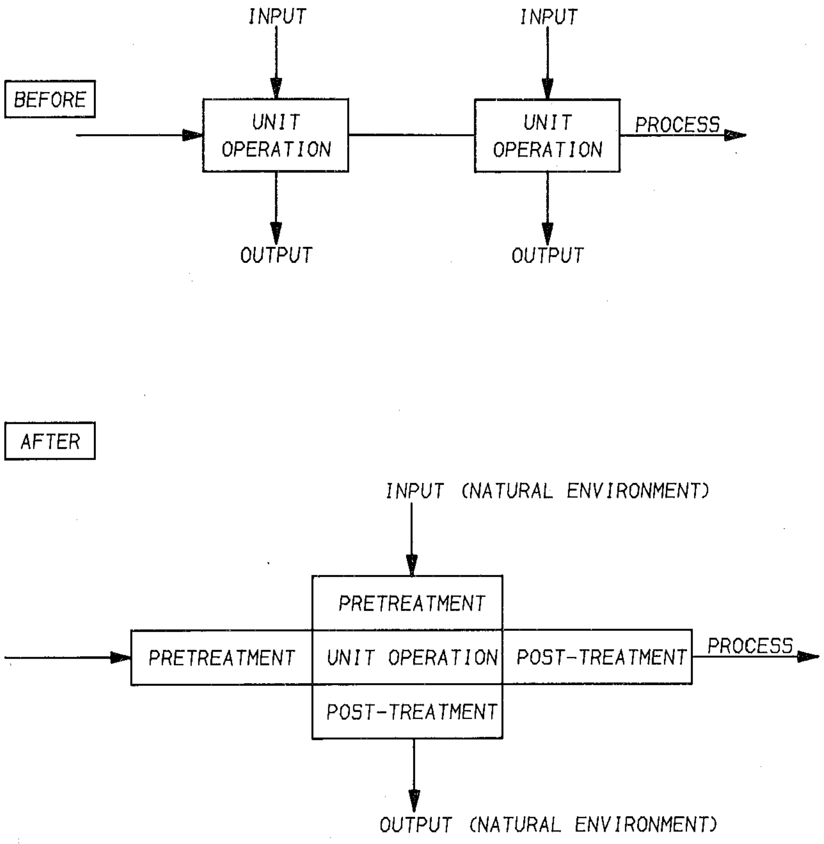
This relatively recent progress in control of ion exchange through automation has, without a doubt, been a decisive factor in the extended use of this unit operation in the sugar industry. Also, automation of the control system has made the industry less inclined to opt for the continuous process over the fixed-bed, since the problems previously associated with fixed beds for continuous processes have been resolved.

D. Ion Exchange and Waste Waters

Waste water was not a sensitive issue, either in the sugar industry or in ion exchange, until the seventies. Since then, governmental pressure and the energy crisis have caused this to become a major problem, not only for environmental reasons, but also for economic reasons, as it was discovered that reducing wastes has a tremendous impact on the utilities consumption of a factory.

As is the case with other unit operations, ion exchange can no longer be considered on the basis of only its own input and output of utilities and wastes, but rather viewed as part of an integrated system which includes the necessary pretreatment of utilities and post-treatment of wastes. Imaginative engineering has brought about considerable improvement in this area. In most cases, this has meant savings in dollars for the factory. (See Figure No. 1.)

EVOLUTION OF THE UNIT OPERATION CONCEPT IN RECENT YEARS



NOW, MUCH MORE THAN IN THE PAST, EACH UNIT OPERATION OF A PROCESS IS CONSIDERED FOR ALL PRE- AND POST-TREATMENTS IT GENERATES, RATHER THAN FOR ITSELF ALONE.

FIGURE NO. 1

1. Water Consumption in Regeneration

Due to the cost of water, one of the first priorities was to decrease water consumption in resin regeneration. For example: In a conventional deliming plant regenerated with lime, it was possible by recovering the water used for the final rinse of resins after regeneration and reusing it at the following regeneration--for purposes such as backwashing, brine dilution, or first rinse--to decrease water consumption by five bed volumes (from 11 to 6 bed volumes). This decreased water consumption, and thereby effluent volume, by 45%.[25]

In another case, the systematic recovery or recycling of water used for the regeneration of the resins in a thin juice demineralization plant resulted in an increase in effluent concentration from 3%-4% total solids to 7.5%-8.5% total solids. The evaporation of these effluents represented a considerable saving in energy.

2. Treatment of Effluents from the Ion Exchange System

Most of the ion exchange systems used in the sugar industry have now been studied for possible treatment of their effluents. An outstanding example is in the concentration of effluents from demineralization or ion exclusion.

The existing demineralization plants for removal of nonsugar from thin juice by H-OH demineralization, or the removal of nonsugar from molasses by ion exclusion, are equipped with specific effluent treatment systems which use concentration and crystallization. In the case of H-OH demineralization, the effluents are concentrated and crystallized for the production of two co-products: a fertilizer, which combines the potassium of the nonsugar with the sulfates and ammonium ions coming from the regenerants; and an organic compound, rich in proteinic substances, which can be used as livestock feed or used to enrich the pulp in amino acids.[14]

The effluents of an ion exclusion plant are usually concentrated to give a residual molasses with a purity of 20%, which can, for example, still be sold as molasses for livestock feed.

Another effort has been in the treatment of effluents from ion exchange decolorization plants which use brine as a reagent. In this area there have as yet been no industrial plants equipped with such treatment facilities--probably due to the fact that most of such sugar refineries are located near the sea and do not face great pressure from the populace or authorities for discharging salty effluents to this environment. There are, however, processes which oxidize the brine,[26] or separate the coloring material from brine by membranes,[27] which will certainly be applied to such treatment in the future.

3. Waste-free Processes

There also exists in the sugar industry the possibility of totally eliminating the effluent stream from an ion exchange process, thus obviating the problem of effluent treatment. The best example of this is use of the Gryllus process[28] in sugar juice deliming, where the regenerant and rinsing fluids are thick juice or low green syrups and thin juice. In this case, there is no water input and, therefore, no effluent is created. The Gryllus process will be discussed in detail in the chapter covering specific processes.

Another interesting endeavor in this field is proposed by Assalini[29] for the regeneration of the Quentin cation exchange resins using Quentin molasses (rich in magnesium), which would avoid the production of waste water in a manner similar to the Gryllus process.

E. INTEGRATION OF ION EXCHANGE IN THE PROCESS

More than any other unit operation of separation, ion exchange in the sugar industry should be considered not only for its direct effect, but also the indirect effects of its presence in the process. These indirect effects have, in fact, proven in many cases to be the reason for the success or failure of a plant.

1. Example 1: Integration of Deliming in a Beet Sugar Factory

The direct effect of a deliming plant is the elimination of calcium from the thin juice in order to decrease fouling of the evaporators.

Deliming plants have for years been running with a brine regeneration system copied from the conventional water softeners--with the following direct effects:

-- Sugar losses in molasses (due to the replacement of calcium by sodium).
-- Sugar losses during the sweetening-on and sweetening-off of the plant.
-- Consumption of water for the regeneration.
-- Consumption of brine.
-- Production of hot waste waters containing chlorides.

All the above can be avoided by integrating the deliming plant in the sugar factory process and using the internally generated products of the factory (thick juice or low green syrup) for the regeneration--a closed loop.[28]

It is interesting to note that although the Gryllus process principle was defined in the late fifties, it was not recognized by the sugar industry until twenty years later, and is now widely used.

2. Example 2: Integration of Demineralization in a Beet Sugar Factory

The direct effect of a demineralization plant in a beet sugar factory is the removal of nonsugar, which increases sugar yield. There are, however, indirect effects. The location chosen, within the process, for the installation of the demineralization plant can have a great impact on the successful operation of the plant. If the plant is demineralizing molasses, it will produce an extra sugar stream which will be sent to crystallization and overload the crystallization process with sugar and recycled nonsugar. This will result in a higher energy demand for crystallization. Conversely, if the plant is demineralizing thin juice, it will remove nonsugar from the main process stream. As a result, the volume of massecuite necessary for the crystallization will be lower and the energy consumption lower.[30]

The diagrams shown represent:

In Figure No. 2 -- Crystallization in a beet sugar factory, with the conventional method, using the remelt of sugar II and sugar III. In this case a massecuite volume of 35.8 l/% beet is necessary for a sugar extraction yield of 84%.

In Figure No. 3 -- Crystallization of the same beet sugar factory, with the demineralization of thin juice. In this case, due to considerable improvement in the color of the standard liquor, it is possible to have a sugar extraction yield of 87.9% with a massecuite volume of 26.7 l/% beet.

3. Example 3: Integration of a Liquid Sugar Plant in a Cane Sugar Refinery

The use of ion exchange for the production of liquid sugar may change drastically the production diagram of a refinery.

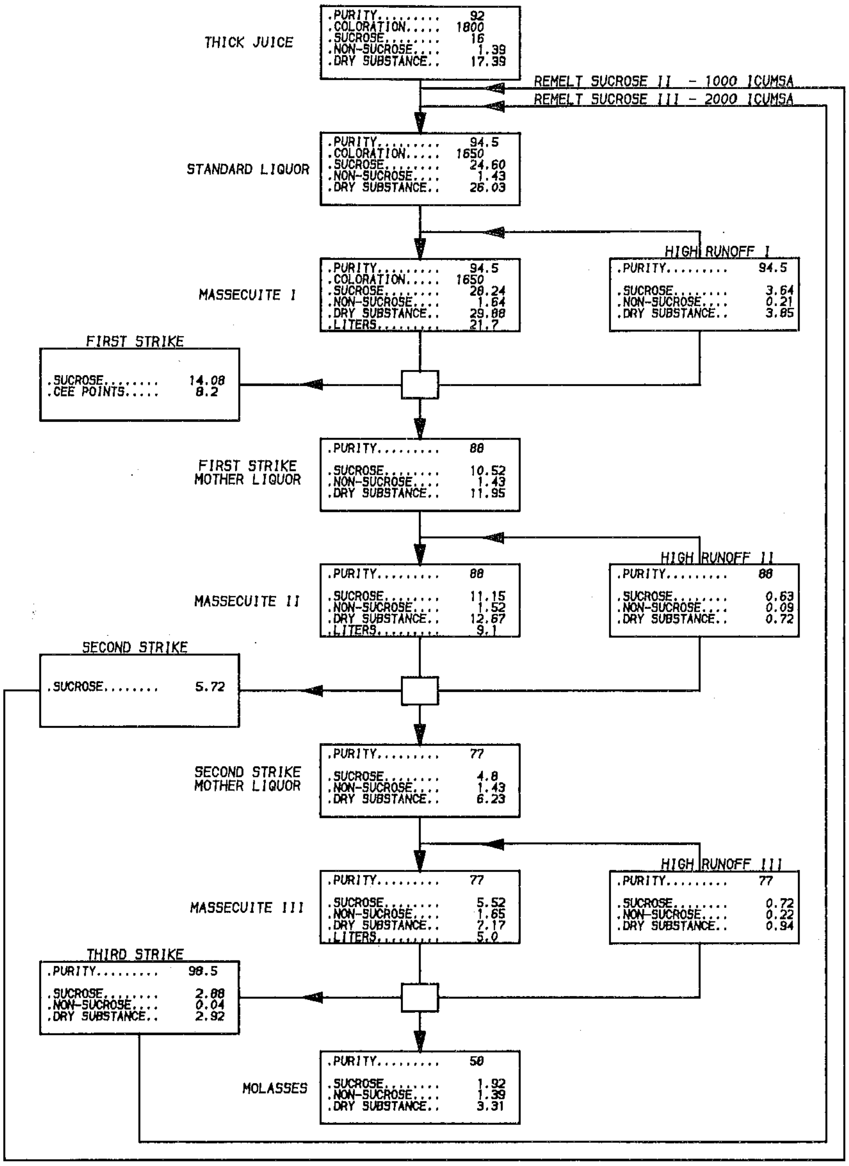
The five diagrams shown here (Figure Nos. 4, 5, 6, 7 and 8) represent the interaction between liquid sugar production and the diagram of the factory--depending on different production capacities for liquid sugar, different raw materials used for the liquid sugar production, and different capacities for the factory itself.

It is interesting to note the interaction between the production of liquid sugar and

- -- massecuite volume,
- -- production of final molasses, and
- -- the possibility of increasing the refinery capacity without increasing the massecuite volume.

From the three examples given, it is obvious that the use of ion exchange technology in the sugar industry has a profound effect on the process itself. When implementing the ion exchange plant, one should at the same time modify the areas of the factory which will be affected by its operation (evaporators, crystallizers, etc.), in order to maintain a good heat and material balance in the modified factory, and thereby benefit from all the good side effects (color removal, massecuite volume reduction, etc.) of the ion exchange plant.

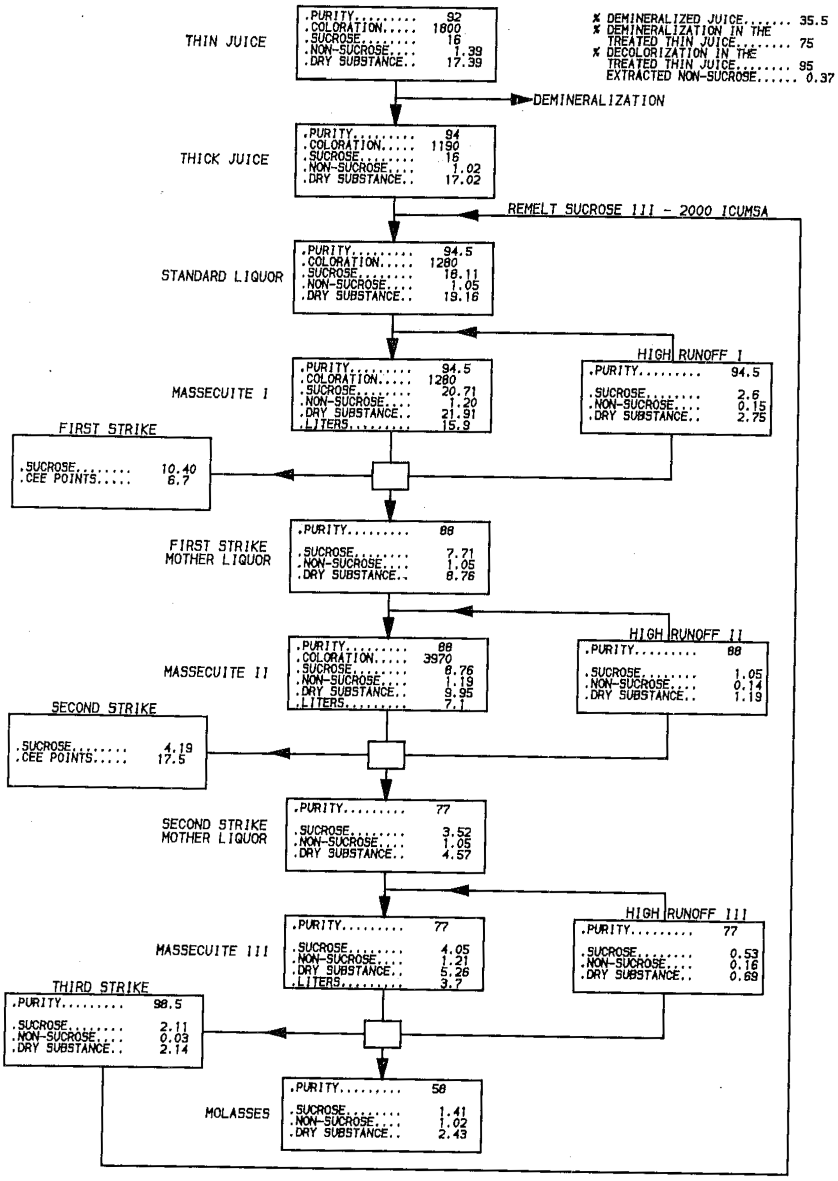
CRYSTALLIZATION WITH REMELT OF SUCROSE II AND SUCROSE III
DIAGRAM NO. 1



LITERS OF MASSECUITE: - 21.7 + 9.1 + 5.0 = 35.8

FIGURE NO. 2

CRYSTALLIZATION WITH DEMINERALIZATION OF THIN JUICE
DIAGRAM NO. 2



LITERS OF MASSECUITE, - 1.59 + 7.1 + 3.7 = 26.7

FIGURE NO. 3

LIQUID SUGAR PROJECT 0
REFINERY DIAGRAM
400 T/D
WITHOUT LIQUID SUGAR PRODUCTION

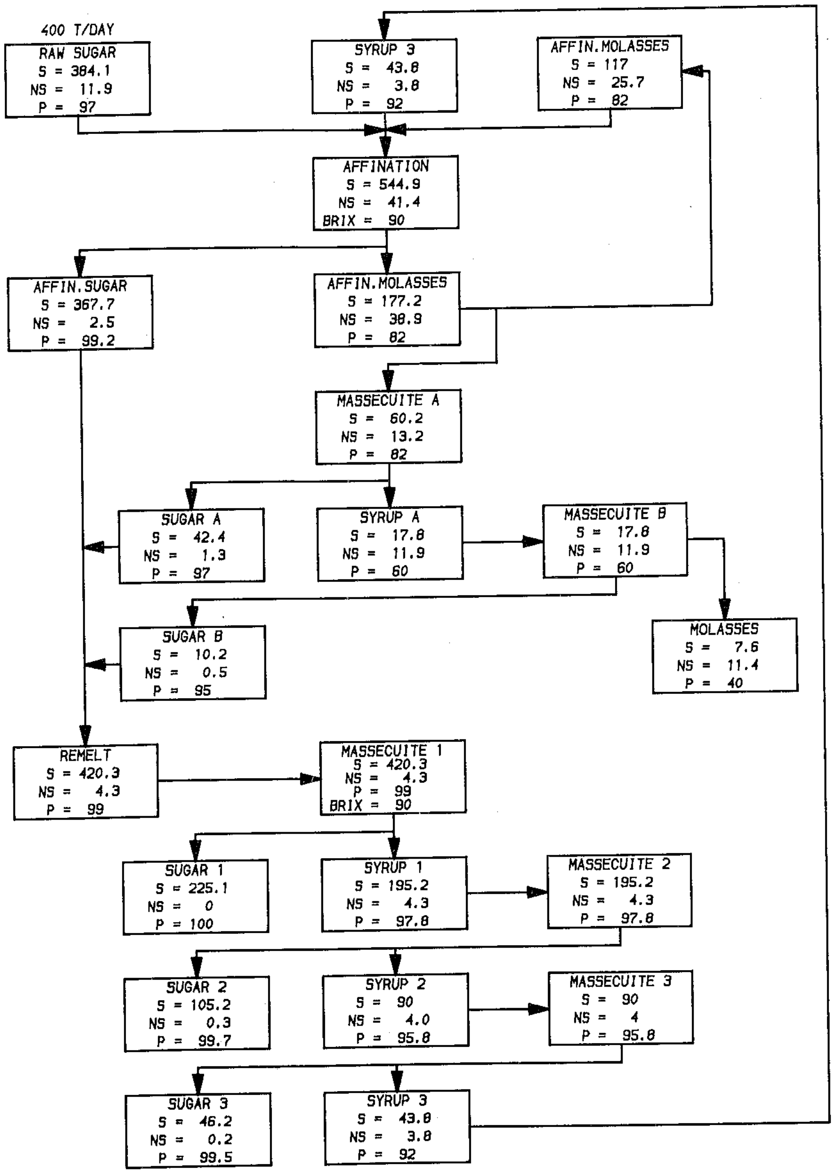


FIGURE NO. 4

LIQUID SUGAR PROJECT 1
REFINERY DIAGRAM
400 T/D
20 T/DAY PRODUCTION OF LIQUID SUGAR

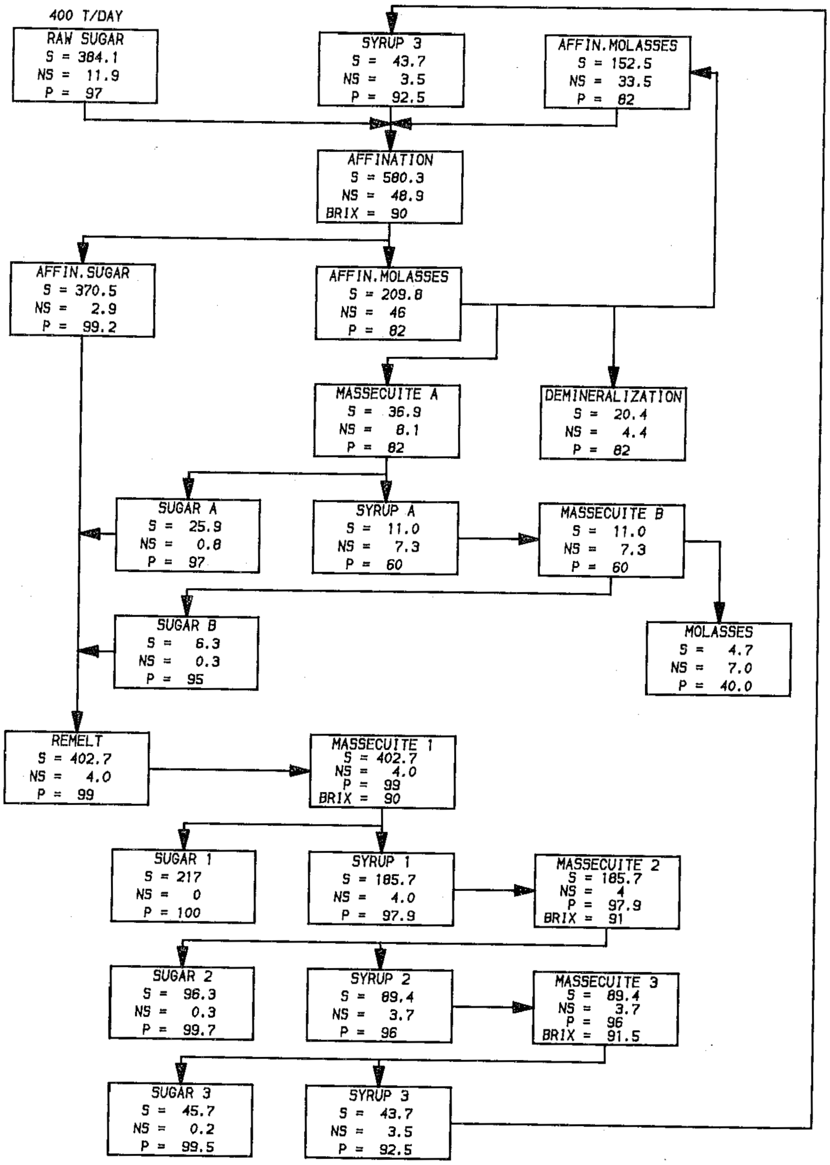


FIGURE NO. 5

LIQUID SUGAR PROJECT 2
REFINERY DIAGRAM
400 T/D
35 T/DAY PRODUCTION OF LIQUID SUGAR

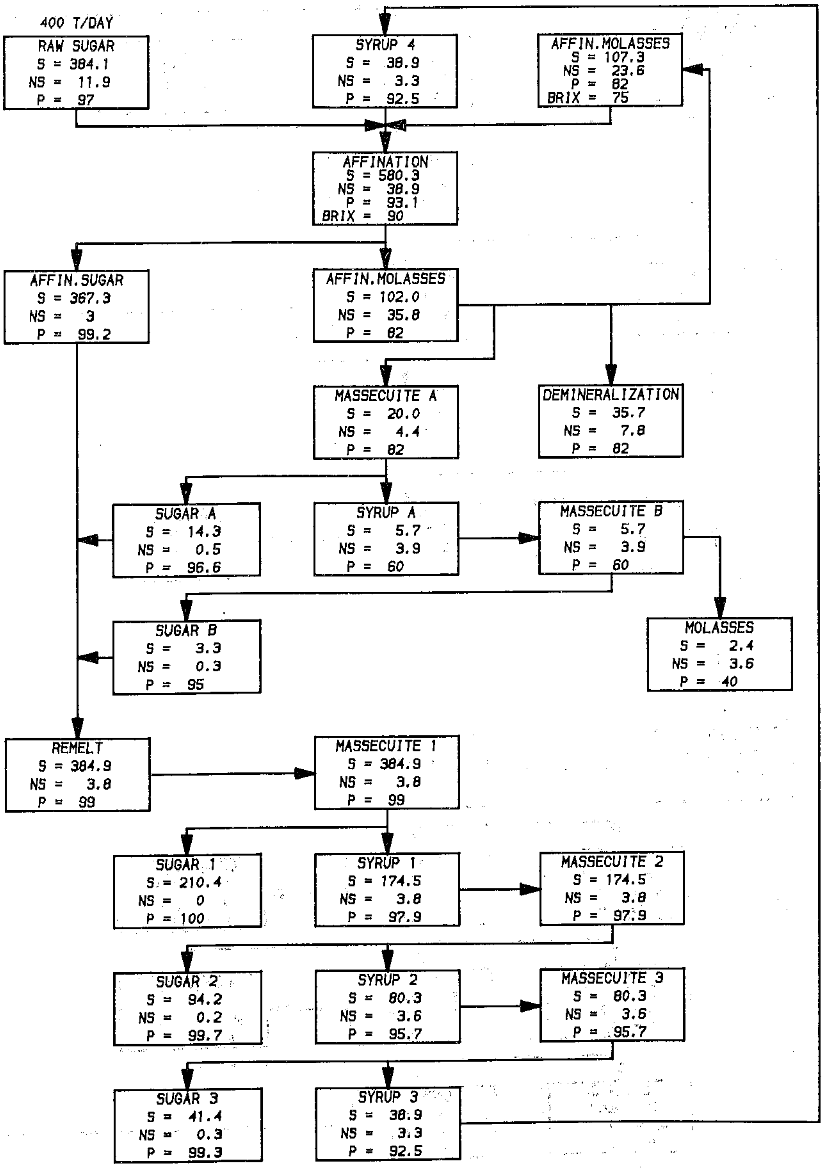


FIGURE NO. 6

LIQUID SUGAR PROJECT 3
REFINERY DIAGRAM
400 T/D
35 T/DAY PRODUCTION OF LIQUID SUGAR, ELIMINATING MOLASSES

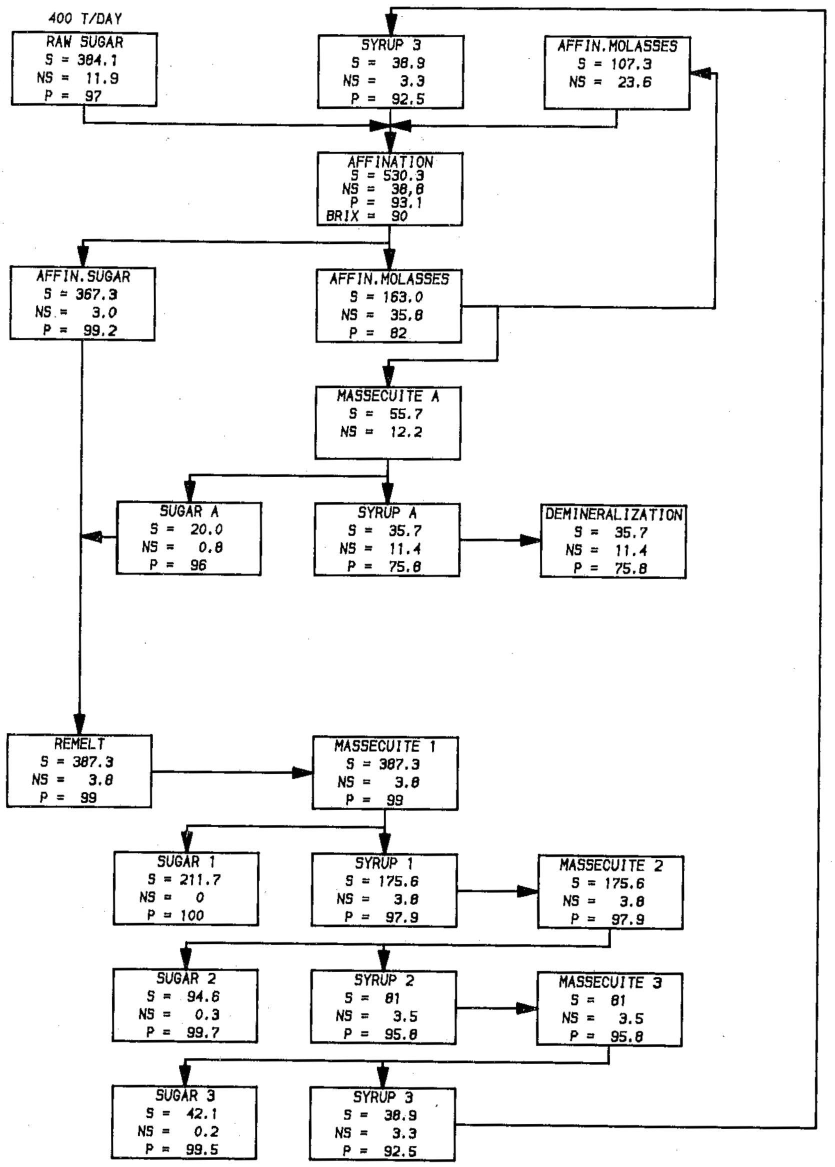


FIGURE NO. 7

LIQUID SUGAR PROJECT 4
REFINERY DIAGRAM
600 T/D
35 T/DAY PRODUCTION OF LIQUID SUGAR

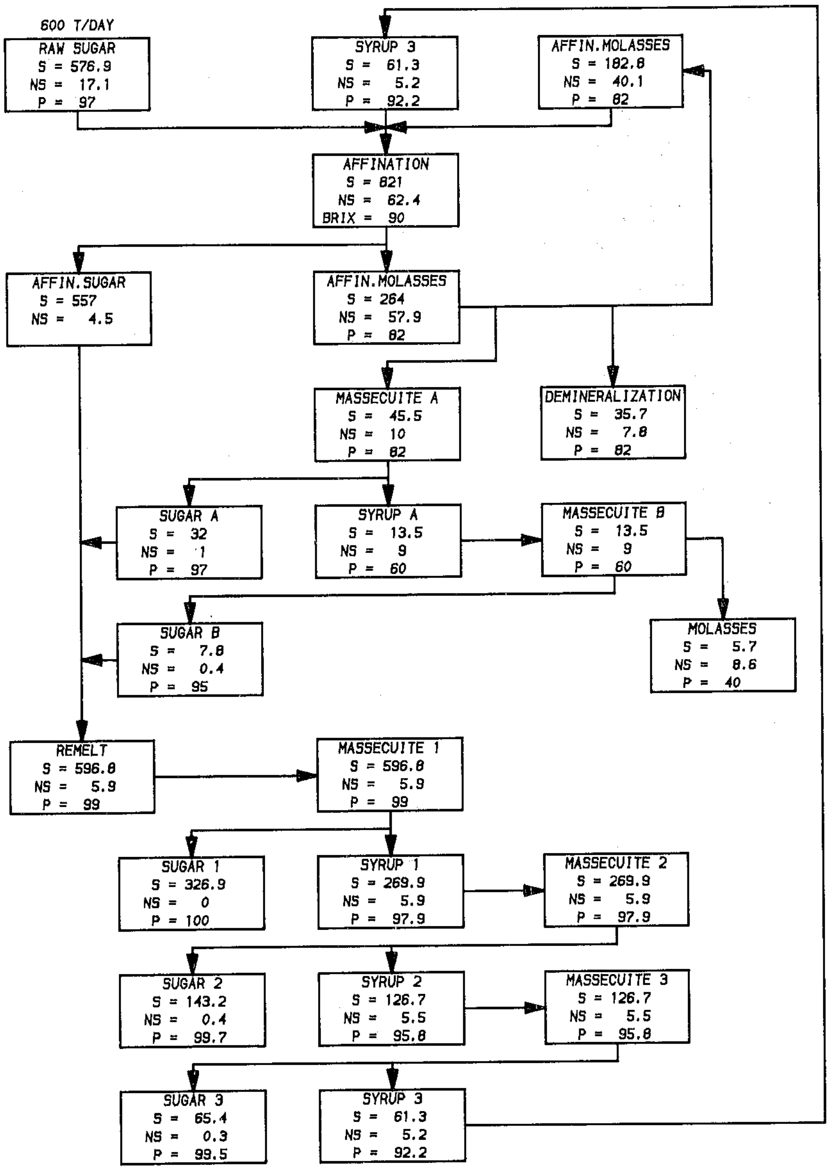


FIGURE NO. 8

III. PRINCIPAL INDUSTRIAL APPLICATIONS FOR ION EXCHANGE IN THE SUGAR INDUSTRY

Following are brief descriptions of typical full-scale ion exchange processes in the sugar industry:

A. Deliming (Beet Sugar Factory)

1. Benefits of Thin Juice Deliming to the Beet Sugar Industry

After two carbonation and two filtrations the purified thin juice contains between 40 mg/l and 200 mg/l soluble calcium, expressed as CaO, depending on the site of the beet sugar factory and the season. This can be even higher if the beets have been altered by too lengthy storage, or due to frost. (Values as high as 600 mg/l can be reached.)

The calcium left in the thin juice has an adverse effect on results at the beet sugar factory, mainly for two reasons:

(1) An important part of this calcium is precipitated on the evaporator tubes in the form of calcium carbonate, which adversely affects the investment, energy and manpower costs of the factory, as explained below.

(2) The calcium left in the thick juice after concentration may, in certain cases, be responsible for the turbidity sometimes observed when white sugar is dissolved to produce liquid sugar.

Although this second possibility can be very costly, especially if you lose a market due to a quality problem, we will at this time consider in more detail the effect of the calcium precipitation on the tube evaporators.

The main effect of this precipitation is to create scaling of the evaporator tubes. As a result, there is a reduction in the overall heat transfer coefficient.

Using a U of 600 Btu/hr/sq.ft./°F for a clean surface, the necessary thickness of calcium carbonate to reduce this value by 50% is only 0.026 in.[32]

The heat transfer coefficient is proportional to the inverse of the surface area considered. Therefore, due to scaling of the tubes in a factory having no deliming system, provision for surface area must be made in advance, taking into account the calcium carbonate scaling. For example: For a beet sugar factory processing 5,500 metric tons of beet per day, if there is no deliming plant, a surface area of 120,000 square feet should be calculated. With a deliming plant, this surface area would be reduced to 90,000 square feet, and the difference in investment would be at least US$300,000. Moreover, for a given surface area, due to the progressive scaling of the tubes, the delta T between steam and juice must be increased in order to maintain the same evaporation--and this results in higher energy consumption.

It is estimated that for a sugar factory having no deliming device, an increase in steam consumption of 20 kg per ton of treated beet must be calculated. This means--for 5,500 metric tons per day, a 150-day season and steam cost of US$6.00/ton--an additional cost of US$100,000 per season. (This figure is based on a coal-operated factory. It should be doubled if the factory is using fuel oil.)

To help maintain a clean evaporator, the sugar factory is usually thermically equilibrated in order to recover all the condensation heat of the vapors on recovery systems.

When efficiency decreases due to scaling, in order to retain the concentration effect, the delta T is increased through control of the vacuum on the last effect, progressively introducing more vapor to the final condenser. At this stage, when the maximum delta T has been reached, it is necessary to proceed with manual cleaning of the evaporator. This means an additional cost in manpower, and this figure must be determined by each sugar factory.

Summarizing the benefits of deliming:

-- No turbidity in remelt from white sugar.

-- Lower investment in evaporation, or no investment necessary to increase factory capacity.

-- Lower steam consumption.

-- Elimination of boilout during the season, representing savings in sugar losses and manpower costs.

2. Normal Configuration of a Deliming Plant

Figure No. 9 shows the usual arrangement of a deliming plant, using the three-vessel configuration. In this case, two reactors are simultaneously deliming thin juice when the third is in regeneration. The main advantage here is that of obtaining a soft thin juice, which is a mixture of the treated juice of one reactor at the beginning of its run and the juice of the other at the end of its run. The resulting mixture, therefore, has a CaO content which represents an average quality soft thin juice.

In some cases, especially where the hardness of thin juice is very high, it is more economical to have a two-reactor configuration (one in deliming and the other in regeneration).

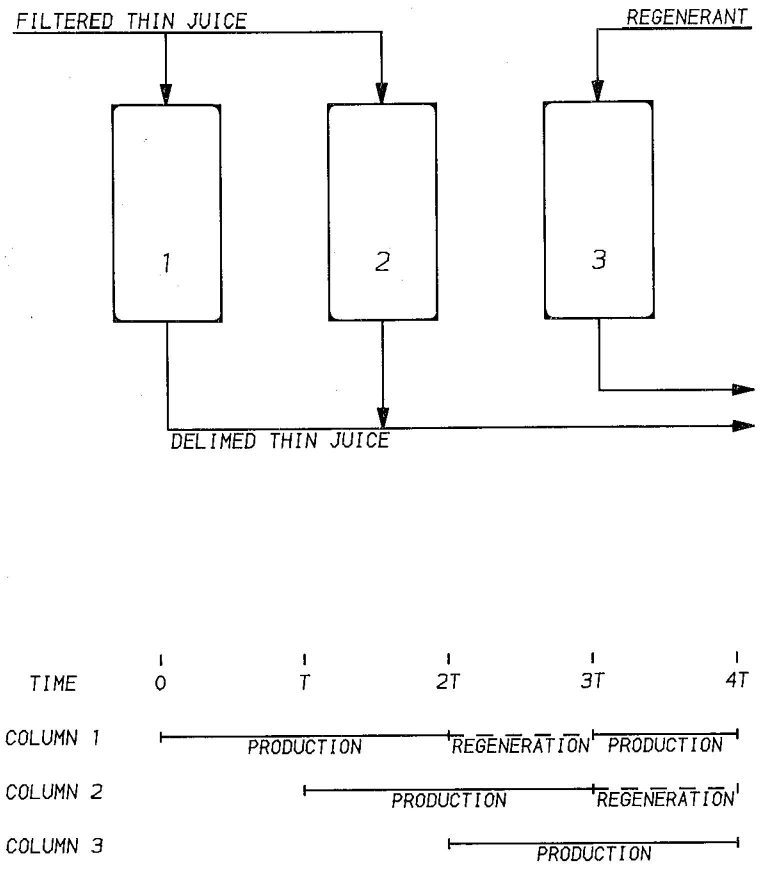
3. Gryllus Process

The material balance shown in Figure 10 outlines the principle of the Gryllus process, using low green syrup for the regeneration of the resin.

It is clear that at the inlet of the system no water is used, only thin juice and low green syrup. Therefore, no dilution occurs in the system.

The low green syrup is used as a reagent for regeneration. Its high potassium and sodium content and high sugar concentration make it very

ARRANGEMENT OF THREE VESSELS FOR THIN JUICE DELIMING

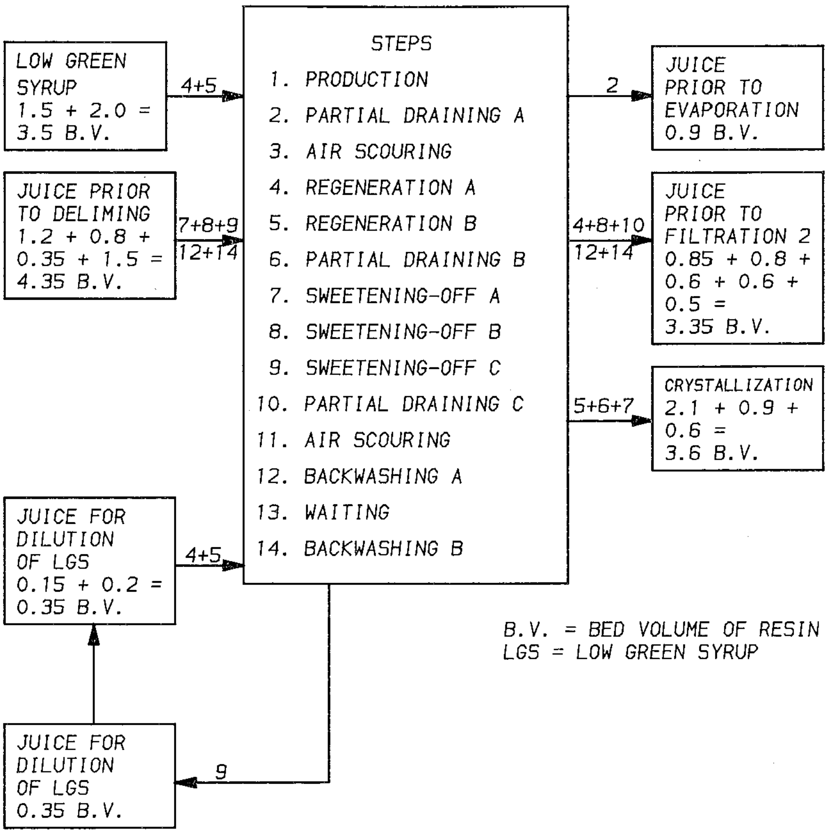


$\theta = (n-1)T$
θ = MINIMUM PERIOD ALLOWED FOR A RUN
n = NUMBER OF VESSELS
T = NECESSARY TIME FOR A REGENERATION

FIGURE NO. 9

GRYLLUS REGENERATION SYSTEM

MATERIAL BALANCE FOR ONE COLUMN



NO DILUTION, NO WASTE, NO CHEMICAL

FIGURE NO. 10

efficient to regenerate the resin after exhaustion with calcium. Therefore, no extra reagent is required for the regeneration.

At the outlet of the system, the juices and intermediate products from sweetening-on and sweetening-off are either recirculated prior to the second filtration or sent to the third crystallization. Therefore, no waste is produced by this system.

One important advantage of the Gryllus system is that no sodium is introduced in the system for the resin regeneration. Since the sodium ion has a melassigenic effect, the sugar factory using the Gryllus system has a better sugar extraction yield, compared with a sugar factory using the conventional process.

This is called "the Gryllus effect".

For an 85-day season, a sugar savings of 550 tons is estimated for a 5,000 tons/day beet sugar factory using the Gryllus process, compared with the same factory using the conventional process.[33]

Figure Nos. 11 and 12 show the integration of the Gryllus system in a beet sugar factory, and a typical regeneration curve for this system.

4. N.R.S. Process[25, 63]

The material balance shown in Figure 13 outlines the principle of the N.R.S. process.

As in the Gryllus process, no water is used, only thin juice. Therefore, no dilution occurs in the system.

For the regeneration, caustic soda is added to cold (40°C) delimed juice at the rate of 40 grams NaOH per liter of juice. One volume of reagent is used to regenerate one volume of resin.

The calcium from the resin is exchanged for the sodium in the juice and forms a soluble calcium-saccharate with the sugar present in the juice.

It is important to maintain a low temperature during the regeneration in order to avoid saccharate precipitation.

At the outlet of the system, the juice is returned either to filtration 2 or to carbonation 2.

The juice containing the calcium removed from the resin is sent to carbonation, where the calcium is separated from the sucrose and calcium precipitated as calcium carbonate.

The calcium carbonate will be removed at the second filtration. The calcium is completely removed from the process with the sludge of carbonation.

Again, it can be seen that with this process no waste is discharged to the environment. Sodium, however, is added to the molasses, having the same melassigenic effect as with a conventional deliming process which uses brine for the regeneration.

INTEGRATION OF THE GRYLLUS SYSTEM
IN THE SUGAR FACTORY

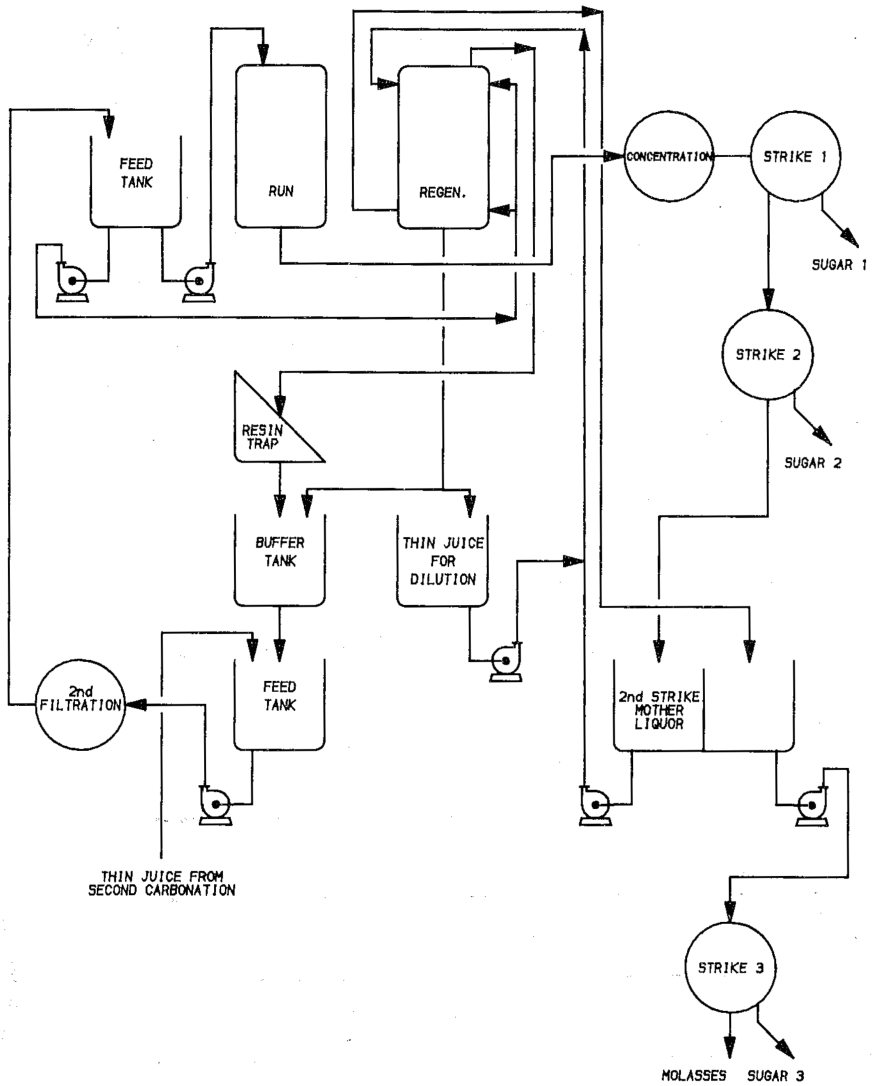
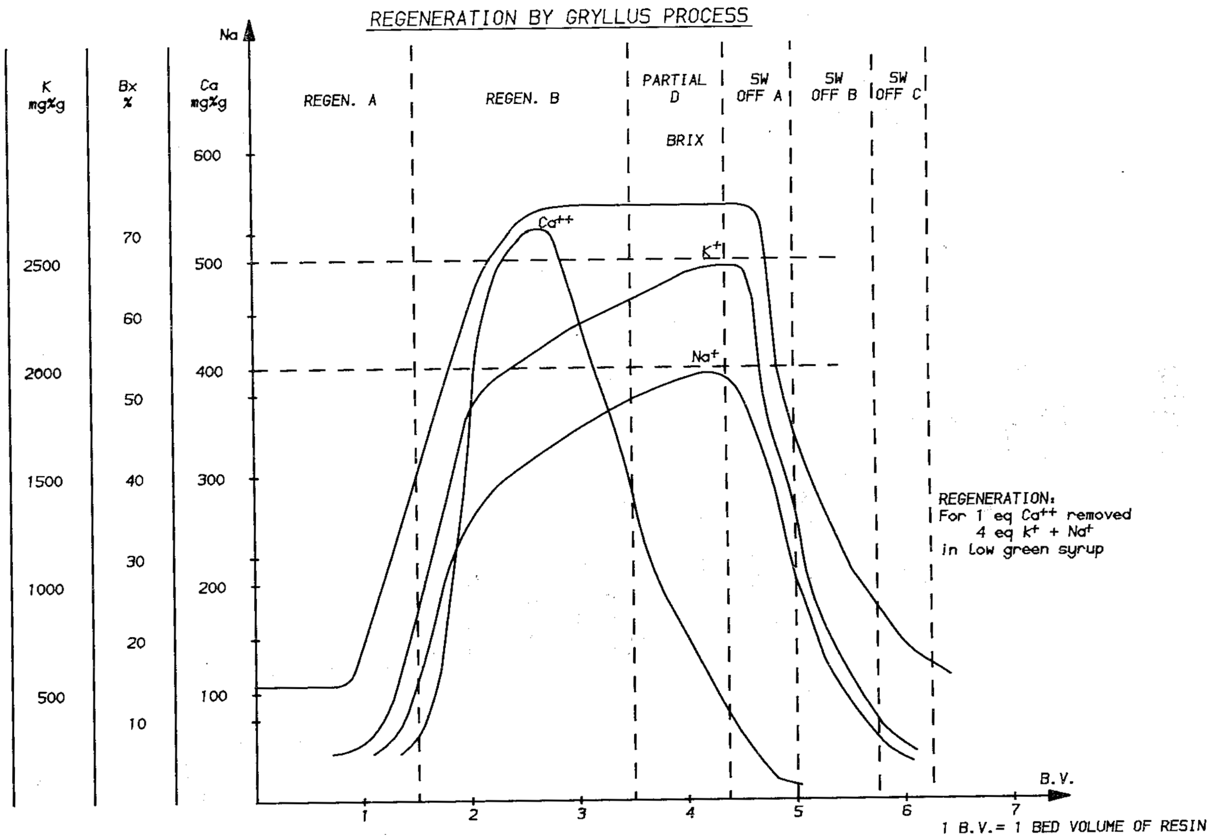


FIGURE NO. 11

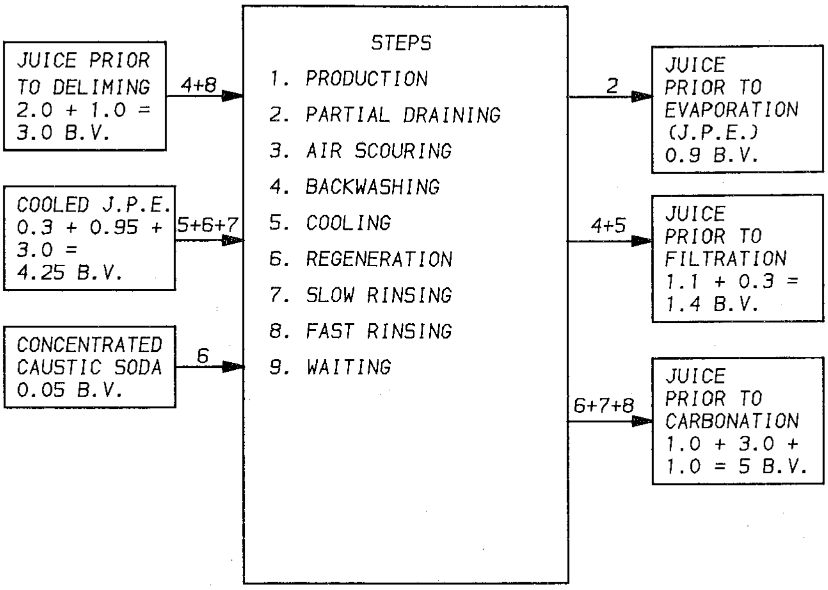


REGENERATION:
For 1 eq Ca^{++} removed
4 eq $K^+ + Na^+$
in Low green syrup

FIGURE NO. 12

N.R.S. REGENERATION SYSTEM

MATERIAL BALANCE FOR ONE COLUMN



B.V. = BED VOLUME OF RESIN

NO DILUTION
NO WASTE
NO ADDITIONAL CHEMICAL (IF CAUSTIC SODA IS BEING USED FOR THIN JUICE ALKALINIZATION)

FIGURE NO. 13

Figure Nos. 14 and 15 show the integration of the N.R.S. process in the sugar factory, and a typical regeneration curve for this system.

5. Softening, Using a Weak Cation Resin in the Hydrogen Form

This fairly recent process has been described by Schoenrock[34] and uses the high affinity of weak acidic cation exchangers for the calcium ions.

The advantages of this system are as follows:

(1) High capacity of the ion exchanger, as compared with other deliming systems (0.8 eq/l for a Gryllus or N.R.S. system versus 2.5 eq/l for this system).

This would reduce the investment cost considerably.

(2) Regeneration of the cation exchanger with a stoichiometric quantity of acid, due to the high affinity of the resin for the hydrogen ion.

(3) Possibility of neutralizing the treated thin juice with active magnesium oxide, contributing to less molasses formation.

(4) Using sulfuric acid for the regeneration, it is possible to use the gypsum formed after the regeneration as a pulp-pressing aid for the pulp dewatering.

These advantages are great, if we compare this system with the conventional system using brine for regeneration.

There are, however, certain things which must be taken into consideration in using this system:

(1) Risk of sucrose inversion in the cation resins in the H^+ form: Flow and temperature parameters must be very carefully controlled.

(2) Sensitivity to suspended solids in the feed: Due to the very high flow rates used to avoid sucrose inversion, the reactors are more susceptible to plugging by suspended materials. The thin juice feed must be perfectly clear.

(3) Resin stability: The weak acidic exchangers are carboxylic resins which have less stability than the conventional polystyrenic strong cation resins. Resin consumption is, therefore, higher.

Comparing this with the Gryllus and N.R.S., where no water is sent to the reactors, this system also has the three disadvantages of the conventional brine regeneration system:

INTEGRATION OF THE N.R.S. SYSTEM
IN THE SUGAR FACTORY

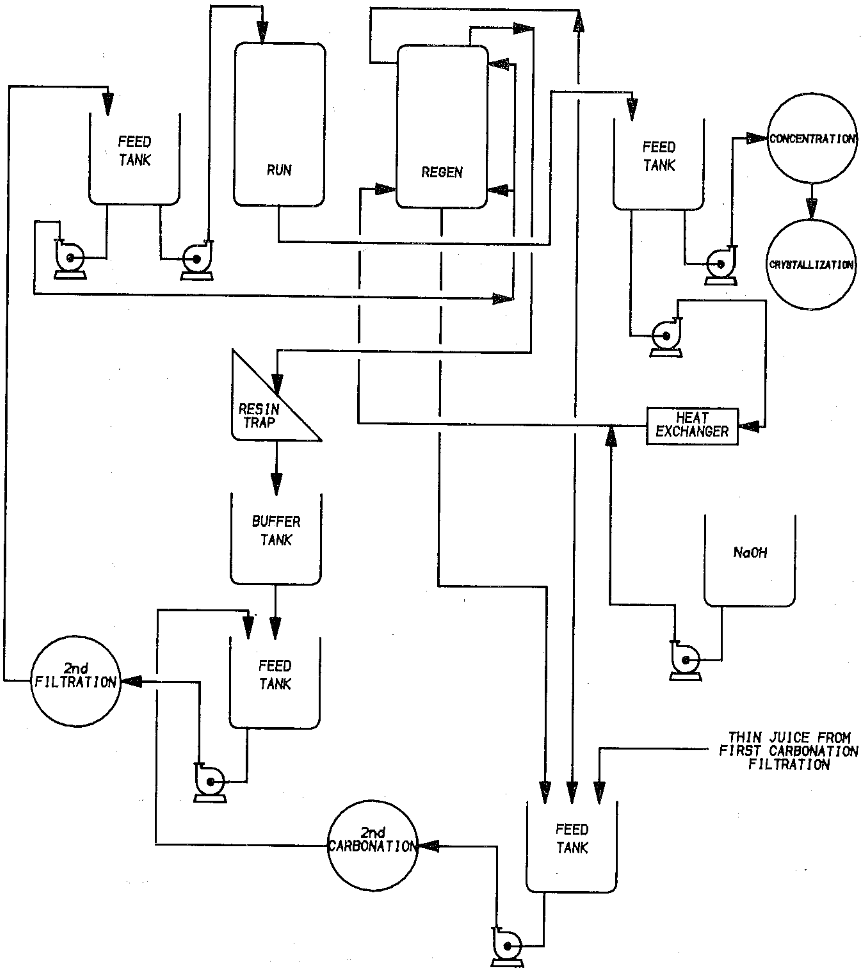


FIGURE NO. 14

REGENERATION BY N.R.S. PROCESS

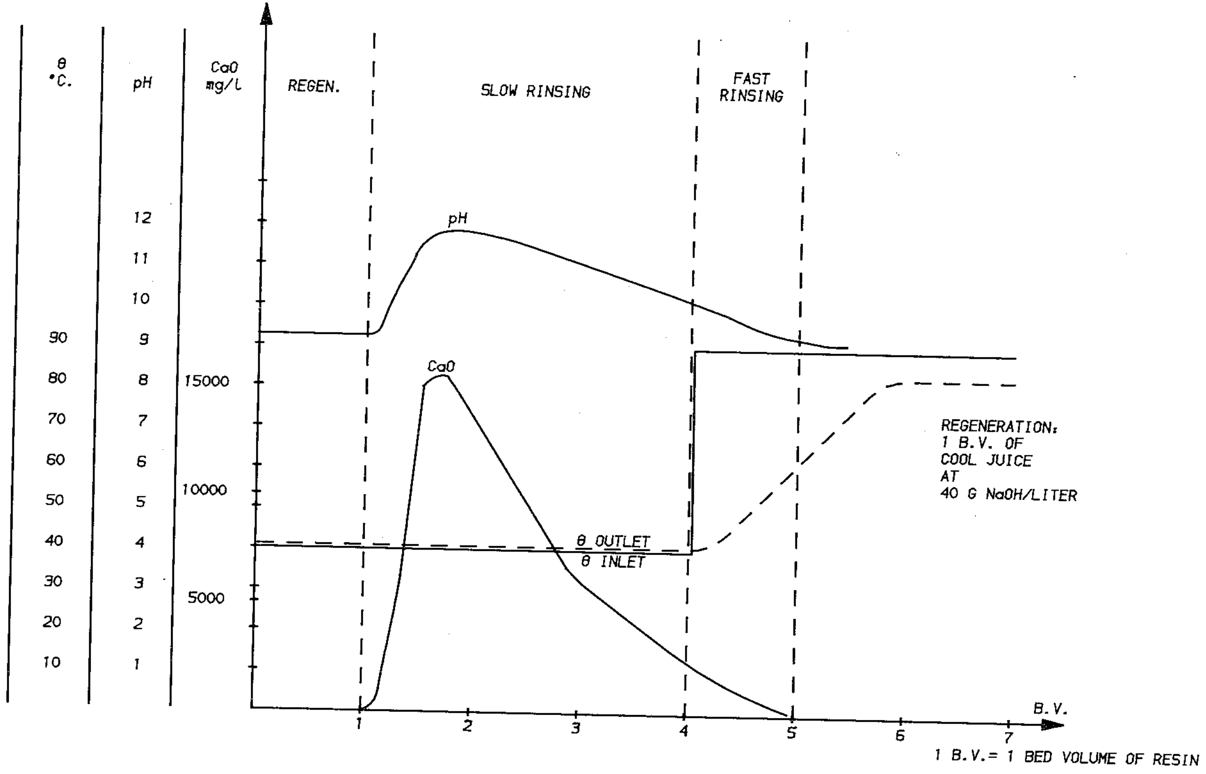


FIGURE NO. 15

-- Consumption of water.
-- Dilution effect on the juice during sweetening-on and -off.
-- Losses in sugar at the end of each cycle.

Figure No. 16 represents the integration of the H^+ softening system in the sugar factory.

B. Nonsugar Removal from Different Streams of the Beet Sugar Factory

After carbonation and filtration, the thin juice of the beet sugar factory has a purity varying between 88% and 92%, depending on the factory setup.

For the conventional factory, the amount of nonsucrose present in the thin juice after carbonation and filtration will directly determine the amount of sucrose lost in molasses. This can be calculated as follows: For each ton of nonsucrose sent to crystallization, one and one-half tons of sucrose will be lost in molasses. This is estimated to represent an extraction loss of 12%-16% of the sucrose contained in the unprocessed beet.[35]

1. Brief Review of the Methods Being Used to Increase Sugar Extraction

Needless to say, sugar technologists have been trying since the birth of the industry to minimize the amount of sugar carried out of the beet sugar factory in molasses.

Various methods have been applied to improve extraction.

(a) Methods for Decreasing Molasses Production of the Factory

(i) Improve crystallization by boiling to high density, cooling to low temperature, and allowing a longer period of time for crystallization.

(ii) Decrease the melassigenic effect of the nonsucrose by partially replacing the sodium and potassium in the nonsucrose with magnesium.

(iii) Remove nonsugar from thin/thick juice or low green syrup by demineralization. This reduces the molasses produced in proportion to the amount of nonsugar removed.

(b) Methods for Molasses Re-treatment

(i) Precipitate a calcium saccharate from the molasses for recycling to factory carbonation (Steffen process).

(ii) Separate sucrose and nonsucrose in molasses by using ion exclusion. The sucrose fraction recovered after separation is then recycled through the factory process.

All of these methods are presently used in the beet sugar industry. The factory's improvement in sucrose yield varies, depending on the method chosen:

SOFTENER FLOW DIAGRAM
(Courtesy of the Amalgamated Sugar Company)

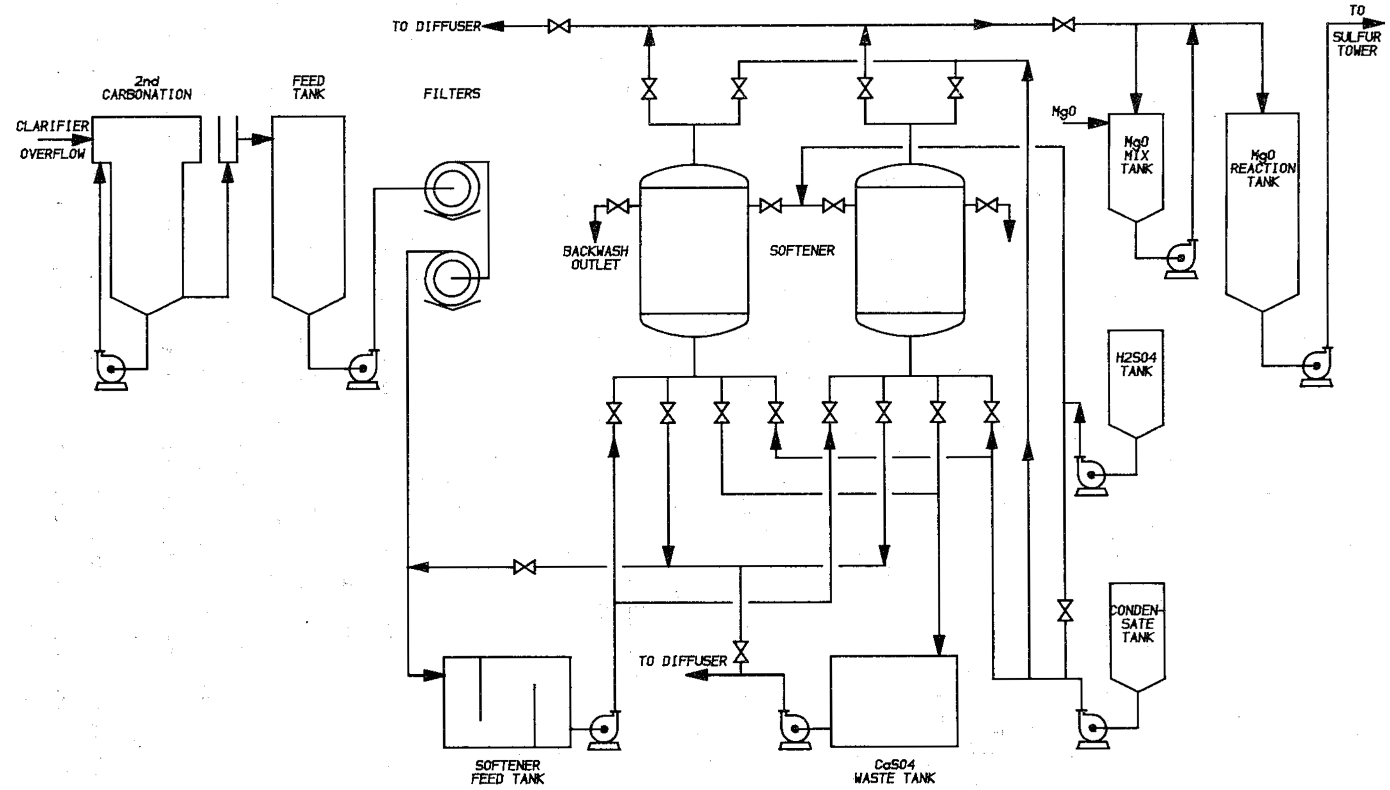


FIGURE NO. 16

- Methods (a)(i) and (a)(ii) increase sucrose recovery by up to 4% of the sucrose present in the beet.
- Methods (a)(iii), (b)(i) and (b)(ii) make possible an increase in sucrose recovery which can exceed 10% of the available sucrose in the beet.

2. Removal of Nonsugar from Thin/Thick Juice or Low Green Syrup by Demineralization

(a) Brief History

The first industrial trials on demineralization of these products were in the United States.[36, 37] Between 1945 and 1949 four units were operating in the U.S.A., but by the early fifties all had been closed down due to the poor economics of the operation.

These plants employed the simple demineralization system, using cation exchangers in the H^+ form and anion exchangers in the OH^- form.

Improvements in this technology brought renewed interest, and in 1957 a French company, Generale Sucriere, started up several new demineralization plants for thin juice demineralization. (It should be noted that some of these plants have been running ever since their start-up, which now represents some thirty years of experience in this technology for each of these plants.) This so-called H-OH demineralization has benefited over the years from the evolution of ion exchange technology in general. The system has been applied in Italy,[12] Japan,[38] and, more recently, again in the U.S.A.[39]

For nonsugar removal by ion exchange, H-OH demineralization using thin/thick juice or low green syrup is the only technology which has been confirmed over the years as being commercially feasible. During its development, several other demineralization processes were proposed and tried, but ultimately failed, e.g.,

- using ion exchange for nonsugar removal and eliminating the carbonation of diffusion juice in the beet sugar factory: Assalini "A" process;[40] and
- recycling the regenerating chemicals necessary for the demineralization process: Moebes process[41] and Vajna process.[42]

Schoenrock[16, 17] recently proposed a new version of the Moebes process, using ammonium bicarbonate as a regenerant. This has not, however, been applied on a commercial scale.

(b) Location of the H-OH Demineralization Plant within the Beet Sugar Process

The best location for the H-OH demineralization plant within the beet sugar process is at the point of thin or thick juice treatment, as already emphasized in Chapter II, paragraph E (2). The reasons for this are:

(i) These products are clear liquids which do not contain suspended materials that could plug the resin bed. They have been clarified by carbonation and filtration. This is always part of the beet sugar process. On the other hand, in the cane sugar industry, the lack of clarification of equivalent products has until now been a barrier for the ion exchange processes.

(ii) These are relatively high purity products which do not exhaust too quickly the ion exchange resins used for their purification.

(iii) Removing nonsugars from the product before crystallization has an indirect and desirable effect on the crystallization diagram.[30] The energy saved in crystallization will counterblance the energy necessary for the concentration and crystallization of the demineralization effluents. Figure 17 illustrates a typical integration of an H-OH demineralization plant in the beet sugar factory.

In an ion exchange process sugar losses are almost negligible, since only the impurities are retained by the resin. Therefore, at the end of a production run, the sugar in the ion exchange reactor can be completely washed out of the resin, for an almost total sugar recovery. The sugar yield obtained is, in fact, in excess of 99.5%.

(c) Practical Arrangement of an H-OH Demineralization Plant

The average demineralization plant is designed to receive continuously the flow of juice to be treated.

It consists of three identical lines, each having a strong cation exchanger in the H^+ form and a weak base anion exchanger in the OH^- form.

The juice, at a concentration which can vary from 16 to 35 Brix, is passed through two exchangers in succession at a temperature of 12°C. In the cation exchanger the mineral cations (potassium, sodium, calcium, magnesium, etc.) and the organic cations (betaine, amino acids, etc.) are retained. In the anion exchanger the mineral anions (chlorides, sulfates, nitrates, etc.) and organic acids (glutamic acid, weak acids produced by sugar degradation, etc.) are retained. Low temperature of the juice is necessary in order to avoid inversion in the cationic resin, which would be detrimental to the production of granulated sugar.

When the resins of one line are exhausted, this line is prepared for regeneration. Sulfuric acid is usually used for the regeneration of the cation exchanger, and ammonia for the regeneration of the anion exchanger.

Time necessary for regeneration is approximately double that required for the production cycle.

SCHEMATIC DIAGRAM OF DEMINERALIZATION INTEGRATION IN THE SUGAR FACTORY PROCESS

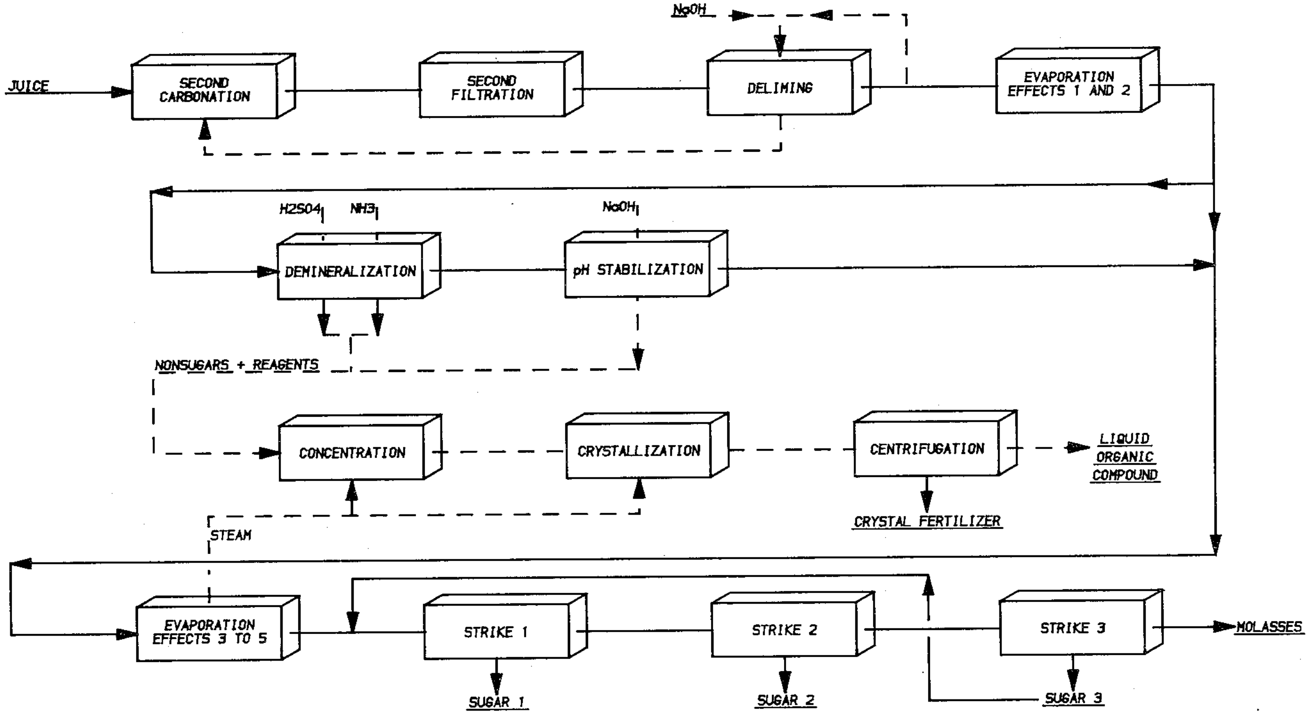


FIGURE NO. 17

Therefore, a continuous system, with three lines of cation and anion exchangers, runs as follows:

Line 1 P R P R P R
Line 2 R P R P R P R
Line 3 R P R P R P

P = Production
R = Regeneration

In the system indicated, one line is always in service while the other two are in regeneration.

It is the responsibility of the ion exchange engineer to choose the correct volume of resin and the proper ratio of cationic resin to anionic resin, based on the type of resin selected and the type of product to be treated.

It should be noted[14] that some variations of the system have been designed to recover valuable nonsugars such as betaine, amino acids and pyrrolidone carboxylic acid (PCA).

Bichsel[43, 44] developed a very interesting concept--which was applied at the Holly Sugar Corporation's beet sugar factory in Hamilton City, California, and later at American Crystal Sugar's beet sugar factory in Moorhead, Minnesota--where the cation and anion exchangers run independently and are controlled by conductivity and pH, respectively. In this system two weak anion exchangers (primary and secondary) are run in succession. This allows full loading of the primary anion exchanger with nonsugar at each production cycle.

At the Nassandres (France) beet sugar factory of the Generale Suciere (whose demineralization plant was built by Applexion),[45] the demineralization system includes two strong anion exchangers in the OH^- form, for the purpose of pH adjustment prior to concentration of the demineralized juice.

All existing improvements to the H-OH demineralization plant have not been published, partly to protect the confidential interests of the end-users. Actually, this process, which is in full operation in many countries (France, Italy, Holland, Japan, etc.), has been in a state of ongoing evolution since its beginning--shortly after World War II.

(d) Treatment of the Effluents of Ion Exchange Demineralization

The effluents of the modern demineralization plant are never rejected to the environment, but are treated for the production of co-products from the nonsugar which has been recovered from the juice plus reagents which were used for regeneration of the resins.

Two principal co-products are normally manufactured: a solid fertilizer containing mainly potassium and ammonium sulfate; and a liquid organic concentrate, rich in proteinic nitrogen, which can be used as a dietary supplement in animal feed. The methods normally used to separate the minerals from the organics are fractionation directly at the elution of the resins,[46, 47] or by crystallization[45, 48] of the minerals after concentration of the total effluents. Experiments have also been done using spray drying[49] of the mineral fraction for the production of special types of fertilizers.

To ensure the best economics for a demineralization plant, it is essential that the energy required for the production of the co-products be offset by the energy savings brought about by the use of the demineralization plant in the sugar factory. Marketing of the co-products is also a very important consideration. If these products are properly marketed, the profit derived from their sale adds to the overall profitability of the demineralization process.

(e) Indications of the Economics of the H-OH Demineralization Process

The figures given below represent the published commercial performance[39] of a modern plant running at 80% of its maximum design capacity:

- -- Nonsugar elimination: 155 g of nonsugar per liter of resin (cation + anion) per day.
- -- Water to be evaporated from effluents and sugar streams: 40.9 tons per ton of nonsugar eliminated.
- -- 100% H_2SO_4 : 0.8 ton per ton of nonsugar eliminated.
- -- 100% NH_3 : 0.32 ton per ton of nonsugar eliminated.
- -- Additional sugar produced by the factory: 1.32 tons of sugar per ton of nonsugar eliminated (or 204 kg of sugar per cubic meter of resin installed per day).

The above figures are not given as the general rule or as the final state of the art (Guerin[14] indicates a performance by a commercial unit of 405 kg sugar recovered per cubic meter of resin installed per day). They can, however, be taken as solid, conservative figures for the study of this technology.

It is not possible to complete a cost estimate for the introduction of H-OH demineralization in a beet sugar factory without an integration study to evaluate all the side effects of demineralization on factory economics. Demineralization cannot be placed in a beet sugar factory as a complement to the conventional process. It must be introduced as a new, essential part of the general process, modifying radically the crystallization diagram.

3. Removal of Nonsugar from Molasses by Ion Exclusion

(a) Brief History

Landi and Mantovani[1] relate the history of the laboratory and pilot scale development of ion exclusion--from Wheaton's[50] research in the early fifties to the encouraging data compiled by Gross[51] in the early seventies.

The real commercial development of ion exclusion on beet molasses began at the plants of The Finnish Sugar Company[20] and Pfeifer und Langen Company.[52] A few first generation commercial plants were built in Europe during the seventies, using the discrete fraction recirculation system, i.e., discontinuous ion exclusion system. Since that time, however, development of this technology has been very slow. Ion exclusion technology, as reported by Kunin,[53] by the mid-eighties had not yet shown any "commercial promise".

New hope for the development of ion exclusion has been raised more recently, with the appearance on the market of the better performing resins,[54] and the use of the simulated moving-bed technology (continuous chromatographic separation). This technology, invented by Broughton and Gerhold,[55] and applied successfully since the early eighties for the separation of glucose and fructose, improves the actual performance of the ion exclusion process. Schoenrock[56] indicates the existence of two commercial units in Japan, in operation in 1987, using the simulated moving-bed technology, and considers "highly probable that the universal application of ion exclusion may be unavoidable in the sugar industry if this industry is to stay competitive against substitute sweeteners".

(b) Location of the Ion Exclusion Plant in the Beet Sugar Process

The principle of ion exclusion--the chromatographic separation of sucrose and nonsucrose--makes impractical the total recovery of the sucrose entered in the separation system. Yields of 70%-85% are currently observed for commercial plants using the discontinuous system.[57, 58] With sugar yields such as this, it is impossible to place an ion exclusion system for the purification of products such as thin or thick juice--or even machine syrup. In fact, all the existing commercial plants have been using beet molasses as raw material.

The sucrose fraction obtained after ion exclusion is a product having a purity of 90%-95%, which is usually sent to the head of the sugar factory process at the carbonation step.

The nonsucrose load of the purified molasses must be added to the normal nonsucrose of the main stream. This is very important to consider for the avoidance of "surprises" in sugar quality and overload of the crystallization equipment. Adriaensen[57] reports an increase in thin juice color--from the normal value of 900 ICUMSA, up to a value of 1390 ICUMSA units--and a thick juice color of 3500 instead of 1700 ICUMSA, due to the recycling of purified molasses.

Progress has been reported[56] recently, and sugar yields as high as 97% have been claimed possible. This means that future plants could use ion exclusion starting from products having a higher purity than molasses, such as machine syrup, or even low green syrup.

(c) Practical Arrangement of an Ion Exclusion Plant

The molasses to be treated must be delimed and filtered.

Deliming is essential, since the cationic resin used for the chromatographic separation is in the Na^+ form. If calcium and magnesium are present in the molasses, they will be exchanged in the resin for sodium ions, and progressively exhaust the resin. As a result, the resin will lose its separation efficiency.

To avoid rapid fouling of the resins by suspended materials, which will necessitate frequent backwashing, good filtration of the molasses prior to entering the chromatographic separation unit is also essential.

The pretreated molasses, diluted to 40-70 Brix, is sent at high temperature to separation. The water used for the chromatographic separation must be either softened or condensed water.

In order to avoid degassing of fluids within the separation column, which could create channelling and disturb the chromatographic process, it is necesary to degasify fluids prior to their entry in the column.

The separation principle is primarily the application of the Donnan membrane theory: In the resin bed, the ionized molecules are rejected and, therefore, advance more rapidly through the column than the non-ionized molecules such as sucrose. An additional effect of molecular sieving is the creation of a separation between the non-ionic molecules. Raffinose, for example, progresses more rapidly than sucrose.

The following illustrates the three-stage evolution of the technology for separating sucrose from nonsucrose in an impure sugar solution through the use of a chromatographic resin separator.

(i) First Generation: One passage through the resin separator of all the solution to be separated.

At measured intervals a portion of feed solution is introduced into the top (inlet) of the separator, each portion being separated by elution water. At the bottom (outlet) of the separator, a steady stream of diluted solution emerges.

For each portion of feed solution and its directly succeeding elution water, there is a portion of diluted sucrose-nonsucrose solution. This represents one elution cycle. (See Figure 18, diagram 1.) It is possible to change the overall composition of this sucrose-nonsucrose solution by diverting part of the solution flowing from the main stream. For example: If the first part of the elution, rich in nonsucrose, is diverted from the main stream, the overall purity of the main stream leaving the separator will be sucrose enriched. This simple system cannot be applied commercially, however, for two reasons:

THREE DIAGRAMS ILLUSTRATING THE EVOLUTION OF ION EXCLUSION

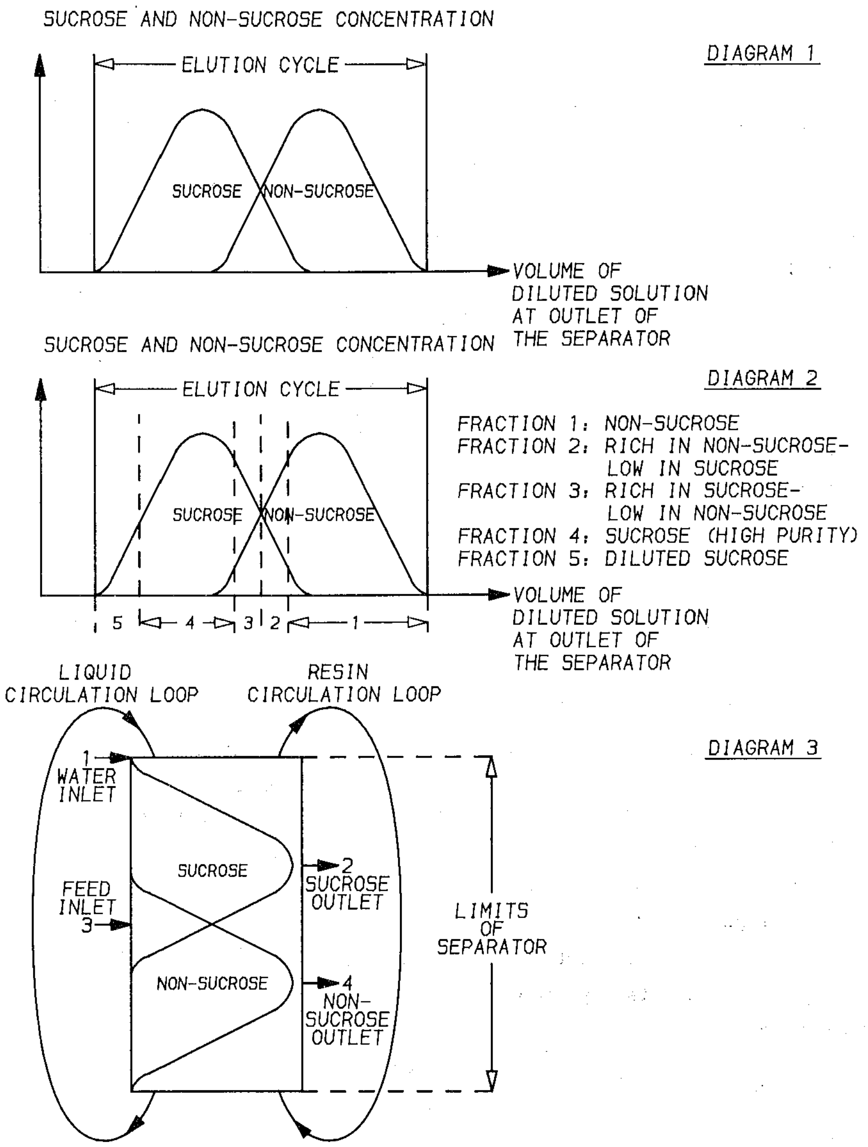


FIGURE NO. 18

- the increase in purity of the mainstream would be limited, and
- the elution water necessary would be too great.

(ii) Second Generation: Discontinuous separation using fraction recirculation.

To obtain a high purity sucrose fraction using a limited amount of elution water, the main stream of diluted solution representing an elution cycle is divided into several different fractions at the outlet of the separator. (See Figure 18, diagram 2.) The different fractions (1 through 5) are collected and destined as follows:

F-1 Nonsucrose: Sent to concentration to produce the secondary molasses.
F-2 Recycled through the separator.
F-3 Recycled through the separator.
F-4 Sucrose (high purity): Final product.
F-5 Diluted sucrose: Recycled through the separator.

Fractions F-2, F-3 and F-5 are cycled through the separator in the following sequence:

First - Fraction F-2
Second - Feed (solution to be treated)
Third - Fraction F-3
Fourth - Fraction F-5
Fifth - Elution water

This is the system usually applied in the discontinuous separators, so called because the molasses and elution water are not continuously entering the separator.

(iii) Third generation system: Continuous separation using the simulated moving-bed technology.

The third generation system essentially follows the setup shown in Figure 18, diagram 3:

- As the resin continuously circulates from the bottom to the top of the separator, in a closed resin circulation loop,
- the liquid continuously circulates from the top to the bottom of the separator, in a closed liquid circulation loop.
- At points 1 and 3 (diagram 3) the water and feed solution are continuously pumped into the separator.
- Sucrose, which is temporarily absorbed by the resin, rises to the upper part of the separator along with the resin, where it is desorbed by the water elution. Sucrose is collected at point 2 (diagram 3) of the separator, the point of its maximum concentration.

- In the liquid circulation loop, nonsucrose--which is not absorbed by the resin--is washed down towards the lower part of the separator, where it is collected at point 4 (diagram 3), the point of its maximum concentration.
- At points 2 and 4 of the separator, high purity sucrose and low purity nonsugar are being continuously extracted.

The most difficult problem in applying this principle is the establishing of the resin circulation loop. This problem is solved by simulating the movement of the resin. Instead of moving the resin around fixed introduction/extraction points, the resin remains a fixed bed with the different introduction/extraction points moving around the resin bed.

The advantages of the simulated moving bed are obvious:

- Continuous and smooth introduction/extraction ensures the reliability of the system.
- Highest purity extracts (sucrose and nonsucrose) are obtained.
- It has the lowest water and resin requirements per unit of sugar separated, since no intermediate fraction is taken out of the system, blended and then reinjected.

For optimum performance from the system, absolute control of the flow rates through the different sections of the separator, and absolute control of the composition of the fluid at each point of the separator, are essential.

The chromatographic separation system usually consists of one separator, or several separators working in parallel, depending on the amount of molasses to be treated. A separator may consist of only a single column, or several columns in a row, depending on the manufacturer's design. If the system is the discontinuous type, there are additional tanks and pumps for holding and pumping the different recycled fractions. If the system is the continuous type (simulated moving bed), no additional tanks are necessary for fraction recycling, since the fluids are being continuously circulated through the separator in a closed loop.

(d) Treatment of the Effluents of the Ion Exclusion Separator

The effluents of the ion exclusion separator come from the nonsucrose fraction. This nonsucrose fraction contains the nonsucrose separated from the molasses, plus the sucrose lost in the process. The concentration of this product is very low (3%-5%), and it is necessary to concentrate this secondary molasses with an evaporator to 55%-60% total solids. Depending on the system used, the purity of the secondary molasses can vary between 10% and 20%. This molasses is usually sold as a cattle feed ingredient.

(e) Indications on the Economics of Ion Exclusion Separation As Applied to Beet Molasses

The figures given below represent published commercial performances[57] of an ion exclusion plant using the *fraction recirculation* system:

- Nonsugar elimination: 116.8 g of nonsugar per liter of resin per day.
- Water to be evaporated from effluents and sugar streams: 23.3 tons per ton of nonsugar eliminated.
- Additional sugar produced by the factory: 1.09 tons of sugar per ton of nonsugar eliminated, or 127 kg of sugar per cubic meter of resin installed per day.

These figures are representative of the performances of present ion exclusion systems. They are not, however, to be taken as the general rule or as the final state of the art, but rather as conservative commercial figures for studying this technology. In order to complete the calculations for introducing ion exclusion in a beet sugar factory, it is very important to conduct an integration study, evaluating all the side effects of the ion exclusion on the factory process--particularly the increased color and nonsugar load on the crystallization circuit.

3. *Prospective:* Nonsugar Removal Using Ion Exchange in the Cane Sugar Factory

Very little experience is reported today on the use of ion exchange in the cane sugar factory. This situation is probably going to change within the next decade due to the new trends in the cane sugar industry.

Until recently, the cane sugar industry was divided into two very distinct activities:

- One seasonal activity: the production of raw sugar from cane.
- One year round activity: the refining of raw sugar into white granulated sugar.

In recent years[59] we have seen white granulated sugar being produced in the cane sugar factory by the addition of integrated refining processes to the conventional cane sugar factory.

Unlike the beet sugar factory, which clarifies and filters its sugar juices thoroughly in order to produce refined sugar, the raw sugar-producing cane factory does not need a sophisticated clarification system, and it does not employ juice filtration procedures. Therefore, the quality of cane sugar juices and syrups does not meet the ion exchange clarity requirements. This, of course, explains the very limited development--until now--of ion exchange in this industry.

Now with this new trend mentioned, the cane sugar factory is obliged to introduce in its process a complete clarification and filtration system, either in the refining stage--which is the conventional method--or on the main stream of cane juice. This will open the way for application in this industry of the entire range of ion exchange technology already used by the beet sugar industry.

C. Production of Liquid Sugar without Preliminary Crystallization

The production of liquid sugar without preliminary crystallization is a relatively recent advent. This is due to the fact that firmly embedded in the sugar technologist's mind was the belief that only crystallization can purify sucrose totally--freeing it of all impurities, taste and odor. It is also due to the technical difficulties which had to be resolved for the systematic removal by ion exchange of these impurities.

Zanto and Bichsel[44] were among the first to promote the idea that it is possible to produce liquid sugar from thick juice. This conclusion was reached after recognition of the very good quality of the sugar solutions obtained after H-OH deionization of diluted thick juice at the Holly Sugar Corporation's beet sugar factory in Hamilton City, California.

In a pilot plant demonstration, Devillers[60] showed how it is possible to produce very pure sugar syrups from beet sugar diffusion juice by means of ion exchange.

Herve[5] emphasizes the importance of "direct" liquid sugar production using ion exchange, which not only avoids the loss of sugar in molasses, but also lowers operating costs when compared with the conventional method.

Again in the late seventies Bichsel[61] mentions the advantages of using ion exchange for the year-round production of liquid sugar from thick juice. The first commercial application of this concept was at the Vauciennes (France) [24, 45] beet sugar factory, where a liquid sugar plant built by Applexion S.A. was put on-stream in early 1983. Figure 19 compares the two methods of producing liquid sugar: ion exchange purification versus the conventional method, which uses the remelt of crystallized sugar to produce the liquid sugar.

An economic comparison of the two systems should include the following considerations:

1. Sugar yield.
2. Equipment in-service time.
3. Raw material storage cost.
4. Energy cost.
5. Reagent cost.
6. Value of co-products.

The evaluation of these points should be based on the economic conditions of each factory. At the liquid sugar plant in Vauciennes, Foucart[24] reports a considerable savings in fuel consumption after the factory switched from the conventional to the ion exchange system. He also reports good sales of the co-products on the French market, but does not give any comprehensive data on the economics of the process.

PRODUCTION OF LIQUID SUGAR FROM BEET THICK JUICE

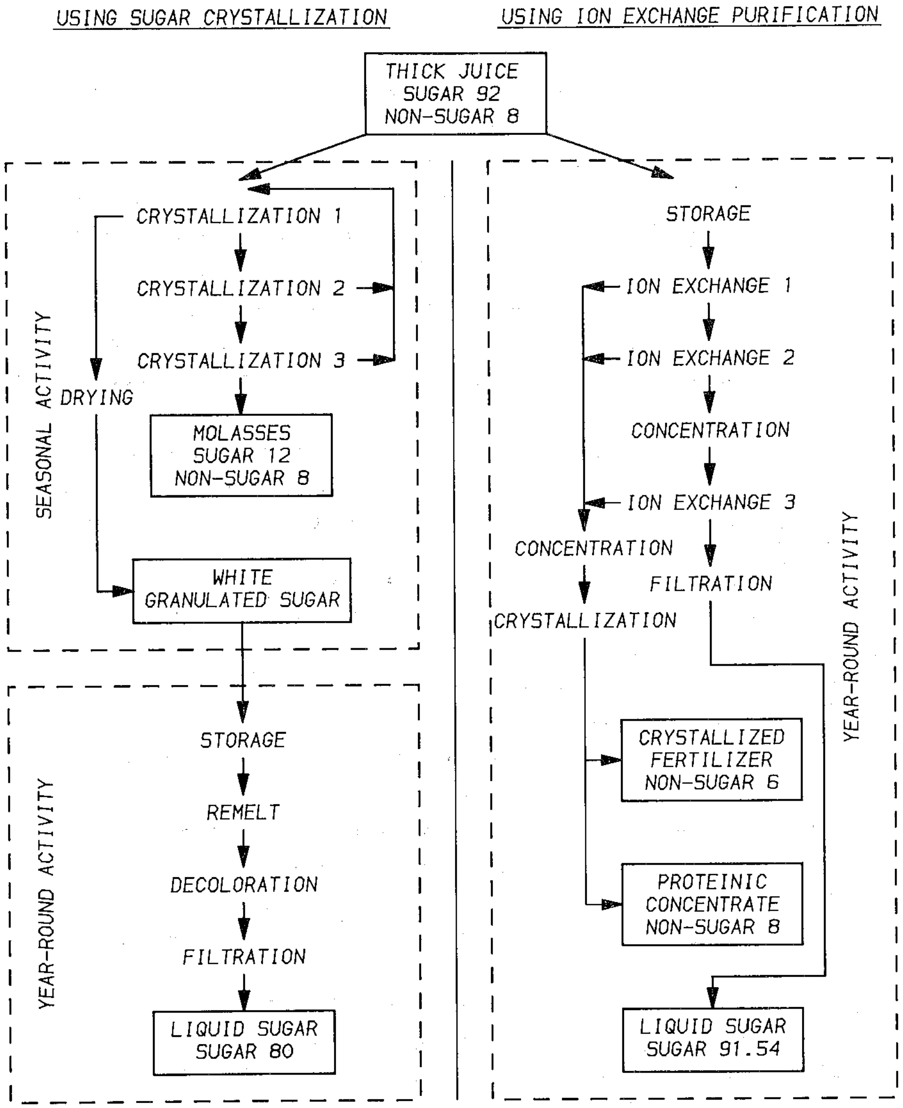


FIGURE NO. 19

In a recent article Herve[64] proposes a new concept for the sugar industry, cane or beet, where the activity of the industry would be separated into two units: agricultural and refining.

--During the season the agricultural unit would produce thick juice or cane syrup, which would be stored.

--The refining plant would process this syrup on a year-round basis, producing liquid sucrose, refined crystallized sucrose, invert sugar, etc.

Figure 20 is a schematic process diagram of the refining plant as it applies to cane sugar syrups. The same diagram, without the flocculation and filtration steps, applies to the beet sugar syrups.

One very unique feature of this process is the crystallization of refined sucrose in one strike from the refined liquid sugar produced by ion exchange. Pisano[62] was the originator of this idea, and it has been successfully applied at the Vauciennes sugar refinery.[24] Among its advantages are:

--A very high quality refined sucrose is produced.

--The mother liquor of the crystallization being liquid sugar, it is not necessary to have several crystallization steps, since no molasses is produced in the process.

--If continuous crystallization is applied, the vapors of the vacuum pan can be recompressed and used for the energy requirements of the ion exchange refining process, making the operating costs very low.

Table 1 shows us the energy and chemical requirements of an Applexion process, starting from a syrup at 92% purity (beet sugar industry) or a syrup at 87% purity (cane sugar industry).

Efforts to produce liquid sugar from beet or cane by more economical methods are sure to continue:

--The use of liquid sugars in the food industry has increased tremendously in the last thirty years.[64, 65]

--In the field of liquid sweeteners, competition from high fructose corn syrup compels the conventional sugar industry, in countries such as the United States, to lower its liquid sugar manufacturing costs. If not, the industry will be limited to the liquid sucrose market.

D. Other Well-Established Ion Exchange Processes Used in the Sugar Industry

1. Quentin Process in the Beet Sugar Industry

As indicated in Chapter II, paragraph B (1), the Quentin process is a method currently used by the beet sugar industry to increase sugar extraction. Like deliming, this method has been widely applied, although primarily in the European beet sugar industry.

APPLEXION PROCESS

FOR THE PRODUCTION OF LIQUID SUGARS
AND PREMIUM GRADE GRANULATED SUGAR
IN THE CANE SUGAR FACTORY

(COURTESY OF APPLEXION)

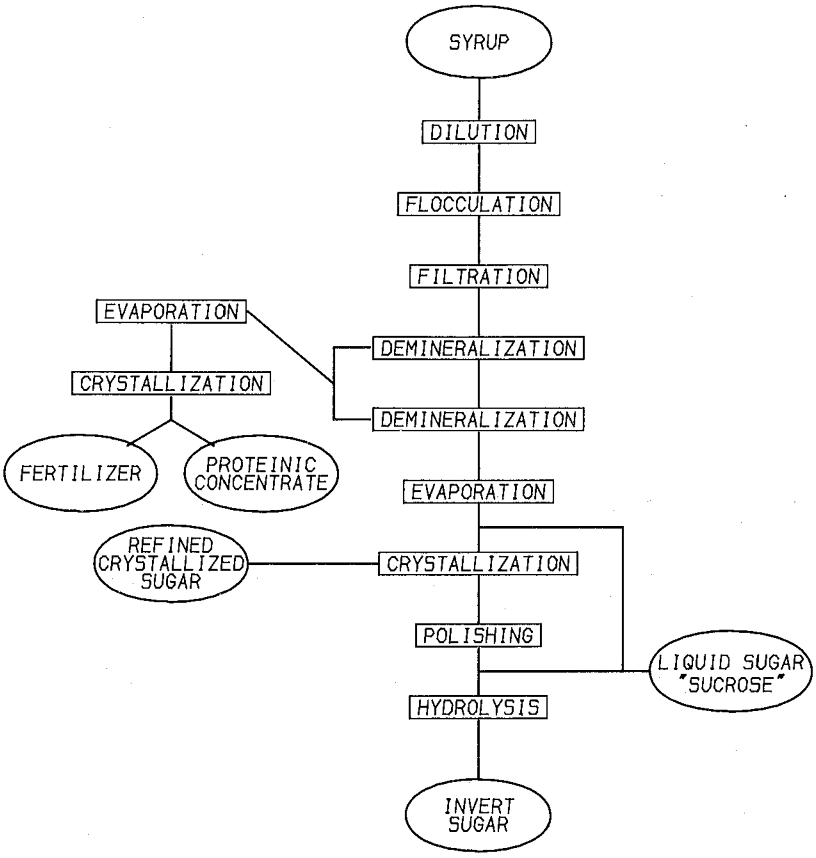


FIGURE NO. 20

TABLE 1

ENERGY AND CHEMICAL REQUIREMENTS FOR THE PRODUCTION OF LIQUID SUGAR FROM BEET OR CANE SYRUP

		BEET		CANE	
		PER TON OF SUGAR (2)	PER TON OF NON SUGAR	PER TON OF SUGAR (1)	PER TON OF NON SUGAR
SULFURIC ACID	100 % (kg)	50.86	582	72.8	477.3
AMMONIA	100 % (kg)	11.71	134	14.9	97.7
CAUSTIC SODA	100 % (kg)	8.48	97	6.3	41.3
PHOSPHORIC ACID	100 % (kg)	-	-	7.5	49.17
LIME (CaO)	100 % (kg)	-	-	9.3	60.97
FILTER AID	(kg)	-	-	12	78.7
PAPER FOR FILTRATION	(m2)	1.4	16.02	1.4	9.18
ACTIVATED CARBON	(kg)	0.25	2.86	5	32.8
FLOCCULANT	(kg)	-	-	1	6.55
CATIONIC RESINS	(L)	0.2	2.3	0.5	3.28
ANIONIC + ADSORBENT RESINS	(L)	0.4	4.6	1.5	9.93
WATER	(m3)	0.4	4.4	0.6	3.93
ELECTRICITY	(kWh)	58.5 (3) (4)	1150 (3) (4)	81	531
STEAM	(t)	0.13 (4)	3.45 (4)	2.7	17.7

(1) PER METRIC TON OF LIQUID SUGAR EXPRESSED AS DRY MATTER FOR A SYRUP PURITY OF 87.
(2) PER METRIC TON OF LIQUID SUGAR EXPRESSED AS DRY MATTER FOR A SYRUP PURITY OF 92.
(3) EVAPORATION IS BY MECHANICAL VAPOR RECOMPRESSION.
(4) THESE FIGURES MUST BE ADDED.

(COURTESY OF APPLEXION)

This process bears the name of its inventor,[66, 67] who demonstrated that the difference in the solubility of sucrose in molasses depends on the cations present in the solution. The following order applies:

$$K^+ > Na^+ > Li^+ > Ca^{++} > Mg^{++}$$

The solubility of sucrose in molasses containing potassium is higher than that in molasses containing magnesium. This is due to the difference in degree of hydration: The magnesium has the highest degree of hydration, which leaves less water available for sucrose in molasses. The sucrose is, therefore, less soluble in magnesium molasses.

Replacing potassium with magnesium also reduces the weight of the nonsugar, thereby producing less molasses: 1 eq of magnesium represents 12.16 g of nonsugar, while 1 eq of potassium represents 39.1 g of nonsugar.

Ion exchange is used industrially to replace potassium and sodium with magnesium in machine syrup. A macroreticular, strong cation exchange resin is used for the process. Forty percent of the potassium and sodium ions are exchanged in the resin for magnesium ions. The treated machine syrup is then crystallized, producing molasses in smaller quantity and at a lower purity. The first commercial unit using this process was commissioned in Germany in 1956. Since that time, numerous units have been operated successfully. It is presently estimated that 0.4 to 0.6% beet can be saved in sugar extraction by using this process.

Figure 21 shows a typical flowsheet for a modern unit using fractionated sweetening-on/off, reagent and water recovery systems.

Schoenrock[68] gives the following guidelines for an economic evaluation of the Quentin process:

$Na^+ + K^+$ exchanged per 100 g nonsugar	0.37-0.55 eq
Exchange rate	30-55%
Extraction gain	0.3-0.6% on beet
Brine consumption (30% $MgCl_2$)	0.5-0.8% on beet
Dilution	0.2-0.6% on beet
Sugar loss	0.01-0.05% on beet
Waste water	6-10% on beet

In the decision as to whether or not to install a Quentin unit, the first economic consideration is the difference in price between refined sugar and the sugar in molasses. The second consideration is the availability of magnesium salts for regeneration. Magnesium chloride is a cheap chemical in Germany and in the Great Salt Lake area of the United States. In England, Oldfield et al.[69] reported success with the use of magnesium sulfate for regeneration.

When compared with demineralization, or ion exclusion technologies, the Quentin process has one very big advantage: the capital expenditure for such a plant is quite modest. Two disadvantages must also be considered, however:

QUENTIN PROCESS

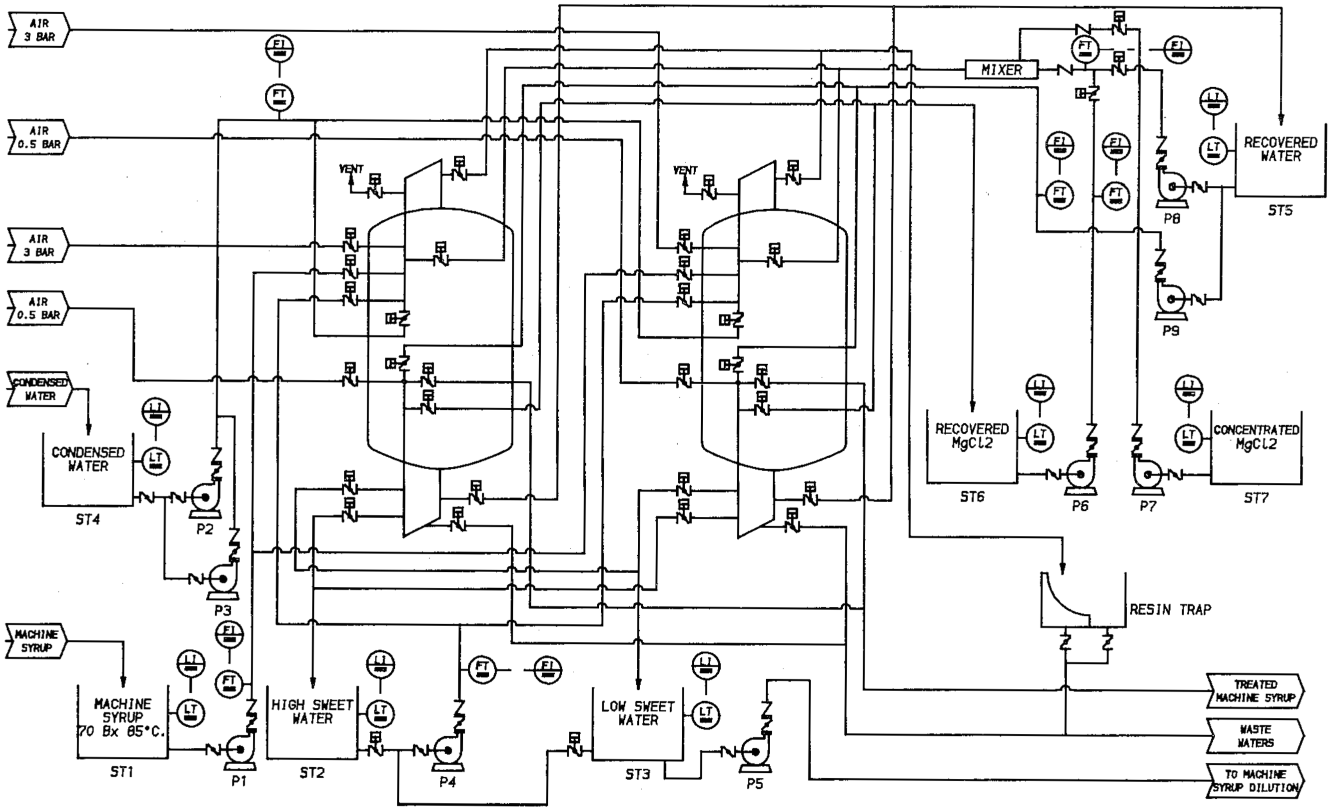


FIGURE NO. 21

--the limited amount of sugar which can be saved by this method, and

--the production of waste waters, which cannot be recirculated in the water circuit of the beet sugar factory.[70]

Since the mid-seventies, environmental protection agencies have made it more and more difficult for sugar factories to discharge wastes--even the mineral type wastes. Presently, waste water production is probably the most serious drawback for the Quentin process. In Chapter II, paragraph D (3), an interesting *solution*[29] *to this problem is proposed.*

2. Decolorization of Fine Liquor in the Sugar Refinery by Means of Strong Anion Resins in the Chloride Form

Decolorizing fine liquors by means of strong anion resins in the chloride form is not a new application of ion exchange in the sugar industry. Fries[71] reports the correlation between the progress of this technology and the improvement in ion exchange resins dating back to the early fifties. In the beginning, only gel type resins were available, and their use was limited to polishing of decolorized fine liquor which had already been passed through bone char or activated carbon. The physical stability of the resins was low, and their irreversible fouling by color molecules was quick. Resin decolorization was, therefore, applied only when ultra-white sugar was required.

When the macroreticular resins became available in the sixties, and then the acrylic resins in the seventies, the possibilities for the use of resins in the decolorization of fine liquor were considerably extended--in fact, resins were now capable of fully replacing bone char and activated carbon in the sugar refinery.

Since the late seventies, for any fine liquor decolorization project in the sugar refining industry, the ion exchange alternative has always been considered--and, in most cases, has won the support of the decision-makers.

(a) *General Comments on Refining Prior to Decolorization*

The general principle for the refinement of sugar has not changed. Now, however, this principle is applied mostly in the refining of cane sugar. (Beet sugar is now usually produced directly as white sugar at the beet sugar factory.)

Raw sugar is first affinated to remove surface impurities from the crystals. Then, it is melted, clarified, filtered and decolorized prior to conventional crystallization. The decolorization step is the last stage of refinement prior to crystallization and, therefore, determines the quality of the refined sugar obtained. Each refiner adapts his decolorization procedure in accord with the following:

--the quality of refined sugar desired,

--the type of clarification used: phosphatation or carbonation, and

--the load of color to be removed, which depends on the quality of the raw sugar.

Guerin[72] makes the distinction between the two types of raw sugar: plantation raw, delivered wet--as produced in Cuba, Brazil, Mexico, etc.; and plantation white, delivered dry--as produced in Guadeloupe, La Reunion Island, the Philippines, etc. The composition of these two types of raw sugar is as follows:

	Plantation Raw ("sucre gras")	Plantation White ("sucre sec")
Sucrose %	96.3-97.2	99.20-99.40
Ash %	0.5- 0.7	0.10- 0.15
Reducing Sugars %	0.2- 0.4	0.15- 0.20
Nonsugars %	1.3- 1.6	0.10- 0.45
Water %	0.8- 1.0	0.10- 0.15
Color (ICUMSA)	4000-5000	1000-2000

The plantation raw is easily affinated, while the plantation white is more difficult to affinate. The affinated sugar usually obtained has the following characteristics:

	Affinated Sugar from Plantation Raw	Affinated Sugar from Plantation White
Purity %	99.30-99.5	99.40-99.5
Ash %	0.06- 0.12	0.08- 0.12
Reducing Sugars %	0.1	0.08- 0.15
Color (ICUMSA)	1200-2500	1000-1300

The affinated sugar is then melted, clarified and filtered. Either of two processes is used for this treatment: phosphatation or carbonation process. Both of these processes have a decolorization effect; carbonation has, in addition, the effect of decreasing the content of ash and reducing sugars. Currently, the color of the so-called "fine liquor" before decolorization varies between 600 and 1200 ICUMSA.

(b) Examples of Fine Liquor Decolorization Systems Using Resins for Part or All of the Process

(i) Using Resins for Part of the Decolorization

Martin[73] reports that since 1981 the Tate and Lyle Westburn Refinery in Scotland has used resins for decolorizing fine liquor after the carbonation process. The procedure is as follows: After carbonation the fine liquor is first passed through a macroreticular acrylic resin bed, which decreases the color from 600 to 250 ICUMSA. Then, it is passed through the char house, where the color is further decreased to an average of 90 ICUMSA. Finally, the fine liquor is passed through a macroreticular polystyrenic resin bed, which decreases the color to 45 ICUMSA units.

Prior to this, the refinery was using only the char house to decolorize the fine liquor from 600 to 90 ICUMSA. Table 2 shows the difference in operating costs between the old system, which used only char, and the new system using char plus resin. Operating costs are reduced by 41%, and the high quality of the final liquor sent to the first pan leads to an increase in the ratio of premium grade granulated sugar produced by this pan and a decrease in the ratio of back-boiling in the refinery.

TABLE 2

DECOLORIZING COSTS COMPARED

WESTBURN REFINERY

(Courtesy, Tate and Lyle)

	(A)	(B)
	11% Char	4% Char + Resin
	%	% Total (A)
New char	10	4
Fuel oil (kiln)	16	6
Steam	18	6
Resin - acrylic	-	5
- styrenic	-	1
Salt + chemicals	-	3
Process labor	27	16
Maintenance	15	10
Sugar loss	14	6
Ash increase	-	2
Total	100	59

Ramm-Schmidt[74] describes the use since 1983 of a combination of acrylic-polystyrenic resins, of the type recommended by Fries,[71] at Finnish Sugar's Porkkala (Finland) refinery. In this case the fine liquor treated is produced by a carbonation process. After carbonation the fine liquor color is at 650 ICUMSA. The first stage of decolorization is by means of powdered activated carbon. This decreases the color to 470 ICUMSA. The liquor is then passed successively through a macroporous acrylic resin bed and a macroporous polystyrenic resin bed. This decreases the color of the fine liquor to 70 ICUMSA.

Hickey[75] reports that since 1987 the Redpath Sugar Refinery in Toronto (Canada)--a carbonation and char decolorization refinery--has employed a new polishing system which uses macroporous polystyrenic resin to equalize the decolorization rate of the char system. Only the first half ("la belle") of the liquor coming out of the char cistern is sent directly to crystallization. This part has an average color of 40 ICUMSA. The second half ("le sirop clair "), having an average color of about 100 ICUMSA, is sent to the new resin decolorizer, where it is decolorized down to 40 ICUMSA prior to going to crystallization.

(ii) Using Only Resins for the Entire Decolorization Process

Martin[76] lists the following advantages of resin decolorization processes over black adsorbents:

1. Flow rates are much greater in terms of bed volumes per hour - hence, a large contraction in the number of plant vessels and the space required.

2. Regeneration is fast - a higher proportion of the material stock is thus on stream.

3. Low energy, non-thermal regeneration - the way to go when fuel prices are leading the inflation of material costs.

4. Manning levels - a process that lends itself to semi or complete automation, and one in which maintenance can more readily be designed out.

5. Hygiene - an enclosed and compact plant. No dust, no handling problems, whether you are using an in situ or external regeneration.

6. Sugar loss - lower because of (a) shorter hold-up times at elevated temperatures and (b) easier desweetening of much smaller material quantities.

In view of the above advantages, it is not surprising that some refineries have chosen to use only resin for their decolorization process.

Cox[77] reports the replacement in 1978 at the Huletts Sugar Refinery in Durban (South Africa) of a complete bone char plant--including fifty-six char cisterns and a stock of 1600 tons of char--by only four resin reactors containing a total of fifty tons of resin. In this particular case, clarification is by carbonation. The color of the liquor before decoloration is about 800 ICUMSA. After a single pass through a macroreticular acrylic resin bed it is possible to obtain a color of 350 ICUMSA. This is considerably lower than the 340-450 ICUMSA, obtained previously with the char system, which is necessary to produce a refined sugar at 50-60 ICUMSA.

Celle[78] describes the replacement at the Generale Sucriere Refinery in Marseille (France) of the old bone char decolorization plant ("... where Emile Zola would have been able to find some good examples for his social novels.") by a new resin decoloriztion station in 1979. In this case macroreticular polystyrenic resins are used with a double-pass system in upflow. Prior to treatment the average color of the liquor is 905 ICUMSA. After treatment the average color of the fine liquor is 120-140 ICUMSA.

Cheong[79] reports the use of a resin decolorization station at the Malayan Sugar Manufacturing Company in Malaysia. In this case the clarification process is the phosphatation type. There is no bone char or activated carbon system to protect the resin station from fouling.

(c) Important Points to Consider in Using Resin Decolorization in Sugar Refining

(i) Using Resin After a Carbonation or Phosphatation Process

Using resins after a carbonation or phosphatation clarification process presents no problem. The clarified liquor must, however, be carefully filtered before entering the ion exchange station, and be free of high molecular weight molecules such as colloidal substances, which could foul the resin. Needless to say, the filter aid employed (such as diatomites) should remain on the filter and not be allowed to reach the resin reactors. A safety filtration prior to entering the resin reactor is always recommended.

(ii) Types of Resin to Be Used for Decolorization

--Strong Base Anion Polystyrenic Type Resin

These resins have proven over the years their excellent characteristics for fine liquor decolorization. Their aromatic structure makes them particularly efficient in fixing the aromatic type coloring materials present in the liquor. At the end of a refining process, polystyrenic resins are almost always used to obtain the lowest ICUMSA color level. They also are used successfully[78] for the entire decolorization process without preliminary bone char treatment. When using polystyrenic resins it is important to avoid overloading the resin with coloring substances which would increase the "irreversible absorbed coloring matter" part[80] which cannot be regenerated, and, therefore, shortens resin life.

--Strong Base Anion Acrylic Type Resin

The acrylic resins are used extensively in fine liquor decolorizing. Although they do not retain the coloring substances as well as the polystyrenic resins, they have an excellent decolorization effect--particularly on liquors having high ICUMSA color levels. They are less subject to irreversible fouling than are the polystyrenic resins, since their skeleton structure is not aromatic and, therefore, has less affinity for the coloring substances present in the sugar liquor. For this reason the efficiency of their regeneration is superior.

(iii) Design Guidelines

--Arrangement of the Decolorization Plant

Depending on the problem of a particular refinery, the refiner and the ion exchange engineer have several different options:

--using the acrylic or polystyrenic resins, or a combination of both types;

--running a single-pass or a double-pass system (some[76] even suggest the triple pass):

--when using a double-pass system, have a merry-go-round arrangement where each resin cell becomes in turn the secondary and primary decolorizer before being regenerated; or

--have a system where the primary decolorizer is never used as a secondary decolorizer.

--Flow Rate Through the Resin Bed

Flow rates of 1.5 to 10 BV/h (1 BV/h is one volume of liquor per volume of resin per hour) for liquors at 65 Brix have been reported. It is important to point out, however, that a reasonable range is between 2 and 3.5 BV/h. This is due to reasons of quality, the liquor being best decolorized at lower throughput. Also, pressure drop problems and premature resin breakage occur when too high flow rates are applied.

The advantages of a resin system over a black adsorbent system are sufficient to allow the ion exchange engineer to design a plant with safe process parameters and optimum performance capabilities--and avoid the "race car" design.

--Upflow or Downflow Design

Decolorizing fine liquors at high density also calls for very serious consideration of the advantages of upflow technology. (See Chapter II, paragraph B.) Here again, the choice of an experienced ion exchange engineering company is the determinant for success. Unfotunately, in the hope of saving on capital investment, the refiner too often turns to experimental, in-house designs. The performance of plants built from such designs cannot, of course, approach that of the plants designed and built by specialized enginneering firms, with the technical know-how that is derived from years of study, research and field experience.

--Countercurrent Regeneration

The importance of countercurrent regeneration for the regeneration of resins in this particular application has been demonstrated.[4] For such regeneration, solutions of 10% NaCl are very efficient for separating the light bond between coloring substances and the resin structure. By means of countercurrent regeneration it is possible to reduce the 100% NaCl consumption from 220 g/l of resin to 120 g/l of resin. It may be a good idea to take advantage of this low NaCl consumption of the countercurrent regeneration by decreasing the length of the decolorization run. This would decrease the color load at each cycle and thereby increase resin life. Using countercurrent regeneration, and with the proper design, it is also possible to ensure that a color body removed from the resin bed never reaches a part of the resin bed that it has not reached during the preceding decolorization run.

To improve regeneration, the use of NaOH or HCl at low concentration in the brine solution is advised. The percentage of concentration depends on the resin used and the quality of liquor being treated.

(iiii) Effluents of Regeneration

As is true with any ion exchange process, the treatment of the effluents of a resin decolorization station must be considered. Although many refineries are located on or near the sea, which simplifies considerably the problem of waste effluents, since the salty solution can easily be discharged into the water, many other refineries are located inland and are thus under greater pressure to treat the effluents of regeneration. Oxidation by means of hypochlorite or ozone[4] is an experimental technology which would reduce the amount of brine rejected to the environment to approximately 5-10% of its present level.

Ultrafiltration, or loose reverse osmosis, has also been under study for several years[77] as possibly a sophisticated technique for concentrating the color and recycling the brine.

Other more conventional processes (aerobic or anaerobic treatment, for these effluents alone or in conjunction with municipal effluents) have been used.

3. Ion Exchange in Sucrochemistry

As stated by Herve,[62] as we near the end of this century, it is most essential that the sugar industry produce not only sucrose, but also all possible sucrose derivatives:

- invert sugar syrups
- glucose syrups
- fructose syrups
- crystallized glucose (anhydrous or monohydrate)
- crystallized fructose
- sorbitol

etc.

Ion exchange is playing an important part in the industry's evolvement from a conventional sucrose to a diversified sweeteners industry. Table 3[13, 81] cites examples for each type of application of ion exchange technology. The term "porous beads" is used instead of "resins" in order to cover not only the conventional polystyrenic, polyacrylic or formophenolic beads (which mainly comprise the ion exchange and adsorbent resins), but also to include the mineral beads and immobilized enzymes. The table shows the four different functions which characterize these porous beads, ion exchange being only one function.

Three typical applications of porous bead technology in sucrochemistry, which are already in use commercially, are:

(a) Molecular Transformation by Catalytic Reaction

The hydrolysis of sucrose by means of catalytic resin is the best known in this category. Discovery of the possibility of producing invert sugar from a sucrose solution by means of a solid catalyst is not new.[82] A number of researchers[83, 84, 85] have studied the heterogeneous hydrolysis of sucrose using

TABLE 3

FIELD OF APPLICATION
POROUS BEAD TECHNOLOGY

SOLUTE ALTERATION BY MEANS OF POROUS BEADS				
ALTERATION FUNCTION	IMPURITIES ELIMINATION	VALUABLE SOLUTE (S) RECOVERY	VALUABLE SOLUTE (S) SEPARATION	SOLUTE (S) CHEMICAL MODIFICATION
ION EXCHANGE	A	B	C	D
ABSORPTION	E	F	G	
ADSORPTION	H	I	J	
CATALYSIS	K			L

TYPICAL EXAMPLES FOR EACH TYPE OF APPLICATION

A - Demineralization of thin juice in a beet sugar factory.
B - Recovery of free fatty acids from a vegetable oil.
C - Separation of fatty acids.
D - Thin juice deliming.
E - Decolorization of fine liquor in a cane sugar factory.
F - Anthocyanin recovery from grape residue.
G - Purification of polysaccharides in glucose syrup at high D.E.
I - Recovery of sucrose from beet molasses by ion exclusion.
J - Separation of glucose and fructose from invert sugar or high fructose syrup.
K - Elimination of traces of sucrose in an invert sugar solution.
L - Sucrose hydrolysis producing invert sugar.

catalytic resins. The most important advantage of heterogeneous hydrolysis over homogeneous hydrolysis using an acid is that with heterogeneous catalysis, the final products of the reaction are separated from the catalyst. Invert sugar solutions obtained in this way are therefore of the highest purity, with a very low ash content. On the other hand, invert sugar obtained by homogeneous hydrolysis, using hydrochloric acid for example, must be neutralized by an equivalent amount of caustic soda, resulting in appreciable salinity (15-20 meq/l of syrup) of the product.

Commercial plants have been built--notably in France and Germany--which use catalytic resins for the production of invert sugar.

Siegers[86] gives the ideal parameters for inversion using catalytic resins: The use of macroporous resin is recommended; the reaction temperature must be as low as possible (40°C) to avoid formation of colored hydroxymethyl furfural. With these conditions, a sucrose solution at 60% T.S. can be hydrolyzed at 99% if the contact time of the solution with the resin is at least fifty minutes. Work has been done recently using immobilized enzymes for the production of invert sugar, and this technology also gives excellent results.

(b) Separation of Glucose from Fructose by Means of Adsorption Chromatography

The development of this technology has appeared mainly since the late seventies in the corn refining industry,[2] where it is used for the production of high fructose corn syrups at 55% fructose and fructose syrups at high purity, from H.F.C.S. 42. It can also, however, be used to produce glucose or fructose syrups from invert sugar. The resin used for this technology is primarily a cationic resin in the calcium form. The separation process is very similar to that described in Chapter III, paragraph B (3) covering ion exclusion. As with ion exclusion, the state of the art for this technology is the so-called "simulated moving bed" system.

(c) Purification by Means of Ion Exchange

In sucrochemistry it is often necessary to purify the products obtained after a reaction or separation. Ion exchange systems are used to remove impurities such as color or minerals. One of the most popular systems used for high purity products is the mixed-bed technology. Mixed beds contain a mixture of cation and anion exchange resins, in suitable proportion. The mixed-bed system gives very good purification results not only in deashing but also in decolorization. A current application for the mixed beds is in liquid sugar refining.

We have limited our brief descriptions of ion exchagne applications in the sugar industry to those processes which are now being used commercially by the industry. Even so, the wealth of applications for ion exchange is obvious. Today's sugar technologist recognizes it as one of the best tools available to him.

SUMMARY

In the last decade ion exchange has made impressive strides. This is amply demonstrated by its growing use in the sugar industry.

Basically, the reasons for this progress are:

- Better resin characteristics
- Better ion exchange engineering
- Better plant control
- Inclusion of waste water treatment in the ion exchange process
- Optimum integration of the ion exchange system in the general factory process

Examples of commercial applications of ion exchange (or, more precisely, porous bead technology) are described briefly, and among these are:

- Gryllus process (deliming)
- NRS process (deliming)
- Deliming by means of weak cation resin
- H-OH demineralization of thin or thick juice (beet sugar industry)
- Ion exclusion for beet sugar molasses
- Production of liquid sugar from thick juice (beet sugar industry)
- Quentin process (beet sugar industry)
- Fine liquor decolorization (cane sugar refining)
- New operations in sucrochemistry, such as
    - sucrose hydrolysis
    - glucose-fructose separation by adsorption chromatography
    - sugar refining with mixed beds

These many and varied applications evidence how deeply rooted ion exchange is in the sugar industry today and how important it is to the industry's future growth and profitability.

REFERENCES

1 S. Landi and G. Mantovani, Sugar Technology Review, Vol. 3 (1975).
2 P.H. Blanchard and E.O. Geiger, Sugar Technology Review, Vol. 11 (1984).
3 Robert Kunin, Amberhilites, No. 161 (Spring 1979).
4 William Fries, International Sugar Journal, Vol. 84 (1982).
5 D. Herve, Process Biochemistry (May and June 1974).
6 William Fries, S.I.T. (1982).
7 Dow Chemicals, Form No. 177-1372-85.
8 Colin Loker, S.I.T., Vol. XLII, Paper No. 499 (1983).
9 Robert Kunin, Meeting of the Cane Sugar Refining Research Project, Inc., 1980 (Pub. 1981).
10 Rhone Poulenc, Industries French Application 79/29360 (November 1979).
11 J. Bouchard, Industries Alimentaires et Agricoles, 82 (1965).
12 G. Assalini and G. Brandoli, Sucrerie Belge, 91 (1972).
13 X. Lancrenon and D. Tondeur, Cahiers du G.I.A., ENSIA (1976).
14 Jean Guerin, Colloque Applexion, Paris (June 1975).
15 J. Elmer, H. Hitzel and E. Moebes, Proc. XIV C.I.T.S. (1971).
16 Avinash G. Gupta and Karlheinz W.R. Schoenrock, Sucrerie Belge, 95 (1976).
17 K.W.R. Schoenrock, A.S.S.B.T. Meeting (1985).
18 A. Zsigmond and E. Gryllus, Zucker (1966).
19 Y. LeHenaff and D. Herve, Industries Alimentaire et Agricole, 94 (1977).
20 H.J. Hongisto, International Sugar Journal, 940 (1979).
21 J.C. Drogerys, Colloque Applexion, Paris (June 1975).
22 F.B. Martinola and G. Siegers, Proc. I.W.C., Pittsburgh (1981).
23 F.B. Martinola and G. Wutte, Proc. I.W.C., Pittsburgh (1985).
24 J. Foucart and J. Paleos, British Sugar Conference (1986).
25 X. Lancrenon and P. Printemps, International Sugar Journal, Vol. 86 (1984).
26 G.T. Wilson and E.L. Bateman, S. African ZA 77/5145.
27 S. Kishihara and M. Komoto, Seito Gijutsu Ken Kyu Kaishi, 28 (1978).
28 Vilmos Gryllus, Cukoripar (1976).
29 G. Assalini, Europen Patent Application EP 16992 (1980).
30 G. Rousseau and X. Lancrenon, Industries Alimentaires et Agricoles (1983).
31 D. Herve and X. Lancrenon, Industries Alimentaires et Agricoles (July-August 1981).
32 C.C. Chou, S.I.T., Vol. 18, Paper 509 (1984).
33 J. Ponant, British Sugar Conference (1982).
34 K.W.R. Schoenrock, A.S.S.B.T. Meeting (1985).
35 E.H. Hungerford and R.A. McGinnis, Beet Sugar Technology, Third Edition (1982).
36 D.M. Stromquist and H.E. Ellyson, Sugar, 45 (February 1950).
37 T.E. Maudru, Ind. Eng. Chem., 42 (1951).
38 Duolite, Ion Exchange Resins in the Treatment of Sugar Solutions (1977).
39 S.E. Bichsel, H.A. Davis and A. Sandre, La Sucrerie Belge, Vol. 98 (March 1979).
40 G. Assalini and G. Brandoli, A.S.S.B.T., 11 (1961).
41 E. Moebes, Zucker, 14 (1961).
42 S. Vajna, Zucker, 12 (1959).
43 S.E. Bichsel and D.A. Hoover, 1969 Journal of A.S.S.B.T., 15(4) 324-331.
44 L.T. Zanto and S.E. Bichsel, 1970 Journal of A.S.S.B.T., 16(2) 149-155
45 M. Shore, N.W. Broughton and coll., American Chem.Soc. Mtg. April 5-10, 1987, AGFD 031
46 P. Devillers, M. Loiliers and J.C. Chartier, Ind.Agricoles et Alimentaires, 81 (1964).
47 S.E. Bichsel and Carpenter, U.S.Patent 3,700,460 (1972).
48 R. Johnson, Jr., 1952 Proc. A.S.S.B.T., 729-732.
49 R.F. Olson, A.M. Sandre and S.E. Bichsel, Meeting of A.S.S.B.T., 1978.
50 R. Wheaton and W.C. Bauman, Ind. Chem. Proc. Dev., 45 (1953) 228.
51 D. Gross, International Sugar Journal, 73 (1971) 298.
52 H.G. Schneider and J. Nikule, Int.Sugar Journal, 77 (1975) 259/294.
53 R. Kunin, Ion Exchange Resin (1985), R.E. Krieger Pub.Co., Malagar, Florida.
54 Upen Bharwada, Sugar y Azucar, August 1987.
55 D.B. Broughton and C.G. Gerhold, U.S. Patent 2,985,589 (1961).
56 K.W.R. Schoenrock, 18 Gen.Assy. of C.I.T.S. (June 1987).

57 O. Adriaensen, La Sucrerie Belge, Vol. 98 (1979).
58 Leif Ramm-Schmidt, Amern.Chem.Soc. Meeting April 5-10, 1987, AGFD 039.
59 M.C. Bennett, S.I.T., 1985, paper No. 519.
60 P. Devillers, Industries Alimentaires et Agricoles (1971)
61 S.E. Bichsel, Proceedings of Tech.Session of Cane Sugar Refin. Res. 1977, 150-161.
62 D. Herve, Industries Alimentaires et Agricoles (July 1987).
63 Pannekett, Industries Alimentaires et Agricoles (1980), 97, 757-760.
64 P. Noynak and G. Bollenback, This Is Liquid Sugar, Yonkers, NY (1966).
65 B. Guerin, Colloque Applexion, 1975.
66 G. Quentin, Zucker, 7 (1954), 407.
67 G. Quentin, Zucker, 10 (1957), 408.
68 K.W.R. Schoenrock, Beet Sugar Technology, 3rd Edition (1982).
69 J.F.T. Oldfield, M. Shore, D.W. Gyte, C.W. Harvey and G.C. Jones, British Sugar Corporation Technical Conference (1978).
70 J.N. Doucerain, Proc. Colloque Applexion, 1975, 95-115.
71 W. Fries and R.W. Walker, Proc. Tech. Sess. Cane Sugar Refin. Res. 1980(pub. 1981).
72 J. Guerin, unpublished (1982).
73 D.S. Martin, W. Hunter and B.W. Drean, Sugar Industry Technologists Meeting, May 198
74 L. Ramm-Schmidt and G. Hyoky, Sugar Ind. Tech. Meeting (1984), paper No. 516.
75 B.F.R. Hickey and M.J. Elliott, Sugar Ind.Tech.Meeting (1987) paper No. 558.
76 D.S. Martin, Sugar Ind.Tech. Meeting (1984) paper No. 508C.
77 M. Cox, Tech. Sess. Cane Sugar Refin. Res. 1980, pub. 1981.
78 R. Celle and D. Herve, Industries Alimentaires et Agricoles No. 78 (1980).
79 Ong Ie Cheong and H. Mussebah, International Soc. of Sugar Cane Tech. (1980).
80 F. Schneider, D. Schliephake and J. Paleos, proc. of the C.I.T.S. (1967).
81 X. Lancrenon, The World Biotech Report 1986, Vol. 2, Part 3.
82 F.E. Rice and S. Osugi, Soil Sci. 5 (1918) 333.
83 E. Mariani, Ann. Chim. Appl. Vol. 39 (1949).
84 G. Bodamer and R. Kunin, Ind. Eng. Chem., Vol. 43(1951) 1082.
85 P.L. Devillers and M. Loilier, Industrie Alimentaire et Agricole, Vol. 75 (1958) 465-470.
86 G. Siegers and F. Martinola, Bayer Technical Bulletin No. 20.394e (1984).

Sumario

En la última década los adelantos en la técnica de intercambio iónico han sido impresionantes. Esto queda ampliamente demostrado por su creciente uso en la industria del azúcar.

Básicamente, las razones de este progreso son:

- Mejores características de la resina.
- Mejor ingeniería del intercambio iónico.
- Mejor control de las plantas.
- Inclusión de tratamiento de aguas residuales en el proceso de intercambio iónico.
- Integración óptima del sistema de intercambio iónico en el proceso general de fabricación.

Se describen brevement ejemplos de aplicaciones comerciales de intercambio iónico (o con mayor exactitud, tecnologia de partículas porosas).
Entre ellos:

- Proceso Gryllus (descalcificación).
- Proceso NRS (descalcificación).
- Descalcificación mediante resina de cationes débiles.
- Desmineralización H-OH de jugo de baja o alta viscosidad (industria de azúcar de remolacha).
- Exclusión de iones para melazas de remolacha.
- Producción de azúcar líquida a partir de jugo de alta viscosidad (industria de azúcar de remolacha).
- Proceso Quentin (industria de azúcar de remolacha).
- Descolorido de licor fino (refinado de azúcar de caña).
- Nuevas operaciones en la química del azúcar, como
  - hidrólisis de sucrosa
  - separación glucosa-fructosa por adsorción cromatográfica
  - refinado del azúcar en lechos mixtos.

Estas numerosas y variadas aplicaciones son evidencia de la importancia y el lugar del intercambio iónico en la industria del azúcar.