

An Evaluation of a Multiple Bed Deionization Process for Beet Sugar Recovery

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Received for publication February 28, 1964

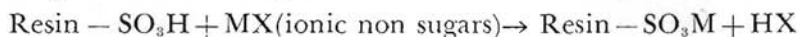
Introduction

The concept of deionization of thin beet juice by ion exchange had appeared only briefly before active programs were initiated by the beet sugar industry to study this process. Throughout the 1940's and early 1950's considerable work was done using the two bed process. Plant trials were completed, ion exchange processes were installed, and some promising results were reported. On the other hand, shortcomings were exposed, various economic factors changed, and many of the ion exchange installations in the United States beet industry were abandoned.

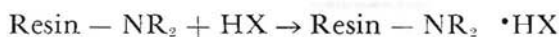
European beet sugar producers followed a similar course during the development stage and since then have successfully adapted IER purification for their juices. For a number of reasons, the process has expanded in many parts of the world. European operations have continued to use the two bed process with various modifications for the processing of beet juices. In addition to a growing number of installations, several elegant special processes employing ion exchange resins either in multiple beds or in mixed beds have appeared and these have received considerable attention during the past few years. The Assalini processes which have been described before this Association are examples of these developments (1, 2)².

It is the intention in this paper to return to the simple, original two bed scheme, the chemistry of which is outlined as follows for ionic non-sugars.

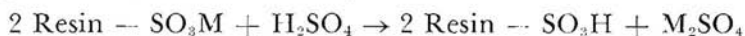
Loading Cation Exchange Resin



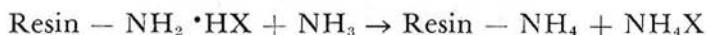
Loading Anion Exchange Resin



Regeneration, Cation Exchange Resin



Regeneration, Anion Exchange Resin



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² Numbers in parentheses refer to literature cited.

Only two fundamental modifications in processing will be introduced here. Instead of a single cation exchange column in the initial stage, the juice is to be passed through two columns of cation exchange resin. The first is to pick up the inorganic cations. The second is to pick up the amino acids thus relieving the anion exchange resins of that role. Secondly a high capacity weak base anion exchange resin will be used to take advantage of greater regeneration economics than were realized when strong base resins or lower capacity weak base anion exchange resins were used.

Modern ion exchange resins have been developed having high capacity and improved physical and chemical resistance to sugar liquors. While in principle, they perform the same chemical changes as those found in earlier resins, the new resins are known to perform these exchange reactions with greater efficiency. In this paper, the properties of commercially available ion exchange resins are outlined and some of their properties are described in connection with their use in sugar juice treatment.

Cation Exchanger Selection

In this process, the cation exchange resin operates in the hydrogen circle to convert non-sugar salts to their free acids. The process is somewhat more involved however than simple exchange and neutralization due to the nature of the non-sugars in the sugar liquors. Figure 1 shows a typical breakthrough curve for a 14° Brix second carbonation juice of 91% purity. This juice has 135 grams per liter of sucrose and 10.8 grams of non-sugars. If it is assumed that $\frac{1}{2}$ the non-sugar salts are inorganic salts having an equivalent weight of 100, the concentration of salts will be 0.108 equivalent/liter or about 5400 ppm as CaCO_3 . The equivalent weight of the non-sugars has been determined from a variety of tests with Amberlite IRA-68, and this will be discussed in the section on anion exchangers.

It is apparent from Figure 1 that the inorganic cations are present as salts of weak acids since a large amount of buffering exists in the system. The titration curves for a strong acid (HCl) and a typical weak acid (acetic) are plotted to demonstrate this buffering effect in a qualitative sense. These curves are calculated based on the assumption that actual breakthrough for ion exchange occurred at 15 bed volumes, a figure reached by using a column capacity of 1.6 eq/liter which is typical for a fully regenerated bed of Amberlite IR-120.

$$\text{Capacity} = \frac{1.60}{0.108} = 15 \text{ bed volumes}$$

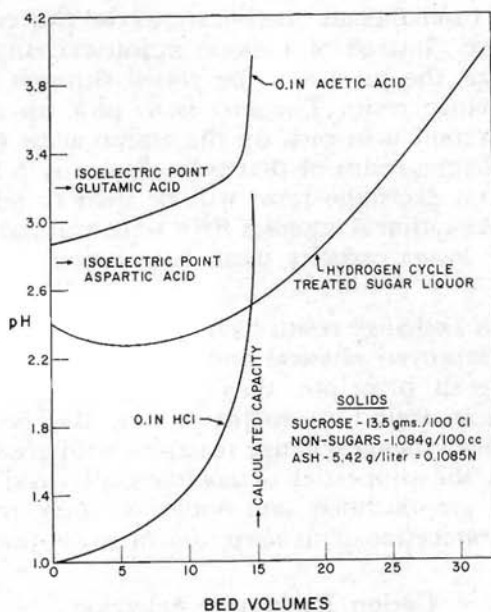


Figure 1.—Hydrogen cycle treatment. 2nd carbonation juice. 14° brix, 91% purity.

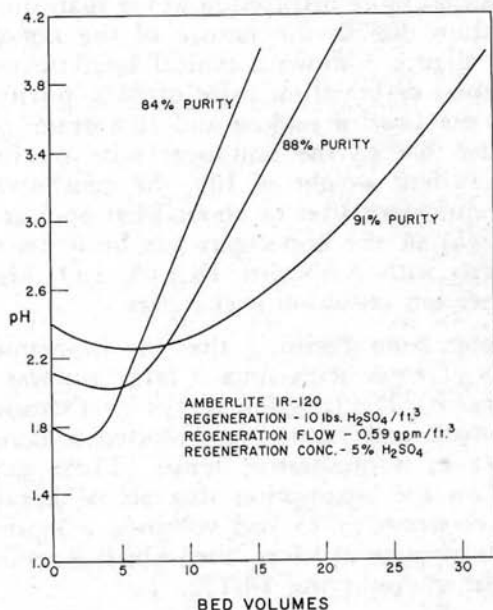


Figure 2.—Hydrogen cycle treatment, 2nd carbonation juice. 14° brix, Ambrelite IR-120H.

In Figure 2, three curves have been plotted showing the effect of purity on the effluent pH curve. The curves have been based on laboratory results on various juices. Possible variation due to changes in the ash to total non-sugar ratio cannot be predicted without extensive data on this subject. The extensive buffering evident in pH breakthrough curves is due in a large degree to the amino acids which are present in the juice. Glutamic acid, pyrrolidone carboxylic acid (PCA), aspartic acid, tyrosine, leucine, and isoleucine are usually found. The quantity of these materials in some typical beet liquors has been previously reported (3, 6).

The amino acid content of a typical beet sugar juice amounts to 15-20% of the total non-sugars and represents 30-40% of the organic non-sugars. It is evident that these represent major constituents in the liquor. Their recovery is worthy of consideration and their properties will certainly have an important bearing on the endpoint of the cation exchange cycle.

In this study it has been considered desirable to operate the cation exchange system in what is called a merry-go-round operation. This permits the recovery of the amino acid fractions at the same time permitting full loading of the cation exchange resin. Furthermore, it provides for the accumulation of the amino acids on the cation exchange resin, rather than requiring additional volumes of the more expensive anion exchange resin.

This merry-go-round system has as its aim the accumulation of the nitrogenous fraction on one bed. It is necessary to balance the cycle so that the bed which receives the amino acids can operate until it is well loaded with the amino acid fraction. At any given moment, two columns of cation exchange resin are operated in series with the amino acids being accumulated on the second column. A question to be answered is how much amino acid can be loaded on the second column before the effluent pH rises above 3.5 at which point the glutamic acid will begin to leak. To discuss this, consider first an "average" beet sugar liquor which is assumed to be as follows:

Table 1.—Composition of 91 purity beet liquor.

Component	Grams/liter	Equivalent Weight	Eq./liter
Sucrose	135	—	—
Inorganic non-sugars	5.42	50 (average)	0.1085
Organic non-sugars	5.42	—	—
Betaine	1.30	119	0.0109
Amino acids	1.41	147	0.0096
Nitrogenous fraction/ash	—	—	0.19

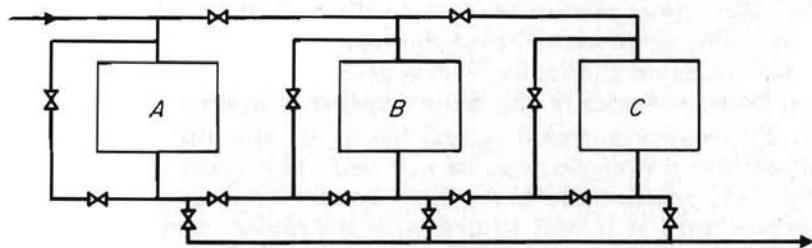
These figures indicate that the ion loading due to amino acids is about 20% of the inorganic non-sugars. For calculation

purposes, it should be assumed that the exchange of amino acids and other nitrogenous materials follow the ratios in Table 1, although experimental evaluation will be required for a firm recommendation.

An examination of the pH curve in Figure 1 shows the importance of careful operation to insure full utilization of the cation and anion exchange resins. To prevent dumping of amino acids, it is necessary to stop the loading before the effluent pH rises above 3.5. The column which collects the amino acids can be used in connection with 2 or more other columns since the columns picking up the inorganic ions will undoubtedly be exhausted before the column picking up the amino acids. Two examples of merry-go-round systems of this type, one involving three columns, the other a total of four cation exchange columns are shown in this paper.

Three column merry-go-round

The following description will serve to outline a recovery procedure based on three columns in the cation set.



MERRY - GO - ROUND FLOW DIAGRAM

The stream of second carbonation juice will pass through column A, then through column B, both of which will load until the pH of the effluent of A raises to 3.8-4.0. Column B now contains about 20% of its exchange sites in combination with amino acids and betaine. It is also likely that other organic non-sugars will be held but it is not known in exactly what portion. This area requires more study. Once the columns have reached this condition, the A column can be dropped off for regenerations. The C column is started up and the flow is now through C to B. This process continues until the pH of C effluent reaches 3.8-4.0. Column B now is about 40% loaded with amino acids. C is then regenerated and A operated through B until a similar breakthrough occurs. Regeneration of B can now be accomplished while loading in a cycle of low flow rate

continues on C. Once A or B is regenerated, either one can be used to accumulate the amino acids on the next cycle.

Four column merry-go-round

With a three column merry-go-round system it is necessary to operate an occasional cycle at low flow to keep the system from getting out of phase. It is likely that a fourth column would greatly assist in this matter. It is suggested that a four column merry-go-round should be used in cases where continuous operation with amino acid recovery is practiced.

The ultimate recovery of the amino acids is involved in the elution of column B with a base. In Europe 10% ammonium hydroxide or NaCl is used for this step. The recovery of amino acids from beet sugar plants is practiced in Europe as a byproduct industry. The effluent mixture is heated with lime and the ammonia recovered after separation of the insoluble calcium glutamate. The precipitates are collected at a central factory where the various fractions are purified and recrystallized for sale as food supplements.

Regeneration efficiency

The expenditure of acid for regeneration is a major factor in the operation of the cation exchanger. Relatively little work has been done on this subject in the sugar industry but certain effects can be estimated accurately in regard to acid consumption. The exchange is largely hydrogen for potassium and in monovalent exchange, leakage can be expected which will affect materially the shape of the breakthrough curve. These factors have been evaluated for Amberlite IR-120 in Figure 3 which shows the relationship between capacity (bed volumes) and acid usage. Figure 4 gives an estimate of the monovalent cation leakage as a function of regeneration level.

Figure 4 shows breakthrough curves for various purity liquors being treated with Amberlite IR-120 regenerated at 10 lbs. H_2SO_4/ft^3 . These curves are quite typical and the values check reasonably well with the estimated leakage of about 8% in the flat range prior to breakthrough.

Sucrose Losses

Since the major purpose of ion exchange treatment of beet juice is the recovery of sucrose, any losses of sucrose in the process would cause much concern. In the cation exchange treatment there are two possible sources of sugar loss. The most significant are losses due to displacement and other mechanical handling operations. The second most important loss is involved with catalytic inversion of the sucrose. Careful consideration shows that these causes for sugar loss are not sufficient reason for rejecting ion exchange treatment.

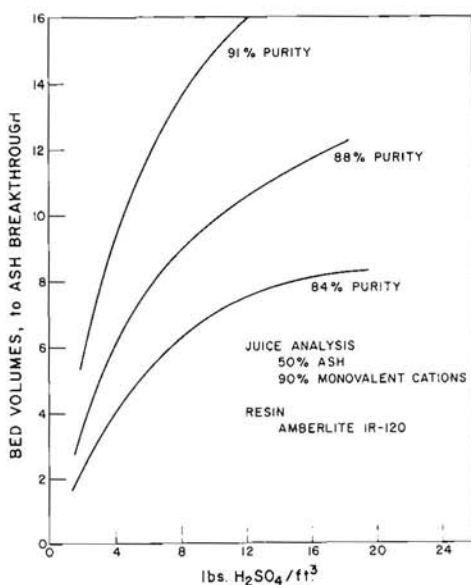


Figure 3.—Relationship between capacity and regeneration level for second carbonation juice.

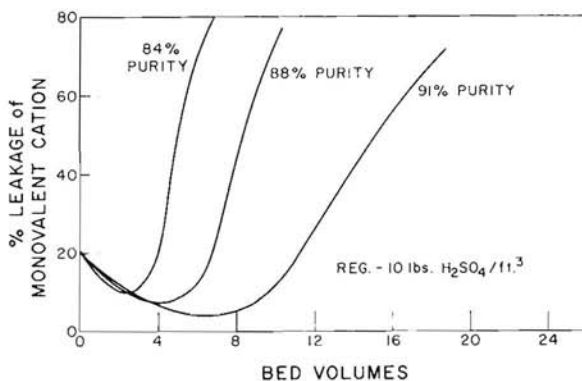


Figure 4.—Potassium leakage as a function of regeneration level and juice purity. Amberlite IR-120.

Losses Due to Displacement

In arriving at the loss of sugar due to the displacement processes, estimates must be made on the basis of empirical field data due to the variables of design and operating conditions. In general, the displacement will be a function of bed void volume, sugar liquor density, liquor viscosity, and resin bead porosity. In addition, liquid heights in the column, flow rates

and under-drain volume will play an important part in the displacement process. From a practical standpoint, there are two problems, namely, the added cost of evaporating diluted juice and the loss of sugar in sweet waters resulting from continued rinsing.

The idealized displacement involving no kinetic considerations would be a sharp step function which would occur when the displacement had filled the bed and underdrain voids. Sucrose molecules which have diffused into the resinous structure reduce this sharpening effect and require time to diffuse out at the end of the displacement. These effects result in a round frontal displacement with a tailing off at the end of the displacement.

The concentration of the sugar liquor plays an important role during "sweetening on". A thick liquor will tend to diffuse down the column under the influence of gravity. This will result in an irregular displacement within the bed. Displacement of a heavy liquor by water in a "sweetening off" step may present a drag problem due to viscosity but it is possible to correct this by using hot water. Flow rate can play an important part in these matters. Generally, flow should be as slow as practical but the improvement in displacement is usually not considerable below about $\frac{1}{2}$ gpm/ft³.

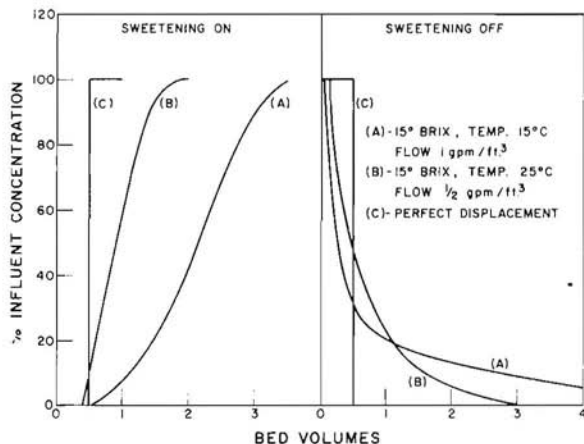


Figure 5.—Displacement curves, plant studies.

In Figure 5 are drawn displacement curves for a typical operation in a beet sugar factory. These curves indicate the influence of flow rate but do not represent an optimum situation in regard to this important operating function. Detailed studies of the variables have been carried out.

The displacement in juice treatment is an important one from an economic standpoint. It is apparent that "sweeten-

ing on" results in a slight overall dilution when dilute juices are involved. This is not serious in average purity liquors but could become important for low purity liquors where runs will be short. Losses are more important during the "sweetening off" step where a considerable tailing may result. These liquors may be used for makeup water to the diffusion station and for the water used for slaking the lime as shown in a later section.

The dilution of typical thin juice as a function of purity has been estimated for a typical bed displacement step in Table 2. It is assumed that displacement is accomplished at $\frac{1}{4}$ gpm/ft³, and that the liquor is of constant concentration. No estimate of equipment voids are allowed for in this estimate.

Table 2.—Displacement dilution of sugar liquor, Flow Rate— $\frac{1}{4}$ gpm/ft³.

Purity %	Concentration Brix	Temperature °F	Bed Volume treated juice net	Total bed volumes (with dilution)	Dilution %
91	14	50	16	18.3	12.8
88	14	50	11	13.3	18.5
84	14	50	8	10.7	25.0

Although a number of factors in this study show that ion exchange treatment is most economical when one is working with low purity juices, in this instance the advantage of working with high purity liquors becomes apparent. It is expected that the dilution water can be returned to the diffusion plant. Therefore, the values recorded above do not represent additional actual evaporator load. The detailed operation of this phase of the plant will be estimated in the sections on economics and plant design.

Invert Formation

Inversion during cation exchange treatment can be broken down into two separate but related processes designated here as heterogeneous and homogeneous inversion. The inversion of sucrose to fructose and glucose is catalyzed by hydrogen ion. The exchange sites when converted to the hydrogen form provide a source of highly acidic materials which give a typical heterogeneous catalytic reaction, when the sucrose diffuse into the resin beads. During the exchange process, hydrogen ions are also liberated from the resin. These ions enter the solution where they are available to act as homogeneous catalysts for the inversion.

Existing data on several cation exchangers have been evaluated and inversion estimated as a function of contact time and temperature. These values are based on the assumption that pure

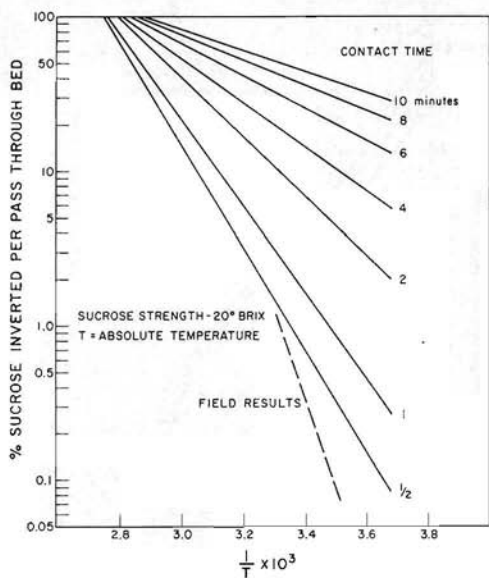


Figure 6.—Inversion with Amberlite XE-100 as function of temperature and contact time.

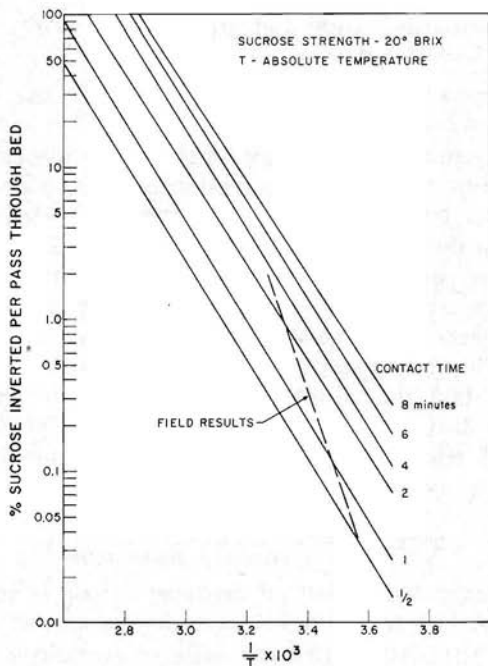


Figure 7.—Inversion with Amberlite IR-120 as function of temperature and contact time.

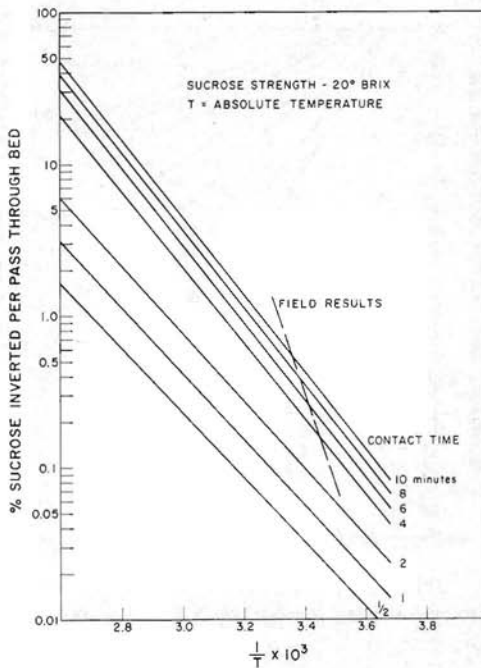


Figure 8.—Inversion with Amberlite 200 or IR-124 as function of temperature and contact time.

sugar solutions are being treated so that only the heterogeneous reaction is involved.

The curves in Figures 6, 7, and 8 show the amount of inversion which will occur when a pure sugar solution at a certain temperature contacts a bed of cation exchanger for a definite period of time. It is assumed here that a 20° Brix liquor is being treated. For most thin juices it is expected that Figures 6-8 will give a reasonable description. Less invert would be expected if a more dilute juice were used and, of course, a greater amount would invert if the liquor were of appreciably higher concentration. A plot of field data for which, unfortunately, the contact time is unknown, is drawn in each graph to show that the calculated values are of the same order of magnitude as those from the field. The flow rates are expressed as contact times.

$$\text{gpm/ft}^3 = \frac{7.48}{\text{contact time (min.)}}$$

Since the concentration of hydrogen ion is related directly to the rate of inversion, it is necessary to measure the amount of time that the cation effluent will exist before neutralization by the anion exchanger. In Figure 9 data from Sadter are plotted as summarized by Payne (5), which enables inversion due to

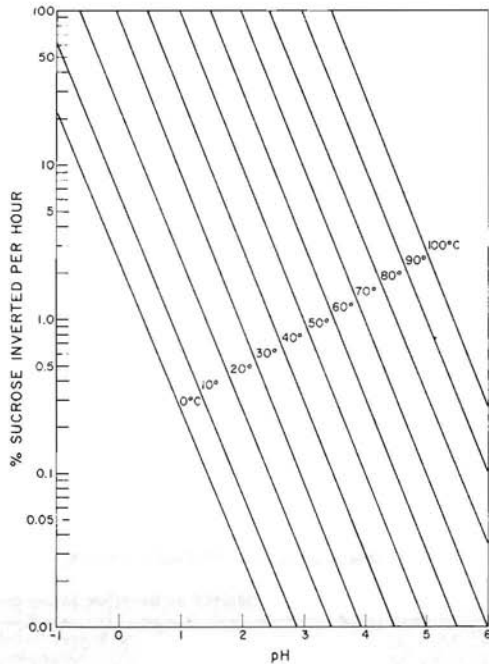


Figure 9.—Homogeneous inversion. Data of Sadter Honig, Principles of Sugar Technology. Volume 1—page 448.

homogeneous catalysis to be estimated. While the amount of inversion by homogeneous catalysis is not as great as that caused by a fully regenerated bed, it must be taken into account.

The graphs developed for inversion can be used quite effectively to calculate inversion for a variety of process conditions. There are four process variables which deserve consideration. These are: (1) Effect of temperature in a standard two bed system; (2) Effect of flow rate in a standard two bed system; (3) Effect of a merry-go-round operation and (4) Effect of regeneration levels. These situations are examined in the following sections.

Effect of temperature

A standard operation with a 90% purity liquor at 15° Brix which will contact a single bed of cation exchanger at 4 minute contact time (1.87 gpm/ft³) will be assumed. The acid generated will pass on to a bed of anion exchange resin. In Table 3, the amount of inversion estimated from Figures 6-9 is listed for the various resins at several temperatures. A sample calculation follows:

Amount due to homogeneous catalysis

At the start of the run the bed is completely in the acid form and there is free space equal to the volume of juice in the cation exchange column above the anion exchange resin. The pH generated is 2.1 (Figure 2).

Time through cation bed = 4 minutes

Time in piping and above anion exchange bed = 4 minutes

Temperature = 0°C (using Figure 9)

$$\% \text{ sucrose converted} = \frac{8}{60} (0.02) = 0.00267\% \text{ inverted}$$

Since the cation exchanger will be exhausted at about the same rate (geometrically) as the anion exchanger, the void displacement will remain relatively constant as the run progresses so that the inversion due to homogeneous catalysis will remain roughly constant throughout the run.

Amount due to heterogeneous catalysis

Using Amberlite IR-120 and the contact time of four minutes,

Table 3.—Summary of invert estimated as function of contact time.

Temperature	Position on run	Contact Time	Homogeneous catalysis	% Invert based on sugar solids heterogeneous catalysis		
				Amberlite XE-100	Amberlite IR-120	Amberlite IR-124
0°C	Start	8	0.006	21.5	0.25	0.073
"	Middle	"	"	5.80	0.12	0.045
"	3/4 quarter	"	"	1.55	0.075	0.026
"	Start	2	0.005	1.52	0.072	0.026
"	Middle	"	"	0.26	0.027	0.015
"	3/4 quarter	"	"	0.085	0.016	0.009
20°C	Start	8	0.056	35.0	1.80	0.33
"	Middle	"	"	14.0	0.70	0.20
"	3/4 quarter	"	"	5.4	0.50	0.90
"	Start	2	0.014	5.30	0.50	0.092
"	Middle	"	"	1.45	0.19	0.053
"	3/4 quarter	"	"	0.60	0.11	0.030
40°C	Start	8	0.62	53.0	9.0	1.30
"	Middle	"	"	28.0	4.5	0.75
"	3/4 quarter	"	"	16.0	2.6	0.29
"	Start	2	0.155	16.0	2.6	0.28
"	Middle	"	"	5.50	1.10	0.16
"	3/4 quarter	"	"	3.40	0.53	0.09
60°C	Start	8	6.66	75.0	34.0	3.8
"	Middle	"	"	55.0	18.0	2.2
"	3/4 quarter	"	"	39.0	9.9	0.76
"	Start	2	1.66	39	9.8	0.76
"	Middle	"	"	22	4.40	0.42
"	3/4 quarter	"	"	15	2.50	0.23
80°C	Start	8	66.4	100.0	100.0	10.0
"	Middle	"	"	100.0	64.0	5.6
"	3/4 quarter	"	"	90.0	34.0	1.8
"	Start	2	16.6	90.0	33.0	1.8
"	Middle	"	"	65.0	16.0	0.96
"	3/4 quarter	"	"	53.0	4.0	0.54

the heterogeneous catalyzed inversion for various parts of a run can be estimated by reference to Figure 7.

Start of run —Contact time (acid resin) = 4 minutes
Inversion = 0.12%

Middle of run —Contact time (acid resin) = 2 minutes
Inversion = 0.075%

$\frac{3}{4}$ of run —Contact time (acid resin) = 1 minute
Inversion = 0.026%

In Table 3, the effect of contact time is examined in the same manner for a variety of resins, temperatures and contact times.

Effect of merry-go-round operation

It becomes apparent that the time during which sugar liquor is in contact with regenerated cation exchanger, is very important in so far as invert formation is involved. For example, the merry-go-round operation would result in an increased time that the liquor would exist in contact with acid resin. If one were to compare the invert formation in a conventional two bed system vs. a merry-go-round operation containing two cation exchanger beds and a double anion exchanger, we would expect the contact time to be doubled.

The effect of a merry-go-round system on invert has been examined for a four minute contact with Amberlite IR-120, a conventional, commercially available cation exchanger of average crosslinkage. These estimates are given in Table 4.

Table 4.—Effect of merry-go-round operation on heterogeneous catalyzed invert formation, 90% purity - 15° Brix Amberlite IR-120H.

Temperature	Contact Convention	% Invert
C°	Minutes	
0	4	0.07
0	8	0.125
20	4	0.40
20	8	0.75
40	4	2.2
40	8	4.4

These figures show that the merry-go-round operation will roughly double the invert formation over that experienced for a conventional two bed system.

On the other hand, numerous studies show that Amberlite 200 and Amberlite IR-124 give less than half the inversion noted for Amberlite IR-120. At high temperatures the homogeneous catalytic reaction will play an increasingly important role so that inversion will tend to increase at a rate greater than that indicated above. Variations in the process can be examined by the methods developed in the previous sections.

Effect of regeneration level

The effect of regeneration level on the amount of invert formed is of interest. Theoretically, the effect will depend on the regeneration efficiency of the acid which in turn is a measure of the amount of hydrogen form available for catalytic inversion. This may be translated to the contact time that the liquor has with the hydrogen resin. The curves used in this report are based on highly regenerated resin (20 lbs sulfuric acid/ft³).

A contact time corrected for regeneration efficiency can be employed to predict the amount of invert formation. The calculation of corrected contact times is illustrated in Table 5.

Table 5.—Effect of cation exchanger regeneration efficiency on invert formations Amberlite IR-120, 90% purity - 15 Brixes.

Regeneration Level lbs H ₂ SO ₄ /ft ³	% Saturation Capacity	Time, minutes	
		Initial contact (saturation)	Corrected contact time
2.5	31	4	1.24
5	49	4	1.98
10	72	4	2.88
15	76	4	3.04
20	81	4	3.25
25	83	4	3.3
Full	100	4	4.0

These concepts can be used to derive a curve for the performance of Amberlite IR-120 when operated at 5 lbs/ft³ using a contact time of 6 minutes. The temperature for the run is 15°C.

Fully regenerated bed:contact time = 6 minutes

$$\text{So at 5 lbs H}_2\text{SO}_4/\text{ft}^3, \text{ Contact time} = \frac{1.98 \times 6}{4}$$

$$= 2.9 \text{ minutes contact at the start of the run.}$$

Heterogeneous inversion = 0.28% of sucrose solids.

Homogeneous Catalysis = 0.07 (6/60) = 0.007% of sucrose solids.

Total = 0.28% heterogeneous inversion of sugar in liquor.

50% point: % heterogeneous inversion = 0.14%

% homogeneous inversion = 0.007

Total = 0.147% of sugar solids

75% point: % heterogeneous inversion = 0.07

% homogeneous inversion = 0.007

Total = 0.077% of sugar solids.

The results of such calculations have been plotted and compared with actual measurements in Figure 10.

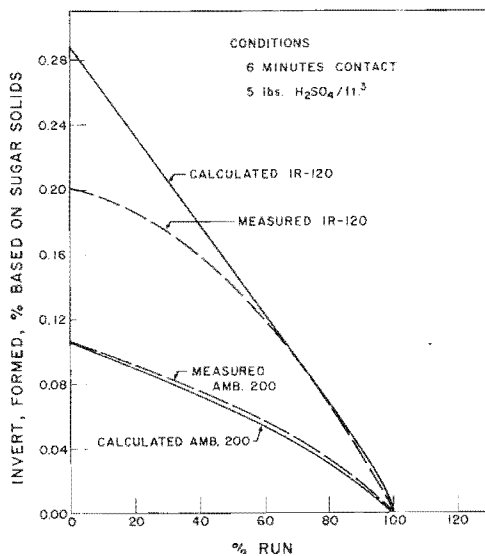


Figure 10.—Comparison of calculated invert formation with experimental values.

The results of these estimates for inversion show that the calculated values are fairly consistent with those obtained by experimentation. The calculation methods give a somewhat higher value but these can easily be accounted for by particle size variation, failure of the displacement scheme due to channeling, etc.

Anion Exchange Resins for Sugar Treatment

Several anion exchange resins have been studied for sugar processing over the years. Amberlite IRA-68 has been found to be a very suitable resin for this application due to its high capacity for non-sugars and its ability to decolorize the liquors to a high degree. Its high loading is a chief virtue but its stability against fouling is also important. Also Amberlite IRA-68 is more resistant to thermal degradation than strong base anion exchange resins. Since this resin shows some instability at very high temperatures, it is necessary to examine this variable in regard to resin life.

In the following sections it will be assumed that Amberlite IRA-68 is used after a merry-go-round operation on Amberlite IR-120. The average cation endpoint will be assumed to be below pH 2.6. It will be assumed that the anion exchanger is regenerated with ammonia but that the ammonia is recovered with lime. Column studies have been employed to define capacity and effluent quality as a function of juice purity.

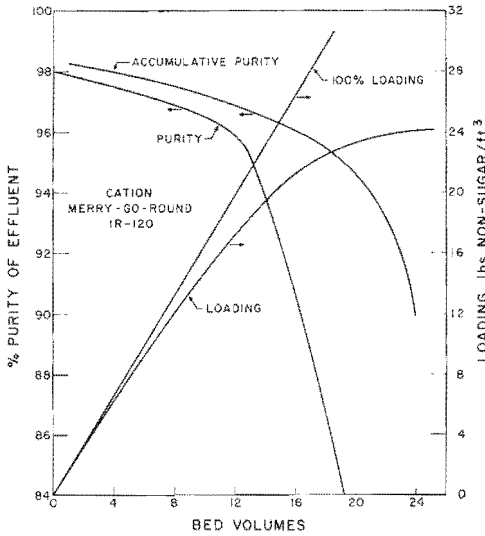


Figure 11.—Amberlite IRA-68 effluent characteristics. Juice of 81.4% initial purity.

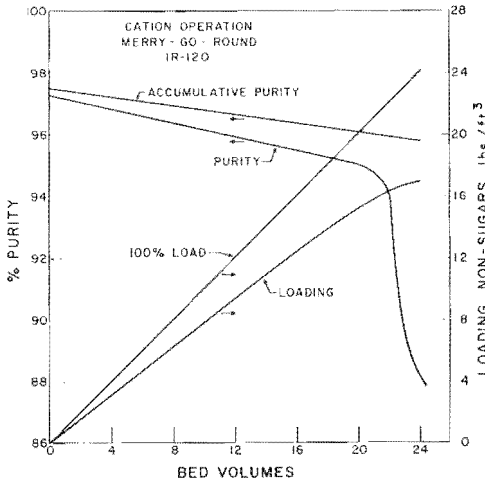


Figure 12.—Amberlite IRA-68 effluent characteristics. Juice of 88.2% initial purity.

Capacity as a Function of Purity

The capacity values of Amberlite IRA-68 have been related to the characteristics of the sugar juice. It is not the intention to develop this matter in detail at this time but a few examples of a typical operation will be used to illustrate a relationship between influent purity and capacity.

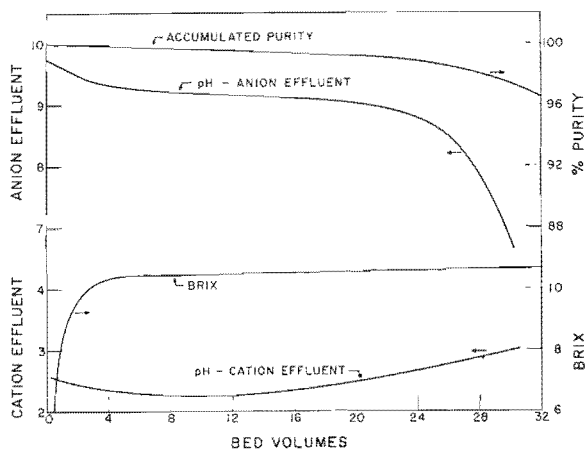


Figure 13.—History of the effluent from Amberlite IRA-68 in deionization of a 91% purity juice loading 19.2 lbs/ft³.

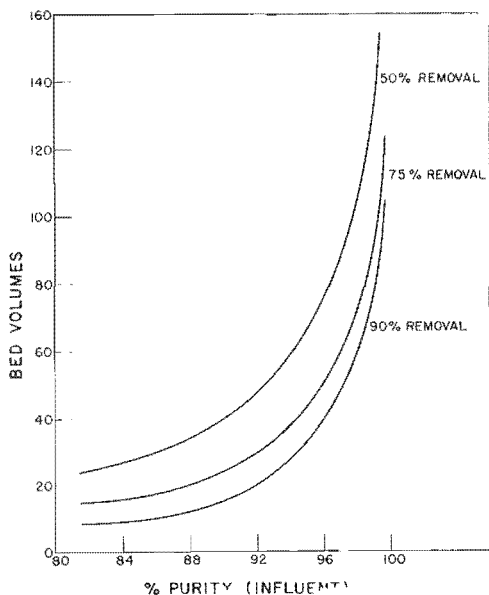


Figure 14.—Effect of juice purity on capacity of Amberlite IRA-68 with merry-go-round operation of Amberlite IR-120 beds.

In Figure 11 we show a typical run on a low purity juice (81.4% purity) and Figure 12 shows a run on 88% purity juice. The most interesting results were obtained on a typical 91% purity beet juice in France and these results are summarized in Figure 13.

The utilization of these results in a general manner is required if an estimate of the capacity of Amberlite IRA-68 is to

be obtained for average sugar liquors. For this purpose the accumulative curves for purity were plotted and values picked off to construct a plot of bed volumes treated to a purity endpoint as a function of influent purity. Within the purity ranges available the curves are plotted in Figure 14. The curves have been extended toward 100% purity by extrapolation.

The capacity of Amberlite IRA-68 is about 1.70 equivalents/liter. This figure will permit an estimate of the capacity provided the equivalent weight is known. Unfortunately, the average equivalent weight of non-sugars vary considerably so that a study is required to fix the equivalent weight.

The results shown in Figures 11-13 can be used to calculate equivalent weights for these particular runs and this is shown in Table 6. These values are approximated from the loading data and the composition of the liquors. The values compare favorably with those obtained by an accurate analytical procedure.

Table 6.—Equivalent weight estimates for typical beet liquors, Amberlite IRA-68.

% Purity	Capacity lbs. non-sugar/ft ³	Equivalent capacity lbs. Eq/ft ³	Equivalent weight lbs. or grams
81.4	24	0.106	226
88.2	17	0.106	160
91	19.2	0.106	181

Regeneration Efficiency

The regeneration of low molecular weight acids from Amberlite IRA-68 is not difficult. Complete regeneration of the sites results from a contact with an equivalent amount of ammonium hydroxide or caustic. For a fully exhausted bed (1.7 meq/liter) a regeneration level of 1.75 eq/liter is suggested. In English units, the requirement becomes 4.37 lbs NaOH/ft³ or 1.86 lbs NH₃/ft³.

The best recommendation is to regenerate with ammonia and then to recover the regenerant with lime. Caustic is normally not employed due to its cost.

Effluent Characteristics

An examination of the effluent curves shows a gradual leakage of non-sugars which increases progressively until breakthrough occurs. It should be recognized that the curves shown in Figures 11-13 represent almost complete breakthrough. The cycles were so operated to obtain complete utilization of the resin. The procedure results in a 50% reduction in non-sugars when calculated on an accumulative basis.

A consideration of the magnitude of the capacity values in terms of bed volumes treated would show that accumulative purity will not change sufficiently to be used for control pur-

poses. It appears that a breakthrough point based on effluent pH is the most suitable one for a sugar application.

Brief mention should be made concerning the non-sugars which are leaking through the bed. It is expected that very weakly ionized acids and non-polar non-sugars would pass through the bed without being retained by ion exchange mechanisms. While it is possible that some of these materials will be held by absorption, no allowance has been made for such process. It is likely that the slight leakage, almost from the beginning of the runs, has been caused by large molecular weight acids and non-polar substances. The exact nature of these components has not been properly established and their effect on the sugar application has not been measured in these studies.

Some interesting work on liquors containing large amounts of invert has shown that these acidic sugars are held at least to some degree on partially exhausted beds of Amberlite IRA-68. This interesting discovery has not been considered in this paper but may be useful in removing invert from high quality liquors.

Thermal Stability of the Anion Exchanger

No problem is expected in regard to the thermal stability of Amberlite IRA-68 in the cold multiple bed process. However, the importance of this property cannot be overlooked and the question of optimum operating temperature requires an answer. In general, it is expected that the process temperature will be fixed by the formation of invert and not by resin instability.

Considerable information has been collected on the thermal stability of Amberlite IRA-68. The mechanism of thermal degradation follows first order reaction kinetics. This result was useful in extrapolation to the low temperature values. The magnitude of the temperature effect on resin half life is summarized in Table 7.

Table 7.—Thermal stability of Amberlite IRA-68, Half Life values for IRA-68.

Temperature °C	K value Days ⁻¹	Half/time Days	Comment
105	1.38×10^{-2}	50	measured
100	9.75×10^{-3}	71	measured
90	5.83×10^{-3}	119	measured
70	1.5×10^{-2}	460	measured
50	3.0×10^{-4}	2,300	extrapolation
40	1.3×10^{-4}	5,350	"
20	1.9×10^{-5}	36,300	"
10	6.6×10^{-6}	105,000	"

Anion Exchange Resin Life

It must be emphasized that thermal life may not be related directly to actual life except at high temperatures. It is not ex-

pected that Amberlite IRA-68 will last 60,000 days (165 years) if operated at 15°C. Other factors will be involved such as oxidation of the resin, fouling with organic matter and operational attrition. Practice has indicated an average life of anion exchangers at 1×10^6 gallons of treated liquor per cubic foot of resin. A more conservative figure will be used in the later economic evaluation.

Selection of Process and General Assumptions

The process that has been discussed is one which involves efficient removal of cations from second carbonation juice by passing it through a cation exchange system utilizing Amberlite IR-120 (H). The acidified juice is then passed through Amberlite IRA-68 for the removal of anions and color bodies. Since Amberlite IRA-68 is a weakly basic anion exchanger, it is not surprising that the best loading is accomplished in a feed liquor which has been converted completely in the cation exchange installation. Constancy of effluent composition from the cation exchange components can best be accomplished in a feed liquor which has been converted completely in the cation exchange installation, and this can best be accomplished by a merry-go-round operation of the units. This procedure will also help in the recovery of amino acids.

There are several places where this process can be performed in the sugar production flow sheet. It is believed, however, that best performance would occur after the second carbonation step. This selection of feed liquor would insure that the juice is of good quality, well established in regard to colloids, and yet not too viscous. It is undesirable to heat liquors being passed through a multiple bed system of this type and consequently, dilute liquors are desirable. Generally, it is undesirable to force heavy liquors through ion exchange beds under pressure. By the way, pressure drop in an ion exchange bed is a function of flow rate, resin particle size, and viscosity. The pressure drop increases almost linearly with the viscosity of the flowing liquor.

An examination of the cumulative purity curves on the treated juice versus the instantaneous effluent curves clearly shows that considerable difficulty will result if blending of the effluent was not employed to deliver a treated liquor of constant purity to the evaporator. To avoid the problem of boiling high purity unbuffered liquors which would degrade rapidly in the evaporators, one might employ a surge tank to allow the mixing of the effluent from the anion exchange installation or one might blend in some untreated juice.

For the purposes of the calculation given in this paper, it shall be assumed that the temperature is controlled at 15-20°C and that the flow rate is 2 gpm/ft³. Under these conditions, inversion will be of the order of 0.2 - 1.0% depending on the regeneration level of the cation exchanger and the method of operation. The information on the invert formation has been derived from theoretical considerations and data obtained in the field and in the laboratory. For the purposes of this calculation, a figure of 1.0% appears to be conservative for both invert and mechanical losses.

Development of the Process

The multiple bed process will be evaluated by a series of calculations based on typical plants. The initial evaluation will be with a 6,000 ton per day plant having a juice of variable purity. The details of the calculations are as follows (4):

Quantity of beets per day = 6,000 tons

Composition 14.97% sugar on beets
 0.39% sugar on beets pulp loss.
 0.02% sugar on beets lime, flume loss.
 14.97-0.41 = 14.56% sugar on beets in the
 juice.

Solids in juice = 14.0° Brix

Purity = 85.5% based on solids

Tons of sugar in juice/day = 6000 × 0.1456 = 874 tons

Tons solids in juice/day = $\frac{874}{0.855}$ = 1021 tons

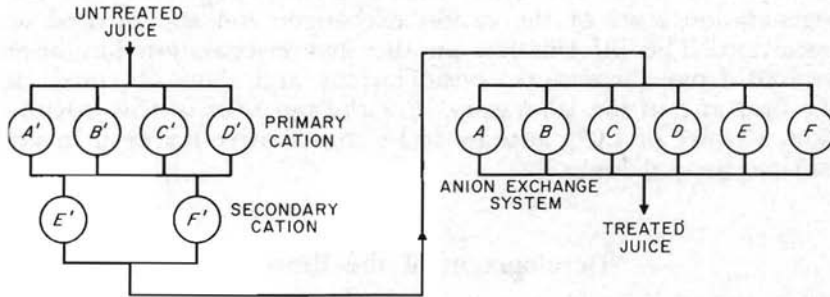
Tons thin juice/day = $\frac{1021}{0.14}$ = 7300 tons = 1.66 × 10⁶
 gallons

Flow = $\frac{1.66 \times 10^6}{24 \times 60}$ = 1150 gallons/minute

Weight in non-sugars = 1021 - 874 = 147 tons/day = 2.94
 × 10⁵ lbs/day

Ion exchange plant

A typical but not optimized system has been used as outlined in the diagram.



SCHEMATIC DIAGRAM OF ION EXCHANGE SYSTEM

Cation exchange system

Cation Exchange Resin—Amberlite IR-120 in six beds.

Capacity—8.5 bed volumes/cycle on a single bed based on laboratory data or say an average of 16.5 bed volumes on each primary bed in a merry-go-round operation. Assume each primary bed is used 6 times/day.

$$\text{Volume} = \frac{1,660,000 \text{ gallons}}{7.46 \times 16.5} = \frac{1,660,000}{123 \text{ gallons/ft}^3} = 13,500 \text{ ft}^3$$

of resin required/day.

$$\text{Volume per Bed} = \frac{13,800}{6 \times 4} = 560 \text{ ft}^3/\text{bed based on a cycling}$$

schedule.

$$\text{Flow Rate} = 2 \text{ gpm/ft}^3$$

Amberlite IR-120 Inventory = $6 \times 560 = 3360 \text{ ft}^3$ resin installed.

$$\text{Regenerant Requirement} = 7.5 \text{ lbs H}_2\text{SO}_4/\text{ft}^3.$$

Anion exchange system

Anion Exchange Resin—Amberlite IRA-68 in six beds.

Capacity—22 bed volumes based on laboratory data.

$$\text{Volume} = \frac{1,660,000}{7.46 \times 22} = \frac{1,660,000}{164} = 10,000 \text{ ft}^3 \text{ Amberlite}$$

IRA-68 required in 24 hr day.

$$\text{Volume per Bed} = \frac{10,000}{6 \times 4} = 420 \text{ ft}^3/\text{bed}$$

Amberlite IRA-68 Inventory = $6 \times 420 = 2520 \text{ ft}^3$

Regenerant Requirement = $1.8 \text{ lbs NH}_3/\text{ft}^3$.

Capital and Depreciation Costs

The cost of ion exchange equipment varies roughly as the resin bed volume according to the empirical formula

$$\text{cost} = 200 (\text{Bed Volume})^{0.7}$$

In addition to the initial outlay, installation cost is usually about equal to the equipment cost less resin. Depreciation of installed equipment can be figured at 5 years under normal conditions although an actual life of 20 years is not unusual for well maintained installations.

The depreciation of resin cost is a difficult matter to calculate. The experience with cation exchangers would lead to the conclusions that treated volumes of the order of 2×10^6 gallons per cubic foot would be a reasonable value. Field knowledge of anion exchanger stability would indicate a life ranging between 500,000 and 1,000,000 gallons per cubic foot. These figures can be used to arrive at a life for these components: 4,070 days for Amberlite IR-120 and 3,030 days for Amberlite IRA-68. However, this intuitively seems to be too long and a five year (100 days/operating year) depreciation figure on the resin and on the equipment will be utilized. This appears conservative on the basis of field experience.

Labor requirement

The labor required to operate a given plant will vary with the amount of automation used and with the composition of the beet juice being processed. A technically trained person will be required for about $\frac{1}{3}$ to $\frac{1}{2}$ of an 8 hour shift. The shift group would be usually 2 men with some mechanical help.

Other considerations

An evaluation of the deionization process requires examination of its effect on auxillary factors including cooling, sweet water quantities, waste treatment, and steam requirements. These matters are reviewed in the following sections.

Cooling costs

The need for the cooling of juice is an important requirement due to invert formation in the cation exchanger bed and also possible thermal instability of the anion exchanger. Cooling costs are much a function of plant location and availability of large quantities of cooling water. Since heat recovery is usually practiced, it is necessary to balance the capital cost of heat exchange surface with the cost per BTU lost in the process. The cost of invert formation increases rapidly with temperature and becomes the major consideration.

The magnitude of these factors for a typical installation has an important influence on the selection of the cation exchanger. Since invert formation increases with operating temperature and

decreases with increasing crosslinkage of the cation exchanger, the optimum operating temperature can be increased by the proper selection of exchanger. For example, Amberlite IR-120 shows a minimum cost value at 16°C. while Amberlite IR-124 gives an optimum cost at 30°C.

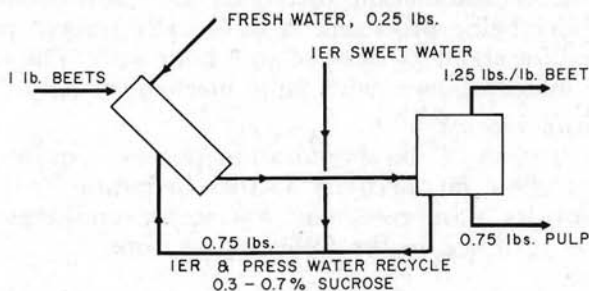
Steam requirement

Dilution of juice during displacement will occur and is much dependent upon the purity of the juice. It would be expected that the deionized juice would evaporate efficiently without scale formation so that the steam usage due to dilution would be counterbalanced by improved efficiency in the evaporator. It is also unlikely that all the juice would be processed so that the actual difference in steam requirement must be evaluated for each plant.

Sweet water utilization

The ion exchange process will result in varying amounts of sweet water production depending on the juice purity. The utilization of this sweet water in the diffuser and for lime water make up becomes an important problem in the reduction of sugar losses. The following calculation will attempt to establish how much sweet water can be handled in a 6,000 ton/day factory operating with ion exchange on beet liquors of varying purities.

The following scheme will be used for the calculation



SWEET WATER RE-USE SYSTEM

In practice 50-75% return from presses is used with a water requirement of 1.0 lbs water/lb beets. It should be possible to substitute sweet water from the ion exchange plant for the press water without hurting purity while the press water can be used for lime preparation. We could also use high levels since the ion exchange sweet water does not contain as much non-sugars as the press waters.

6,000 ton/day plant—water balance (lime plant)

Fresh Water = 6,000 (0.25) = 1,500 tons/day

Sweet Water and Press Water = 6,000 (0.75) = 4,500 tons/day

Lime Feed = 2.5% on beets

Lime Salts = $\frac{2.5}{100} (6,000) = 150$ tons lime/day

In a 30% Slurry = $\frac{150}{0.3} = 500$ tons/lime slurry/day

Water Required, Lime System = 350 tons/day

Water from ion exchange

The amount of sweet water will depend on the success in the design and operation of the equipment. It is likely that the sweet water will not exceed about 4 bed volumes for each bed volume in operation. For a 6,000 ton/day plant on 85.5% purity, the amount of sweet water will be:

$$\frac{4 \times 23,500 \times 8.33}{2,000} = 391 \text{ tons of sweet water}$$

For the other purities under consideration, the sweet water generated by ion exchange becomes:

Table 8.—Production of sweet water as a function of purity.

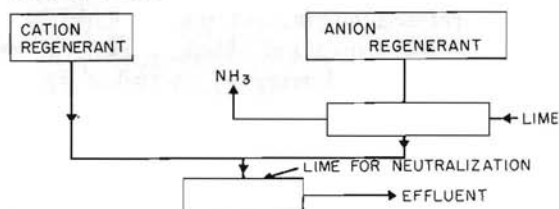
Purity, %	Sweet water, tons
82	495
90	248
96	146

It is evident from these estimates that the sweet waters produced by ion exchange can be returned either as lime slurry or as part of the pulp water returned to the diffuser.

Ion exchange system waste disposal

Since it is likely that amino acid recovery cannot be justified at the present time due to economic reasons, the spent regenerant from the ion exchange plant will require treatment as a waste. An indication of the actual amount of waste produced by ion exchange is of interest in the adaptation of the process to an existing factory. The 6,000 ton per day mill will be used operating on a 85.5% purity juice as the basis for calculations.

WASTE FLOW



Cation regenerant

About 50 tons of sulfuric acid will be used in regeneration of which about 50% is converted to salts during regeneration.

Volume of spent regenerant will be about five times the total cation resin volume required for a day's operation.

$$13,500 \times 5 \times 7.46 = 505,000 \text{ gallons}$$

$$\begin{aligned} \text{Concentration of Solids} & \left(\frac{68}{49} \right) \frac{50 \times 2,000}{505,000} = \frac{100}{505} \\ & = 0.28 \text{ lbs/gal or } 3.2\% \end{aligned}$$

Anion regenerant

About 9 tons of NH_3 are required and this in turn is treated with lime to yield 15 tons of a spent lime slurry containing a mixture of non-sugars. The non-sugar loaded on Amberlite IRA-68 amounts to about 16 lbs/ft³.

$$\text{Load} = 16 \times 10,000 = 160,000 \text{ lbs}$$

$$\begin{aligned} \text{Waste} & = \text{Lime} + \text{non-sugars} \\ & = 30,000 + 160,000 = 190,000 \text{ lbs} \end{aligned}$$

The spent regenerant would have a volume about five times the total anion exchange resin volume required for a day's operation.

$$10,000 \times 5 \times 7.46 = 374,000 \text{ gallons}$$

$$\text{Concentration of Solid} = \frac{190,000}{374,000} = 0.5 \text{ lbs/gallon (or } 6.1\%)$$

The BOD requirements of the ion exchange waste would be expected to be similar to that found in a Steffen process. The ion exchange waste amounts to about 150 gallons per ton of beets while values of about 120 gallons per ton are reported for Steffen's process by McGinnis (4). The BOD would probably be about 50% of the total amount found in the process water and would be concentrated in about 10-20% of the total waste effluent. Backwash water from the beds would be used in the flumes and condensers and as such would not be considered as a dirt waste related to the ion exchange process.

Economic Considerations

The economic evaluation of this deionization process requires detailed knowledge on the particular mill involved. A judgement on profitability requires an estimate on the future market price of refined sugar and molasses during the period that the plant is being amortized. Certain general values can be reached however which will serve as an index for the economic evaluation of the process.

The purity of the juice and the mill size are important influences on the required capital investment. For example, a 6000 ton per day mill treating of juice of 82% purity will cost about \$860,000 or 143 dollars per ton of capacity. Capital cost is also related to non-sugar removal and is roughly \$10,000/ton of non-sugar removed/day. For a 6000 ton per day mill, an

increase of 1% in purity would decrease the capital investment by \$35,000. A proportional reduction would be found for smaller plants.

The cost of removal for non-sugars varies from 2.8 to 8.6 cents/lb for a 6000 ton per day mill treating juices having purity ranges of 82 to 96%. The cost rises sharply above 90% purity and the operation becomes unprofitable at a refined sugar price of 7 cents per lb and a molasses price of 3 cents/lb. For small plants the cost of removal is somewhat higher but follows the same pattern.

The operating cost breaks down roughly according to the following distribution: depreciation (41%), chemicals and water (49%), fuel (5%), and labor (5%). The contribution of labor would increase for small plants since it is almost as difficult to operate a 1500 ton per day mill as a 6000 ton/day mill. As expected the contribution of fixed charges is very high and closely related to the method of cost accounting used in the mill. The ion exchange resin contributes about 30-35% of the total capital cost and its depreciation represents about 14-15% of the total daily cost when depreciated on a 5 year-100 day/year basis.

Comparison with the Steffen Process

Steffen's process has long been used to increase the extraction of sugar from beets. While it is a simplification to state that the ion exchange process is a substitution for the Steffen's House, it is important to compare the two processes from an economic standpoint. The following table gives a comparison for a 6,000 ton/day beet plant which would feed a Steffen's House rated at 400 tons molasses/day.

Table 9.—Comparison of the ion exchange and Steffen processes.

	(6,000 Tons Beets/day)	
	ion exchange	Steffen's
Total capital cost, \$	757,000	1,600,000
Extraction	87%	95%
Operating cost, \$/day	1,902	4,630
Tons sugar recovered	127	192
Cost/100 lbs. sugar, \$	0.75	1.20

In addition to the tabulated comparison, a number of points should be kept in mind. The degree of extraction for the Steffen process is related to the amount of raffinose which is present in the beet molasses. The capital cost for the Steffen process has been estimated from rough values available for smaller plants. A working cost of \$11.50/ton of molasses has been used for the total cost calculation and no value has been included for depreciation of the Steffen process or of the ion exchange plant since the equipment used in the processes differ widely. The

cost per 100 lbs of sugar recovered indicate a significant advantage for the ion exchange process.

Conclusions

Modern ion exchange resins have been developed which have affected materially the economics of a two bed deionization process. Under proper conditions it is possible to show a significant gain in sugar recovery at a capital cost of about 100-125 dollars/ton of beets processed. The capital write-off period not including taxes was in range of 120-200 operating days. The cost for non-sugar removal varied from 4-5 cents/lb depending on juice purity and plant size.

A comparison with the Steffen House process was quite favorable to ion exchange when compared at the same depreciation rate. The waste problems were not aggravated and the sweet water utilization was not unreasonable. Cooling water would be a serious problem which can be controlled at least in part by proper section of the cation exchanger.

Acknowledgements

The author is grateful to members of Society MINOC, a subsidiary of the Rohm & Haas Company for collecting data on field operation of the two bed system; to Japan Organo for providing valuable field data on invert formation; to Dr. M. Andrus of Rohm & Haas Company for valuable advice, direct assistance and much editorial help, and finally to many individuals in the American Beet Sugar Industry who have given critical advice and stimulating discussion when this paper was in its early stages.

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