RECOVERABLE STATIC REGENERANT ION EXCHANGE TREATMENT OF THOMPSON SEEDLESS GRAPE JUICE[1]

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The utility of ion exchange in processing fruit juices and their derivatives has been fairly well established (1, 2, 8). Among the problems encountered are: chemical and organoleptic changes, the need for a multiple-step operation (regeneration, wash, sweetening on, service run, sweetening off, regeneration), and regenerant cost. Some of these problems could be solved by using regenerants which, when evolved from the resin by the counter-ions of the treated material, could form an insoluble compound. With the proper technique this can remove a polar material without introducing foreign ions. A juice processed in this manner will not exhibit gross changes.

The answer to the cost problem appears to be a regenerant which could be used repeatedly. Reusable thermolabile regenerants have been described (5, 9). Their use entails recovery by distillation, which limits their use with fruit juices and allied products because heating usually harms the treated material. Recourse to a property of the regenerant other than its boiling point, such as low solubility, is indicated (16).

Since an important feature of any food processing operation is relative freedom from contamination by toxic substances, salts of the lighter elements would appear usable — but alkali metal salts are very soluble and magnesium and aluminum salts are laxative. Calcium salts remain. Undissolved calcium compounds have been investigated before as regenerants (7, 3, 6, 14, 16).

The predominant anion in grape juice is tartrate; its calcium salt is sufficiently insoluble (11), and the difference in affinities (10) of the calcium and tartrate ions for the exchangers is small enough to allow a reasonable regeneration and a long service run. Relatively few counter-anions are exchanged.

Calcium tartrate as regenerant offers the advantage of easy recovery of its excess by mechanical means because of its low solubility. The excess is necessary for a high regeneration level. During the treatment of grape juice, the counter-ions present (e.g., potassium, sodium, malate, sulfite) are held and the evolved ions form calcium tartrate. The largest part of the evolved calcium tartrate is present as precipitated solids and is readily available for the next regeneration. Since ion exchange is not a chemical reaction in the orthodox sense (the heat of exchange is usually on the order of less than 2 kcal/mole), calcium tartrate is almost fully recoverable, and available for full reversion of the system from which it evolved without expenditure of energy.

Ion exchange of grape juice at 40 meq of potassium per liter in metathetic exchange for the calcium ion, with the non-tartrate anions exchanging for tartrate, results in 5200 ppm calcium tartrate in the system (10) The solubility of calcium tartrate is on the order of 300 ppm (11), so recovery of over 94% of the regenerant is a matter of mechanics. One mechanical approach is to allow the formed precipitate to remain in the exchange column itself. Change of product flow to water flow with simultaneous change in direction reverts the equilibrium conditions, and the regeneration will occur in a manner similar to that described by Deuel et al (7).

This study shows how substances in complex solutions of polar and nonpolar solutes can be removed by exchange for a spar-

ingly soluble polar compound. We used Thompson Seedless grape juice because its flavor is mild, delicate, and easily impaired. Studied besides regenerant recovery was removal of SO_2 used for preservation, and inhibition of enzymatic browning. Elimination of nontartrate anions and the labilogenic potassium bitartrate without undue change in pH of the juice was also investigated.

EXPERIMENTAL PROCEDURE

The experimental assembly consisted of a column 125 cm long and 5.5 cm outside diameter. This was filled with 1270 ml of a sulfonic polystyrene resin and 1270 ml of a trialkylalkanolammonia (TKA) polystyrene resin. The cation exchanger, cross-linked with 12% divinylbenzene, was in the calcium and the anion exchanger in the tartrate form. The resins were inti-

mately mixed and poured into the column in small portions suspended in water. The water was constantly drawn off to avoid separation by specific gravity. The bottom of the column was fitted with a filter, and the empty top space was filled with Float-screen (4).

Filtered Thompson Seedless grape juice pressed from grapes grown in the Imperial Valley, California, was treated with SO_2 prior to filtration and then passed through the column downflow. One-liter portions were sampled and analyzed for SO_2 by the modified direct colorimetric method (12). Total acid was determined by the A.O.A.C. method, and potassium by flame spectrophotometry.

Flow direction was reversed and the system regenerated by solution of the deposited calcium tartrate. The input liquid was distilled water. The regeneration progress was determined by measuring de-
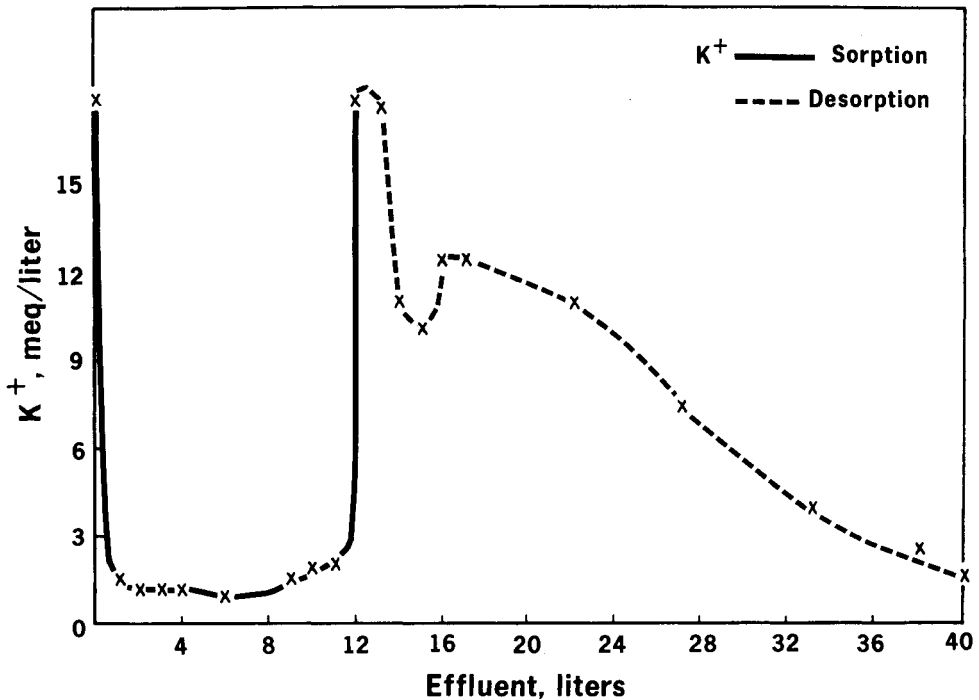

Figure 1. Sorption of the potassium ion from input juice at pH 3.7. Desorption with distilled water.

sorbed components. Also studied was the degree of regeneration in terms of potassium and SO_2 sorption and desorption.

RESULTS AND DISCUSSION

Table I gives the hydrogen-ion content changes during the treatment phase of the experiment. There appear to be discrepancies in sorption of the hydrogen and potassium ion and between the cations and the sulfite. The inconsistency actually shows the difference in affinity of the particular ionic species for a given resin. Thus the potassium ion substitutes for calcium in the resinate form much more rapidy than does the hydrogen ion. Table 2 provides data on the desorption of the hydrogen ion removed from the treated grape juice.

Figures I and 2 give an overall picture of sorption and desorption of the potassium and sulfite ions. The difference in

TABLE I

Sorption of Hydrogen Ions from Grape Juice during Ion Exchange in the Calcium Tartrate Cycle

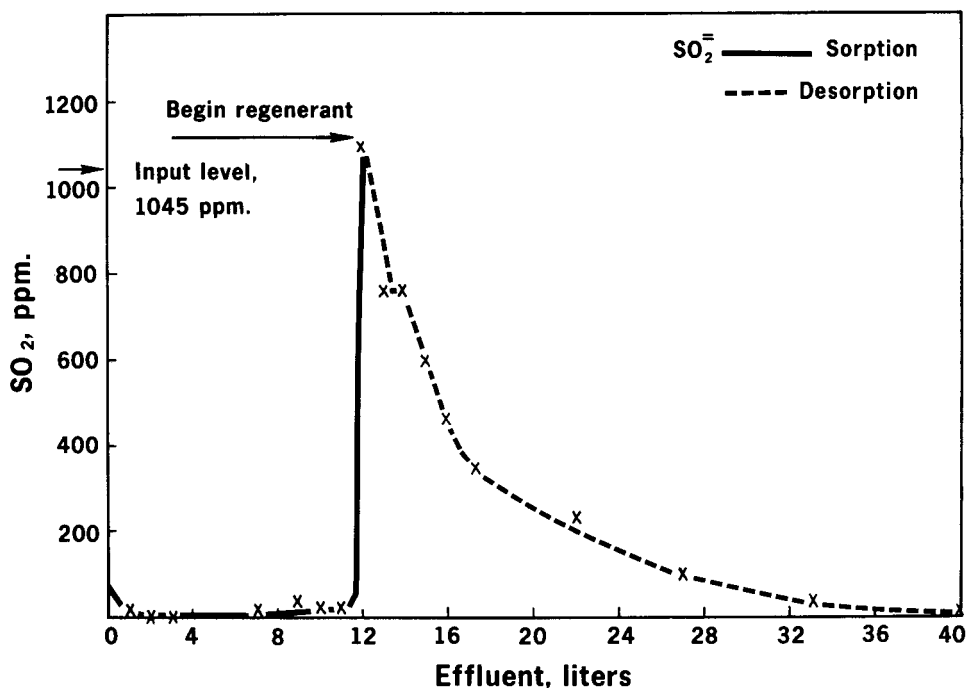|	H^+ meq/l
Control	750
Effluent (ml):	
1000	100
2000	80
3000	140
4000	40
5000	40
7000	40
9000	40
10000	40
11000	80
12000	160

Figure 2. Uptake of sulfurous acid by the ion exchanger from input juice at pH 3.7 expressed in ppm SO_2.

the slope of desorption curves of potassium sulfite illustrates the difference between the affinity of the calcium ion for

TABLE 2

Regeneration Expressed in Desorbed Hydrogen Ion
Input: distilled water

Effluent (ml)	H+ meq/l
1000	360
2000	480
3000	720
4000	640
5000	600
10000	140
15000	200
21000	40
26000	20
28000	40

the sulfonic resin and the tartrate ion for the trialkylalkanolammonia resin. These affinities, however, must be considered in the light of those of the desorbed species. Figure 3 shows juice treatment and regeneration results in terms of soluble solids. The breakpoint is evident at the 12-liter throughput.

The results show that calcium tartrate, as an organometal salt representative of slightly soluble alkaline earth metal compounds, can be used as a recoverable regenerant for ion-exchange systems. The unstable potassium acid tartrate is removed from the juice. There is reason to believe that other very slightly soluble compounds can also be used to treat fruit juices (10, 14). The advantage of such a system is primarily in regenerant cost and labor. Further, it does little harm to the juices since changes in pH are very small and there is no observable loss of flavor.
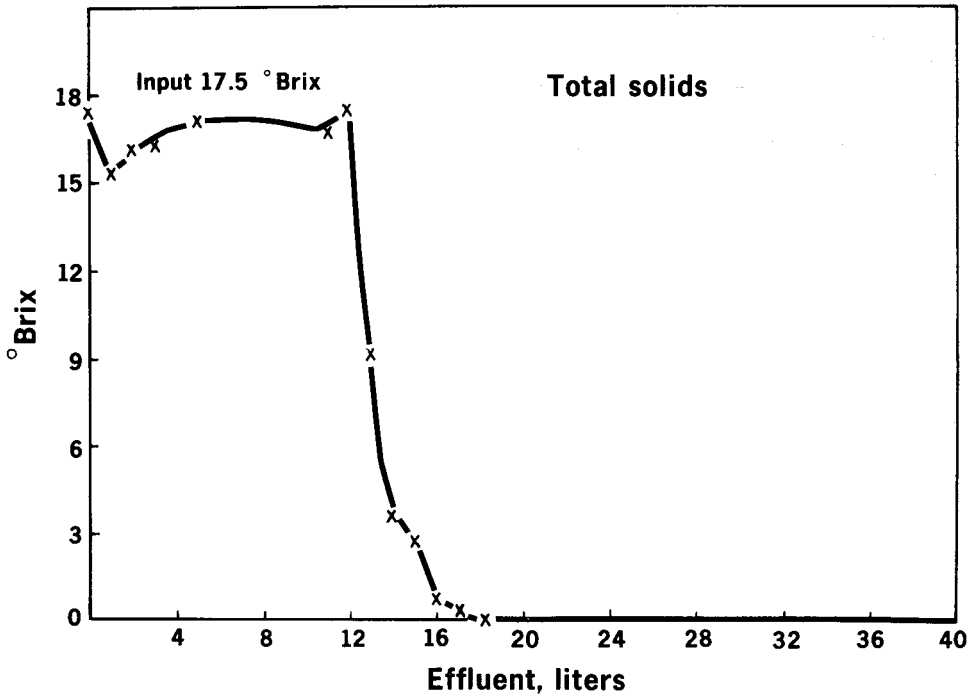

Figure 3. Monitoring of the service run and regeneration. Total solids taken for criterion.

The changes were essentially those to be expected from chill-proofing plus removal of SO_2. The principle of recoverable static regenerant can thus be applied to ion-exchange purifications of high-ash low-cost materials.

SUMMARY

Calcium tartrate was the regenerant in ion-exchange treatment of grape juice. Reuse for subsequent regeneration was nearly quantitative without the need for handling.

ACKNOWLEDGMENTS

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