Weak Cation Exchange Softening: Long Term Experience and Recent Developments

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M. Kearney and D. E. Rearick
Amalgamated Research Inc., 2531 Orchard Dr. E., Twin Falls, Idaho USA 83301

Introduction

Weak cation softening systems operate in several factories in the U.S. beet sugar industry including the highest slice location (16,000 tons/day at the Amalgamated Sugar LLC's Mini-Cassia factory in Paul, Idaho). The earliest installed system, in Twin Falls, Idaho, has been operating since 1984. Although a novelty at the time, this system is now the longest operating beet juice softening system in the U.S. and weak cation softening is now looked upon as a time proven process. The technology continues to advance with the introduction of process intensified fractal configurations.

Weak cation juice softening with sulfuric acid regenerant is the only ion exchange process in the sugar industry where the used regenerant has a higher value than the original regenerant. This higher value by-product is used as a necessary pulp pressing aid. As opposed to all other regeneration methods, weak cation softener regeneration is a profitable operation.

Due to the weak acid functionality of the resin, the softener can be operated in the very efficient hydrogen form with no significant inversion of sucrose. Twenty years of factory data has demonstrated that there is no increase in molasses invert or thick juice color due to weak cation softening. A first favorable result is that compact softener cells are used since the capacity of weak cation resins is more than double that of strong cation resins. Additionally, the fast kinetics of weak cation resin allow operation at about 50 bed volumes/hour compared to the typical 10 bed volumes/hour for strong cation softeners. This provides a further reduction of softener size. The weak acid characteristics also allow for extremely efficient regeneration. Regenerant use is about 110% on operating capacity.

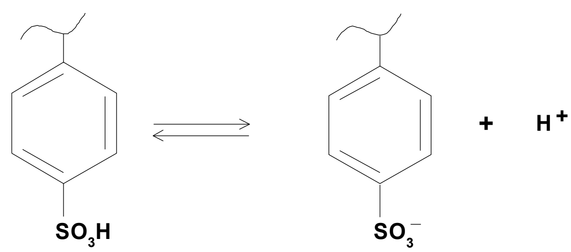
Amalgamated Research Inc.'s recent introduction of fractal softener configurations has further reduced cell size, resin requirements and system cost. These modern systems operate up to 500 bed volumes/hour. As a result, the fractal weak cation softener uses only about 2% to 4% of the resin compared with strong cation juice softening and is operated using correspondingly small cells. Although operating at very high specific flowrate, the fractal configuration exhibits very low pressure and negligible pressure drop. The extremely high flowrates also allow rapid regeneration turn-around.

A. Characteristics of Weak Cation Softening

Several important factors distinguish hydrogen form weak cation softening from the commonly encountered strong cation exchange processes. These differences relate to use of the process with sucrose solutions, regeneration efficiency, and the necessity for solution alkalinity.

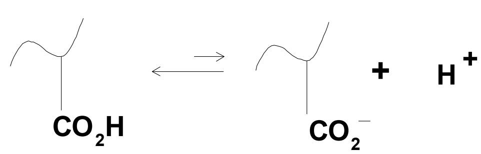
There is a common misconception that the use of hydrogen form weak cation exchange resins in the softening of sugar solutions presents a serious risk of sucrose hydrolysis (inversion). This idea is undoubtedly due to the fact that <u>strong acid</u> cation exchange resins in the hydrogen form are good catalysts for sucrose hydrolysis and, in fact, can be used as heterogeneous catalysts in continuous systems for invert syrup production.[1] There is, however, a vast difference in chemical structure and the resulting acidity between weak and strong cation exchange resins. The strong cation exchange resins typically used in water softening applications contain sulfonic acid functional groups (Figure 1) which are strongly acidic.

FIGURE 1
Structure of Strong Acid Cation Exchange Resin



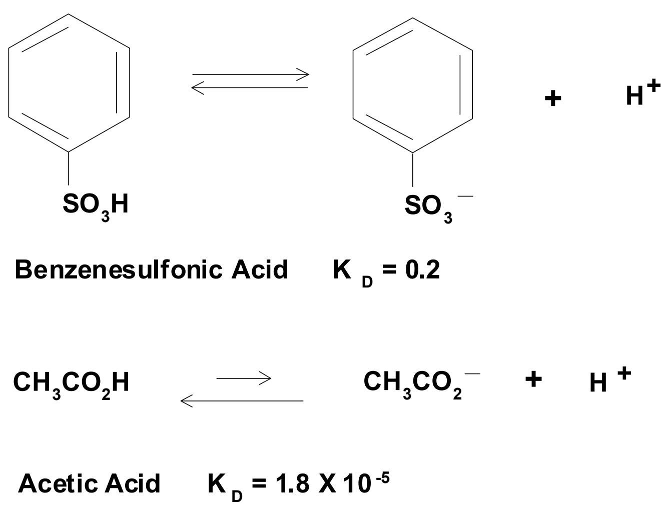
The dissociation equilibrium shown in Figure 1 results in significant levels of the ionized forms on the right side so that in the presence of a sulfonic acid form resin there is an appreciable level of hydrogen ions available to catalyze sucrose hydrolysis. Weak cation exchange resins have carboxylic acid functional groups which are much weaker acids (Figure 2) so that the dissociation reaction shown does not proceed readily.

FIGURE 2
Structure of Weak Acid Cation Exchange Resin



That is, free carboxylate ion (right side of the equation) has a great affinity for hydrogen ion so that the reaction equilibrium lies far to the left, the primary species present is the undissociated acid, and the concentration of hydrogen ions available for catalysis of inversion is very low. For purposes of comparing relative acidities, the structure of strong cation exchange resins is comparable to that of benzenesulfonic acid while the functional group in weak cation exchange resins is like that of the much weaker acetic acid. Hydrogen ion forming reactions and dissociation constants are given for both simple acids in Figure 3.

FIGURE 3
Organic Acid Dissociation



Note that the dissociation constant for benzenesulfonic acid is 0.2 indicating that the ratio of products (sulfonate anion and hydrogen ion) to reactant (benzenesulfonic acid) is 0.2 while the constant for acetic acid is only 1.8×10^{-5} indicating that the ratio of products (acetate anion and hydrogen ion) to undissociated acid is only 1.8×10^{-5} or 0.000018. Thus benzenesulfonic acid is stronger than acetic acid by a factor of 0.2/0.000018 or 11,100.

The low acidity of the carboxylic acid functional group in weak cation exchange resins accounts for three factors that are important in softening of sugar factory process streams:

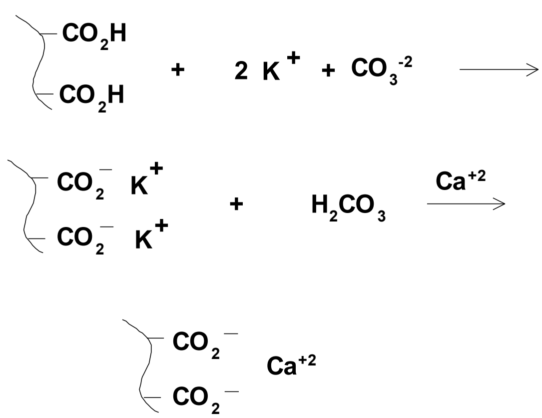
1) A very low catalytic activity for sucrose inversion, as discussed above. The low level of catalytic activity for inversion is easily managed to insignificant levels by process controls such as high flow rate and effluent realkalization.

2) Very efficient regeneration due to the strong affinity of the carboxylate anion in exhausted resin for hydrogen ion. The carboxylate anion efficiently captures hydrogen ions from regenerant acids to produce the hydrogen form resin in nearly stoichiometric amount. Strong

cation exchange resins, in contrast, regenerate by a reversible exchange process that requires a significant excess of regenerant acid.

3) Solution alkalinity is necessary for efficient calcium exchange. Because the hydrogen form resin exists mostly as the unionized acid, it cannot exchange for calcium directly. Solution alkalinity results in loss of a hydrogen ion forming the carboxylate anion which is then available for capture of calcium ion. In the case of thin juice, where the predominant cations are monovalent species (potassium and sodium), the weak cation exchanger first is converted to the monovalent cation form by a neutralization reaction and the monovalent form then undergoes exchange to remove calcium from solution (since these resins have a much higher selectivity for divalent cations). Softening of thin juice thus normally proceeds as shown in Figure 4.

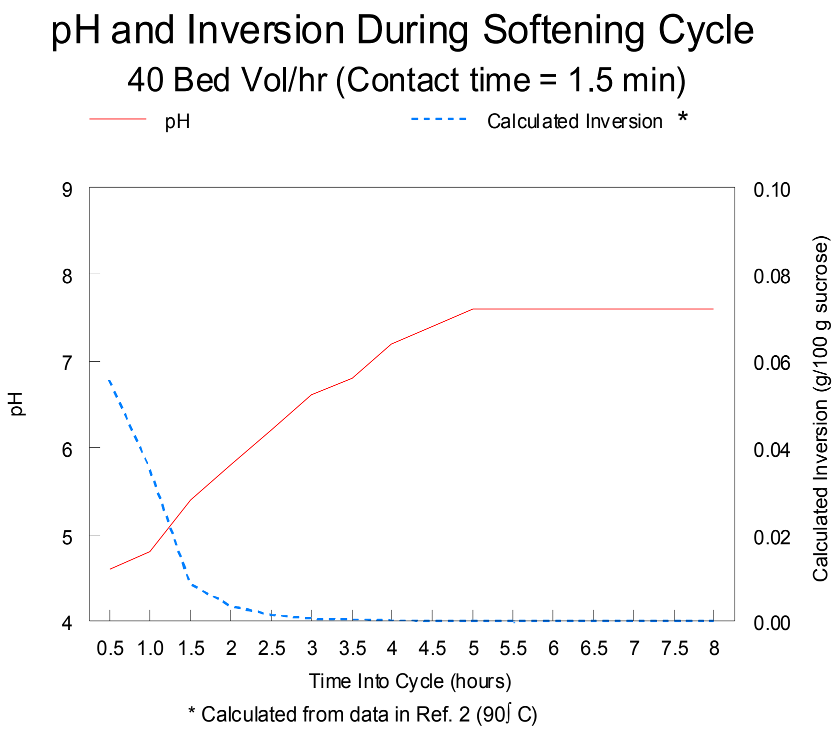
FIGURE 4
Steps in Thin Juice Softening



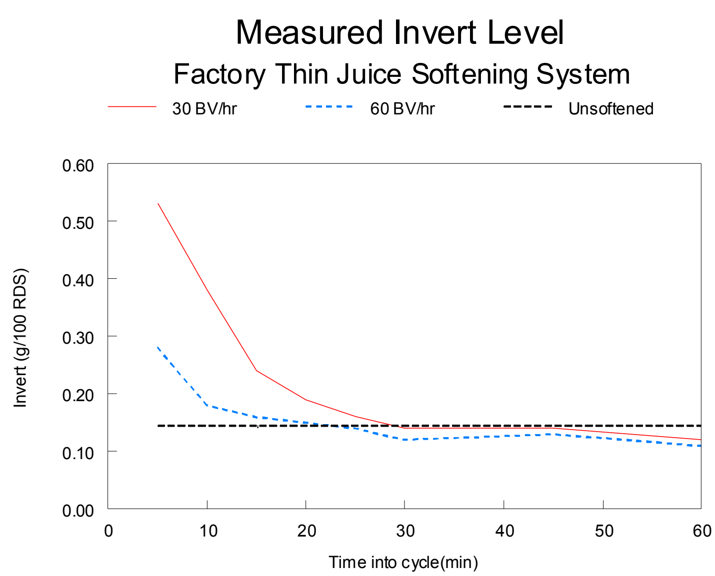
B. Sucrose Stability During Weak Cation Exchange Softening

In addition to the theoretical basis (discussed above) for low sucrose inversion during hydrogen form weak cation softening, extensive data has been collected over the years of such softening operation in factory systems. The first graph (Figure 5) shows the measured effluent juice pH value (solid line) during a typical softening cycle at a flow rate of 40 bed volumes/hour (BV/hr). Note that during the early part of the cycle hydrogen form resin neutralizes juice alkalinity and lowers the pH to 4.6. The pH then rises to a stable level of 7.6 as resin is converted to the monovalent cation form. At this flow rate, thin juice is at the indicated pH only during the brief contact time (1.5 minute); juice is then realkalized by addition of sodium carbonate. Inversion during contact with resin at the given pH values was calculated for 90EC from data given in Reference 2. Average expected inversion for the full eight hour cycle is 0.0066 g/100 g sucrose).

FIGURE 5



The low fraction of sucrose inversion predicted from measured pH values and literature inversion rates is actually even higher than values obtained when invert levels are measured in softened juice. The following graph shows measured invert levels in unsoftened juice along with measured invert levels at 30 BV/hr and 60 BV/hr. Note that measurable inversion only occurs during the first thirty minutes of the softener cycle, even though the pH has been shown to take longer to return to initial levels. From values for increase in invert, calculated from the Figure 6



data, a value for total invert formed during each five minute interval can be calculated using the total throughput values for this system of 200.6 kg dissolved solids/min at 30 BV/hr and 401.2 kg DS/min at 60 BV/hr. These values are given in Table 1.

TABLE 1
Invert Formed in Factory Softener System

Time Into Cycle (min)	Invert formed (g)	
	30 BV/hr	60 BV/hr
5	4330	2650
10	2390	700
15	950	360
20	420	220
25	150	0
30	10	0
Total Invert	8250	3930

For this system, the total throughput of solids in a 10 hour cycle (at 60 BV/hr) is 241,000 kg and of this quantity 3.93 kg (or 0.0016%/DS) is converted to invert. At the slower flow rate of 30 BV/hr, total solids throughput is the same (in a 20 hour cycle) so the fraction of inverted sucrose is roughly twice as high, at 0.0034%/DS.

As shown by the above typical measurements, invert formation across a weak cation exchange softener under normal process conditions (60 BV/hr; 90EC) with subsequent juice realkalization results in only an insignificant amount of invert formation. Historical records at Amalgamated Sugar's four factories with thin juice softening have shown no increases in molasses invert levels or thick juice color (which would be affected by destruction of excess invert) in the years since the installation of softening equipment.

C. Regeneration produces a high value pulp pressing aid

The weak cation softening process is waste free. During regeneration, the sulfuric acid regenerant is converted to higher value calcium sulfate. The calcium sulfate is then added to the diffuser as a necessary pulp pressing aid. Discussion of weak cation softening always includes a discussion of pulp pressing since weak cation softeners provide multiple service to the sugar factory. They are also pulp pressing aid production units.

The increased value of regenerant across the softener can be demonstrated as follows (year 2002 bulk prices):

H_2SO_4, 93%:	($.039/lb solution)/.93 = $0.04194/lb acid
$CaSO_4$:	$0.0352/lb calcium sulfate

The acid used for ion exchange softening and the calcium sulfate used as a pulp pressing aid function on an equivalent basis. Interestingly, the calcium sulfate interaction with pulp is also an ion exchange phenomena[3]:

H_2SO_4:	(49g/eq) H ($0.04194/454g) = $0.00453/eq
$CaSO_4$:	(68g/eq) H ($0.0352/454g) = $0.00527/eq

At year 2002 prices the value of regenerant increases by about 16% across the weak cation softener.

As long as pulp pressing aid is needed, the strategy of using the regenerant twice (in two very different applications) is an important advantage with this process. Either the softener regenerant or the pulp pressing aid can be considered to be no cost.

D. Fractal weak cation softeners

The most recent implementation of weak cation softening uses fractal cell configurations. The fractal weak cation softening process exhibits several unique characteristics[4,5]. These include:

! An order of magnitude reduction in weak cation resin requirement. The resin bed depth is typically only 6 inches. Resin requirement is only 10% of that used in conventional weak cation softening and only about 2% to 4% of that used in NRS or other strong cation softening systems [6,7].

! Cells are extremely small. The vessels are only marginally wider (in the vertical direction) than the vessel's sight glass (Figure 7). The small size significantly reduces capital costs and provides a major savings in space.

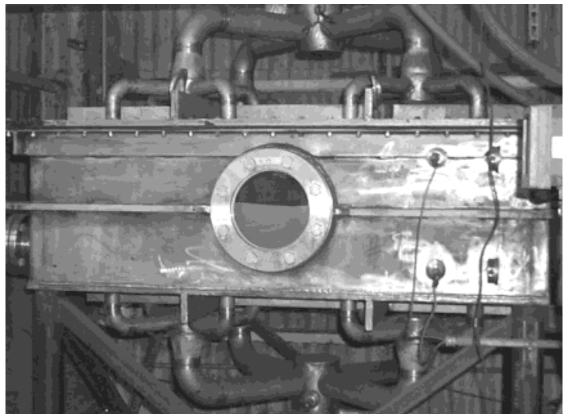
! Low pressure vessels. The vessels operate at less than 15 psi. This further reduces capital cost and is also a safety benefit. ASME stamp is not required.

! Very low pressure drop. Although operating at up to 10 times the flow rate per unit of resin compared with conventional systems, the low bed depth and fractal distribution eliminates nearly all pressure drop. The distributor/collector ΔP plus the resin bed ΔP is only about 1 to 2 psi.

! Rapid regeneration turn around. A complete cycle of sweet-off, regeneration, regeneration rinse and backwash is completed in 25 minutes. This provides very flexible scheduling.

! Entirely uniform backwash. Due to mirror image fractals at the top and bottom of the cell, flow is equally uniform in the upward direction. Because of the very small amount of resin configured as a flat bed, backwash with 100% expansion can be accomplished on a regular basis within the small amount of freeboard.

FIGURE 7
A fractal ion exchange cell



Acknowledgment

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