TEN YEARS EXPERIENCE WITH ACRYLIC ANION RESINS AS CROSS DECOLORIZER IN CANE SUGAR REFINING

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ABSTRACT

The use of acrylic anion exchange resins as a gross decolorizer in the carbonation refinery was more advantageous compared to the classical carbon—styrene anion exchange resin polishing system. Even with heavy color loading, these acrylic anion exchange resins gave an economical life of 450 cycles representing approximately 14,000 mt refined sugar produced/cu. m resins

INTRODUCTION

Conventional styrene anion exchangers have been employed by cane refineries simply as polishers after powdered carbon, granular carbon or bone char. As the color load increased markedly above 2.0 stammer units, the useful life of these materials dropped. They were able to handle the increased color load for short periods of time, but were soon fouled irreversibly. It was universally held that this fouling trend was an inherent limitation for all strongly basic ion exchangers. Theory assumed that the basicity of the ion exchange site caused it to ionically capture and hold the polar portions of complex colorants. Statistically, some colorants would never be removed because of the strength of the electrostatic (ionic) charges.

A study by Gustafson and Lirio\(^1\), however, showed that electrostatic charges, alone, were not responsible for the irreversible binding of organics by anion exchangers. In fact, their study led to the theory that Van der Waals forces (covalent bonding) played a more dramatic role in this fouling phenomenon than anyone had ever reported.

The Gustafson and Lirio work compared strongly basic anion exchangers having styrene backbones with acrylic backbones. The difference in selectivity is summarized in Table 1.

\( K_{Q1} \) is a measure of the selectivity (preference) of the ion exchangers for the organics over chloride. If \( K_{Q1} \) were equal to unity (= 1), the ion exchanger would have no preference. The higher the \( K_{Q1} \) value, the greater the preference of the ion.

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exchanger for the organics over chloride. Two effects can be observed from the data. Firstly, as the polarity system decreases, going from water to an alcohol-water mixture, the value of $K_C$ decreases. This indicates that the organic species is being held more strongly by the less polar solvent than by water. Although alone these data are inconclusive, they do indicate that Van der Waals forces are overcoming the electrostatic (ionic) charges. Comparing the differences in $K_C$ between the styrene matrix and acrylic matrix resins (both are strongly basic, Type 1, anion exchangers), a difference in value of several percent, perhaps even as high as a two-fold factor might be expected. Gustafson and Lirio, however, measured an order of magnitude difference in selectivity between a styrene and an acrylic matrix resin for the same organic under the same conditions. They conclude that a hydrophilic matrix resin (acrylic) would be less prone to fouling compared to a hydrophobic matrix resin (styrene).

This study reverses the practice of limiting ion exchangers to polishers in cane refineries.

RESULTS AND DISCUSSIONS

Plant Operation

When using anion exchange resins in either polishing or gross decolorization systems, six essential steps are carried out every cycle.

(i) Sweeten on — refinery liquor to be decolorized (carbonated liquor) is pumped through the system to displace remaining water in the resin bed.

(ii) Service run — carbonated liquor of 60-66° Brix and temperature of 70-75°C is metered through the resin bed at a flow rate of 2-3 bed volumes/hr for a specific length of time determined by the color value of the effluent.

(iii) Sweeten off — at the end of the service run, air and water are used to displace remaining sugar liquor in the resin bed.

(iv) Backwash — water is pumped in an upflow direction to hydraulically expand the resin bed. Accumulated dirt and resin fines are removed during backwash.

(v) Regeneration — sodium chloride solution of 10% concentration and temperature of 70°C is metered through the resin bed at 2 bed volumes hour.
Once used sodium chloride regenerant is recycled as the lead portion followed by fresh sodium chloride regenerant.

(vi) Displacement

the regenerant is displaced with water followed by a fast rinse to remove residual chloride ions.

As shown in Fig. 1, one anion resin column as a pre-decolorizer and 5 anion resin columns as gross decolorizers was used. The effluent of the pre-decolorizer column is blended into the influent of the gross decolorizer columns. The advantages of such an operation is the reduction of input color load on the gross decolorizers and the utilization of the decolorization ability of the anion resins as much as possible, i.e. when an anion resin has completed 450 cycles in any gross decolorizer columns, this resin was continuously used as a pre-decolorizer until another column is ready to take its place. This gives an overall resin life of approximately 650 cycles.

![Simplified flow diagram of gross decolorization columns](image_url)
Photograph: Fully automated gross decolorization columns using Amberlite IRA-458S at Malayan Sugar Manufacturing Co. Bhd., Malaysia

Resin Performances

The decolorization system originally employed in the refinery was powdered activated carbon and styrene anion polishing. Clear liquor having the following characteristics:

\[
\begin{align*}
\text{brix} & = 60 - 64^\circ \\
\text{temperature} & = 70 - 75^\circ \text{C} \\
\text{color} & = 5.2 - 5.4 \text{ Stammer Units} \\
\text{pH} & = 7.5 - 8.0
\end{align*}
\]

TABLE 1. Selectivity coefficient (KC1) for adsorption of sodium naphthalene-sulfonate by strongly basic anion exchangers.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Styrene Matrix</th>
<th>Acrylic Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>133</td>
<td>11.3</td>
</tr>
<tr>
<td>50% CH\textsubscript{3}OH</td>
<td>8.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

was typical influent to the styrene anion polishers. Color removal of these resins declined gradually from 200 to 300 cycles then dropped sharply after 300 cycles. The styrene anion resin had to be replaced after 350 cycles. Even when using gel or macroreticular type styrene anion resins, the same irreversible fouling trend was observed as shown in Table 2.

TABLE 2. Performance data of styrene anion resins in polishing system.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Thru/Cycle</th>
<th>Input Color in SCV (av.)</th>
<th>Color wt. loaded/cycle in Stammer Units</th>
<th>Color Removal (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 200</td>
<td>48 BV</td>
<td>5.2</td>
<td>982</td>
<td>85%</td>
</tr>
<tr>
<td>201 - 300</td>
<td>48 BV</td>
<td>5.4</td>
<td>1,020</td>
<td>76%</td>
</tr>
<tr>
<td>301 - 350</td>
<td>45 BV</td>
<td>5.3</td>
<td>938</td>
<td>64%</td>
</tr>
</tbody>
</table>

Stammer Units

Color wt. input = 343,000
Color wt. output = 85,750
Color wt. removed = 257,250 after 350 cycles
Since operating variables such as brix, color and throughput change from time to time, a simplified equation was used to calculate input colors adjusted to a color weight basis for comparative purposes:

\[
\text{Color wt. input/cycle in stammer units} = C \times T \times RV \times B \times D
\]

where:

- \( C \) = average input color in stammer units
- \( T \) = throughput in bed volumes
- \( RV \) = resin volume in cubic meters
- \( B \) = average brix divided by 100
- \( D \) = density of liquor at the average brix

In March 1970, we switched one of the 5 styrene anion polishing columns to Amberlite IRA-458S; an acrylic gel type anion resin was used. The input color load to this column was increased gradually. Performance data of this first column, summarized in Table 3, clearly shows improved overall performance. At 350 cycles, where a styrene anion resin would have been replaced, more than 80% color removal with the acrylic resin can still be obtained, even though input colors consistently higher. This column of Amberlite IRA-458S was replaced only after 550 cycles.

**TABLE 3.** Performance data from March 1970 to October 1971 using Amberlite IRA-458S as Gross Decolorized in one column.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Throughput/Cycle</th>
<th>Input Color in OS CV (av.)</th>
<th>Color wt. loaded/cycle in stammer units (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–200</td>
<td>48 BV</td>
<td>5.4</td>
<td>1,020</td>
</tr>
<tr>
<td>201–300</td>
<td>45 BV</td>
<td>6.1</td>
<td>1,080</td>
</tr>
<tr>
<td>301–400</td>
<td>45 BV</td>
<td>6.9</td>
<td>1,222</td>
</tr>
<tr>
<td>401–450</td>
<td>45 BV</td>
<td>7.7</td>
<td>1,363</td>
</tr>
<tr>
<td>451–500</td>
<td>42 BV</td>
<td>7.9</td>
<td>1,305</td>
</tr>
<tr>
<td>501–550</td>
<td>34 BV</td>
<td>7.0</td>
<td>936</td>
</tr>
</tbody>
</table>

*Using 450 as resin replacement period. Stammer Units

\[ 
\text{Color wt. input} = 527,063 \\
\text{Color wt. output} = 92,236 \\
\text{Color wt. removed} = 434,827
\]
In view of this significant performance, all of the styrene anion resins were switched to acrylic anion resins and we gradually eliminated activated carbon while maintaining consistent refined sugar quality. This switch resulted in a cost savings of about $2.00/mt refined sugar produced in the refinery. Table 4 shows typical performance data of Amberlite IRA-458S when activated carbon was totally eliminated. These results compare favourably with our first column results (Table 3).

Having fully established that acrylic resins (Amberlite IRA-458S) as the decolorization system are more viable than the classical carbon-styrene anion resin polishing system, the next logical step was to see a macroreticular acrylic anion resin could even be more effective.

**TABLE 4.** Performance data using other lots of Amberlite IRA-458S in Gross Decolorization System.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>ThruPut/Cycle</th>
<th>Input Color in °SCV (av.)</th>
<th>Color wt. loaded/cycle in Stammer Units</th>
<th>Color Removal (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 200</td>
<td>45 BV</td>
<td>7.7</td>
<td>1,363</td>
<td>82%</td>
</tr>
<tr>
<td>200 - 300</td>
<td>42 BV</td>
<td>7.3</td>
<td>1,206</td>
<td>80%</td>
</tr>
<tr>
<td>301 - 400</td>
<td>42 BV</td>
<td>8.0</td>
<td>1,322</td>
<td>78%</td>
</tr>
<tr>
<td>401 - 450</td>
<td>42 BV</td>
<td>7.5</td>
<td>1,239</td>
<td>72%</td>
</tr>
<tr>
<td>451 - 500</td>
<td>36 BV</td>
<td>7.5</td>
<td>1,062</td>
<td>60%</td>
</tr>
</tbody>
</table>

Using 450 cycles as resin replacement period:

<table>
<thead>
<tr>
<th>Stammer Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color wt. input = 577,125</td>
</tr>
<tr>
<td>Color wt. output = 126,968</td>
</tr>
<tr>
<td>Color wt. removed = 450,157</td>
</tr>
</tbody>
</table>

**TABLE 5.** Performance data using Amberlite SDC-301 in Gross Decolorization System.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>ThruPut/Cycle</th>
<th>Input Color in °SCV (av.)</th>
<th>Color wt. loaded/cycle in Stammer Units</th>
<th>Color Removal (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 200</td>
<td>42 BV</td>
<td>7.4</td>
<td>1,253</td>
<td>82%</td>
</tr>
<tr>
<td>201 - 300</td>
<td>42 BV</td>
<td>7.2</td>
<td>1,219</td>
<td>81%</td>
</tr>
<tr>
<td>301 - 400</td>
<td>39 BV</td>
<td>7.5</td>
<td>1,179</td>
<td>76%</td>
</tr>
<tr>
<td>401 - 450</td>
<td>36 BV</td>
<td>7.6</td>
<td>1,103</td>
<td>69%</td>
</tr>
<tr>
<td>451 - 500</td>
<td>33 BV</td>
<td>7.4</td>
<td>984</td>
<td>57%</td>
</tr>
</tbody>
</table>

Using 450 cycles at resin replacement period:

<table>
<thead>
<tr>
<th>Stammer Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color wt. input = 534,825</td>
</tr>
<tr>
<td>Color wt. output = 123,010</td>
</tr>
<tr>
<td>Color wt. removed = 411,815</td>
</tr>
</tbody>
</table>
In theory, some of the color bodies present are too large to be adsorbed by the gel resins. The high surface area and open structure of the macroreticular resin could accommodate these larger bodies, thus affecting better color removal. Furthermore, this structure is expected to provide better elution of colorants during the regeneration stage. Thus, the need for employing a macroreticular acrylic anion resin will probably depend on the nature of the colorants. This need would probably not become evident until the resins have been tested for several hundred cycles. Amberlite SDC-301, an acrylic anion resin having a macroreticular structure, was installed to identify whether our refinery required this degree of sophistication. The results are summarized in Table 5.

The plan data indicated marginal difference in performance between the acrylic gel and macroreticular anion resins for the conditions in the refinery. It should be emphasized that this is not a universal conclusion. There are other refineries in the Asean countries, and in other parts of the world, (Cooper2) who have found Amberlite SDC-301 to be the resin of choice.

Work on New Anion Resins

It has been observed that styrene anion resins have a higher selectivity for colorants than the acrylic anion resins. When operating as a gross decolorizer, this is a drawback because of premature fouling resulting in shorter resin life. When operating as polishers, however, this property has an advantage. Styrene anion exchange resins are able to remove better the last traces of colorants than the corresponding acrylics. This trend becomes highly evident when treating an influent liquor of less than 1.0 stammer units. However, the need for such highly refined liquor is rarely encountered.

Nevertheless, because of variation in liquor quality and since color removal decreases with each cycle, there are times in the course of plant operation when a little extra decolorization power is desired. A mixture of styrene and acrylic anion resin would be one approach. The fear of course, is that the styrene portion of the mixture would foul at a faster rate than the acrylic, thus prematurely eliminating the advantage of such a mixture.

Another approach is to increase the hydrophobicity of the acrylic anion resins. This could be achieved by placing an aromatic nucleus nearby the ion exchange site. Such an approach is expected to represent a favourable trade off. While the resin life is expected to be less, the decolorization power (amount of color removed per cycle) is expected to be better. This would result in better color control, higher throughput per cycle, less sweetwater production, better salt efficiency, lower waste volume, or a balance of the above factors depending on the needs of the refinery.

A new acrylic anion exchange resin, Amberlite XE-338 developed with characteristics of higher hydrophobicity was evaluated in our laboratories together with
Amberlite SDC-301 (macroreticular) and Amberlite IRA-458S (gel) as gross decolorizers under identical conditions. Laboratory test commenced in August 1978.

The test parameters are:

- Resin volume in each test column: 100 ml
- Resin bed depth: 30 cm
- Influent liquor: refinery brown liquor
- Decolorization flow rate: 1 liter/hr (10 BV/hr)
- Temperature: 75 - 80°C
- Thruput (volume of liquor decolorized): 40 BV/cycle
- Regeneration: 500 ml/hr (2.5 BV/hr)
- Operational steps: identical to plant operation

The average influent characteristics of the brown liquor after 50 test cycles completed at the time of this report were:

- Brix = 64.0°
- Color = 8.7 Stammer Units
- pH = 7.5

Gross decolorization performance of the three acrylic anion resins under the conditions outlined above is shown in Figure 2. These results indicate that Amberlite XE-338 does have approximately 5% higher color removal efficiency.

**FIGURE 2.** Gross Decolorization of Acrylic Anion Bins in the Laboratory
This study, of course, is inconclusive. A plant scale operation has to be undertaken to demonstrate the overall economics and utility. It is important to point out that anion resin improvements are possible and that they are being made continually as shown in our lab studies.

CONCLUSION

The past ten years of experience with acrylic anion resins as gross decolorizer have shown that the acrylic anion exchangers can replace the classical carbon-styrene anion resin polishing system in cane refinery decolorization operation. Further they are more advantageous than the classical decolorization system due to their higher capacity for color adsorption; longer useful life; and favorable economics. Though details are beyond the scope of this paper, other advantages seen in the refinery for acrylic anion resins in gross decolorization are the negligible sugar losses; ready expansion and automation of the plant; essentially trouble-free operation, and further reduction in operation cost by recovery of waste sodium regenerant.

REFERENCES


10 AÑOS DE EXPERIENCIA USANDO RESINAS ANIONICAS ACRILICAS PARA DECOLORACION TOTAL EN LA REFINACION DE CAÑA DE AZUCAR

I. Cheong y H. Mussebah

RESUMEN

El uso de resinas intercambiadoras anionicas acrilicas para la decoloracion total en nuestra refineria de carbonatacion nos ha dado importantes ventajas en comparacion con la clasica combinacion de carbon-resina intercambiadora anionica de estireno usada para pulir el licor solamente. Aun con altos colores, estas resinas intercambiadoras anionicas acrilicas han tenido una vida economica de 450 ciclos lo que corresponde aproximadamente a 14,000 toneladas metricas de azucar refinada producida por metro cubico de resina.