EVALUATION OF A MAGNETIC ION EXCHANGE (MIEX®) RESIN FOR DECOLORISATION APPLICATIONS WITHIN A RAW SUGAR FACTORY

By

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Abstract

DECOLORISATION of sugar syrup prior to crystallisation improves the quality of raw sugar produced and reduces costs in further refining processes. The use of ion exchange resins for this purpose has been discussed in many publications and specialised resins are used in sugar refineries. This paper describes laboratory and mill prototype trials to evaluate the potential of a magnetic ion exchange resin (MIEX®) for application within a raw sugar factory to decolorise syrup. Simple jar tests proved that MIEX® resin outperforms an existing industry resin when used at equal capacity. Further detailed laboratory testing showed that logarithmic relationships exist whereby decolorisation efficiency decreases with increasing brix and with resin contact time, but increases with higher dry resin doses. Simulated long-term stability studies showed that the MIEX® resin retained similar efficiency under factory treatment conditions (70°C with 50 brix syrup) than it did under extended testing (ambient temperature) with drinking water, and did not suffer significant physical degradation. A prototype reactor unit was constructed for sugar factory testing and was capable of treating up to 30 m³/h of 45 brix syrup in a fluidised bed system with a 5 minute resin contact time. Higher brix solutions could not be used within the fluidised bed design due to viscosity problems and resin overflow. Typical experiments to examine resin exhaustion showed initial decolorisation rates of around 70% which dropped slowly to 20% after just over 200 tonnes of syrup (or around 90 tonnes syrup brix) had been processed. A series of tests designed to produce average decolorisation efficiencies of around 50% were conducted and were successful with no apparent drop in this efficiency until around 80 m³ syrup had been treated, which required a 4 hour run. These results showed that the initial laboratory experiments could be replicated on a factory prototype scale with the resin showing acceptable and reproducible performance.

Introduction

The process of producing refined sugar from harvested sugarcane has changed very little in the past 100 years. On the whole, sugarcane juice is obtained from the cane stalk by extraction or diffusion prior to clarification, concentration and crystallisation to produce raw
sugar. This raw sugar is further refined using affination, decolorisation and crystallisation processes to produce a white refined sugar. The number and nature of purification steps used to produce white sugar exist because raw sugar colorants encompass a wide variety of chemical classes and molecular sizes and cannot be removed using a single, widely applicable, decolorisation technology.

During the refining of raw sugar, the remnants of impurities and colorants are removed during crystallisation. However, in order to achieve a low colour crystalline product, it is critical that the feed syrup or liquor prior to crystallisation is of good quality. Traditionally, this liquor is decolorised by either activated carbon or ion-exchange resins.

Due to the potential extraction of premiums for higher quality (usually lower colour) raw sugar, there have recently been a number of technologically driven advances facilitating the production of higher quality raw sugars in the sugar mill. These advances include technologies such as membrane filtration to assist during juice clarification and ion-exchange chromatography to directly remove colorants, and serve to increase the value of sugar mill products as well as directly reducing the cost of subsequent refining. As summarised by Jensen (2007), many processes have been patented that are capable of directly producing white or near white sugars in a sugar mill from clarified cane juice (Kearney et al., 1995; Kwok et al., 1996; Monclin, 1995; Saskatchewan, 2000; Fechter et al., 2000; Shimanskaya et al., 2002). The implementation of the White Sugar Mill (WSM) process at the Felixton Mill in South Africa is probably the best example of new technology application within an existing sugar mill to dramatically improve product quality and unlock additional value from the sugars remaining in molasses (Jensen, 2007).

Orica Watercare has developed a proprietary magnetic ion exchange resin (MIEX®) used within commercial drinking water treatment plants to remove negatively charged dissolved organic carbon impurities. MIEX® resin has been developed specifically for drinking water applications and critically, can be employed within a continuous process that is capable of treating very large volumes. There are sixteen operational plants currently using MIEX® resin, with over ten others under design and construction. One such example at Wanneroo in Western Australia treats over 100 million litres of water per day in a continuous process. The MIEX® resin has several key advantages over conventional ion exchange resins warranting its consideration in the decolorisation of sugar factory process streams.

- **Bead chemistry:** The resin is a strong-base macroporous ion exchange resin, containing an evenly dispersed magnetic particulate (ferromagnetic iron) which causes each bead to act as a weak magnet in solution. This provides aggregation behaviour and allows the design of continuous process solutions since these aggregates form larger faster settling particles which ‘fall’ in solution and can be physically separated from a treated liquid stream which exits treatment vessels at an overflow point.

- **Rapid decolorisation kinetics:** The small MIEX® bead size (200 μm diameter versus conventional resins of 500–2000 μm) provides enhanced surface area to volume ratios and permits rapid colorant uptake. MIEX® processes therefore require smaller resin quantities, smaller inventories, reduced spent regenerants and smaller footprints for installation to meet performance objectives relative to conventional ion exchange methods.
Process flexibility: MIEX® resin can be used in various formats, including continuous or batch stirred contactors and fluidised beds. The trials conducted at Mulgrave Central Mill in this paper have used a fluidised bed design which is a higher performance version of traditional chromatography in which the resin column is run with a reverse or bottom to top flow. The magnetic qualities of the resin allow higher flow rates and efficiencies than for existing resins.

This paper describes the application of MIEX® resin from the laboratory scale up to a working raw sugar factory prototype unit capable of treating and decolorising syrup at flow rates up to 30 m³/h.

**Experimental**

MIEX® ion exchange resin was manufactured by Orica Watercare (Melbourne, Australia) and used for bench scale experiments and the pilot plant application. It was supplied as a suspension in solution and inventories used are measured by the total volume of the suspension, not by weight. The standard dry resin concentration supplied is 220 g/L of total volume.

**Laboratory scale evaluation**

Initial laboratory experiments investigated decolorisation performance, optimum contact time, temperature effects and the maximum loading of colorants by the MIEX® resin from consecutive syrup treatments. The ranges of these parameters investigated are outlined in Table 1. Colour measurements were made according to standard procedures within the Laboratory Manual for Australian Sugar Mills – Volume 2. Brix measurements were made using an Atago hand-held refractometer.

<table>
<thead>
<tr>
<th>Table 1—Experimental conditions for laboratory scale evaluation.</th>
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<tbody>
<tr>
<td>Syrup soluble solids content (brix)</td>
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<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>Contact time (min)</td>
</tr>
<tr>
<td>MIEX® dry resin dose (g/L syrup)</td>
</tr>
</tbody>
</table>

The laboratory trials were designed to answer fundamental questions to determine the likelihood of MIEX® resin being able to function in a sugar mill environment.

Does the resin remove raw sugar colorants?

How does the resin perform under much higher colorant loadings than for water treatment?

Do resin operating conditions need alteration to suit different mill substrates?

Are there process conditions where the resin is unsuitable for application?

Does resin performance degrade significantly after multiple regeneration cycles?

Are there resin stability issues under mill conditions, particularly under a constant high brix and high temperature regime?

MIEX® resin was vacuum filtered to produce a paste and the moisture content was determined for each trial run to calculate an accurate dry resin dose. Sugar syrup was obtained from the final evaporator stage from the Mulgrave Central Mill and was diluted with
demineralised water for the various experimental conditions. This syrup had an average colour of 16,000 ICUMSA colour units, an ash content of 1.5–2% and a soluble solids content of approximately 70 brix.

The decolorisation performance of the resin was tested using 500 mL syrup solutions to which were added appropriate resin quantities. This suspension was heated in a water bath, agitated for the desired contact time, filtered through Whatman 100 filter paper and the colour of the treated syrup measured. In addition to the raw sugar factory syrup samples, refinery sourced filtered raw liquor (FRL) and raw sugar syrups (64 brix) prepared by melting raw sugar were subjected to similar testing as described by Lindeman and O’Shea (2001).

An ion exchange resin, sourced from an Australian sugar refinery where it is employed to decolorise FRL, was tested under similar conditions.

**Mill prototype unit**

In order to transfer laboratory trials to the sugar mill on a meaningful scale, a prototype reactor unit was constructed to use MIEX® resin in a fluidised bed system.

The reactor was made of carbon steel and had fluidisation zone heights and diameters of 2400 mm and 1900 mm respectively, and a disengagement zone diameter of 2900 mm at the top of the column (Figure 1). The incoming flow at the bottom of the reactor unit was distributed by a distribution plate (500 mm x 500 mm) and travels upwards through a fixed gravel bed consisting of coarse gravel (100 mm depth), fine gravel (80 mm depth) and filter sand (120 mm depth).

![Fig. 1—The prototype MIEX® reactor unit installed at Mulgrave Central Mill.](image-url)
The gravel bed was enclosed by cloth on both sides to ensure separation of resin and filter sand when emptying the column. A sparger unit was installed over the gravel bed to facilitate mixing and to assist in achieving resin fluidisation. The designed upflow linear velocities in the fluidisation and disengagement zones were 10 m/h and 5 m/h respectively. The column was closed by a perforated steel plate to achieve an additional pressure loss and to prevent resin carryover. All relevant plumbing and pumps were installed to operate within the existing raw sugar production process. Typical operating conditions for the reactor unit are listed in Table 2.

Trials were conducted using the prototype reactor unit at the Mulgrave Central Mill during 2006 and 2007. The reactor was fully integrated into the mill process and was fed using final evaporator vessel syrup of approximately 70 brix which was diluted to 40–45 brix with water in the pipe leading to the reactor, enabling relatively accurate brix control. The average flow rate used during testing was approximately 20 m$^3$/h, although the unit was capable of processing at a maximum rate of 30 m$^3$/h.

<table>
<thead>
<tr>
<th>Table 2—Operating conditions for the prototype reactor unit.</th>
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<tbody>
<tr>
<td>Column height</td>
</tr>
<tr>
<td>Bed height (if different)</td>
</tr>
<tr>
<td>Syrup flow rate</td>
</tr>
<tr>
<td>Settled bed volume (calculated)</td>
</tr>
<tr>
<td>Fluidised bed volume (calculated)</td>
</tr>
<tr>
<td>Operating temperature</td>
</tr>
<tr>
<td>Resin inventory (supplied suspension)</td>
</tr>
<tr>
<td>Approximate resin mass in column</td>
</tr>
<tr>
<td>Average contact time</td>
</tr>
<tr>
<td>Average syrup brix</td>
</tr>
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</table>

The reactor was operated and regenerated in an upflow mode. During a typical decolorisation run, syrup was sampled every 15 minutes from both the inlet and outlet of the column. Process parameters such as flow rate and temperature were carefully monitored, and the syrup samples were subjected to brix and colour analysis.

The plant was operated for 8 hours, after which it was rinsed with hot water until the brix of the outflow was less than 2, before undergoing regeneration with 5000 L of a saturated NaCl solution at ambient temperature. After filling the reactor with the NaCl solution, the resin bed was sparged with air to evenly distribute the brine and the mixture was allowed to soak for one hour. The regenerant brine solution was drained through the bottom outlet of the reactor by gravity and the retained resin was rinsed with approximately 40 m$^3$ water in an upflow mode to remove excess salt and the process was re-started by the introduction of further syrup again as an upflow with the sweeten-on outflow going to waste until the brix was greater than 30. The total regeneration process was not optimised for time and required 3–4 hours.

Results

Laboratory scale study

Table 3 presents the results of initial experiments using a jar test to evaluate MIEX® resin against an industry used ion exchange resin. These simple tests examined the percentage
decolorisation from raw sugar syrups and from refinery sourced FRL samples under identical conditions. In all cases, the MIEX® resin outperformed the industry resin. This positive result led to a subsequent stage of detailed laboratory experiments (Figures 2 and 3).

**Table 3**—Decolorisation of raw sugar syrup and refinery filtered raw liquor (FRL).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Resin dry weight (g)</th>
<th>Time (min)</th>
<th>% Decolorisation (average of 3 tests)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sugar syrup (64 brix)</td>
<td>1</td>
<td>15</td>
<td>37 (Industry resin) 72 (MIEX®)</td>
</tr>
<tr>
<td>Raw sugar syrup (64 brix)</td>
<td>1</td>
<td>15</td>
<td>31 (Industry resin) 71 (MIEX®)</td>
</tr>
<tr>
<td>FRL (61 brix)</td>
<td>1</td>
<td>15</td>
<td>76 (Industry resin) 88 (MIEX®)</td>
</tr>
<tr>
<td>FRL (61 brix)</td>
<td>0.5</td>
<td>15</td>
<td>57 (Industry resin) 82 (MIEX®)</td>
</tr>
</tbody>
</table>

Figure 2 shows the results of the laboratory scale decolorisation experiments for a range of diluted raw sugar factory syrups at constant temperature (70°C) and resin dose (20 g/L).

The plot clearly shows that the percentage decolorisation exhibits a strong logarithmic relationship where increasing brix dramatically reduces resin efficiency.

This is presumably directly related to the increased solution viscosity. As expected, the data distinctly shows that decolorisation efficiency improves with increasing resin contact time so long as the resin does not become fully loaded during the experiment.

Fig. 2—Laboratory scale decolorisation of diluted raw sugar factory syrups at various brix levels and contact times, with a constant dry resin dose of 20 g/L at 70°C.

A further set of experiments showed the dependence of the decolorisation performance with the dry resin dose (Figure 3). As for previous experiments with constant contact times and various brix, the relationship between syrup decolorisation efficiency and
resin dose was logarithmic. The series of plots clearly show the expected outcome of decreased decolorisation efficiency with increasing brix of the syrup being treated.

![Graph showing decolorisation efficiency vs. resin dose and brix](image)

**Fig. 3**—Laboratory scale syrup decolorisation of diluted raw sugar factory syrups at various brixes across a range of resin concentrations. All experiments used a 5 minute contact time and a temperature of 70°C.

Other experiments evaluated the stability of the resin under sugar mill operating conditions. Simulated long term treatment of the MIEX® resin was conducted using a 12 week laboratory treatment with 50 brix raw sugar syrup at 70°C followed by morphological and functional examination. Microscopic examination of the resin beads indicated that this treatment had no deleterious effect and that the high osmotic shock from consecutive treatment with syrups and regenerants did not affect bead stability. Resin efficiency (capacity) after 10 consecutive regeneration cycles was found to be within a similar range experienced with extended drinking water treatment (results not shown) as measured by chloride capacity of the resin.

**Mill prototype study**

The results of the laboratory tests were used to design the prototype reactor. From the laboratory work (Figure 3), the necessary resin concentration and contact time required to achieve a target decolorisation efficiency can be readily calculated. The first series of tests with the prototype reactor unit were designed to confirm these laboratory results. The actual operating conditions were as shown in Table 2.

Figure 4 shows syrup decolorisation in a typical exhaustion experiment where the column was continually treated with syrup sourced from the evaporator stage (around 45 brix) until the resin was unable to further remove colour effectively, or was in effect, fully loaded. The graph shows that the prototype decolorisation behaviour with tonnes syrup brix processed also showed a logarithmic relationship which proved comparable to earlier
laboratory results. Initial decolorisation performance was approximately 70% colour reduction, before dropping to around 20% when around 90 tonnes of syrup brix had been processed.

![Graph showing decolorisation performance over syrup brix processed](image)

Fig. 4—Prototype unit decolorisation of evaporator syrup at 45 brix.

![Graph showing operating parameters](image)

Fig. 5—Operating parameters for the prototype unit decolorisation experiment shown in Figure 4.

The process parameters from this experiment are depicted in Figure 5, where the brix, temperature and flow profiles through the unit are recorded. The graph shows that there was effective temperature control across the process run with temperatures remaining largely
between 60–70°C. Flow measurements through the reactor unit increased gradually to a maximum value of approximately 24 m³/h and remained steady during the run time after this point. The brix value of the output from the reactor unit increased to a maximum of 47 brix during the process run due to the sweetening on process used to begin the cycle. This process was required since exposing the resin to an immediate change in viscosity after regeneration would have resulted in very high resin loss or carryover out of the top of the reactor unit, with the added difficulty that the syrup output could not be mill processed due to resin contamination in the overflow. Further experimentation showed that higher brix streams could not be effectively processed with the current fluidised bed setup without risking major resin loss. This is due to the increased viscosity of the syrup stream which significantly affects resin fluidisation behaviour. Under a different process setup such as a traditional column, higher brix syrups could be processed with the MIEX® resin.

**Discussion**

Ion exchange processes have been regularly examined by sugar technologists over a long period of time. Despite being proven for refinery applications, they have not found routine application within sugar mill situations. The primary reasons for this include short decolorisation cycles due to heavy salt and colorant loadings in juice/syrup streams, cost of regenerants, waste disposal problems, resin fouling and the impacts of cane supply variation, particularly with respect to poor weather affecting harvesting. A further major disadvantage is the fact that such processes are usually conducted in batches and are not amenable to continuous application.

The MIEX® resin has been specifically developed for continuous application, however, its designed application for drinking water treatment is a very different operating environment than for a sugarcane juice or syrup stream. For water applications, the resin was designed to remove dissolved organic carbon (DOC) which is usually present at around 10 mg/L in source waters. Traditional water treatment using MIEX® resin is a regime using temperatures of around 20°C and employs contact times of between 5 and 20 minutes.

Colorant loadings experienced by the resin in raw sugar factory applications are considerably higher than this, and the process streams treated are of higher viscosity. This is critical in applications using a fluidised bed process which rely on the fact that the magnetic resin needs to aggregate and fall in solution at a sufficient rate to provide satisfactory performance. In addition, there are also elevated temperatures to consider which may impact on the kinetics of both decolorisation and aggregation processes, as well as questions of resin stability and longevity under more aggressive operating conditions.

Laboratory scale testing indicated that the higher temperatures used for syrup experiments enabled more efficient contact between syrup and resin which reduced the necessary time for a 50% syrup colour reduction to approximately 1 minute for low brix solutions and approximately 5 minutes for higher brixes (Figure 2). Interestingly, there are significant differences in percentage decolorisation when contact times were increased from one minute to five minutes. Unfortunately 10 minute contact time results were not conclusive, due to experimental error. Assuming that the resin does not become fully loaded with colorants, it is expected that decolorisation for a contact time of 10 minutes will be similar to or greater than decolorisation achieved during 5 minutes contact time. The plot shows that when using a dry resin concentration of 20 g/L under laboratory conditions, sugar syrup of less than 13 brix will undergo an 80% reduction in solution colour for a 5 minute contact time.
Further laboratory experiments using increased resin concentrations showed that levels of decolorisation beyond 60% could be obtained for any syrup solution up to 70 brix in a single 5 minute contact time (Figure 3). However, it is likely that such high resin doses are not commercially sensible.

Decolorisation experiments both in the laboratory and the prototype reactor unit demonstrated that a strong logarithmic relationship exists between the percentage decolorisation and both resin concentration and the syrup brix (Figures 2, 3 and 4). As expected in the laboratory experiments, percentage decolorisation decreased with increasing brix, reflecting the increased colour loading of the syrup and the increased viscosity which affects the kinetics of colour removal and resin settling.

During the reactor unit trials, steady state fluidisation was initially difficult to achieve due to the potential for resin loss through the overflow at the top. Maintaining the substrate brix around 40–45 brix permitted steady state operations with an effectively fluidised bed, while virtually eliminating resin loss.

The decolorisation performance illustrated in Figure 4 could be directly compared to the laboratory work by estimating the reactor unit resin concentration and measuring the substrate brix. The reactor unit contained an initial MIEX® resin inventory of 3800 L (836 kg dry weight) within a fluidised bed volume of around 9.24 m$^3$, which translates into an approximate dry resin concentration of 90 g/L in the fluidised bed.

By reading off the graph in Figure 3, it can be seen that treatment of a 45 brix solution with 90 g/L dry weight resin would be expected to produce a decolorisation efficiency of almost 60% based on laboratory trials using a 5 minute resin contact time at 70°C. As shown in Figure 4, the percentage decolorisation in the reactor unit begins at around 70% before starting to tail off. This result is affected to some degree by errors in estimating the actual resin volume and fluidised bed volume but provides confidence that the laboratory work is an effective predictor of larger scale decolorisation experiments and can be used to guide the design of scaled up equipment.

Further work not delineated here examined shorter decolorisation runs of approximately 2 hr in duration using the same conditions established above. Performance across six separate trials was relatively constant and achieved an overall decolorisation efficiency of 50% at a syrup flow rate of 20 m$^3$/h, which equated to the treatment of around 40 m$^3$ of syrup (or approximately 18 tonnes of syrup brix) prior to regeneration. Three of these trials were extended to the treatment of double this quantity of syrup before the observation of any significant decrease in percentage decolorisation. This work provides confidence in the regeneration regime used and the performance of the resin after regeneration.

Conclusion

The laboratory and prototype reactor unit tests show that effective decolorisation of a highly coloured sugar syrup stream is possible using MIEX® resin and that laboratory results can be replicated on larger scales. Further, the extensive laboratory trials also provide a means of designing larger scale equipment by providing relationships between process stream brix, MIEX® resin dose and decolorisation efficiency.

A prototype fluidised bed setup with a liquid inlet from the bottom and a simple gravel distribution system was able to process sugar syrup up to a solids content of 45 Brix and decolorise the syrup by up to 70%.
Further work is being undertaken to optimise resin regeneration conditions and to minimise brine waste generated during regeneration in order to finalise designs for large scale mill installations. Future studies will also focus on stabilising decolorisation performance and achieving an integrated fully continuous system.

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