

REFEREED PAPER

AFTER FOUR DECADES: A NEW LOOK AT ION-EXCHANGE RESIN AT THE TONGAAT HULETT REFINERY

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Abstract

In November 1978 the bone char decolourisation plant at Tongaat-Hulett Refinery (Hulref) was replaced with five ion-exchange columns. This change had major benefits for the refinery in terms of chemical and energy costs, and refined sugar quality.

In order to improve the liquor decolourisation, a further five secondary stage resin columns were installed in 1987. This improved the overall decolourisation from 60 to 70%.

Since 1978 the resin plant has been using the same macroporous strong base anion acrylic resin. Having a single supplier of resin for the refinery has been identified as a risk. In view of this it was decided by the refinery management to evaluate resin from other suppliers. In the paper the work done to evaluate an alternate resin supplier will be discussed.

The following areas will be covered:

- Technical performance of the resin at various cycle times
- Commercial evaluation of the resin
- Technical support from the suppliers
- Resin lifetime prediction based on analysis.

The trial has also allowed the refinery to re-evaluate process conditions, and the lessons learnt from the exercise are expected to benefit the refinery in the long run.

Keywords: ion-exchange, resin, decolourisation, effluent, colour removal

Introduction

The Refinery was established in 1910. An outline of its history and the current refining operations are described in detail by Tayfield (1996), and Moodley and Cockburn (2015). The original decolourisation processes employed by Hulref was carbonatation, followed by bone char. Due to the bone char plant being old and in need of extensive repairs, it was decided to evaluate the option of replacing the plant with ion-exchange resin.

After extensive pilot plant investigation and due to the success of ion-exchange in other part of the world it was decided (Cox, 1980) to replace the 56 char cisterns with five resin vessels. This change had major benefits in terms of cost and quality of refined sugar.

In 1987 (Kirkiridis, 1992), to meet the refined sugar quality requirements of the export market, a secondary resin decolouring stage was added. The addition of the secondary stage improved the overall decolourisation from 60 to 70%.

In the original pilot plant evaluation both macroporous strong base anion acrylic resin and styrenic resin were evaluated (Cox 1980). It was found that for the carbonated liquor feeding the resin plant at Hulref the macroporous strong base anion acrylic resin gave the best results of terms of fouling resistance, colour removal and cycle time (Loker, 1983). In view of this, since 1978 Hulref has been using the macroporous strong base anion acrylic resin from a single supplier.

Having a single supplier of resin for the refinery has been identified as a risk. It was thus decided by the refinery management to evaluate resin from other suppliers. In this paper data from a 24 month evaluation study on an alternate resin supplier is presented.

Resin selection

Ion-exchange resins will have an affinity for various colour bodies contained in refinery process solutions (Getaz, 1990). There are a variety of compounds that are present (Davis 2001), and most are removed by standard precipitation and coagulation techniques, carbonation being an example (Figures 1 and 2).

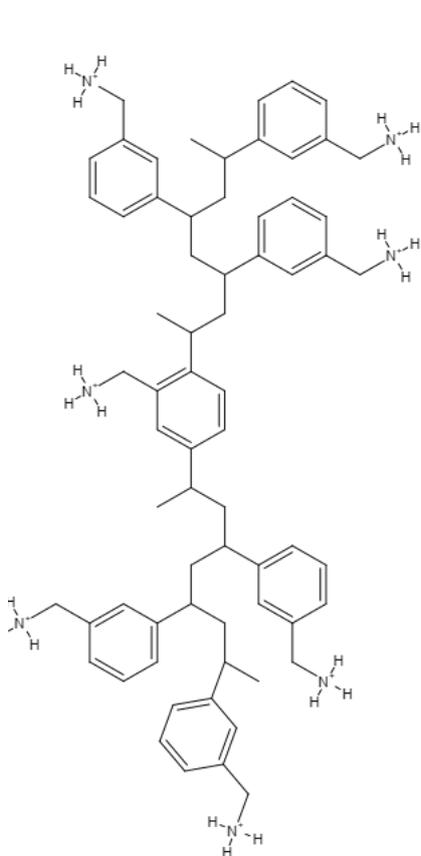


Figure 1. Crosslinked polystyrene resin.

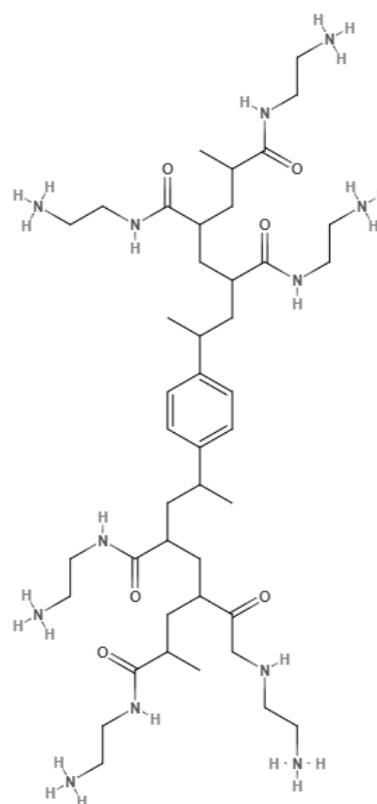


Figure 2. Crosslinked polyacrylate resin.

The mechanism of adsorption on ion-exchange resins is either by van der Waal's attraction to the matrix, or by electrostatic attraction to the functional group. Most of the chromophores are negatively charged, and thus resins with positively charged functional groups are used. These are generally referred to as strong base anion resins.

While the styrenic resins in Figure 1 are superior in their loading of aromatic polyphenolic compounds, they are also more difficult to regenerate. This produces a better quality of sugar as measured by colour value, but the resins are more expensive to regenerate, with a consequent increase in effluent volumes.

Acrylic resins in Figure 2 are more commonly used for this reason and they are also able to operate at higher capacities. Due to the amidic linkage to the functional groups, which are hydrolysed at high temperatures, these resins lose capacity faster than styrenic types.

The resin types used in decolourisation are almost always of the macroporous type. This means that the resin has been produced using a porogen solvent that increases the pore diameters to 100 nm, as opposed to the gel types that have pores of the region of 1-2 nm, and are only able to remove small organic molecules of sizes below 500 daltons. For example a sucrose molecule is 342 daltons. Gelular type resins also show poor kinetics for all but inorganic ionic species.

For this reason an acrylic strong base anion resin with a macroporous structure is most often chosen for the first stage of ion-exchange decolourisation. In some cases a second stage using a styrenic strong base anion resin is used as a polisher, effectively removing the colour bodies that have a lower affinity to the acrylic types (Bento, 1998).

Operational information

Brown liquor from the carbonatation station feeds the four primary vessels. Primary liquor from all vessels is collected in the primary liquor tank and fed to the four secondary vessels, again in parallel. The average liquor flow through the vessels is at 2.5 bed volumes per hour (BV/h). Six vessels have stone beds which differ in the liquor outlet configuration; three have laterals covered in mesh and one has wedge wires.

At any stage the fifth pair of vessels will be on regeneration. A caustic brine solution with 0.4% caustic and 10% salt is used to regenerate resin at 2.5-3 BV/h. Based on the performance of the vessel pair, at approximately 15 cycles an acid wash with 4% HCl is performed. The regeneration is in sequence and not performance based. When resin is exhausted after approximately 350 cycles, it is discarded. Resin from the secondary vessel is transferred to the primary vessel and new resin is charged into the secondary vessel.

The resin plant performance and brown liquor colour for the 2017/18 season is shown in Figure 3.

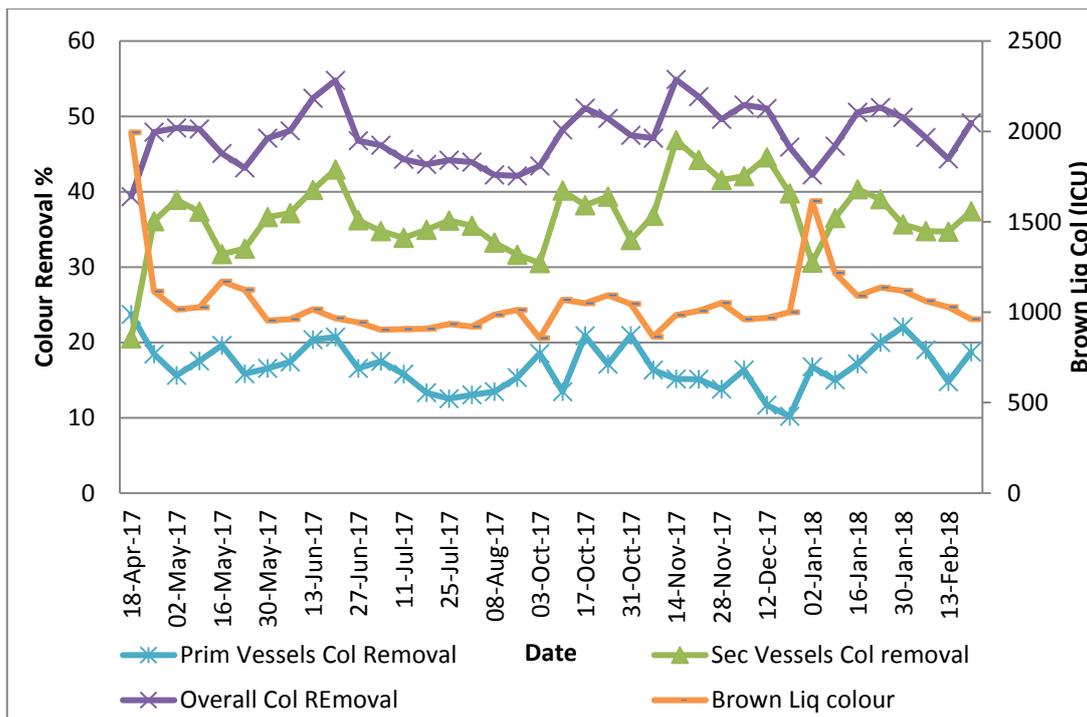


Figure 3. Resin plant performance from 24 hour composite samples.

The following comments can be made from Figure 3:

- The colour of the brown liquor feeding the resin plant varies from 800 to 2000 icu.
- The resin plant total colour removal varies from 40 to 55%.

It must also be noted that the colour of the raw sugar entering the refinery can vary from 1500 to 3000 icu. This will have an adverse effect on the performance of the resin plant.

The cycle times for all vessels are shown in figure 4. The cycles depicted are affected by operating conditions and plant time efficiency. During plant stoppages, the vessels are assumed to be online thus increasing cycle times. Typical cycle times recommended by resin manufacturers are 24-72 h.

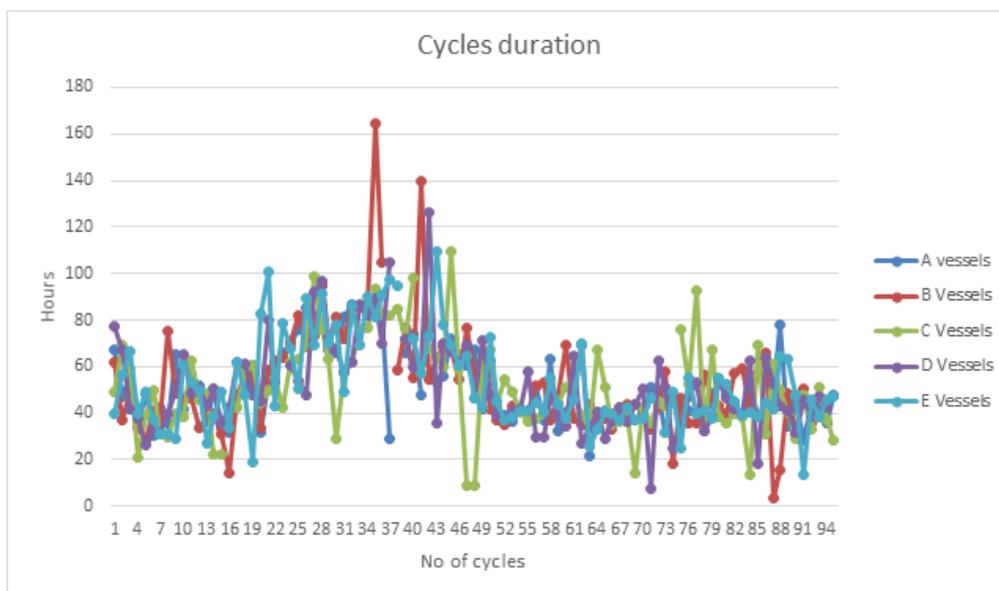


Figure 4. Resin vessels cycle times.

Trial conditions for resin evaluation

Two polisher vessels were filled with media within a week of each other for the most comparable trial. Vessel A2 was changed out with the current resin and Vessel D2 was changed out with Lewatit S5528 in March 2016. After 190 cycles on Vessel A2, and 184 cycles on vessel D2, the resins were changed from the polish position to the lead position (vessels A1 and D1 respectively). The relevant dates are detailed in Table 1.

Table 1. Trial overview details.

	Current Resin	Lewatit S5528
Fill date (polisher position)	12/03/2016	19/03/2016
Polisher vessel	A2	D2
Number of cycles in the polish position	190	184
Moved to primary position	23/09/2017	10/06/2017
Primary vessel	A1	D1
Number of cycles in the primary position to date (up until 22/02/2018)	54	70
Total number of cycles to date (22/02/2018)	244	254

Initially, during the change out procedure, the vessels were filled with 13 000 litres of resin. The vessels were run through one cycle, including backwash, before being topped up with the final 3 000 litres of resin on the first regeneration.

The bedvolume of each vessel was approximated at 13 000 litres once fines are removed by backwash. Top up volumes are detailed in Table 2.

Table 2. Resin volumes (litres) and top up.

	Current Resin	Lewatit S5528
Initial volume installed	13 000	13 000
Initial top up	3 000	3 000
Top up volume	5 500*	1 000
Date	10/07/2017	26/06/2017
Number of cycles	185	180
Top up volume	4 500	4 000
Date	11/12/2017	08/01/2018
Number of cycles	222	236

*The top up of the current resin was far greater than that of the Lewatit S5528. It could not be established whether this was due to resin breakage.

Particular attention was given to the resin volumes throughout the trial. A previous trial where huge losses were experienced had to be abandoned, and for this reason there was a perceived risk. To reduce this risk, the resin volumes were visually checked every week by an operator (it is a standard procedure to check resin volumes every week). Further, during this

trial the two trial resins were sent for analysis, and cracked and broken beads were reported (see below Figure 9: Physical condition of resin beads over time).

Commercial information

The relationship between a customer and a supplier is often complex, as both entities have competing priorities. The customer often utilises the leveraging of competition as the most common method of procurement and achieving cost-competitiveness, whilst the supplier prefers fixed, structured long term arrangements, often without price flexibility.

In this particular case Hulref has been using the same supplier of Resin for 39 years, thus creating a situation of non-competitive 'Sole Source' procurement. A sole source procurement process can be defined as any contract entered into without a competitive process based on justification that only one known source exists, or that only one single supplier can fulfil the requirements (NASPO, 2015).

This unsatisfactory situation creates the following procurement risks:

- **Lack of Cost Competiveness and Cost Degradation:** The supplier, aware of the Hulref procurement process, adopts a resource-monopoly position and becomes more powerful in negotiations whilst adopting price inflexibility. The lack of competition has therefore unintentionally created an increase in the Total Cost of Ownership of the goods.
- **Supply Chain Risk:** Lack of Supply for whatever reason from the Sole Source Supplier can have a devastating impact on production and factory performance.
- **Quality Risk:** A serious quality defect could cause irreparable damage to the market reputation of Tongaat Hulett.
- **Complacency:** A long term relationship with a key supplier can result in both sides accepting the status quo without seeking excellence and innovation.

To mitigate the risks above, and in terms of the Porters 5 Forces Model (Figure 5), (which is a model used to understand the forces that shape competition within a supply market) it was imperative for Hulref to transfer power away from the supplier to the customer.

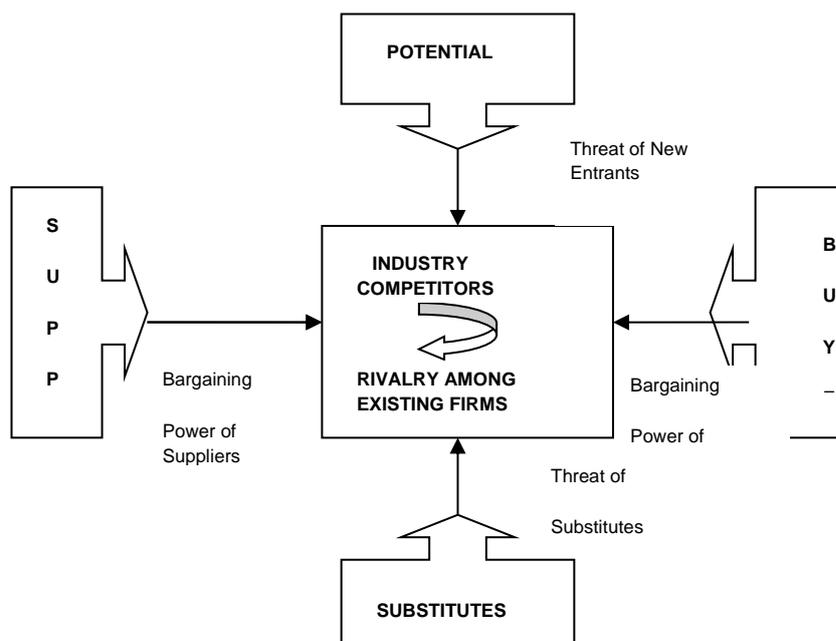


Figure 5: Porters 5 Forces Model (Lynch, 2000).

The sourcing strategy adopted was to undertake a competitive bidding process to test for cost-competitive alternates. The request for proposal (RFP) process yielded the results shown in Table 3.

Table 3. RFP competitive pricing.

	% Savings
Existing Supplier	23%
Cwenga/ Lanxess	41%
Supplier A	16%
Supplier B	32%
Supplier C	23%

The tender process yielded significant gains as all bids received were more competitive than the budget price. Expectedly the introduction of competition also pressurised the existing supplier to reduce prices by 23%. However, the most cost competitive resin was the Lanxess resin resulting in a saving of over 41.37%.

Results and Discussion

Overall ion-exchange performance

Throughout the entire trial period the colour around the ion-exchange unit process was recorded as 24-hour composite samples (Figure 3). The brown liquor colour level remained fairly constant throughout the majority of the initial phase of the trial where the resins were in the polish position. An improvement was seen after the April shut, just before the resins were changed to primary positions.

The outlet from the polish ion-exchange stage (secondary liquor) overall has become better in quality, and this might be attributed to the fact that one of the resin trains was changed out earlier than scheduled, to accommodate the trial. Efforts were also made to shorten regeneration times, and therefor run lengths, leading to a more efficient decolourisation over the resins.

Decolourisation performances of resins on trial

During phase 1 of the trial the resins were both placed in the polish position. After 184 cycles on the Lewatit and 190 cycles on the current resin, the resins were changed from the polish position to the lead position. As of writing, the resins are still in the primary position, and will continue for another 50-100 cycles.

While the resins were in the polish position the decolourisation performances of the two resins were near indistinguishable. When the resins were transferred from polish position to lead, it can be seen in Figure 6 that the decolourisation ability of the Lewatit resin drops and then rises again to meet the performance of the current resin. This was attributed to the timing and the extra volume of top up required for the current resin, while the Lewatit resin was not topped up to the same degree.

Resin analysis

Samples of the two trial batches of resin were taken for analysis. These samples were sent to both Lanxess (Table 4) and the current resin manufacturer (Table 5) for testing.

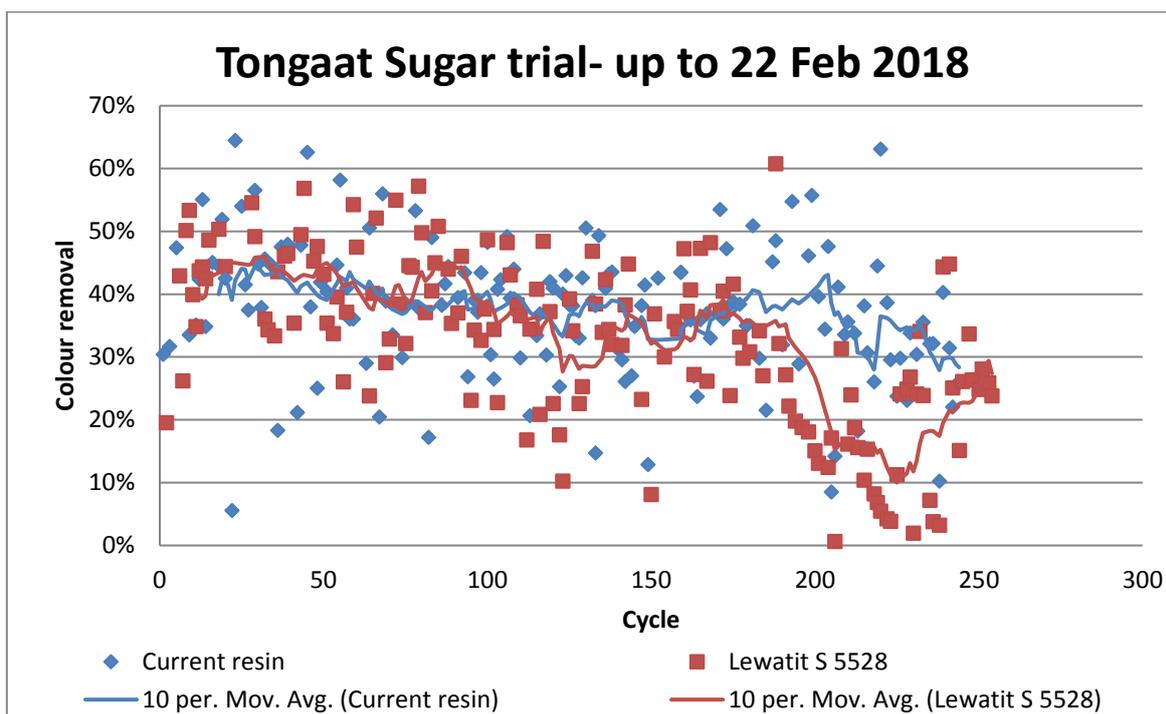


Figure 6. Comparison of colour removal per cycle throughout trial.

Table 4. Results from LANXESS Deutschland GmbH (Ulrich Litzinger).

Parameter	Current resin			Lewatit S5528		
	0	97	192	0	112	184
Number of cycles						
Colour	White	Dark brown	Dark brown with beige	Bright yellow	Brown	Dark brown
Perfect beads (%)	99	99	99	99	99	99
Cracked beads (%)	0	0	0	0	0	0
Broken beads (%)	1	1	1	1	1	1
Total strong capacity (eq/l)	0.71	0.5	0.77	1.1	0.65	0.72
Decolourisation performance (%)	85.4	85.7	82.6	86.1	85.9	80.1
Swelling % (Cl - OH)	22	20	1	18	10	1

Table 5. Results from current resin (RST labs with comments from Peterlan Consulting).

Parameter	Current resin			Lewatit S5528		
	133	174	196	143	184	206
Number of cycles						
Colour						
Perfect beads (%)	95.1	94.9	95.3	97.3	95.3	92
Cracked beads (%)	3.2	3.5	2.8	2.2	2.7	5.1
Broken beads (%)	1.6	1.6	1.9	0.5	2	2.9
Total strong capacity (eq/l) OH form	0.47	0.45	0.54	0.49	0.5	0.5
Total strong capacity (eq/l) Cl form	0.49	0.45	0.55	0.52	0.52	0.52
Strong base capacity %	63.3	55.6	61.8	73.1	59.6	59.6
Moisture Holding Capacity % (Cl-)	69.6	68.7	69.5	70.4	71	70.3
Dry Matter g/l (Cl-)	198	204	199	190	185	195
Swelling % (Cl - OH)	4.2	Nil	2	7.1	4.9	3.4

The dry matter is a measure of the irreversible fouling of the resins. The differences between the two types of resin are not significant at this stage. The moisture holding capacity, likewise, gives an indication of the free-pore volume, higher values being preferable.

A particular interest was taken during the trial in whether the resins experienced losses due to physical damage of the beads. It is expected that over time factors such as chemical exposure and physical movement of resin can cause damage to the beads.

The broken beads and fines are backwashed out and would result in total loss of volume. The percentage of broken beads was found to be very low from both laboratories (Figure 7). This points to improved resin manufacture techniques from both suppliers. However, the figures from the Lanxess laboratory were lower than those obtained by RST, which were attributed to differences in analytical method.

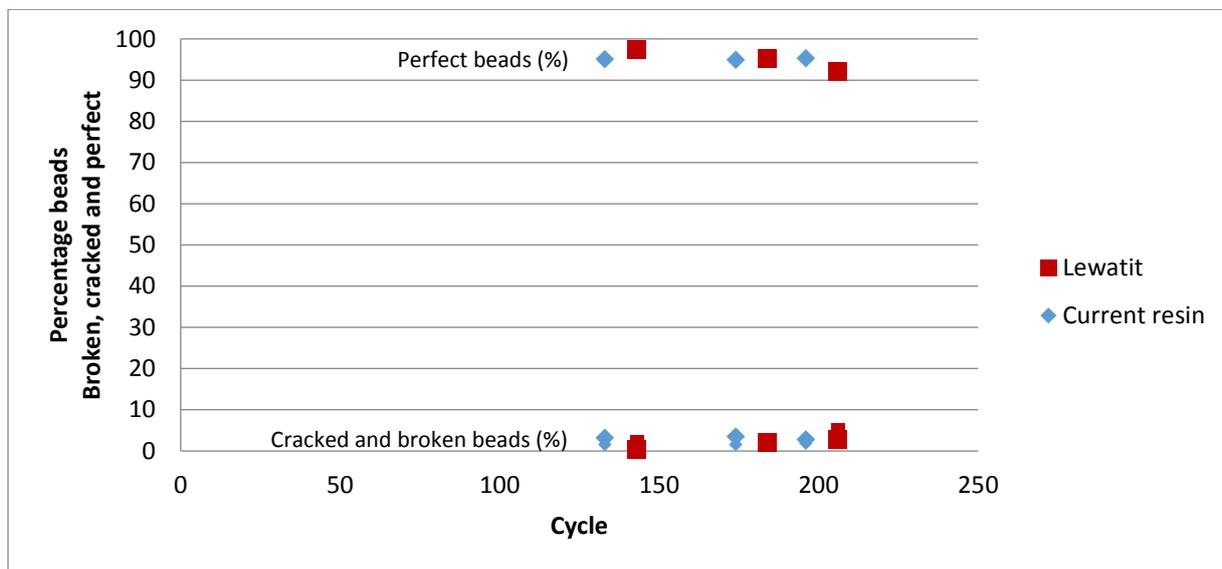


Figure 7: Physical condition of resin beads over time.

The total strong capacity of the resin was analysed to give an indication of the number of functional groups still available for exchange. The decrease in strong base capacity is as expected for an acrylic resin, due to the hydrolysis of the amidic bonds and the conversion of quaternary amine groups into tertiary amine (Figure 8,).

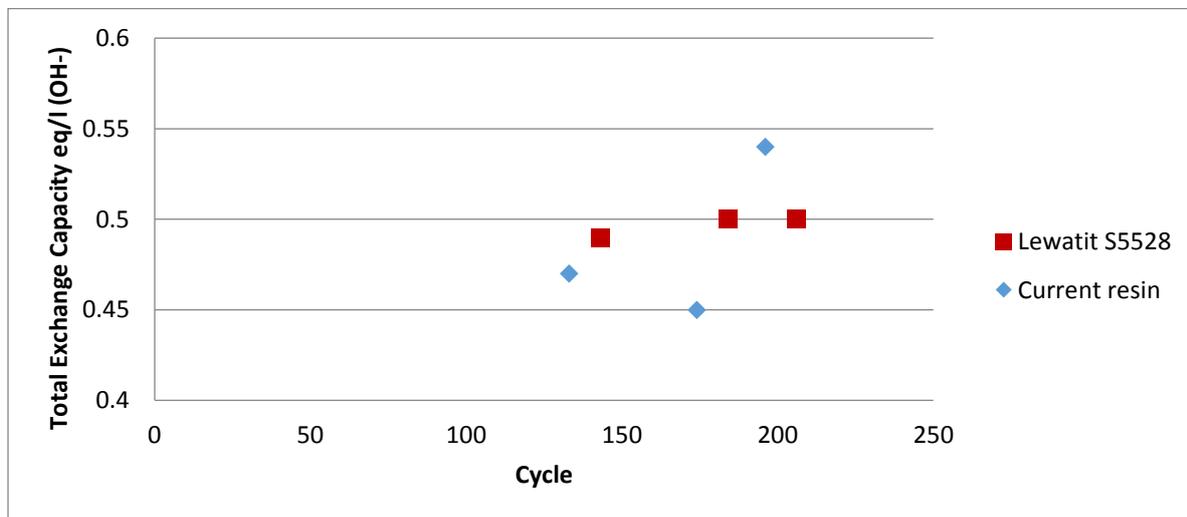


Figure 8. Total strong capacity over time.

This can be seen in Figure 8, where the total strong capacity of the Lewatit S5528 drops slightly over time. A similar effect can be seen on the first two data points of the current resin, but before the third sample capture, the vessel was topped up with about 40% new resin, skewing the result upwards.

These capacity losses are related to the effects of time and temperature. The capacities affect the adsorption of ionic and strongly polar colour bodies on to the functional groups, but not the adsorption onto the matrix of the resin.

Challenges faced during trial

A number of challenges were faced during the trial period that may or may not have affected the results. Because of the parallel nature of the trial, any effects should have been fairly similar between the two vessels.

Severe storms and flooding during 2017 caused a longer stoppage than usual on the plant. This has extended the period of the trial, but, as most data has been reported with regards to number of cycles, this should not affect any calculations on resin lifetime.

Extended cycle times were experienced due to delays in regeneration. Efforts were put into place to reduce the time that each train spent in the regeneration stage, such as running the regens of primary and secondary vessels in parallel. This in turn allowed for shorter run lengths, and the overall colour removal performance has benefited from this minor change. Plant issues caused some downtime, but the number of cycles is the basis of comparison.

At the end of the first stage of the trial, the resins were moved from the polish to the lead position. In the case of the Current resin the levels of resin have dropped to a greater degree than the Lewatit resins. This was attributed to a faulty backwash water valve that was under-reading, resulting in high water flow and hence carryover of resin during backwash. As a result the quantity of top up was considerably higher and the Current resin initially showed a high colour removal. After a number of cycles this difference decreased.

Conclusion and recommendations

The following conclusions can be drawn from this intensive 2 year evaluation trial:

- The performance of both resins was very similar in all aspects.
- The cost of the Lewatit resin is about 32% lower than the current resin used by the refinery.
- A new source of ion-exchange has been technically and economically evaluated and found acceptable in both regards.

In view of this major benefit it was decided by the management of the refinery to replace 50% of the current resin with the Lewatit. This translates to an annual savings of R2.1 million. In addition, a number of control parameters have been identified that will result in improved plant operation.

Acknowledgments

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