

REFEREED PAPER

PRE-TREATMENT OF REFINERY FINAL RUN-OFF FOR CHROMATOGRAPHIC SEPARATION

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Abstract

In the case of a back-end refinery, the final run-off or return syrup of 92-95% purity and 75° brix is generally returned to the raw mill to be combined with raw syrup and boiled in the A-pans. Approximately 8% of the input raw sugar brix into a refinery is returned, consequently locking up A-pan capacity and, in the case of a factory with marginal pan capacity, cane throughput is restricted. In addition, energy consumption is increased and sugar losses in final molasses are elevated. A number of processes have been considered to eliminate recycling refinery run-off, most of which require pre-treatment and/or high capital investment with a high degree of commercial risk. Test work was undertaken at the Tsb Malalane cane sugar refinery to determine the optimal pre-treatment option for decolorising and softening refinery return syrup. The pre-treatment results indicate that chemical softening, followed by the addition of a cationic colour precipitant and pH adjustment with sulphur dioxide, yields appreciable calcium reduction and modest decolourisation. The overall benefit indicates that the treated final run-off is of suitable quality to apply another crystallisation step and/or alternatively consider for further purification by chromatographic separation and/or resin decolourisation.

Keywords: sugar refining, final run-off, return syrup, pre-treatment, softening, chromatographic separation

Introduction

The Malalane mill refinery is a typical back-end cane sugar refinery. Decolourisation is achieved by carbonatation followed by sulphitation. Further purification is achieved by traditional evaporative crystallisation. Normally four or five boiling stages are necessary to maximise sugar recovery. This refining process is adequate to meet the commercial bottlers and EEC2 refined sugar specifications. The final refinery run-off (also termed 'Jet 4', 'return syrup' or 'refinery molasses') is approximately 8% of the input raw sugar brix into the refinery and is returned to the raw mill to be combined with raw cane syrup and crystallised in the A-pans. The typical quality of Malalane mill refinery run-off is given in Table 1.

In reviewing technologies to produce white sugar, Walthew and Jensen (2002) described crystallisation as a well-established technique for purifying and separating materials that has proved itself in the sugar industry to be robust and reliable and each recrystallisation step is highly effective at improving the quality. However, its main drawbacks are:

- Energy demand each time sucrose is redissolved, recrystallised and centrifuged.
- Recrystallisation requires a large investment in pans and centrifuges.

Table 1. Typical quality of refinery run-off.

Brix (%)	76 - 78
Purity (%)	92 - 95
CaO (ppm)	2000 - 4500
Colour (ICUMSA)	6000 - 8000
Invert (%)	2 - 2.5
Sucrose (%)	66 - 68
Conductivity ash (%)	1.2 - 1.5

The interdependence of the refinery and raw mill streams in a back-end refinery and the number of crystallisation steps are shown in Figure 1. When compared to a stand-alone refinery, the practice of reprocessing final run-off in the raw mill is operationally less complicated and utilises existing raw mill process plant. However, combining refinery run-off (low colour and high purity) with cane syrup (higher colour and lower purity) diminishes the benefits of lower feed material colour and higher purity for crystallisation. The additional brix load on the A-pan station demands more pan capacity and, if this is a constraint area, pan exhaustions will suffer with consequent increased final molasses and undetermined losses. Of greater consequence for a factory with marginal A-pan capacity is that cane crushing capacity is restricted by the additional brix loading from final run-off, as well as from the resulting higher recirculation from the B and C-pans.

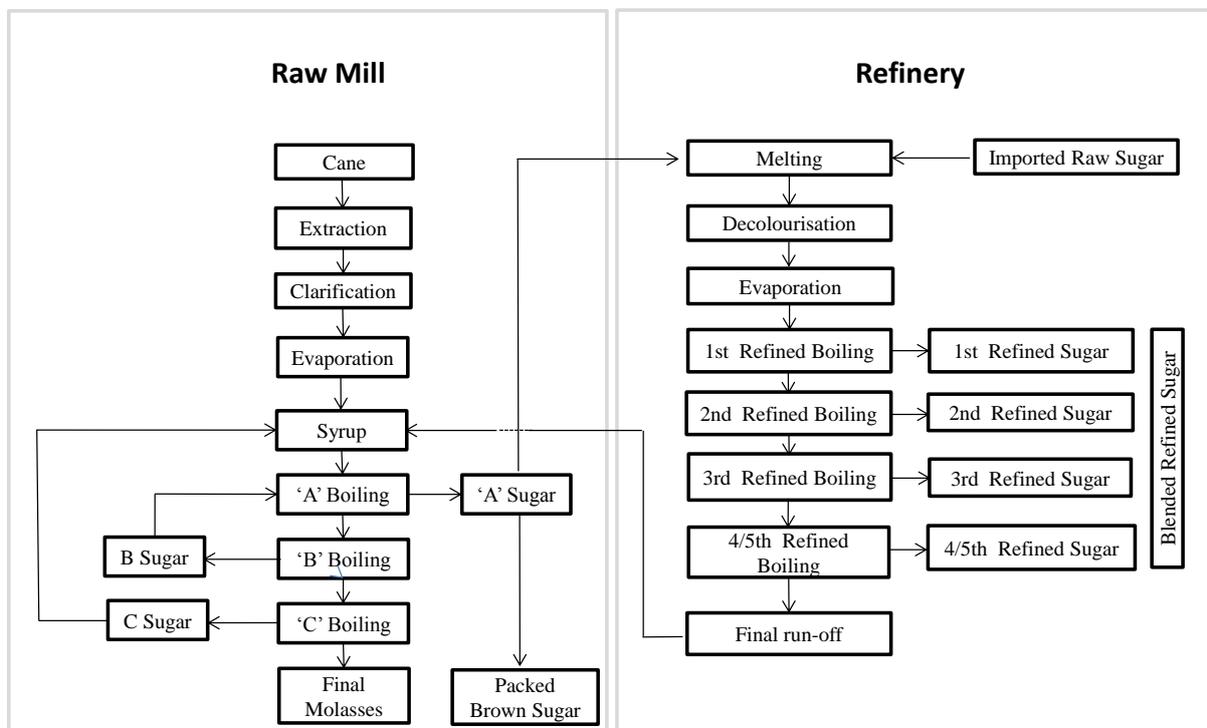


Figure 1. Malelane raw mill with back-end refinery flow streams.

The negative impacts from processing refinery final run-off at the Malalane refinery have been quantified and are presented in Table 2. Although the recoverable refined sugar value

still makes the reprocessing worthwhile, the cane crushing capacity benefit and opportunity to reduce costs make a strong case to find an alternative, more cost effective solution.

Table 2. Annual impact of reprocessing refinery run-off at the Malalane refinery.

Refinery capacity Refining rate: 56.3 ton raws/h → 55 ton RSO/h → 350 000 ton RSO p.a. Final run-off: 5 m ³ /h → 3.8 ton brix/h → 28 000 ton brix p.a. → 25 000 ton sugar p.a.	
Impact on cane crushing capacity Brix loading in final run-off is equivalent to 23 ton cane/h Cane capacity loss is 120 000 ton cane p.a. Sugar opportunity loss	= 14 000 ton sugar p.a.
Impact on final molasses loss <i>Crushing season</i> High purity brix load in the raw mill increases final molasses losses Additional molasses loss of 2% (derived from O/C refining performance)	= 5000 ton sugar p.a.
<i>Off-crop refining</i> Higher molasses losses during off-crop refining Molasses loss	= 800 ton sugar p.a.
Impact on refining loss Refining loss is estimated to be 0.7% (UDL + sludge) Refining loss due to recirculation in the refinery	= 200 ton sugar p.a.
Total sugar loss	= 20 000 ton sugar p.a.
Impact on steam usage Recovery boiling in the raw house increases HP steam usage by ±5 ton/h Coal requirement for recovery boiling (in and off-crop)	= 5000 ton coal p.a.

Alternative options for handling refinery molasses

Over the past few years, the mill has considered several options to eliminate the negative impacts of processing refinery run-off in the raw mill.

Speciality by-products

These are supply and demand driven. Some candidate technically viable by-product options were considered and found to be capital intensive with a high degree of commercial risk.

Sale of final run-off to a distillery or other by-products plant

This has proved nonviable due to the fact that the recoverable refined sugar value greatly surpasses its value as raw material feedstock. Transport and logistics also increase the costs.

Production of a speciality product such as golden syrup

The market demand for such products is far too small to absorb a significant proportion of the final run-off.

The production of speciality low colour liquid sugar

This would require major capital, significant decolourising and de-ashing resin inventory, and the disposal of regeneration streams would be problematic.

Membrane filtration

This was considered and the extremely low flux rates at the brix level in final run-off currently render this option uneconomical.

Improved recovery through crystallisation

The refinery operations staff have revisited crystallisation practices with a view to optimising refinery yields and thereby reducing the quantity of refinery final run-off. This is on-going optimisation work.

Chromatographic separation

This technology offers a means of purifying refinery run-off to eliminate the negative impacts that arise from its reprocessing.

Chromatographic separation

Chromatographic separation is a well-developed process and is being successfully applied for desugarisation of beet molasses and purification of high fructose corn syrup. Work on ion exclusion desugarisation of refinery Jet 4 done by the Sugar Milling Research Institute (Peacock, 1996) has demonstrated the technical feasibility of treating carbonation refinery run-off. The benefits identified from this laboratory trial were:

- 90% recovery of sucrose from the feed
- 88% decolourisation
- 71% ash reduction
- 64% less oligosaccharides
- 74% less monosaccharides.

Subsequent crystallisation in a pilot pan showed that the benefits continued through to refined sugar.

Walthew and Jensen (2002) described chromatography as an attractive off-the-shelf technology; however, with the following drawbacks:

- Low brix recovered streams.
- The feed material must be free of divalent ions.
- The feed material must be free of suspended matter.

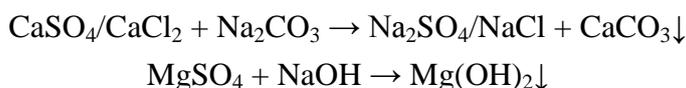
Peacock (1996) stated that divalent ions in the feed, notably Ca^{2+} and Mg^{2+} , replace the Na^+ ions in the resin. The large size of these cations when compared to the size of the sodium ions results in a decrease in the sizes of the pores within the resin beads. The effect decreases the efficacy of the resin in separating components.

Provided that softening can be accomplished cost effectively, that turbidity can be reduced to an acceptable level and that the low brix streams can be accommodated without an onerous energy requirement, chromatographic separation would be a viable option for decolorising and de-ashing final run-off with a view to recycling all or part of the final run-off within the refinery, or to consider it for a speciality product.

Softening refinery run-off

Refinery run-off contains divalent cations which originate from the carbonatation process. A prerequisite to make the chromatographic option viable is a softening and turbidity removal pre-treatment step. Thompson *et al.* (1994) examined the feasibility of using ion exclusion to increase the exhaustibility of refinery Jet 4. They concluded that ion exchange resins can be used to remove calcium, but the run-off would need to be diluted and the treatment of regeneration effluent would need to be addressed. As an alternative, the authors concluded that chemical softening could be used to reduce the calcium level to <300 ppm, this being the limit for industrial ion exclusion plants desugaring cane B-molasses. Davis (1995) conducted pilot plant trials to examine chemical pre-treatment of fourth jet by adding sodium hydroxide and simultaneously sparging with sulphur dioxide followed by powdered activated carbon. The test work achieved 20-30% decolourisation and reduced calcium to <300 ppm.

The tried and tested technique to soften potable water utilises sodium carbonate to precipitate hardness. Chemical softening using sodium carbonate not only precipitates calcium and magnesium, but the precipitate serves as filtration media for the removal of suspended matter. This aspect, combined with simplicity, lower equipment cost and robustness, supports the choice of chemical softening over ion exchange for the softening. Chemical softening is achieved by addition of sodium carbonate (Na₂CO₃) in an alkaline medium to precipitate calcium and magnesium as calcium carbonate and magnesium hydroxide respectively, and subsequently filtering out the precipitate. The reactions for non-carbonated hardness are depicted as:



Calcium precipitates as a carbonate at a pH of 9.25; however, magnesium is precipitated from solution as a hydroxide at pH >10.5. Restoring the solution to its original pH is done by either sulphitation or phosphatation. This last step has the added advantage of some decolourisation.

Objectives

To determine the suitability of chromatographic separation for the purification of refinery run-off, Malelane has considered a phased test programme as follows:

Phase 1: Laboratory testing of chemical softening of final run-off.

Phase 2: Pilot plant testing of chemical softening of final run-off.

If phases 1 and 2 are successful, then the test work will proceed to evaluate phases 3 and 4.

Phase 3: Lab testing of chromatographic separation and/or resin decolourisation.

Phase 4: Pilot plant testing of the preferred solution after phase 3.

Progressing in a phased programme from lab testing to pilot plant work and only then to slip-stream factory trials before installing full scale plant would minimise the risk associated with new technology. This paper covers phases 1 and 2 of the programme, viz. to gauge the efficacy of the softening process when applied to the mill's own refinery run-off.

The test work set out to evaluate:

1. Softening by sodium carbonate followed by pH correction and filtration. The primary purpose for the chemical softening of refinery run-off was to determine the viability of reducing the calcium content from the 2000-4000 ppm level to <300 ppm. "This is the limit used for industrial scale ion exclusion plants desugaring cane B-molasses." (Thompson *et al.*, 1994).
2. Use of additives in combination with the above to further reduce the colour and the ash content of final run-off.

Laboratory trials

The focus of the laboratory trials was to establish the optimum dosage rates and corresponding degree of calcium removal. The method involved treating the refinery run-off and then filtering under vacuum. Samples were analysed for pH, brix, colour, conductivity and CaO. Conductivity readings rather than ash % was used due to uncertainty about the conductivity/ash relationship with different inorganic species as well as different concentrations. The ICUMSA method (Anon, 1985) was used for colour measurement and the EDTA method was used for CaO determination. Tests were done in triplicate and the average results are shown in Table 3.

Table 3: Laboratory chemical softening trials

Test No.	Type of test	Brix	pH Start→End	Colour reduction (%)	Conductivity reduction (%)	CaO reduction (%)	CaO Start→End (ppm)
Na₂CO₃ dosage							
1	Softening at 80°C: Na ₂ CO ₃ at 1.0% on brix → filtration	62°	6.4→10.5	-21	-68	78	2545→560
2	Softening at 80°C: Na ₂ CO ₃ at 1.5% on brix → filtration	62°	6.4→11.3	-24	-70	85	4727→709
3	Softening at 50°C: Na ₂ CO ₃ at 1.0% on brix → filtration	50°	5.8→10.3	13	-66	78	3985→885
4	Softening at 50°C: Na ₂ CO ₃ at 1.5% on brix → filtration	50°	5.8→11.0	15	-68	83	3985→664
Na₂CO₃ dosage and pH adjustment							
5	Softening at 50°C: Na ₂ CO ₃ at 1.5% on brix → filtration → pH adjustment using H ₃ PO ₄	50°	6.0→11.4 11.4→6.5	11	-34	75	1640→410
6	Softening at 50°C: Na ₂ CO ₃ at 1.5% on brix → filtration → pH adjustment using SO ₂	50°	6.4→11.4 11.4→6.4	25	-29	80	1640→328
Cationic polyamine dosage							
7	Polyamine at 100 ppm → filtration	62°	6.2	14	73	2	4844→4747
8	Polyamine at 150 ppm → filtration	62°	6.2	71	69	11	4327→3851
9	Polyamine at 200 ppm → filtration	62°	6.6	56	62	12	4302→3786
Combined treatment: Na₂CO₃ + polyamine + SO₂							
10	Softening at 50°C: Na ₂ CO ₃ at 1.5% on brix → filtration → 150 ppm polyamine + SO ₂ → filtration	50°	5.83→11.0 11.0→6.4	20	-23	93	3985→277
11	Softening at 50°C: Na ₂ CO ₃ at 1.5% on brix → filtration → SO ₂ + 150 ppm polyamine → filtration	50°	5.82→11.0 11.0→6.4	26	-19	93	3985→277

Runs 1, 2, 3 and 4: Softening by NaCO₃ followed by filtration

No pH adjustment was carried out in these runs so as to evaluate the efficacy of Na₂CO₃ dosage on its own. The softening was initially done at 80°C and caustic soda was used to elevate the pH. High temperature runs 1 and 2 showed significant increases in colour, attributed to the formation of alkaline degradation products of fructose (ADFs), which are acidic in nature, as well as from melanoidins that result from reaction of amino acids with sugars under heat (Davis, 2001). For runs 3 and 4 the temperature was reduced to 50°C to match factory conditions and the brix was lowered to accommodate filtration at a lower temperature. CaO reduction was similar to the high temperature runs. Conductivity increased

in all the runs and is attributed to the addition of sodium carbonate. Based on these results, 50°Bx, 50°C and 1.5% Na₂CO₃ dosage were selected as the standards for further testing.

Runs 5 and 6: NaCO₃ followed by filtration + acid followed by filtration

The pH was restored to the starting level in these runs with the intention of evaluating the impact on CaO reduction by precipitation with an acid. The H₃PO₄ test (run 5) showed 11% decrease in colour and 75% reduction in the CaO level. The SO₂ test (run 6) showed better results, i.e. 25% decrease in colour and 80% reduction in the CaO level. The phosphoric acid treated sample filtered extremely slowly. This is to be expected with phosphatation floc, which is colloidal in nature. The SO₂ treated sample filtered relatively quickly. This aspect coupled with better colour reduction and slightly higher CaO reduction, supported the use of SO₂ for pH adjustment for further trials. The dosage rate of SO₂ was determined by stoichiometry to be 4000 ppm on brix.

Runs 7, 8 and 9: Polyamine followed by filtration

A low molecular weight cationic polyamine currently being used for refinery melt decolourisation was dosed at rates of 100, 150 and 200 ppm on brix to evaluate the impact on decolourisation of refinery run-off. The purpose of this test was to determine whether the decolourisation without any further treatment was significant enough to benefit the A-pan performance.

The samples were dosed with the cationic polyamine, vigorously stirred for 5 min, left to stand for 5 min and then filtered. The results showed significant colour reduction. These results were consistent with the decolourisation benefits reported by Moodley (1993) that the addition of a colour precipitant (polyamine) significantly improved decolourisation of refinery melt.

An unexpected benefit of treating final run-off with a cationic polyamine was a ≈65% ash reduction and ≈10% CaO reduction. This is consistent with work done by Runggas (1978) in his investigation of cationic flocculants in the carbonatation refining process. He observed that one of the flocculants tested consistently lowered ash levels. It is speculated that the conductivity reduction is due to the positively charged polyamine forming bonds with ash species which exist as negatively charged colloidal complex. The conclusion drawn from these results supported dosing 150 ppm of cationic polyamine to enhance decolourisation and ash reduction.

Runs 10 and 11: Combined treatment (Na₂CO₃+polyamine+SO₂)

By combining the benefits from the earlier trials, Na₂CO₃ at 1.5% dosage on brix, followed by filtration, then dosing 150 ppm cationic polyamine, followed by SO₂ for pH adjustment and final filtration, was selected for the combined treatment of refinery run-off. The colour improvement observed in the combined treatment test was not as dramatic as with the polyamine on its own. To test the impact of high pH on polyamine dosage, two runs (one at high pH and the other at low pH) were carried out. No appreciable difference in decolourisation between the two runs was observed. This aspect needs further investigation. Both runs 10 and 11 showed similar levels of conductivity increase (≈20%) indicating that the benefit of polyamine dosage on ash reduction was not fully replicated. This aspect also needs more investigation. The CaO levels when compared to the runs with pH adjustment improved from the 80% to the 90% level. The overall benefit of lower colour and lower CaO supported adopting this technique for the pilot plant trial.

Pilot plant trials

The purpose of the next phase of testing was to determine whether the lab results for the combined treatment (Na_2CO_3 + polyamine + SO_2) could be replicated in a factory pilot plant. The softening pilot plant, comprising a contact tank and pilot filter, is shown in Figure 2.

The test methodology involved slip-streaming 500 L of refinery run-off into the contact tank, adjusting the brix to 50° and then dosing industrial grade Na_2CO_3 . The softening trial was conducted with unheated run-off at approximately 50°C. The Na_2CO_3 was introduced as a solid directly into the contact tank. Agitation was achieved by a stirrer installed in the contact tank and after 15 min the treated liquor was filtered on the 12 frame pre-coated pilot plate and frame filter shown in Figure 2.

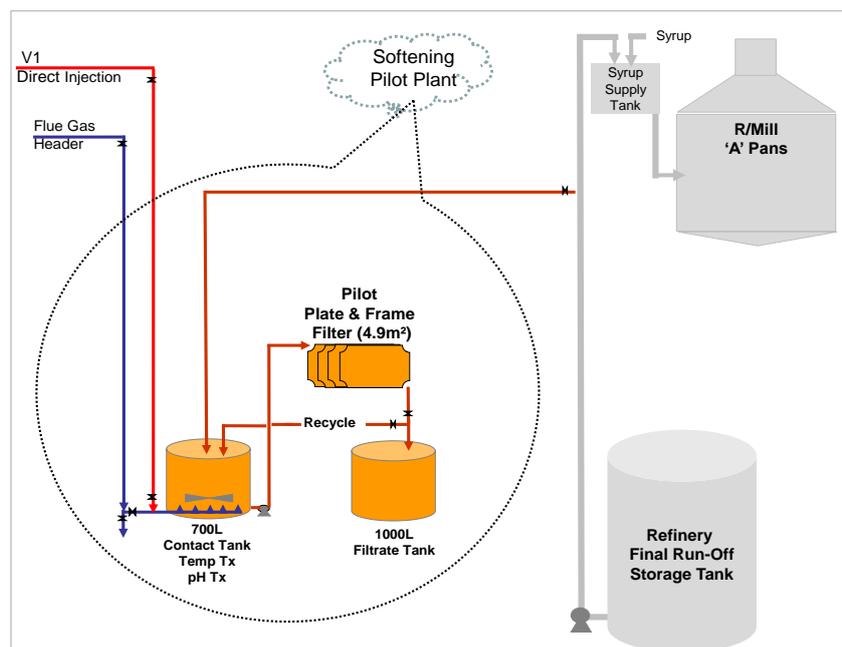


Figure 2. Pilot plant process flow diagram.

The temperature and pressure of the feed liquor was recorded for each run. First runnings from the filter were recycled back to the contact tank. Once the liquor became clear, the valves were switched and the filtered liquor was diverted to the filtrate holding tank. When the contact tank was empty, the filtrate was returned to it and dosed with the polyamine at 150 ppm. The filtrate was then vigorously stirred and then bubbled with the SO_2 until the pH dropped to 6.4, and then re-filtered through the pilot filter. Rather than stopping the neutralisation at a pH of 7, a lower pH level of ± 6.5 (corresponding to the initial run-off pH) was selected to maximise the decolourisation by sulphur dioxide. Samples were analysed for pH, brix, colour, turbidity, conductivity ash and CaO. Tests were done in triplicate and the average results are shown in Table 4.

Two runs were undertaken with the aim of determining the optimal Na_2CO_3 dosage rate under plant conditions. The 1.5% Na_2CO_3 run showed marginally better results for decolourisation and CaO reduction, indicating potential for chemical dosage optimisation. More tests at different dosage rate will need to be done. The conductivity increase in both

runs was at the 20% level, which is similar to the results of the lab trial. This aspect will be investigated in further test work.

Colour reduction was at the 30% level for both runs. Run 2 (1.5% Na₂CO₃) met the <300 ppm requirement for residual CaO. Turbidity after the final filtration step was reduced by 80%. Filtration proceeded rapidly and no increase in pressure drop across the filter was observed.

Table 4. Pilot plant chemical softening trials.

Test No.	Type of test	Brix	pH Start→End	Colour reduction (%)	Turbidity reduction (%)	Conductivity reduction (%)	CaO reduction (%)	CaO residual (ppm)
Combined treatment: Na₂CO₃ + polyamine + SO₂								
1	Softening Na ₂ CO ₃ at 1.0% on brix → filtration → 150 ppm polyamine + SO ₂ → filtration	50°	6.2→10.7 10.7→6.2	28	75	-19	90	336
2	Softening Na ₂ CO ₃ at 1.5% on brix → filtration → 150 ppm polyamine + SO ₂ → filtration	50°	6.3→11.5 11.5→6.3	30	82	-21	93	298

Costs

The equipment required to soften 5 m³/h of refinery run-off scaled up from the pilot plant will comprise two tanks, pumps and two sets of plate and frame filters. An indicative capital estimate is in the order of R2.5 million. The process chemical cost is estimated to be R3 million per annum.

Conclusions

Laboratory and pilot plant chemical softening trials have been undertaken at the Malalane refinery to determine the optimal pre-treatment option for softening refinery final run-off for further processing by resin based processes. The pre-treatment results indicate that dosing 1.5% Na₂CO₃ and pH adjustment with SO₂ is a viable method to soften refinery run-off. The addition of 150 ppm cationic polyamine enhances CaO removal. After the final filtration step the residual CaO was <300 ppm, 80% turbidity reduction was achieved and the 30% decolourisation that has been achieved is considered a bonus. Indications from the pilot plant test work suggest that further optimisation in process chemicals is possible. The overall benefit indicates that the treated final run-off is of suitable quality to be considered for further:

- Crystallisation albeit the impact of higher sodium levels on molasses losses is still to be assessed.
- Purification by chromatographic separation and/or resin decolourisation.

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