Abstract

The Arabian Sugar Company refinery in Bahrain was commissioned towards the end of 2013. It is a carbonatation / ion exchange refinery designed to process VHP sugar. As with most refineries in the region, water availability is an issue and therefore it was designed with indirect condensing to optimise water consumption. As a consequence, it is also a refinery with low effluent discharge, most of the environmental loading coming from the ion exchange regeneration.

The specialist ion exchange subcontractor designed a system with a stated 90% brine recovery using nanofiltration and brine evaporation. It incorporates various holding tanks to optimise the use of water while sweetening off and on. The operating manual, issued during commissioning, reported that the effluent would be 44.8 m³/d at full capacity with 15 kg of chemical oxygen demand [COD] content, equivalent to 307 ppm of COD and therefore comfortably within the required limit of 600 ppm for permitted discharge to the municipal sewer.

In the event, the local treatment plant could not cope with the refinery effluent discharge which was both puzzling and worrying. It turned out that the effluent was nothing like that claimed with both higher volumes and much higher COD loadings. This paper describes the investigations and solutions developed for the issues found so that others can learn from the experience.

Introduction

The Arabian Sugar Company refinery in Bahrain was commissioned towards the end of 2013. It is an 1800 t/d melt, carbonatation / ion exchange refinery designed to process VHP sugar. The ion exchange regeneration includes brine recovery with nanofiltration (NF) and brine evaporation.

As with most refineries in the region, water availability is an issue and therefore it was designed with indirect condensing to optimise water consumption through re-use of the evaporator and pans vapour condensate. As a consequence, it is also a refinery with low effluent discharge, most of the environmental loading coming from the ion exchange regeneration:

![Figure 1: Simplified Water Balance](image-url)
Bahrain Sugar Refinery: Effluent Issues and Solutions
Dr Mike Inkson, Sugar Knowledge International and Kanada T Korea, Arabian Sugar Company

The water balance data in Figure 1 is theoretical. The total effluent flow is 9.5 t/h. At 1800 t/d [75 t/h] melt, the 12.52 t/h water consumption is about 17% on melt. It is too early in the life cycle of the refinery to comment on how close it will come to the theoretical.

The effluent is treated in the local sewage treatment plant which was designed to process ‘typical’ domestic effluent as specified by the local regulations. The key components of the specification are shown in Table 1:

<table>
<thead>
<tr>
<th>Component</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6 to 9</td>
</tr>
<tr>
<td>BOD</td>
<td>400 mg/l</td>
</tr>
<tr>
<td>COD</td>
<td>600 mg/l</td>
</tr>
<tr>
<td>Suspended Solids</td>
<td>400 mg/l</td>
</tr>
<tr>
<td>Turbidity</td>
<td>35 NTU</td>
</tr>
<tr>
<td>Detergents</td>
<td>30 mg/l</td>
</tr>
<tr>
<td>Oils and Fats</td>
<td>50 mg/l</td>
</tr>
<tr>
<td>Total N</td>
<td>50 mg/l</td>
</tr>
<tr>
<td>Total P</td>
<td>10 mg/l</td>
</tr>
<tr>
<td>Sulphates</td>
<td>400 mg/l</td>
</tr>
<tr>
<td>H₂S</td>
<td>10 mg/l</td>
</tr>
</tbody>
</table>

Table 1: Short Form Effluent Specification

Below the data given there is a range of limits for metals ranging from 5 mg/l [Al, Fe, Pb] down to 0.001 mg/l [Hg].

During the conceptual design phase, the focus was on the COD/BOD. The contractor reported that the COD burden from the average 2.4 m³/h of regeneration effluent would be 46 kg/day and that from the average 1.0 m³/h of NF CIP effluent would be 5 kg/day. That equates to 622 mg/l of COD but as there were two blowdown streams with a similar flow, it was not considered an issue.

Decolourisation Design Concept

Overview

There are three columns of 30 m³ bed volume each, two operating in parallel at any one time. The third column is either being or has been regenerated. The columns each have two separate cells of 15 m³ each and the operational flow is upwards.

The regeneration is also traditional: caustic brine is used to flush off the colour bodies and replace them on the resin with chloride ions; at intervals an acidic brine regeneration followed immediately by a caustic brine regeneration is undertaken. Regeneration was scheduled for once every 30 bed volumes (BV) with an acidic brine regeneration once every ten caustic regenerations. In practical terms that meant three regenerations per day at full capacity and an acidic brine regeneration approximately every three days.

The system includes various water tanks in order to optimise water consumption.

In brine recovery, the spent caustic brine is processed through a three stage nanofiltration plant to create a dilute recovered brine which is then concentrated back up in a triple effect evaporator to full concentration. The condenser of the brine evaporator is cooled by dilute brine from a small brine cooling tower so some of the evaporation is achieved with atmospheric evaporation.
Process Description

When a column comes off line it is sweetened off in two stages with downflow water. Initially the displaced syrup is returned to the carbonatated liquor tank and then, as the brix falls, it is sent to the sweetwater tank.

The next stage in the process is an upflow backflush to loosen the beds and remove any accumulated debris. This is undertaken on each cell separately and the water is sent to a settling tank where the solids are segregated so that, with time, the clear water can be pumped to the recovered water tank. The remaining water is discarded.

Once the backflush is complete the regeneration itself takes place. The brine is drawn from the recovered brine tank which itself is kept topped up as necessary from the brine preparation plant. The target is a brine at 100 g/l concentration flowing down through the column. The first fraction of the eluent flowing out of the column is classified as ‘recovered water’, after which the second fraction is classified as ‘salty water’. Each is sent to the appropriate storage tank for re-use. As the colour and COD start to appear the eluent is classed as spent brine which is sent to the spent brine tank. Once all of the COD has gone and the colour is off the shoulder of the curve the eluent is again classified as ‘salty water’ and is sent to the salty water tank.

Once the regeneration is complete the column is rinsed. The first stage rinsing is with salty water which is followed by a second stage using recovered water and finally a third stage is undertaken with fresh hot process water. The first stage rinsings are sent to the spent brine tank, as is the first part of the second stage rinsings. As the conductivity of those rinsings falls, they are sent to the salty water tank. The third stage rinsings are sent to the recovered water tank.

Thereafter the column is ready for sweetening on in preparation for re-entering service. The sequence is the reverse of the sweetening off sequence.

The spent caustic brine is diluter than the feed brine [57 g/l according to the mass balance]. Nanofiltration is operated at that concentration. The process design does not allow the spent acidic brine to be treated by NF: it is sent to the neutralisation pit for disposal.

The NF skid consists of 10 membrane modules arranged in three feed and bleed loops. The permeate is essentially dilute brine which is sent to the brine evaporator feed tank and the highly coloured retentate is sent to the molasses tank for blending with molasses. NF operates about 22 hours per day, the rest of the time being used for cleaning in place (CIP). The CIP is triggered by the build-up of pressure in the system. As with regeneration, the system is optimised for water consumption and effluent quality. Powerful surface active agents are used during the cleaning.

The brine is a conventional, albeit very small, triple effect plate heat exchanger unit. There is no issue with salt being heat labile and therefore, unlike a sugar liquor evaporator, it is arranged in the much more efficient counter-current mode with the live steam evaporating the most concentrated brine. The process condensates are sent to the recovered water tank.

As mentioned previously, all of the cooling required [NF skid and brine evaporation] is achieved with a brine cooling tower, the evaporative cooling contributing to the overall evaporation duty.

Mass Balance

With a semi-continuous process and intermittent activities such as CIP, the mass balance was presented on a ‘per cycle’ and also a daily basis. A simple flow diagram with quantities per cycle is shown in Figure 2 and the daily balance is shown in Table 2. The flow diagram does not show the NF CIP, that only comes to account in the daily balance of the table.
Figure 2: Simplified Flow Diagram with Quantities per Cycle
Table 2: Daily Mass Balance

The data comes from the operating manual handed to ASC after commissioning and as the subcontractor was leaving site. The water input is the gross water requirement, 59.7 m³ of which is satisfied by the Hot Condensate. The net water demand is stated as 215 m³ per day.

Summary

The balances don’t exactly balance but clearly a lot of work had gone into process optimisation since the conceptual design phase. Table 3 compares the two sets of effluent data, the earlier data having been converted to a daily basis:

Contractor’s Early Data

<table>
<thead>
<tr>
<th>Volume [m³/d]</th>
<th>COD [kg/d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regeneration Effluent</td>
<td>57.6</td>
</tr>
<tr>
<td>CIP Effluent</td>
<td>24</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>81.6</strong></td>
</tr>
</tbody>
</table>

Subcontractor’s Data

<table>
<thead>
<tr>
<th>Volume [m³/d]</th>
<th>COD [kg/d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste [backwash and CIP]</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Table 3: Comparison of Effluent Statements

What was not apparent was that none of the daily data took account of the 2.5 BV of spent acidic brine which would be produced every three days at full capacity and which, according to the subcontractor, could not be passed through NF.

Initial Outcome

When it became evident that the local treatment plant could not cope with the effluent discharge we decided to become directly involved even though the plant was nominally still the contractor’s responsibility. The first thing that we did was to analyse in depth what the real decolourisation effluent was. It turned out that it was made up of three separate streams: backwash, NF CIP effluent and acidic spent brine.
**Backwash**

This effluent is the result of the final sweetening off of the column. Most of it was recovered for use in the next sweetening off but about 10 m³ was sent to the effluent neutralisation tank in order to remove solids that settled out in the conical bottom of the storage/settling tank. There was no rational explanation for dumping 10 m³ when 1 m³ would probably be adequate and, as the sweetwater would be used for melting and hence whatever solids would end up being filtered out, there was no explanation for why it was needed at all.

The COD was measuring at 10 000 ppm. With three regenerations per day that equated to 300 kg of COD per day when the declared total COD load was only 15 kg of COD per day. The high COD also indicates that this is a sucrose loss.

The sucrose content was measured at 1.2 Bx which, as the backwash was subsequently used for the next backwash, was self-defeating. The subcontractor therefore increased the amount of process water used in backwashing from 15 of the total 75 m³ to 35 of 75 m³ and hence reduced the brix of the backwash to 0.5 Bx.

Challenged on the need to dump 10 m³ of backwash every cycle, the subcontractor agreed that it would be possible to dump once every three cycles but still required 10 m³ to be dumped.

The combined effect of these adjustments was that the effluent was reduced to 10 m³ per day of 5 000 ppm COD effluent but that was still 50 kg per day of COD, 3.33 times the total declared COD burden.

**NF CIP Effluent**

The nanofiltration membranes need to be chemically cleaned every three regenerations, that is to say once per day. The total volume flow from the cleaning is about 10 m³.

The COD was measuring at 20 000 ppm which equates to 200 kg of COD per day. Although we had no way of assessing how much of the declared 15 kg of COD per day was to come from the NF CIP process, a guess of 1 000 ppm for the expected COD burden was made.

Clearly something was wrong so the subcontractor returned to site. It was found that the programming of the CIP process was incorrectly set up so that high COD liquor which should have gone to molasses was actually going to effluent. Once this was corrected the NF CIP effluent reduced to 1 000 ppm of COD, equivalent to 10 kg of COD per day.

**Acidic Spent Brine**

Acidic regeneration is required to flush out any build-up of calcium and similar salts which carry-over from carbonatation. The nominal frequency is one every ten normal regenerations and the subcontractor’s technique was to undertake an acidic regeneration first, immediately followed by a normal regeneration to ensure that the resin is in the correct state for normal decolourisation.

The stated position was that the effluent from the acidic regeneration could not be recovered with nanofiltration and all 75 m³ of it had to be dumped. Assuming such a process every three days means about 25 m³/d with a measured COD of 11 000 ppm and hence a daily COD burden of 275 kg.

We had already come to the conclusion that doing a normal regeneration first then doing the acidic regeneration would reduce the COD of the effluent. It required a second normal regeneration afterwards to put the resin into the chemical state needed for it to operate correctly but that wouldn’t need to be a full regeneration.
A trial showed that using the ASC technique halved the COD burden but that still didn’t explain why the acidic spent brine couldn’t be treated with NF and hence eliminate the effluent because the recovered brine would be re-used and the COD would be in the retentate.

The reason given was that calcium and magnesium salts would irreversibly foul the membranes as they would form hydroxides. However, nothing was known about the presence of those salts in the spent brine flow: did they come off first or last or all through the regeneration process. In addition, it wasn’t known whether they would form hydroxides or stay as chlorides.

Remedial Work and Results

It clearly made sense to us to deal with each component of the effluent flow separately.

**Backwash**

This had been reduced to 10 m³ per day of 5 000 ppm COD effluent after discussion with the subcontractor. Our initial approach was to question why 10 m³ needed to be decanted off the bottom of the storage/settling tank each day. A preliminary experiment quickly showed that, at most, substantially all of the solids were discharged after decanting 500 litres so we reduced the procedure to decanting 1 m³ per day.

However, that still gave 1 m³ per day of 5 000 ppm COD effluent when the discharge limit was 600 ppm and the water was taking sucrose with it. Six months ago we took the decision to send the decantate to sweetwater. We initially monitored the process carefully in case there was some unforeseen consequences but nothing was detected and we now feel confident that none will appear.

Accordingly, the backwash effluent has been completely eliminated so we had gone from 30 m³ and 300 kg COD per day down to 10 m³ and 50 kg COD per day initially and then down to nil.

**NF CIP Effluent**

Once the programming error had been corrected the CIP process was known to result in 10 m³ per day of 1 000 ppm COD effluent. We couldn’t avoid CIP and didn’t want to experiment with extending the time between cleans.

On the other hand, diluting with another effluent stream such as the blowdown from the power station would bring the COD level below the permitted 600 ppm so it was accepted that this effluent stream would continue to be discharged. We had gone from 10 m³ and 200 kg of COD per day of effluent down to 10 m³ and 10 kg of COD per day.

**Acidic Spent Brine**

This was an average flow of 25 m³/d with a measured COD of 11 000 ppm. We had already shown that by starting with a caustic regeneration before the acidic regeneration we could halve the COD burden but the better solution, from our point of view, was to treat the acidic spent brine by sending it through NF.

The first thing to do was to examine where the calcium and magnesium salts came out in the regeneration process. It quickly became apparent that they did so at the earliest stages of regeneration. It also became apparent from laboratory tests that hydroxides were not formed on neutralisation although that didn’t mean that they wouldn’t form in practice.

The minimum position was therefore that most of the acidic spent brine could be treated by NF. In order to be conservative we assumed that it would only be 75% but for the purposes of equipment design we assumed 100% would be processed.
The additional equipment was limited to a storage tank, T4201, for the acidic spent brine and a diaphragm pump, P4206, to meter it into the caustic spent brine tank, T4200, whilst that tank was being filled during a normal regeneration. The existing tank T4200 had a capacity of 120 m³ so could cope with the addition of 7.5 m³ of acidic spent brine for each 75 m³ of caustic spent brine. The new tank, T4201, was specified with a capacity of 80 m³.

The system was set up to start the metering pump at the same time as the opening of XV4200.01. Under normal circumstances, if all went well, XV4200.02 would never have to be opened in the future to send acidic spent brine to the neutralisation pit but if we couldn’t process all of the acidic spent brine through NF the option still existed.

Geographically, the new tank could be placed next to the existing tank which made the pipe changes very simple:
Laboratory experiments showed that, although the pH of the acidic spent brine was < 2, the addition of 10% acidic spent brine to caustic spent brine had a negligible effect on the pH of the latter. In fact it took an addition of 32% to reduce the pH from 12.5 to 12.0 so the potential problem of over adjusting the pH of the caustic spent brine was not going to be an issue.

The new equipment is now all installed and we are starting to operate under the new regime. Unfortunately, it is too soon to be absolutely sure that we can process all of the acidic brine through NF although the results are looking promising. [We are expecting that the membranes will be gradually blinded over time if there is an issue with calcium and magnesium hydroxide, there won’t be a catastrophic failure.]

Accordingly, we can only say that it looks as if the acidic spent brine effluent has been eliminated so we have gone from initially expecting none to 25 m³ and 275 kg COD per day possibly down to nil.

Mitigation
In addition to all of the above, we also set about examining the frequency of regeneration and the frequency of acidic regeneration with a view to reducing both.

The starting point for regeneration frequency was treating 900 m³ of sugar solution through any one column before regenerating the column. We slowly increased the throughput between regenerations until we reached 1200 m³ without experiencing any problems and then closely monitored the performance over 20 cycles to make sure that there is no adverse effect. That is a 33% improvement which means that the NF CIP effluent and acidic spent brine production is reduced accordingly.

Rather than continue with that approach we then switched the focus to the frequency of acidic regeneration, increasing that first of all to once in eleven normal regenerations and then to once in twelve. That is a further 20% improvement which must be compounded with the previous improvement meaning that the gross effect on acidic spent brine production is virtually a 60% improvement.

Of course, we have to recognise that as the resin continues to age we may not be able to sustain the 1200 m³ between normal regenerations but as the acidic regeneration is only a result of the carbonatation performance, that improvement should not be affected by resin age.

Conclusions
This is not a scientific paper and so perhaps ‘conclusions’ is too strong a heading: what lessons have been learnt?

First of all, a holistic approach to process design is always essential: the one station cannot be designed in isolation. If that had happened correctly then there would never have been any backwash effluent, it would have been part of the sweetwater system from the outset and there would have been 300 kg less of COD burden in the site effluent.

Secondly, never assume that control systems – particularly batch control systems with lots of on/off valves – are correctly programmed. It took very little time to track down the NF CIP programming error and correct it but in the meantime we were chasing a symptom and not the problem, costing us time and resource.

Thirdly, always challenge what specialists tell you [in a nice way]. We went from a categorical refusal to contemplate NF processing of acidic spent brine to acceptance of it.