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Produced Water Recovery at Seneca Resources Using Short Bed Ion Exchange

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ABSTRACT: As a result of water restrictions in the Bakersfield, California area Seneca Resources has installed a new produced water recovery system. The paper reviews this process, which consists of water knock out and clarification tanks, an IGF unit, a specialized nutshell filter, and a short bed ion exchange softener that is regenerated with salt. The water being treated has a TDS level of 4,000 - 7,000mg/L. The specified target hardness level in the treated stream is <1ppm. In actual service the ion exchange softener is consistently producing water with a hardness level <0.5ppm. Some novel aspects covered in the paper include the following: the use of an air scoured dual-media nutshell filter, the application of short bed ion exchange technology to the treatment of produced water, and an in-situ resin cleaning process.

BACKGROUND

Due to fresh water shortages in the Bakersfield area Seneca Resources decided to install a new produced water system at their North Lost Hills property to permit recycle to supply their OTSG. Their OTSG currently produces 70% steam at 800psig. The original produced water treatment plant consisted of gravity separators and a clarification tank before sending the water to a disposal well. After de-oiling the feed water specification and product targets are given in Table 1.

The new process, Figures 1 and 2 consists of primary oil and solids separation using the pre-existing gravity separators and a refurbished induced gas floatation cell, a specialty nutshell filter, polishing cartridge filters, and a short bed ion exchange softener.

Table 1: Feed and Process Specification

Parameter	**Produced Water**
Suspended solids (mg /L)	
Normal	<10
Excursions	<70
Oil (mg/L)	
Normal	3
Excursions	<70
Hardness (mg-$CaCO_3$/L)	447
Iron (mg-Fe/L)	1.52
Total dissolved solids (mg-$CaCO_3$)	4,000 – 7,100
Temperature (°F)	90 - 160
SiO_2 (mg/L)	150 – 200*
Required product flowrate (gpm)	200
Product water hardness	<1

*To date Seneca has not reported problems with this high silica level and have operated for 15y at their Sunset Midway Field with a level of approximately 130mg/L

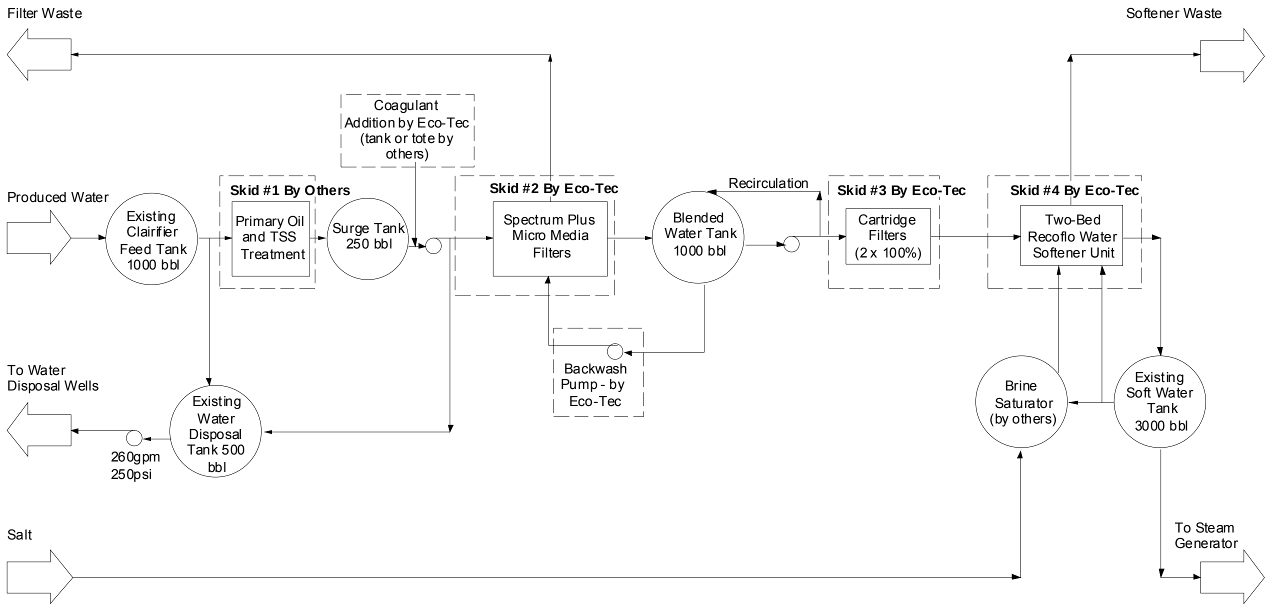

Figure 1: Process Flowsheet

Figure 2: Short Bed Softening System 200gpm (6,857 bpd)

SPECIALTY OIL REMOVAL FILTER

OIL REMOVAL FILTRATION, ORF - The use of nutshell filtration is well established for the treatment of produced water. The most common media used is black walnut shells with a -12/+20 mesh size distribution. Walnut shells are used because the surface is oleophobic, which allows easier oil removal during backwash relative to sand or anthracite. The higher wetting force between oil and these other media makes removal more difficult and increases the risk of mud ball formation and media loss.

Interestingly, it is worth noting that sand filters are commonly used for oil and grease removal in the steel industry. A comparison of design criteria for nutshell and sand filters shows that sand filters have about six times the solids holding capacity, but only 20% of the oil loading capacity (1).

Typically loading of nutshell filters is controlled by measuring differential pressure to a maximum value of approximately 20psi. At this point the backwash process is initiated. This is usually done by either mechanical agitation or a gas scouring backwash process. Filter performance depends upon the nature of the feed and how the filter was operated. Data available in the literature (2) indicates that generally the effluent should contain <10ppm oil. Specific examples provide field and pilot plant data showing the following performance: i) feed oil 9 - 100 mg/L giving an effluent containing 2 – 13mg/L(2), ii) an upset feed oil level of 250 mg/L giving an effluent level of 26 – 125mg/L(2), and iii) feed 24mg/L and effluent 3.2mg/L (1).

SPECIALTY ORF - In the Seneca flowsheet a specialty nutshell media filter (3) is used to remove the residual oil and suspended solids remaining in the produced water after the IGF. The oil and suspended solids levels in the feed were expected to be <3mg/L (upsets to as high as 70mg/L) and <10mg/L (upsets to 70mg/L) respectively. To avoid fouling of the downstream softener, oil and suspended solids must be reduced to <0.1mg/L. To produce the required softened water product flow of 200gpm a single 60” diameter filter was selected, Figure 3.

Figure 3: Specialty Nutshell Filter

The filter contains two layers of media, a relatively finer upper layer of black walnut nutshells (-20/+30mesh) on top of a layer of very fine micro-media (effective size of about 100um). Compared to a conventional filter with a single layer of nutshells this configuration offers the benefit of polishing filtration by the lower micro-media which helps to ensure lower levels of oil and solids in the filtrate. The main features of this filter include the following:

Upper Layer of Walnut Shells Three feet of this media is used to remove the bulk of the oil and the suspended solids.

Lower Layer of Micro Media One foot of this very fine and dense media acts as a polishing layer to remove the residual oil and solids that leak through the nutshell layer. The small particle diameter greatly increases the surface area density improving oil and solids capture efficiency. This also increases pressure drop- DP, however the high operating temperature reduces viscosity giving a DP that ranges from 10 - 15psig. Pressure profile measurements down through the depth of the filter show that run termination, based on DP increase, results from the accumulation of oil and solids at the interface between the layers. Trapping the fine oil droplets and solids here at the end of filter loading, maintains a significant depth of clean micro-media below the interface ensuring that there is no significant oil and solids leakage into the filtrate.

Air Scour and Backwash Cleaning Cycle To ensure oil and solids removal a simultaneous air scour and backwash is used to agitate and wash the media. Air scour or backwash alone are inadequate. Air alone does not lift and expand the media, but simply short circuits through a few rat holes leaving the majority of media untouched. Backwash alone does not provide enough shear force to release the oil and solids from the media surface. Mechanical agitation effectively cleans the media but relative to this procedure is more costly and complex. In some cases the use of natural gas or nitrogen instead of air are proposed to avoid adding oxygen to the backwash waste water. These are of course more expensive options and may not be warranted since the impact on vessel internal corrosion would be minimal and if the waste is recycled the amount of oxygen relative to the full produced water stream is small. In the Seneca installation the filter is backwashed using filtrate. Use of feed water for backwash may be considered depending on the oil and solids levels.

FIELD PERFORMANCE - Figure 4 shows filter pilot plant data for a single cycle when treating a feed containing 30ppm oil and 20ppm of suspended solids. The pressure drop is significantly higher because the feed temperature was only 15C. The graph shows that filtrate turbidity was always at or below

0.1NTU. A composite sample of the filtrate and a grab sample at the end of the loading step were collected and showed no visible signs of oil. The measured oil levels in these samples were <0.5ppm which was the method limit of detection.

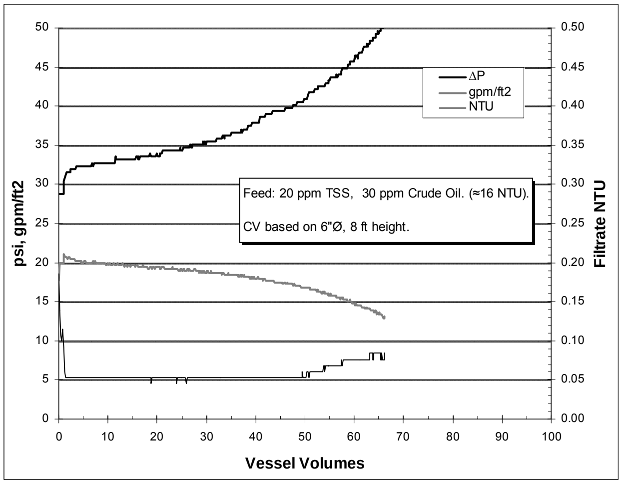

Figure 4: Filter Performance Data

Unfortunately, no field measurements of oil levels in the filtrate were made. During commissioning filtrate turbidity was measured and found to be 0.15NTU and showed no signs of visible oil. It was noted that the turbidity of filtrate samples while initially quite low rapidly increased upon standing. This was due to oxygen exposure and the precipitation of FeS. This effect is shown in Figure 5. A freshly drawn sample from the clarification tank is shown on the left side. On the right side the same sample is shown to be much more turbid after only a few minutes exposure to air.

Figure 5: Effect of Air Exposure

Since the filtrate is stored in a tank that is open to atmosphere, these same solids are formed before being sent to the softener. Gas blanketing of this tank has been recommended to avoid this problem. Currently these solids are captured in the guard cartridge filters that are located immediately before the softener beds. Analysis of loaded cartridges running under normal conditions has confirmed the presence of Fe and showed no presence of oil confirming proper operation of the ORF filter.

Upset conditions do of course occur. The filter was commissioned in mid-December 2009 and the first upset occurred in early February. There was a breakthrough of emulsified oil from the IGF unit, figure 6. No significant amount of oil can be filter from a stable emulsion by nutshell filters. This problem must be resolved by correcting the emulsion breaking process upstream. The impact on the downstream softener is shown in figure 3, which shows a rapid increase in pressure drop across the primary softener bed due to oil fouling of the resin. Once the emulsion was broken normal filter performance was restored without the need for any special media cleaning process.

Figure 6: Emulsified Oil

<u>Lessons Learned</u> - The following lessons learned may be of assistance to those designing and operating nutshell filters: i) Where possible avoid exposing the feed and filtrate solutions to air. The presence of oxygen will precipitate FeS in the filtrate which could then foul the downstream softeners, ii) Stable emulsions are not well filtered by nutshell filters. This

problem must be resolved by regaining control of the upstream emulsion breaking process, iii) A non-contact turbidity meter (i.e. no contact between fluid and light source and detector) should be selected to minimize cell cleaning requirements, iv) To minimize plugging the top lateral system, used to retain the nutshell media during backwash, testing has shown that 0.02" slots running at a velocity of < 1ft/s should be used.

SHORT BED IX SOFTENER

SOFTENER SELECTION - Selection of softener bed design is based upon the targeted hardness level in the product water, feed TDS and hardness, operating and capital cost, and performance reliability. While each case must be evaluated individually, generally as the TDS level rises the configurations progress through the following series: SAC, SAC:SAC, SAC:WAC and sometimes WAC or even WAC:WAC (in the case of low feed hardness and high TDS).

For this application the conventional design would be either salt regenerated SAC:SAC or SAC:WAC using salt to regenerate the SAC and HCl/NaOH to regenerate the WAC. For the SAC:SAC system the product hardness level is primarily a function of the purity of the brine. Equilibrium calculations (4) were used to produce Figure 7 which shows the theoretical impact of brine purity on hardness leakage. The plot for 7,000TDS suggests that to achieve the specified 1ppm hardness target the use of vacuum pan salt would be just acceptable, however these calculations do not account for kinetic factors and therefore in practice use of a higher purity salt would be required. In many cases such salt is not available thus making the conventional SAC:SAC configuration not viable. This is an even greater limitation when product water hardness levels of 0.1 – 0.5mg/L are required. However, at Seneca a high purity salt is available and the target level is only 1mg/L. Therefore SAC:SAC would be a potentially viable configuration.

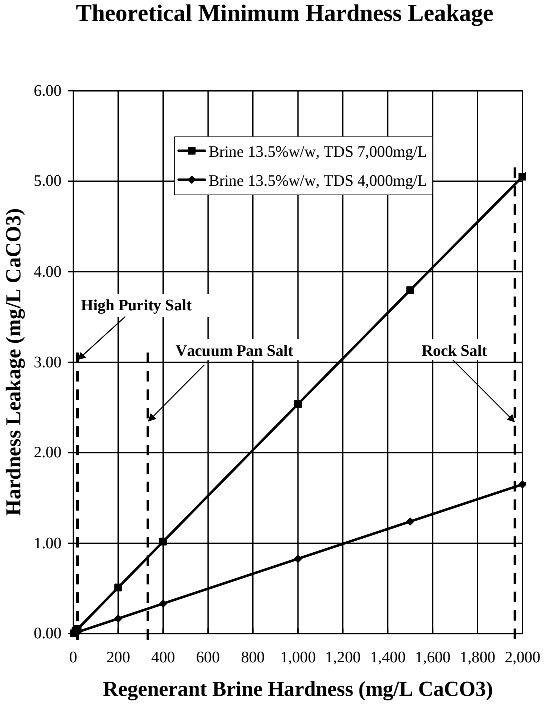

Figure 7: Hardness Leakage vs. Brine Purity

A SAC:WAC system using HCl and NaOH to regenerate the WAC bed was discounted by Seneca because they did not want to store HCl and NaOH on site. After extensive pilot plant testing a short bed SAC:WAC salt regenerated softener configuration, Figure 8 was selected. To produce the 200 gpm product flowrate the beds are 42" in diameter, 6"(5ft^3) and 3"(2.5ft^3) in depth (and volume) respectively and are mounted on a single frame and operated in series. The beds are simultaneously counter-currently regenerated in series using high purity salt.

Figure 8: 200gpm SAC: WAC Short Bed Softener

WAC RESIN SALT REGENERATION - Salt regeneration of a WAC bed is certainly not common practice, though it has been previously reported in the technical literature (5,6) and can be accomplished by using a large amount of high purity brine. Tests were conducted comparing the performance of salt regenerated WAC and SAC resins running as short bed (6”) polishers. The results are shown in Figure 9.

- For these tests a 7,000mg/L TDS feed containing 10ppm hardness was used as this was felt to be typical of primary SAC bed leakage.
- A standard regenerant dosage of 18-20 lbs/ft^3 based on the primary bed was selected. Assuming a 2:1 primary to polisher bed depth ratio.
- A 13.5%w/w high purity brine containing 10ppm hardness was used.
- Product water hardness target level was 0.1mg/L.

The graph clearly shows that for a short bed system the WAC resin has almost ten times the capacity of the SAC. This is probably due to the relative lengths of the mass transfer zone, MTZ. The much higher selectivity of the WAC resin for hardness shortens the MTZ, thus extending the time to breakthrough. WAC resin bed loading at the point of breakthrough is about 4.3kgr/ft^3. This explains why a polishing WAC short bed was selected. It should be noted that a polishing SAC resin bed could be used if the bed depth was significantly longer as is the case with a more conventional design. The benefits of the short bed system would of course be lost.

SHORT BED IX TECHNOLOGY - Short bed IX technology is characterized by use of the following:

- Short bed depths typically ranging from 3” – 24”.
- Use of fine mesh resin typically ¼ the size of conventional beads.
- Fully packed resin bed.
- High hydraulic flowrates of 30 – 50gpm/ft^2
- Counter-current regeneration.

The fine mesh resin greatly increases the rate of exchange thus allowing use of the shallow bed depth and high flowrates with the net effect of significantly smaller equipment. The packed bed easily allows counter-current regeneration, which minimizes regenerant consumption and ensures maximum product purity. However, because the resin is not fluidized during regeneration care must be taken to properly filter all streams entering the resin bed. This is of particular importance when treating produced water because of concerns related to both particulate and oil fouling.

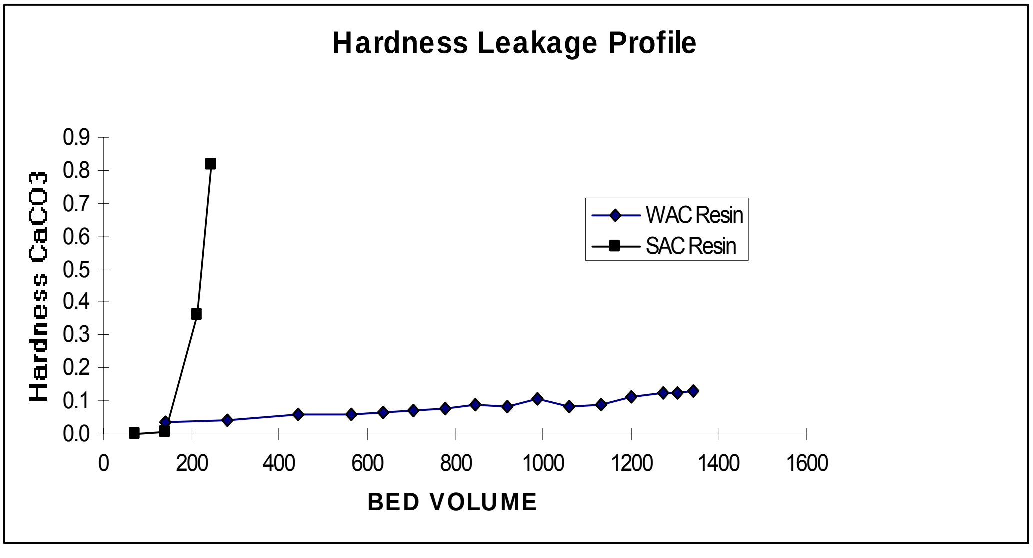

Figure 9: Short Bed SAC vs. WAC Loading Profile

PERFORMANCE DATA -

Table 2: Short Bed SAC: WAC Pilot Plant Test Data

Stream	**Volume (L)**	**Total Hardness (mg/L)**	**TDS (mg/L)**
Feed	14.25	570	6,050
Regenerant Brine – 13.5 %w/w	0.250	15	
Product	14.25	0.075	
Spent Regenerant	0.250	689	
Regenerant Rinse Wash	0.485	15,299	

Regenerant Consumption (lbs/1000 barrels) = 972
Regenerant Consumption (lbs/ft3 – SAC resin) = 8.3

The pilot plant data show that a product water with less than 0.1ppm hardness was produced. Given that the process target is only <1ppm the salt consumption could probably have been reduced.

Table 3: Commissioning Data

Stream	**Volume (gallons)**	**Total Hardness (mg/L)**	**TDS (mg/L)**
Feed	3147	337	3,700
Regenerant Brine – 23 %w/w	18.5	100	
Product	3147	0.21	
Spent Regenerant	34	not measured	
Regenerant Rinse Wash	71	not measured	

Regenerant Consumption (lbs/1000 barrels) = 575
Regenerant Consumption (lbs/ft3 – SAC resin) = 8.7

The above tabulated commissioning data shows that the softener was easily achieving the <1ppm hardness target. The salt consumption per 1,000 barrels was reduced during commissioning relative to the pilot plant testing because of the lower TH in the feed. The salt consumption of 575 lbs/1,000 barrels is slightly less than would be expected for a conventional SAC:SAC system. If a conventional SAC:SAC system is operated with a resin capacity of 26kgr/ft^3 and a salt dosage of 20lbs/ft^3, then salt consumption is calculated to be 632 lbs/1,000 barrels which is 10% more than the short bed system.

The system was commissioned in December of 2009 and has been in service continuously for 6 months at the time of writing this paper. An existing online hardness monitor indicates that a hardness level of <1ppm (the detection level) has been maintained. Additional field samples were collected in January and February and product hardness levels of 0.2, 0.33, <0.13, <0.13ppm were measured. Increasing the salt dosage would allow a further reduction in hardness. Pilot plant testing has shown that maintaining hardness levels below 0.1ppm is possible.

RESIN FOULING AND CLEANING - Resin fouling by oil and suspended solids when treating produced water is very common. Preventing fouling from occurring and dealing with it efficiently are obviously key to ensuring a reliable water treatment plant. As previously mentioned a fouling incident did occur shortly after commissioning when a large amount of emulsified oil was passed into the softener. Figure 10 shows that during this time period of about 1 day the pressure drop across the unit rose as the oil accumulated on the resin. During this upset the product hardness level was maintained below 1ppm without a reduction in run length. Flow through the unit was stopped and the guard cartridge filters were changed. However, the resin columns were not opened and no cleaning procedure was undertaken.

When the upset condition producing the emulsified oil was addressed the softener was restarted and the pressure drop began to fall back down to normal levels over a 2-day period. It seems that the accumulated oil was simply washed off the resin by the warm produced water.

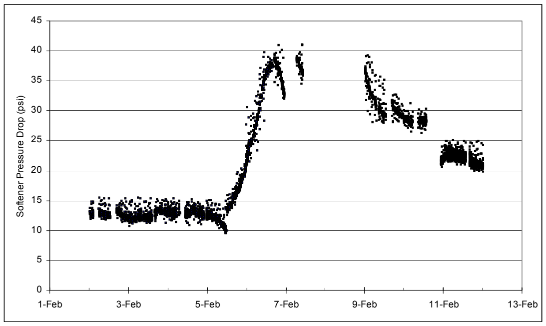

Figure 10

To date no other such upsets have been reported. More severe upsets may not permit recovery of softener performance in this manner. Common practice in this case would be to remove the resin from the vessel for washing using a surfactant. This process requires proper transfer of resin to minimize bead damage, adequate washing to remove the oil, careful separation of the resin and wash water to minimize bead loss, and disposal of the spent wash solution. Completing this process can take anywhere from a half to a few days. Others (7) have also promoted the benefit of using HCl/NaOH regenerated WAC resin as the primary bed since the NaOH helps to remove oil. Of course the operating cost of using HCl and NaOH regeneration are higher than salt and this becomes more significant as flowrate and feed hardness increase.

SHORT BED RESIN CLEANING - A new cleaning process has been developed for use with short bed technology. The resin can be cleaned in-situ by simply pumping in about 1bed volume (5ft^3 or 37gallons for the Seneca unit) of a specialty short bed cleaning solution. The oil is rapidly solubilized as the solution is pumped through the bed. The dirty cleaning fluid is displaced from the bed and if desired can be recovered for re-use and the oil recycled upstream. The cleaning process itself can be accomplished in less than 30 minutes. To date it has not been necessary to use this procedure at Seneca.

Figures 11 show the effect of this cleaning solution on an oil fouled resin in a pilot plant. A feed containing about 10ppm oil was pumped through the resin column until the bed was clogged. Figure 11.1 shows the virgin cleaning solution in the right side beaker as it is being pumped into the bed and Figure 11.2 shows the top of the pilot column as the water is being displaced by the incoming cleaner. Figure 11.3 shows the dirty oil containing cleaning solution flowing out of the bed and being collected in the left side beaker in Figure 11.4.

Figure 11.1

Figure 11.2

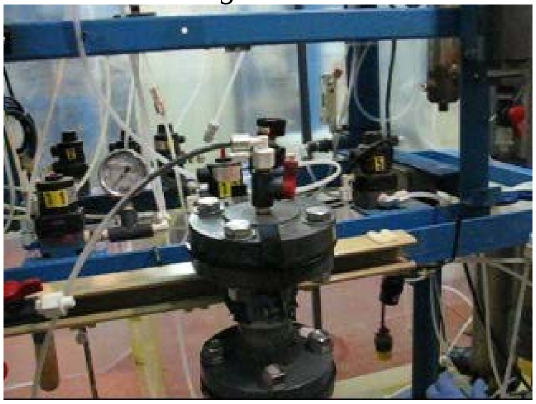

Figure 11.3

Figure 11.4

Figures 12 show the effect of this cleaner on a segment of the guard cartridge filter that was fouled during the upset condition. The as received segment is shown in Figure 12.1. It is loaded with oil and with iron sulphide. As previously explained the iron sulphide was formed in the tank preceding the cartridge filters (but after the nutshell filter) as a result of exposure to air. The first attempt at cleaning using HCl is shown in Figure 12.2. The colours of the solution and cartridge segment show that it was completely ineffective. The segment was then rinsed and immersed in the cleaning solution. This removed the oil and the cartridge was then again immersed in HCl to dissolve the iron sulphide. The final clean segment is shown in Figure 12.3.

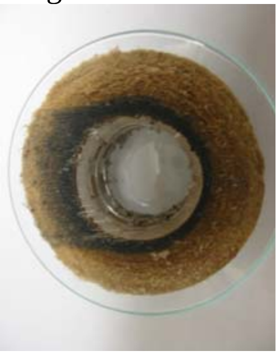

Figure 12.1

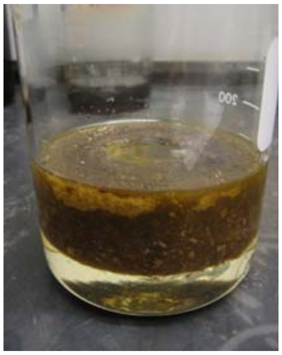

Figure 12.2

Figure 12.3

While this cleaning solution will handle oil the possibility of particulate fouling by iron (or scale carry-over from a softener) remains a potential concern. In situ cleaning to dissolve these particles using cleaners like citric acid (or HCl) can be done and was implemented as a preventative measure at Seneca. In the event of an upset in the prefiltration process that allows a significant amount of insoluble particulates into the resin bed removing the resin from the column would be necessary. For a short bed column this process is facilitated by resin transfer nozzles on the side of the bed spools. This allows resin removal without having to disassemble the resin bed.

SUMMARY

A specialty nutshell filter and short bed ion exchange system have been in continuous operation for 6 months at the time of writing this report. Over this time period the hardness target of <1ppm has been consistently maintained and off site sample analysis has shown values <0.5ppm. A salt regenerated SAC:WAC configuration was selected based on the greater capacity of the WAC resin bed and the desire to avoid onsite use and storage of HCl and NaOH. Resin cleaning has not been required, but the details of a new <30minute in-situ oil cleaning process have been described.

REFERENCES

1. Charles D. Blumenschein et al, “Walnut Shell Filtration for Oil and Solids Removal from Steel Mill Recycle Systems” AISE Steel Technology, April 2001 p33.

2. Produced Water Treatment Design Manual edited by Abbas Zaidi, Thomas Constable, Wastewater Technology Centre, Burlington, Ontario, 1994 p 3-43.

3. Craig Brown et al, “New Process for Reusing Produced Wastewater” Proceedings of the International Water Conference 64th Annual Meeting, October 2003, IWC-03-27, p235 – 239

4. F.X. McGarvey et al, “Water Conditioning for Oil Well Flooding” Proceedings of the 18th Annual Liberty Bell Corrosion Course, Philadelphia, Pa, September 1980.

5. V. Kadlec, "Brackish Water Softening Combining Strong and Weak Acid Cation " Proceedings of the 18th Annual Liberty Bell Corrosion Course, Philadelphia, Pa, September 1980.

6. C.J. Brown, M. Sheedy, "A New Ion Exchange Process For Softening High TDS Produced Water " SPE/Petroleum Society of CIM/CHOA, Calgary, Alberta, November 2002 Paper Number 78941.

7. Guy Mommaerts, "Fouling of WAC and SAC Resins in EOR applications" Proceedings of the International Water Conference 68th Annual Meeting, Orlando, Florida, October 2007, IWC-07-69.