SHORT BED ION EXCHANGE TECHNOLOGY PRODUCES ULTRAPURE WATER WITHOUT USING A MIXED BED

Michael Sheedy
Eco-Tec Inc.,
1145 Squires Beach Road, Pickering,
Ontario, Canada, L1W 3T9.
Presented at the EPRI 8th International Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators, Calgary June 20 –23, 2006

Abstract

Conventional practice when producing water with a conductivity of less than 0.1 umho/cm is to use a mixed bed ion exchange unit. This paper describes a novel short bed ion exchange technology that produces water of this quality using separate columns of cation and anion resin. The principle features of this technology include the use of compressively packed beds only 3” to 6” in depth, fine mesh resins that improve exchange kinetics, counter-current regeneration, and low exchanger loadings. This results in a system that is much smaller and less complex than an installation with a regenerated mixed bed unit. Case studies are presented that describe operation of this technology for the treatment of a surface water source, a municipally treated water source, and RO permeate.

Introduction

High pressure power boilers typically require make-up water that has the following characteristics:

- Conductivity \( \leq 0.1 \text{umho/cm} \),
- Silica 5 – 20 ppb,
- TOC \( \leq 300 \text{ ppb} \),
- Na, Ca, Mg, Cu, SO\(_4\), Cl 3 – 20 ppb.

The flow sheets most commonly considered when trying to produced this quality of water are the following:

1. Roughing demineralization using two conventional deep bed ion exchange columns followed by a mixed bed polisher, SAC/SBA/MB.

2. Roughing demineralization using reverse osmosis followed by a mixed bed polisher or EDI, RO/MB, RO/EDI.

Using Recoflo® short bed ion exchange technology it is possible to produce this quality of water without using either a mixed bed polisher or EDI stack.
Features of Short Bed Ion Exchange

1. **Short bed height and small resin volume** – The most obvious feature of this type of system is the significantly shorter bed height. Typical bed depths for a demineralizer are 3” to 6”. This represents a resin volume that is approximately 10% that of a more conventional deep bed design. Such a dramatic reduction in column size reduces installation cost and footprint. It also allows the equipment to be completely factory pre-assembled and tested prior to shipment, thus reducing commissioning time and cost.

2. **Fine mesh resin** – Short bed systems use resin particles that are about 1/5 the size of conventional resin beads. Reducing the particle size significantly increases the kinetics of the exchange process and allows operation at hydraulic flow rates that are 3 to 5 times higher than in conventional systems. This reduces the diameter of the resin vessels and the required floor space. Finer mesh resins are also stronger and more resistant to cracking due to changes in osmotic pressure1, 2.

3. **Counter current regeneration** – Counter-current regeneration is the most efficient method for contacting resin and regenerant chemicals. It ensures that the exit end of the resin bed is the most thoroughly regenerated thereby minimizing onstream leakage rates and increasing final water quality. It also minimizes the amount of excess regenerant chemical that must be used to ensure target water quality levels are achieved.

4. **Compressed resin bed** – The resin is packed into the column in a slightly compressed condition. This ensures that no flow channeling and ionic leakage occurs. It also prevents any resin movement within the column ensuring that the benefits of counter-current regeneration are realized. Since no freeboard space exists within the column it is essential that suspended solids be removed from the feed stream. This means that some form of pre-filtration equipment must always be provided with a short bed system. Such equipment typically ranges from cartridge to dual media filters depending on the TSS level.

5. **Low resin loading** – Typically less than 20% of the total exchange capacity of the resin is used in a loading cycle. This is significantly less than is used in a conventional system and ensures that only the most easily accessed and regenerated sites are used. In conjunction with counter-current regeneration this helps to minimize chemical consumption. It also minimizes the volume change associated with each loading and regeneration sequence, which helps to reduce resin bead physical stress and cracking.
6. **Short cycle times** – The low resin loading and high flow rates combine to produce short cycle times. For example, a system treating a feed stream with 170 mg/L TDS and producing 3 Megohm.cm quality product water has a total cycle time including regeneration of only 17 minutes. Such short regeneration times can reduce the need for redundant equipment through the use of surge tanks that would otherwise be impractically large for the multi-hour regeneration sequences that are common for conventional systems.

**Theory and Performance of Short Bed Ion Exchange**

Within an ion exchange column there is a relatively shallow layer of resin where the exchange process is actually taking place. Upstream of this layer the resin has already been exhausted while downstream the resin has yet to receive any significant loading. Short bed ion exchange technology is based on the manipulation and control of this shallow layer or "mass transfer zone, MTZ". In effect the depth of a short bed column is reduced to just slightly greater than the MTZ.

Under some conditions the depth of the MTZ can be estimated using the following equation derived by Glueckauf\(^3\) or by the NTU HTU approach outlined by Treybal\(^4\).

\[
Z_B = \frac{(H_p+H_o)}{2} \times \left\{ \frac{1}{(a-1)} \ln\left(\frac{1}{x_B}\right) - \frac{a}{(a-1)} \ln\left(\frac{1}{(1-x_B)}\right) + 1 \right\} \\
+ \frac{(H_f+H_o)}{2} \times \left\{ \frac{a}{(a-1)} \ln\left(\frac{1}{x_B}\right) - \frac{1}{(a-1)} \ln\left(\frac{1}{(1-x_B)}\right) - 1 \right\}
\]

Where

- \(Z_B\) = Half the height of the MTZ for ionic species B
- \(H_p\) = Plate height contribution due to particle diffusion and is directly proportional to resin particle (diameter)\(^2\) and fluid velocity
- \(H_f\) = Plate height contribution due to film diffusion and is directly proportional to resin particle diameter
- \(H_o\) = Plate height contribution from finite particle size
- \(a\) = Resin separation factor for a given ion pair (ie Ca and Na)
- \(x_B\) = Ionic fraction of B

This equation shows that the depth of the MTZ and the kinetics of the exchange process are very dependant on the diameter of the resin bead. A smaller particle helps to reduce the depth of the MTZ while permitting operation at higher flow rates.

In fact, due to the relatively low concentrations being treated during the loading step the kinetics of the exchange process are primarily limited by diffusion across the mass transfer film surrounding the resin bead. Under these conditions the exchange rate is inversely proportional to the bead diameter.
While not used for process design purposes these approaches help to explain the significance of the relevant process parameters such as particle diameter, solution flow rate, and resin selectivity and provide a theoretical basis for the use of short ion exchange beds.

Figure 1 shows experimental data for the measured MTZ in a cation resin column treating a 170 mg/L TDS water source. Under these conditions the product water quality produced after subsequent treatment through a short bed anion column ranged between 3 – 5Megohm.cm.

The two curves show the location of the MTZ before and after loading at steady-state. To produce each curve the resin was extruded from a column and separated into 6 equal portions. Each section was then titrated with NaOH. The curves clearly show the following:

- Consistent with counter-current regeneration, the resin at the top (inlet) of the column and to the left of the curves is predominantly in the salt form, while the resin at the bottom (outlet) of the column and to the right of the curves, is primarily in the acid form.

- The area between the curves represents the actual loading that takes place each operating cycle and is less than 20% of the total bed capacity, which is represented by the area below the max. capacity line.

- The actual depth of the mass transfer zone in this case is only about 3”.

- Since these data were produced from a column at steady-state the MTZ cycles back and forth between these boundaries each operating cycle.

![Figure 1](image-url)
A similar curve could be produced for the anion column. Since the exchange on the anion resin is followed by neutralization of the hydroxyl ion it may be expected that this more favourable equilibrium condition would result in an even shorter mass transfer zone. In practice, the author has found that when trying to produce high purity water the lower capacity of the anion resin and its much lower selectivity for silica prevents operation with an anion bed shorter than the cation bed, unless use of a degassifier is considered.

For a dual short bed system such as the unit shown in the figure 2, typical performance is described in table 1.

![Figure 2](image)

Figure 2

*This Recoflo short bed demineralizer can produce up to 600 gpm (136 m3/hr) of high purity water*

<table>
<thead>
<tr>
<th>Feedwater Conductivity (µS/cm)</th>
<th>Product Water Resistivity (Mohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>340</td>
<td>1-5</td>
</tr>
<tr>
<td>200</td>
<td>10-12.5</td>
</tr>
<tr>
<td>20</td>
<td>16-18</td>
</tr>
<tr>
<td>4</td>
<td>17.5 – 18.1</td>
</tr>
</tbody>
</table>

The less favourable equilibrium condition in the cation bed does explain why there is more sodium leakage from the cation bed relative to chloride leakage from the anion bed. The result being that under most conditions the primary contribution to ionic leakage from a dual short bed (SAC/SBA) demineralizer is sodium hydroxide. The other obvious source of caustic is of course incompletely rinsed regenerant solution.

In a short bed system the problem of residual regenerant is addressed by using a relatively small volume of rinse water, typically about 1 bed volume, followed by a brief period of internal recirculation through both beds before the unit is returned to service.
To further improve performance, the problem of onstream sodium leakage from the cation bed is addressed by adding a small polishing bed of SAC resin to the skid and locating it immediately after the primary anion bed. This Triflo configuration, shown in figure 5 extends the range of feed water conductivity that may be treated to 1,000µS/cm, while still allowing the production of better than 10 Megohm.cm product water.

The TDS fed to this polishing bed is minimal which means that the regeneration frequency is very low and the additional regenerant consumption is insignificant. For the same reason it is possible to operate this bed at almost double the hydraulic flow rate and with a bed depth of only 3”, which is half the depth of the primary units. Furthermore, it is possible to reduce the primary cation bed regenerant dosage since the resulting incremental leakage will be captured by the polishing bed. In this way the overall regenerant consumption can be reduced.

**Short Bed Triflo Case Study**

This Triflo system was commissioned in the fall of 2002 and produces 500 gpm of high purity water with a conductivity of less than 0.1 micromho/cm and less than 4 ppb SiO₂ without using a mixed bed polisher. The water is used to feed a 2,000psig coal fired boiler. The primary water sources are either raw water drawn from one of the Great Lakes or the local municipal supply both with a Total Dissolved Solids (TDS) of about 160 mg/L as CaCO₃, conductivity of about 310µs/cm and the following water analysis.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>95 mg/L</td>
<td>Bicarbonate</td>
<td>111.5 mg/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>50 mg/L</td>
<td>Sulfate</td>
<td>21.9 mg/L</td>
</tr>
<tr>
<td>Sodium</td>
<td>13 mg/L</td>
<td>Chloride</td>
<td>14.1 mg/L</td>
</tr>
<tr>
<td>Other cations</td>
<td>2.2 mg/L</td>
<td>Silica</td>
<td>1.5 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Other anions</td>
<td>0.8 mg/L</td>
</tr>
<tr>
<td>Total cations</td>
<td>160.2 mg/L</td>
<td>Total anions</td>
<td>149.8 mg/L</td>
</tr>
</tbody>
</table>

Turbidity       | up to 100 NTU |
TSS             | up to 100 mg/L |
TOC             | normally <2 mg/L, spikes to 7 mg/L |
pH              | 7.5 – 8.5 |
Temperature     | 35 – 80°F |

This new system has now been in service for almost 4 years and has consistently produced less than 0.1 micromho/cm water.
As the analysis indicates this water will at times contain significant amounts of TSS. To prolong filter run length the initial process design allowed switching to a city water source when turbidity levels exceeded 100 NTU. Feed turbidity is monitored by an online turbidity meter.

To remove TSS three dual-media Spectrum Filters were provided with each capable of delivering 50% of the required net product flow. A photograph of one of the filters is shown in figure 4. Each filter is 66 inches in diameter and is operated at a maximum hydraulic flowrate of 428 gpm (18 gpm/ft^2). The bulk of the suspended solids are removed in the upper filtration layer, which consists of coarse anthracite with an effective size of 0.6 – 0.8mm. The lower layer acts as a polishing filter to remove the residual solids not retained by the anthracite. A unique high-density micro-media is used with an effective size less than 0.1mm.
This filtrate stream is pumped to two short bed Triflo ion exchange trains. Each train was designed to provide a net product flow rate of about 290 gpm. As previously described a Triflo unit consists of three short depth compressively packed ion exchange beds. The primary SAC/SBA columns are 60 inches in diameter and 6 inches in depth and operate at 30 gpm/ft². The final polishing cation resin bed is only 48 inches in diameter and 3 inches in depth and runs at 50 gpm/ft². A photograph of one of the Triflo units is shown in figure 5.
Counter-current regeneration of the primary SAC and SBA resin beds is automatically initiated after processing a fixed volume of solution. The normal onstream loading time for the primary beds is about 10 minutes. The primary regeneration sequence is fully automated and takes about 11 minutes. The conc. Chemicals are injected inline via gear pumps into regenerant DI water.

To ensure adequate removal of silica during anion regeneration the regenerant DI water is heated to 140°F in an electrically heated warm water supply tank. Upon completion of the primary regeneration sequence water is recirculated through the primary cation and anion beds to remove any residual unwashed regenerant chemicals.

As a result of the small TDS load on the cation polisher bed it is only regenerated after 100 loading cycles of the primary beds have been completed. This is also automatically initiated.

Product water conductivity and silica performance data collected from a log sheet monitoring program are shown in the figure below. The data clearly show that product water conductivity was consistently below 0.1 micromho/cm and that silica levels were generally less than 4 ppb. The long-term trend indicates a decline in the silica concentration and more stable readings. Silica levels subsequent to this monitoring period were typically in the 2-4 ppb range. This is attributed to minor program and sampling modifications and the performance of in-situ anion bed cleaning when silica levels start to increase.

![Figure 6](image-url)  
*Triflo product water quality*
Table 2 shows a comparison of regenerant consumption for the Triflo system and the previous SAC/degassifier/SBA conventional system. The Triflo unit has provided a dramatic improvement in product water quality and a substantial reduction in regenerant acid consumption, however the reduction in caustic consumption is more modest, due to the fact that the Triflo system does not use a degassifier as the did the previous system.

<table>
<thead>
<tr>
<th></th>
<th>Old System</th>
<th>Triflo</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Consumption</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid</td>
<td>0.38 gal/kgal</td>
<td>0.17 gal/kgal</td>
</tr>
<tr>
<td></td>
<td>2-3 umho/cm</td>
<td>&lt;0.1 umho/cm</td>
</tr>
<tr>
<td>Sodium</td>
<td>40-80 ppb</td>
<td>Sodium ~1 ppb</td>
</tr>
<tr>
<td>Caustic</td>
<td>0.34 gal/kgal</td>
<td>0.29 gal/kgal</td>
</tr>
<tr>
<td>TOC 500 ppb</td>
<td>TOC 200 ppb</td>
<td></td>
</tr>
<tr>
<td>Silica 5 ppb</td>
<td>Silica 2-4 ppb</td>
<td></td>
</tr>
<tr>
<td>Chloride 5-10 ppb</td>
<td>Chloride 1-2 ppb</td>
<td></td>
</tr>
<tr>
<td>Sulfate &lt;4 ppb</td>
<td>Sulfate &lt;1 ppb</td>
<td></td>
</tr>
</tbody>
</table>

**Short Bed Polisher Case Study**

In 2001 a high purity water treatment system was installed as a replacement system at a nuclear power station. The system has a capacity of 1050 gpm (239 m³/hr). It treats Great Lakes surface water through direct filtration, reverse osmosis (single pass) followed by a double pass through short bed demineralizers, each one consisting of a separate bed of cation and anion resin (see Figure 7 below).

<table>
<thead>
<tr>
<th></th>
<th>Feed Water</th>
<th>Product Water Spec</th>
<th>Actual Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>0.6-1.3ppm</td>
<td>&lt;2.0ppb</td>
<td>0.36ppb</td>
</tr>
<tr>
<td>Sodium</td>
<td>10-13 ppm</td>
<td>&lt;0.2ppb</td>
<td>&lt;0.05ppb</td>
</tr>
<tr>
<td>TOC</td>
<td>1.5-3.0ppm</td>
<td>&lt;10ppb</td>
<td>5.1ppb</td>
</tr>
<tr>
<td>Chloride</td>
<td>20-25 ppm</td>
<td>&lt;0.8ppb</td>
<td>&lt;0.3ppb</td>
</tr>
<tr>
<td>Sulfate</td>
<td>24-27 ppm</td>
<td>&lt;1.8ppb</td>
<td>&lt;0.5ppb</td>
</tr>
</tbody>
</table>
Figure 7

1050 gpm (239m3/hr) capacity high purity system with Recoflo short bed ion exchange polishers in foreground. Large vessels are micro-media filters for surface water direct pre-filtration. Reverse osmosis units are in background.

This system has been operating for 4 years and consistently produces water of the quality indicated in Table 3. The RO permeate quality which feeds the ion exchange polishers is typically in the range of 10-20µS/cm, with 2-3 ppm TDS and 60 ppm CO2. The final quality indicates the purity that can be achieved using this process, without the use of mixed resin beds.

Pilot testing prior to the selection of the system indicated that a single cation/anion short bed polisher could achieve the specified quality. However, since this was the first commercial installation of Recoflo short bed technology at this capacity and product water purity, and since the client was a nuclear power station that needed a reliable, continuous supply of demineralized water, it was decided to install the system in a two-stage configuration.

The first stage demineralizers have a total cycle time of 39 minutes, which includes the 7 minute regeneration sequence. Chemical consumption is 0.33 lb-sulfuric acid and 0.67 lb-caustic soda per 1000 gallons of water produced.

The final polisher is in service for 29 hours and is then regeneration in 11 minutes before returning to service. In both cases the regeneration sequence is fully automated. Chemical consumption of the final polisher is 0.067lbs of sulfuric acid and 0.05lbs of caustic soda per 1000gallons of water produced. For a system producing 500 gpm continuously, this would correspond to a 200 gal (760 l) tote of 93% sulfuric acid lasting for 580 days and a 200 gal tote of caustic lasting 350 days. The waste volume from each of the two final polishers which treat 525 gpm (120 m³/hr) is 418 gal (1653 l) per regeneration.
Summary

The case studies presented in this paper clearly demonstrate that Recoflo® short bed ion exchange technology can be used to produce high purity water for boiler feed make-up without using a mixed bed polisher or EDI cell.

References


