Optimizing the replacement ratio of ion exchange resins in polishing plants by characterization and cost evaluation

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Abstract

An ion exchange process in a power plant was investigated to provide a means to lower operating costs by optimizing exchange ratios of used resins. Ion exchange resins were obtained and tested according to ASTM standards to find the difference of capacity after long term use. Moreover, we used Fourier-transform infrared spectroscopy (FT-IR) methods to identify the adsorbed impurities and exhausted functional groups. The cation and anion exchange resins showed a drop of 0.39 and 0.53 eq/L in total capacity, respectively, also corresponding to the drop and increase of peaks found through FT-IR. Finally, a cost analysis was conducted to optimize the performance of ion exchange resins with the lowest cost possible. Our results showed that ion exchange processes are heavily related to operation costs. A proposed total cost of ownership model will help stakeholders decide on cost-effective ion exchange processes while being able to maintain ultrapure quality. Moreover, results conducted through standardized tests will be able to compare with the results provided.

Keywords: Ion exchange; Ultrapure; Polishing stage; Pure water; Cost optimization

1. Introduction

Conventionally, ion exchange (IX) processes in water treatment utilizes ion exchange resins to remove contaminant salts, in particular hardness causing calcium and magnesium ions, from water [1]. Nowadays, IX processes have further proceeded to apply in food industry [2,3], pharmaceutical and bio processes [4,5], recovery of rare metals [6–8], use in chromatography [9,10] and producing ultrapure. Of the applicants of IX processes, industrial ultrapure production heavily utilizes IX in the main and polishing stages [11,12]. As shown in Fig. 1, in the main stages IX resins exchange hardness causing ions from the water. In the polishing process, however, IX resins are used to remove low molecular organic contaminants and acids before the ultrapure reaches the final point of use [12].

One of the industries that produces ultrapure are power plants [13]. As impurities in the water can scale up in the gas turbines or cause higher boiling points which in turn leads to more energy consumption, power plants use and produce ultrapure, as pure water can address the concerns above and raise the efficiency of power generation itself. Ultrapure production processes take numerous processes into a single production train, sometimes utilizing the same process repeatedly to remove target compounds [12]. Ion exchange in the polishing stage removes unwanted organic matters and ions, thus further refining the effluent ultrapure.

Modern IX processes utilize mixed bed approaches with automated processes that inject regenerants into the exhausted resins to regenerate [1], and the used regenerants are sent directly to waste. Waste regenerants are extremely saline, as salt levels easily reach over 100 g/L and is hard
to treat and meet the stringent environmental laws before disposal [14]. Even more, regenerated resins show lower exchange capacity than their unused counterpart [15]. Due to these reasons, it has become a trend to use the resins as a single use and then dispose, as disposal of resins is typically easier than disposing brine [1]. Disposal of resin are treated just like many other solid wastes, cheap, and easy to meet regulations, despite concerns that brine management has less impact to the environment than disposal of IX resins [1,14,16,17]. Some techniques such as reusing brine are in use, but not as a mainstream process [18].

However, the exchange ratio between new and use IX resins remains unclear. Amini et al. [19] noted that many facilities that uses IX processes exchanged IX resins without monitoring their systems closely, resulting in a 3.5-fold difference on resin exchange interval times. Unless data are collected and operated without trained workers, processes exchange used resins with fresh, new ones at a set ratio at set time intervals. Even more, as IX resins continues to improve in service time (>6 y, differs by application), many processes are shifting from a batch mode (disposing all resins that was used) to replacing a set percentage, improving the total capacity while being able to reduce replacement costs. But it remains unclear how much of the IX resins should be replaced for optimized operation, as costs of resins, alongside the capital expense (CAPEX) and operation expense (OPEX) costs, differs around the globe.

Therefore, to provide a method of calculating optimized IX resins exchange ratio, we took into consideration cost analysis in IX process alongside with results obtained from IX resins from a real operating plant. The IX resins serviced the ultrapure process for 5+ years and is a good control for estimating long term capacity of the resins. Furthermore, we tested the resins through standard methods and evaluated its functional groups through Fourier-transform infrared spectroscopy (FT-IR) techniques. Together, decision makers will have a reference of how to optimize their systems to meet the capacity goals while reducing operation costs.

2. Materials and methods

2.1. Ion exchange resins and experimental setup

All IX resins, new and used, were obtained from a power plant in Korea Midland Power, where IX processes are used to process ultrapure water for power generation. New IX resins were stored as delivered, with no signs of damage in the packaging. Used IX resins were taken directly from the polishing process, and then stored in sodium chloride conditions. Used IX resins were taken and stored in mixed bed conditions and were separated before testing. Specifications of the IX resins can be found in Table 1.

All IX resins were pretreated and tested according to ASTM D2187 [20]. In short, IX resins were poured into a 150 cm long column and backwashed with up-flow water until the effluent was clear. Then 100 g/L NaCl solution was slowly introduced into the columns until the effluent contained NaCl. The anion resins were separated and siphoned out using either a peristaltic pump or disposable spoids, and the remaining cation resins were drained out of the columns using deionized water. The resins were then treated with acids/bases accordingly within the columns, and then again treated with the counterpart base/acid. After rinsing and measuring pH of the effluent water, the resins were drained in a humidified drying apparatus after being weighed for further experiments. All glassware was custom ordered and manufactured at Lab Market (Republic of Korea, Buchner Funnel manufactured in Japan), and were pre-cleaned with acids and deionized water before experiments.

2.2. Testing of total and salt-splitting capacity of IX resins

Testing IX resins for total and salt-splitting capacities was also conducted by ASTM D2187 standards: In short, a filter tube with porous media was fitted into an apparatus to retain the resins while reagents can flow downwards at a rate of 20–25 mL/min through a separation funnel. All
pH conditioning and titrations used an indicator solution; if electronic pH meters were stated as useable, electronic pH meters (MULTILAB, IDS) were used.

### 2.2.1. Cation exchange resins

For salt-splitting capacity, samples were converted to hydrogen form, eluted with sodium chloride solution, and then titrated to determine the hydrogen ion exchanged during this process. First, the samples were treated with hydrochloric acid (Merck, USA) at a rate of 20~25 mL/min (approximately 60~75 bed volumes per hour) to convert the resins to hydrogen form. Then, the resins were rinsed with water at the same rate until the effluent was yellow to methyl orange (Samchun, South Korea). Afterwards, sodium chloride (Samchun, South Korea) solutions were passed at equal rate to elute the exchanged hydrogen ions. The eluent was titrated with NaOH (Samchun, South Korea) solutions using sodium hydroxide solutions with phenolphthalein (Merck, USA) indicators. The results were calculated according to ASTM D2187.

For total capacity, resins were converted to hydrogen form, equilibrated within known excess of standard sodium hydroxide solution in sodium chloride conditions, then titrated of residual hydroxide ions with standard acid. Samples were weighed and transferred into the filter tubes and treated with hydrochloric acid at a rate of 20~25 mL/min (approximately 60~75 bed volumes per hour) to convert the resins to hydrogen form. The resins were rinsed with water at the same rate until the effluent was yellow to methyl orange. Subsequently, sodium chloride (Samchun, South Korea) solutions were passed at equal rate to elute the exchanged hydrogen ions. The eluent was titrated with NaOH (Samchun, South Korea) solutions using sodium hydroxide solutions with phenolphthalein (Merck, USA) indicators. The results were calculated according to ASTM D2187.

### 2.2.2. Anion exchange resins

Anion exchange resins were first converted to chloride form. Then, nonsalt-splitting groups were eluted with ammonium hydroxide (Fujifilm, Japan), followed by elution of salt-splitting groups with sodium nitrate (Samchun, South Korea). Finally, chloride ions were determined by elution through sodium chloride solutions. Resins were first treated with hydrochloric acid to convert into chloride form. Then, certain amounts of ammonium hydroxide were passed through the samples at a rate of 20~25 mL/min (approximately 60~75 bed volumes per hour), followed by water at the same rate until a mixture of 1 L was collected. Then, at the same rate, sodium chloride solutions, followed by water, was treated to the samples, again until a mixture of 1 L was collected. Finally, the resins were treated with sodium nitrate solution at the same rate.

The pH for effluents of ammonium hydroxide were adjusted using nitric acid (Deoksan, South Korea) and ammonium hydroxide. Then, potassium chromate (Samchun, South Korea) solution equal to 50 mg was pipeted in and titrated with silver nitrate standard solutions. The sodium chloride solutions were titrated to pH 3.9 using an electrometrical pH meter with hydrochloride standard solutions. The sodium nitrate solutions were pretreated and titrated with the same procedures as ammonium hydroxide.

### 2.3. FT-IR analysis

FT-IR analysis was done using a Nicolet iN-10 infrared microscope (Thermo-Fisher Scientific) for microscope analysis. To obtain microscopy images of IX resins, about 1~3 mg of resins samples was transferred into 25 mm mesh disks and pictured with autofocus enabled. The resin images were inspected with the naked eye to determine whether the resins were intact or damaged.

Absorbance spectra were obtained with a Nicolet iS50 FT-IR spectrometer for ATR (attenuated total reflection) analysis. To gain a spectra, resins were dried in the pretreatment apparatus. Then, about 4 mg of dried resins were crushed into the finest power possible using a mortar and pestle. The powdered form was carefully transferred onto the crystal disk using stainless spatulas, and then scanned for 32 times for each spectra. The average of the measurements was used for the final spectra. Peaks were identified using the manufacturer provided software, Omnic Picta, while graphs were plotted in SigmaPlot v12.5.

### 3. Results and discussions

#### 3.1. Total and salt splitting capacity of ion exchange resins

As can be seen in Fig. 2, both new and used ion exchange resins were checked to be full and intact before
the experiments. All sampled IX resins were inspected to be whole and intact throughout the experiment, and no particles or debris nor any remnants were found through FT-IR imaging. After the resins were checked that they were intact, resins were pretreated and stored in glass bottles for testing.

3.1.1. Cation exchange resins

As shown in Fig. 3, the salt splitting capacity of new and used cation exchange resins resulted in 2.45 ± 0.11 eq/L and 1.88 ± 0.04 eq/L, respectively, and the total capacity of new and used cation exchange resins resulted in 3.18 ± 0.57 eq/L and 2.79 ± 0.01 eq/L, respectively. The drop of salt-splitting and total capacity for used resins suggests that there were impurities removed by cation IX resins in the polishing stage.

3.1.2. Anion exchange resins

As shown in Fig. 4, the salt splitting capacity of new and used anion exchange resins resulted in 1.87 ± 0.05 eq/L and 1.34 ± 0.01 eq/L, respectively, and the total capacity of new and used anion exchange resins resulted in 2.22 ± 0.02 eq/L and 1.69 ± 0.00 eq/L, respectively. The results are reasonably linked to our hypothesize that used resins will have lower total capacity than their fresh counterparts and suggests that there were impurities removed by cation IX resins in the polishing stage.

3.2. FT-IR analysis

In cation IX resins, a drop can be seen on peaks 1, 177, 1,126, 1,035 and 1,008, as shown in Fig. 5. According to previous literatures [8,13,21], the peaks were assigned as ~SO3H groups, the main functional groups of strong acidic cation resins. In the used resins, notably lower peaks were observed on the same wavelength, suggesting that cation IX resins exchanged ions in the process and exhausted functional groups are found in the form of peak decrease. There were also decreases in the 700 cm⁻¹ area, where the peaks also represent the ~SO3H groups (data not shown).

As can be seen in Fig. 6, in anion exchange resins, there was notable increase of peaks on 1,488, 1,475 and 1,382. From previous literatures [13,22], the found peaks are described in Table 2. Also, an increase was noted on peaks 1,428 and 1,417. These peaks are related with the functional groups on anion IX resins [22]. The increase of peaks suggests that the functional groups of resins have adsorbed impurities associated.

3.3. Cost analysis

In our study, a total cost of ownership (TCO) model was derived to analyze the total cost of IX processes. The cost factors associated with the IX processes was analyzed and considered in the model. The aim of the TCO analysis is to lower the total costs while meeting water quality standards. The results of the ion exchange resins ratio were used for optimizing the ratio in this model.

Next, we collected data on the costs associated with the ion exchange system, including implementation and operation costs. We combined our IX experiment results with the data collected to create a comprehensive TCO model. The TCO model focused on the total costs of the ion exchange process while assuming that the water quality is met when using the optimized IX resin ratio, thus allowing to determine minimized costs while ensuring water quality.

It was found that implementation costs accounts for less than 10% of total costs while most of the ion exchange processes are driven by operating expenses, as reported by previous literatures [23–25].

3.3.1. Implementation costs

Implementation costs in general includes: equipment costs, installation costs, modification costs, engineering...
and design costs, training and supporting costs, etc. In our model, we examined implementation costs, which includes equipment costs and installation costs. Other implementation costs we have found are considered to have little impact in the model, as it doesn’t vary across countries and suppliers, and are treated as ‘other’ factors. The total implementation costs were estimated by adding up each factor, when the resulting equation is represented as follows:

### Table 2
Identified peaks of Fourier-transform infrared spectroscopy attenuated total reflection for new and used ion exchange resins and their associated groups

<table>
<thead>
<tr>
<th>Cation IX resins</th>
<th>Anion IX resins</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,177; 1,126; 1,035; 1,008</td>
<td>-SO₃H</td>
<td>Functional group</td>
</tr>
<tr>
<td>&lt;700</td>
<td>-SO₃H</td>
<td>Functional group</td>
</tr>
<tr>
<td>1,488; 1,475</td>
<td>C–C stretching vibrations of benzene rings and C–H asymmetric deformation vibrations of –CH₃</td>
<td></td>
</tr>
<tr>
<td>1,452</td>
<td>C–H deformation vibrations of aliphatic group –CH₂ and –CH₃ and C=C stretching vibrations, –CH₂ scissor vibrations</td>
<td></td>
</tr>
<tr>
<td>1,382</td>
<td>C–H symmetric deformation vibrations of –CH₃</td>
<td></td>
</tr>
<tr>
<td>1,428; 1,417</td>
<td>–OH bending of carboxylic acids</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Total and salt-splitting capacity of cation exchange resins.

Fig. 4. Total and salt-splitting capacity of anion exchange resins.
Total implementation costs = Equipment costs + Installation costs + Other costs

(1)

3.3.1.1. Equipment costs

The cost of tanks (for water and ion exchange resins), pumps, filters and such equipment are considered in this factor. The buyer should compose an intensive research of these materials as these are always in direct contact with the product ultrapure. Such materials should be tested for leaches and microbial regrowth, which leads to the deterioration of the producing water.

3.3.1.2. Installation costs

Installation costs vary across multiple factors, including initial resin costs, facility size, raw material costs, estate and much more. Of these factors, the size of the facility and the type of resin selected is the decisive factor in the implementation cost. For small systems unavailable to achieve the economics of scale, equivalents to a small water treatment system that serves <10,000 people, there will be added cost in this factor [12,25,26]. The initial ion exchange resins should also be considered for the equipment costs, which should also include rinsing and installation costs. The experiment cost to derive the optimized IX resin ratio also belongs to this factor. The equation will be represented as follows:

Installation costs = Installation rate × Size of system
- × decreasing constant for economics of scale

(2)

3.3.1.3. Other costs

Other costs include trainings for staffs, regulatory compliance, initial startup costs, etc. Although prices vary, they are fairly constant and not a decisive factor for IEX polishing systems. Any other one-time payoffs fall into this category.

3.3.2. Operating costs

As mentioned earlier, operating costs are the main driving factor when considering IX for water treatment [23]. Most of the costs described here are ongoing costs that needs payments on a recurring basis, and can differ by factors including, but not limited to, the factors mentioned below. Operating costs are an essential component of the TCO model, representing the ongoing costs associated with running and maintaining the IX system. The operating costs includes the costs of energy, water, and consumables required to operate the system, as well as the costs needed to replace the ion exchange resins.

The cost of replacing the ion exchange resins represents a significant part of the operating costs, as it is a periodic expense that must be factored into the TCO analysis. The cost of resins can be estimated based on the frequency of replacement and the cost per unit of resin, which is determined by the resulting quality of the ultrapure. The resulting equation is represented as follows:

Operating costs = Operating rate × Size of system
+ Frequency of replacement × Cost per unit of resin

(3)

3.3.2.1. Resins

When operating an IX process, fresh resins should be continuously introduced into the system, whether to replace the resins leaked from a completely mixed flow reactor (CMFR) or to replace a certain amount of ratio in a fixed bed reactor (FBR). Typically, in FBRs, there are no resins that leaks out, so the only consideration is to replace the exhausted resins to new ones. However, in CMFRs, IX resins continues to leak out, and fresh resins must be continuously fed to maintain the performance of the process [19]. Although both reactors should be considered, ultrapure processes utilize an FBR based design, so we considered the FBR model and neglected the leakage of IX resins. Should CMFR processes are in use, leak of resins should be considered.

Fig. 5. Fourier-transform infrared spectroscopy attenuated total reflection spectra of new and used cation exchange resins.

Fig. 6. Fourier-transform infrared spectroscopy attenuated total reflection spectra of new and used anion exchange resins.
3.3.2.2. Brine and reagents

As a result of IX resin regeneration, brine is inevitable. Unless the whole IX process is maintained with single use resins, brines will occur. The most non-saline brine contains about 5 g/L of NaCl, and typically 10 g/L is the minimum concentration that is found in the industry [1,15,27]. Most of these brines are disposed untreated, mostly by dilution with freshwater or by slow disposal to the wastewater treatment plants. Commonly used brine treatments include evaporation and solidification, and cost analysis is required should these methods are used. Very few known processes treats brine for reuse, by employing organic removal techniques for brines or reusing a portion of used brines that has low DOC and conductivity [19]. Brine reuse reduces cost for resin disposal and by using less reagents, and up to 95% cost reduction was reported [26].

Reagents are used to regenerate exhausted resins, neutralize pH of treated water, chemically remove fouling, and more [19]. Most common reagents used are HCl and NaOH for adjusting pH and NaCl for regenerating resins. There are many more unconsidered reagents, such as those used to test the resins, or caustics for removal of fouling.

The cost of reagents and brines is a significant part of the operating costs and must be considered as a factor in the TCO analysis. The cost of reagents and brines can be estimated based on the frequency of usage, the amount used per cycle, and the cost per unit of reagents and brines. The equation is represented as follows:

\[
\text{Cost of reagents and brines} = \text{Frequency of usage} \times \text{Amount used per cycle} \times \text{Cost per unit of reagents and brines}
\]  

3.3.2.3. Energy costs

In Korea, electricity prices are regulated by the Ministry of Trade, Industry and Energy, instead of a supply-and-demand basis. In 2019, the industrial price for electricity in Korea was lower than the IEA median, at 95 USD/MWh (Dollar’s price based on 2019) [28]. Due to low energy prices and low tax compared to other countries, water treatment in Korea is cheaper when it comes to energy costs. In IX processes, the energy consumption of pumps, working pressure, energy prices, etc. should be considered. If the process includes brine management, as discussed above, it should also be considered. The equation is represented as follows:

\[
\text{Energy costs} = \text{Operating rate} \times \text{Size of system} \times \text{Cost of electricity}
\]  

3.3.2.4. Maintenance and repairs

Maintenance costs includes regular maintenance activities and repairs required to keep the IX system in good condition. The equation was represented as follows:

Fig. 7. Sankey diagram of the proposed TCO model. Note that the nodes are not proportional to the actual values.
Maintenance costs = Maintenance rate × Size of system (6)

3.3.2.5. Other operation costs

Where reduced costs will include reuse of regenerants, economic of scale, etc., and all other costs will fall into the expenses. Ongoing costs of labor and salaries should also be considered.

3.3.3. Other considerations

If the whole ultrapure process has extensive waste heat nearby, use of heat exchangers for energy retrieval will help save overall cost in exchange for initial installation costs. For example, heat exchangers can pull waste heat from a power generator nearby to propel a membrane distillation system to treat brine. Such reclaimed value can impact the power generator nearby to propel a membrane distillation system.

For example, heat exchangers can pull waste heat from a power generator nearby to propel a membrane distillation system to treat brine. Such reclaimed value can impact the power generator nearby to propel a membrane distillation system.

3.3.4. Resulting TCO model

In short, the proposed TCO model can be expressed as follows:

Optimised ratio = exchange rate of ion resins when
\[ \sum \text{expenses} - \sum \text{reduced cost} \] is lowest

Which can be further divided into the factors discussed above: the sum of the initial capital costs (C), the annual operating costs (OC), and the replacement costs (RC), as follows:

\[ \text{TCO} = C + \sum (\text{OC}) + \text{RC} \] (8)

where \( \Sigma \) represents the summation symbol and the annual operating costs are expressed as the sum of the costs of reagents (R), brines (B), energy (E), and water (W) over a certain number of years (t):

\[ \text{OC} = \sum (R + B + E + W) \text{ for } t \text{ years} \] (9)

Similarly, the replacement costs can be represented as the cost of replacing the ion exchange resins (IR) over a certain number of years (t):

\[ \text{RC} = \sum (\text{IR}) \text{ for } t \text{ years} \] (10)

- In conclusion, the TCO model we derived provides a comprehensive analysis of the costs associated with implementing ion exchange resins for water treatment. The model includes the costs of purchasing and installing the system, as well as ongoing operating costs, such as the cost of reagents and brines, water, energy, and the cost of replacing the resins. By considering these different factors, the TCO model provides a more accurate estimate of the TCO for the IX system, allowing us to optimize the ratio of cation and anion exchange resins to lower costs while maintaining desired water quality.

4. Conclusions

In this study we tested IX resins from an operation ultrapure production train and evaluated its capacities based on ASTM standards and infrared techniques. Moreover, cost analysis coupled with the IX capacities lead to finding the optimized replacement ratio of IX resins in the processes. Our findings are

- IX resins in the ultrapure polishing plant saw a decrease in total and salt-splitting capacity, which means that IX resins had a hand in the ultrapure polishing process.
- FT-IR results showed that the resins were intact, and peak analysis based on wavelengths revealed that used IX resin function groups decreased when used.
- Cost analysis showed that multiple factors can change the outcome of total costs, and that IX processes are OPEX driven, compared to CAPEX.
- Resin types and the constant need of fresh IX resins are the most decisive factor in the total cost.
- An optimized replacement ratio can be calculated, but many unknown factors still remain to be solved.

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Declarations of competing interest

The authors declare no conflicts that may have afflicted the outcome of this study.

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