Leachables from Strong Acid Cation Exchange Resins

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High purity water is now required in many industries. Ion exchange resins are the best means for obtaining such water. The present study was carried out to obtain the profiles of leachables from typical strong acid cation exchange resins (SACER, three gel and two porous types) widely used for the production of highly pure water. These resins in the H form and fully cleaned were put in purified water which had been purged with nitrogen gas for a hundred days at 50°C. The amounts of organic compounds that could be leached from the SACERs were 4.2 x 10⁻² to 1.7 mg/l per dried resin of liter wet resin as total organic carbon. The leachables from SACERs had similar gel filtration chromatograms and the amounts of components was different from those of the others. The high molecular weight (M,W.) leachables ranged from several hundred thousand by assuming them as polystyrene sulfonate. Phenolsulfonic acid and p-sulfobenzoic acid were found to be present in low M.W. leachable components by reverse phase chromatography.

1 Introduction

Nowadays, a large amount of highly purified water is required in many industries, such as fine chemical, pharmaceutical, medical-related, semiconductor, and power industries. The water qualities are different from users' requirements. For example, pure water for pharmaceutical, and medical-related use must be free from bacteria and pyrogen. Water for semiconductor manufacturing and for various analytical or reagent use is desired earnestly to contain no impurities in ions, microorganisms and organic contaminants. Ion exchange resins are an essential element to make these pure water of ppb or ppt level not only in industrial but in lab. scale. An ion exchange resin is generally used at ambient temperature. The resin has been employing at elevated temperature in a field of purification and separation of a desired constituent or catalysis. It is known trace organic substances leach out from resins as the total organic carbon (TOC) throw in use or during strage. What is the substance and how is the leaching profile have become a matter of great concern in the highly advanced industries. But few studies have been reported on the profile of leachables in terms of the M.W. information and the identification. In this study, concerning commercially available five SACERs obtained from different makers, the leaching behavior of leachables was revealed by soaking the resins into purified water purged with nitrogen gas at elevated temperature (50°C). The soaking time was set to one hundred days because the resin should be used within a couple of months after purchasing it. Information on the components of leachables and their molecular weights was obtained through gel filtration chromatography (GFC) and reverse phase chromatography (RPC).

2 Materials and Methods

2.1 Materials

2.1.1 Ion exchange resin

Five commercially available strong acid cation exchange resins (A～E) with sulfonated cross-linked polystyrene matrix were tested. The resins, A and B are porous type, and C, D, and E are gel type. These are typical resins for water treatment and obtained from leading makers such as Tokyo Organic Chemical Industries Co., Ltd. (Amberlite), Mitsubishi Chemical Industries Ltd. (Diaion), Dow Chemical Co., Ltd.
(Dowex), Bayer Co., Ltd. (Lewatit), Rhom and Haas Co., Ltd. (Duolite). The brand-name of each resin is concealed because the key concern of this study is not to discuss the comparative merits of the resins on performance in purification of water, but to make clear the profile of leachables come out from resins as a characteristic of ion exchangers.

The pre-treatment of resins are shown in Fig.-1.

The general properties of the resins are given in Table-1.

2.1.2 Purified water

Pure water (TOC< 100 ppb) prepared by Puric R (Japan Organic Co., Ltd.) which is an ultrapure water production equipment for lab. use was employed. Prior to use dissolved oxygen in the water was purged away (DO<0.1 ppm) by blowing nitrogen gas into so as to minimize the effect of oxidative decomposition on resin matrix\(^{13,14}\).

2.1.3 Reagent

Polystyrenesulfonated M.W. 1,800, 8,000, 38,180, 114,400, 400,000 (Gaschro Industry Co., Ltd.) and \(p\)-ethylbenzenesulfonic acid (Tokyo Kasei Co., Ltd.) were used to mark the M.W. fitting curve for GFC analysis.

\(p\)-Benzenesulfonic acid, \(p\)-toluenesulfonic acid, \(p\)-ethylbenzenesulfonic acid, \(p\)-phenolsulfonic acid, \(p\)-sulfobenzoic acid monopotassium salt and \(p\)-styrenesulfonic acid of reagent grade (Tokyo Kasei Co., Ltd.) were employed for the identification of leachables. The concentration was set to 10 Cmg/L.

2.2 Analysis of leachable from SACER

First, the sample resins were rinsed again as follows:

1) The resin put into a glass column was backwashed using ten bed volumes of the purified water.

2) Then, 50 mL portions of the rinsed resin was put into a 250 mL volumetric flask and the purified water was messed up to the mark.

3) The flask was stood with gentle stirring in an incubator at 50°C.

4) TOC and pH of the supernatant were periodically monitored.

5) After a hundred days, the solution in the flask was filtered with a 0.22 \(\mu\)m membrane filter (Millipore Industries Co., Ltd.)

6) Sulfate ion concentration in the filtrate was

![Fig.-1 Pre-treatment of SACER.](image)

**Table-1** General properties of SACER.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Moistur holding capacity (%)</th>
<th>Weight capacity (meq/g)</th>
<th>Volume capacity (meq/mL)</th>
<th>Density (g/L)</th>
<th>Effective size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>51.0</td>
<td>4.54</td>
<td>1.77</td>
<td>797</td>
<td>0.54</td>
</tr>
<tr>
<td>B</td>
<td>48.9</td>
<td>4.46</td>
<td>1.84</td>
<td>808</td>
<td>0.57</td>
</tr>
<tr>
<td>C</td>
<td>44.0</td>
<td>4.39</td>
<td>2.15</td>
<td>874</td>
<td>0.55</td>
</tr>
<tr>
<td>D</td>
<td>47.1</td>
<td>4.50</td>
<td>2.00</td>
<td>833</td>
<td>0.60</td>
</tr>
<tr>
<td>E</td>
<td>50.1</td>
<td>4.66</td>
<td>1.77</td>
<td>764</td>
<td>0.63</td>
</tr>
</tbody>
</table>

As salt form.
determined by the bariumchromate method described in JIS*).

7) Molecular weight distribution for the leachables were measured by GFC and their UV spectra were measured. An aliquot of the filtrate was adjusted to 10 Cmg/L solution (the filtrate E; 20 Cmg/L) by using purified water. The components in the leachables were measured by RPC.

2.3 Analytical equipment and condition

TOC : TOC-10 B (Shimadzu Co., Ltd.)
TOC Model 1,800 (Tohre Astro Co., Ltd.)
pH : pH meter Model 130 (Corning Co., Ltd.)
Dissolved oxygen : D.O. meter-IP (Kyusuikagaku kenkyushyo Co., Ltd.)
GFC : HPLC ; HLC-803 D (Tosoh Co., Ltd.)
Detector; SPD-6 A (Shimadzu Co., Ltd.) UV 210 nm
Column ; PWXL4000 (7.5 mm i.d x 30 cm) + PWXL2500 (7.5 mm i.d X 30 cm) (Tosoh Co., Ltd.)
Eluent : 0.2 M Na$_2$SO$_4$+10 % acetonitrile in pure water
Flow rate ; 0.5 mL/min
Injection volume ; 30 μL
Temperature ; 25°C

The calibration curve for GFC is shown in Fig.-2.

RPC : HPLC and detector were the same equipments as GFC analysis
Column ; Silica ODS 80 T$_m$ (4.6 mm i.d x 15 cm) (Tosoh Co., Ltd.)
Eluent : 0.1 M KH$_2$PO$_4$
Flow rate ; 0.8 mL/min
Injection volume ; 50 μL

Temperature ; 25°C
Spectrophotometer : MPS 2,000 (Shimadzu Co., Ltd.)
Incubator : Incubator IB-200 (Ikeda Rika Co., Ltd.)

3 Results and Discussion

Fig.-3 shows the change of TOC in the mixed solution of each SACER and the purified water at 50°C. The general properties for the SACERs after a hundred days soaking were substantially the same as the initial ones given in Table-1. The TOC increased with the soaking time in each solution. Especially in the beginning stage, the TOC increase was proportional to the soaking time, so that the TOC leaching rate was given by the slope. The rates were from 4.2×10$^{-4}$ to 1.7 Cmg/h per dried resin of liter wet resin as given in Table-2. These values were smaller than ones from strong base anion exchange resins (SBAER, 2.0×10$^{-4}$ to 4.7 Cmg/h per dried resin.

![Fig.-2](image)

Fig.-2 Calibration curve of polystyrenesulfonate.

![Fig.-3](image)

Fig.-3 Change of TOC in the mixed solution of SACER and purified water at 50°C.

![Fig.-4](image)

Fig.-4 Change of pH in the mixed solution of SACER and purified water at 50°C.
of liter wet resin) obtained in our previous experiment. The difference in the TOC leaching rates between SACER and SBAER must be due to the difference of the decomposition mechanisms. The most TOC components from SBAER come from the release of the functional group. On the other hand, it is said the TOC from SACER comes to leach out by the degradation of the resin skeleton. Therefore the TOC value from SACER is in general smaller than the one from SBAER. It can be suggested through the bond energy of C-C (347 kJ/mol) of the styrene-styrene chains and C-N (305 kJ/mol) of the functional site.

The TOC leaching rates of the resin A and B were smaller than those of C and D. This may relate the difference of the resin structures, porous and gel. The porous type resin has ordinarily higher crosslinker content than the gel type. The higher crosslink level makes the resin network tight and depresses the expansion of resin, so that it is expected to prevent diffusion of the leachables toward outside from the resin inside. The TOC level coming out from the resin C and D increased proportionally to the soaking time till 40 d. Then the TOC increase rates slowed down. Concerning the resin E showing the extremely low TOC leaching rate, the reason can be thought as follows. According to Higosaki et al. experiment, leachables from SACER were adsorbed on SBAER up to less than 1 ppm level. This resin E was obtained in the mixture with SBAER (OH) of one to one by volume. Most leachables with negative charge leaching out from the resin E must have been adsorbed on the paired SBAER with positive charge in the mixed state.

The pH values for the mixed solutions of each resin and the purified water decreased with increase of TOC of the solution as shown in

<table>
<thead>
<tr>
<th>Table-2 TOC leaching rate of SACER.</th>
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<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
</tbody>
</table>

\(^{a)} \text{TOC in the solution after 7 d soaking.}\)

<table>
<thead>
<tr>
<th>Table-3 TOC, pH, and sulfate ion concentration in the mixed solution after 100 d soaking.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
</tbody>
</table>

\(^{a)} \text{Sulfate ion concentration.}\)

\(^{b)} \text{Amount of sulfate ion.}\)

Calculation equation:
\[ Q_s = C_s \times \frac{(V - R \times D \times MHC)}{(R \times D \times MHC)} \]

where:
- \(V\) : volume of volumetric flask (mL)
- \(R\) : volume of wet resin (mL)
- \(D\) : density of resin (g/L)
- \(MHC\) : moisture holding capacity (%)

Fig.-4. After 100 d soaking, the pH of the solutions indicated strong acid from four to three except for the solution of the resin E. As the TOC of the solutions increased, the pH decreased much. In Table-3, the TOC, the pH, and sulfate ion concentration in the each mixed solution were tabulated. The amounts of sulfate ion leached from each resin were 7.1 to 280 mg per liter dry resin. Hall and Streat propose the following formulas concerning the decomposition of the ion exchange site:
\[
\begin{align*}
R-SO_3H + H_2O & \rightarrow R-OH + H_2SO_3 \\
3H_2SO_3 & \rightarrow 2H_2SO_4 + S + H_2O
\end{align*}
\]

When assumed that the release of proton comes from sulfuric acid, the hydrogen ion concentration which was calculated from sulfate ion measured \((C_s)\) must be nearly equal to the pH value measured. As you can see in Table-4, the hy-

<table>
<thead>
<tr>
<th>Table-4 Hydrogen ion concentration, observed vs calculated.</th>
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<tbody>
<tr>
<td>Resin</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>A</td>
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</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
</tbody>
</table>

\(^{a)} \text{Observed from pH value.}\)

\(^{b)} \text{Calculated from sulfate ion concentration.}\)

Calculation equation:
\[
[H^+] = 2 \times C_s \times 10^{-7/96.1}
\]
Hydrogen ion concentrations obtained from the pH values were higher than those estimated through the sulfate ion concentrations observed ($C_s$) except for the resin E. It suggests that acidic organic compounds came out from SACERs. Consequently the substances caused to decrease pH of the mixed solution as the TOC in the solution increased.

Fig. 5 describes GFC chromatograms of the leachables from SACER after a hundred days soaking. The molecular weight distribution for the leachables were ranged in several hundreds close to a hundred thousand. The major components presented at M.W. 500~600, 1,400~2,000, and 3,100~3,500 (as polystyrenesulfonate) in the chromatograms. The resin C had several low molecular components in addition to the above ones. The peak area of each component was different from each other. But at least these three M.W. components seem to be common in the SACERs.

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Fig. 6 gives the UV absorption spectra of the leachables of the resins B and C. Fig. 7 shows the UV spectra for benzenesulfonic acid derivatives and polystyrenesulfonate of M.W. 1,800. The molecular weight distribution for the leachables were ranged in several hundreds close to a hundred thousand. The major components presented at M.W. 500~600, 1,400~2,000, and 3,100~3,500 (as polystyrenesulfonate) in the chromatograms. The resin C had several low molecular components in addition to the above ones. The peak area of each component was different from each other. But at least these three M.W. components seem to be common in the SACERs.

Fig. 6 gives the UV absorption spectra of the leachables of the resins B and C. Fig. 7 shows the UV spectra for benzenesulfonic acid derivatives and polystyrenesulfonate of M.W. 1,800. Two peaks around 190 nm and 225 nm existed in the both absorption spectra of the leachables of the resins. The absorption peak around 250 nm is assigned to the characteristic benzenoid absorption band of polystyrenesulfonate. This peak was recognized clearly in
the leachable of the resin C. In the resin B, the peak was hidden. These specific absorption peaks in Fig.-6 agreed with benzenesulfonic acids (193-199, around 225 and 250 nm) and the poly-styrenesulfonate as shown in Fig.-7. The fact suggests a certain substance of benzenesulfonic acids should be contained in the low M.W. leachables' components from SACERs.

Furthermore, Fig.-8~12 give the chromatograms by RPC for the leachables of each SACER. Fig.-13 shows the RPC chromatogram for p-phenolsulfonic acid and p-sulfobenzoic acid.
Table-5 Retention time of benzensulfonic acids.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-Sulfobenzoic acid</td>
<td>3.6</td>
</tr>
<tr>
<td>$p$-Phenolsulfonic acid</td>
<td>4.4</td>
</tr>
<tr>
<td>$p$-Ethylbenzenesulfonic acid</td>
<td>11.1</td>
</tr>
<tr>
<td>$p$-Toluenesulfonic acid</td>
<td>44.2</td>
</tr>
<tr>
<td>$p$-Stylenesulfonic acid</td>
<td>75.0</td>
</tr>
</tbody>
</table>

mono potassium salt. Table-5 indicates the RPC retention time of benzensulfonic acids. RPC is known to be a very useful tool to separate low M.W. organic substances' mixture into each component by the difference of polarity. The RPC technique is also available for identifying the aromatic sulfonates (leachables) by the retention times for the known substances under the defined analytical conditions. The retention times (3.5~3.6 min and 4.3~4.4 min) of the two peaks in the RPC chromatogram of every leachable solution coincided with the time for $p$-sulfobenzoic acid (3.6 min) and $p$-phenolsulfonic acid (4.4 min). Consequently it was found out that these two substances were contained in the low M.W. leachable components released by SACERs. The results on the identification of leachables in SACERs are of interest in the meaning that the identified components in our study is the same materials in the latest study on the prediction and identification of leachables from SACERs by the oxidative stress procedure using hydrogen peroxide\(^{4}\). With respect to the formation mechanisms of leachables in the SACERs put into water at the elevated temperature, energetic works will be needed.
4 Conclusions

Based on the results of this study on the profile of leachables come out from SACERs at 50°C, the following conclusions were drawn.

1) The TOC throw out of SACERs used was in the range of $4.2 \times 10^{-2}$ to 1.7 Cmg/h per dried resin of 1 L wet resin in purified water at 50°C.

2) Porous type SACER (A, B) were less amounts in TOC throw than gel types (C, D).

3) SACER (E) which had mixed with SACER from the beginning showed the least TOC throw.

4) The high molecular weight substances in the leachables were in the M.W. range of several hundreds to about a hundred thousands as polystyrenesulfonate, and the prime common components were M.W. 500-600, 1,400-2,000, 3,100-3,500.

5) p-Phenolsulfonic acid and p-sulfobenzoic acid were detected in the low M.W. teachable components.

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References


15) JIS K0102, 129 (1986).


