**Temperature stability of anion exchange resins**

**Introduction**

The functional groups of anion exchange resins are only moderately stable and undergo degradation at high temperature. When treating cold water, this degradation is very slow. However, with hot condensate, or when the caustic regenerant is heated, anion resins lose capacity. This Tech Fact discusses various usage scenarios and the behavior of anion exchange resins under these conditions.

**Main types of anion exchange resins**

The functional groups of the most common polystyrene-based anion resins are shown in the table below.

\[
\begin{align*}
\text{SBA type 1} & : & R - \text{CH}_2 - N^+ - \text{CH}_3 \\
\text{SBA type 2} & : & R - \text{CH}_2 - N^+ - \text{CH}_2 - \text{CH}_2 - \text{OH} \\
\text{WBA} & : & R - \text{CH}_2 - N - \text{CH}_3 \\
\end{align*}
\]

In the above pictures, R represents the polystyrene backbone. Strongly basic anion exchange resins (SBA) have a quaternary ammonium group, whereas weakly basic anion exchange resins (WBA) have a tertiary amine group. Anion resins based on acrylic polymers have groups similar to SBA type 1 and WBA, but have slightly different properties. SBA acrylic resins are similar in stability to type 2 styrenic resins.
**Degradation reaction**

The basic thermal degradation reaction is called Hofmann’s reaction, shown here for a type 1 resin:

\[
\begin{align*}
R - CH_2 - N_2 &+ CH_2 - N_3 \\ R - CH_2 OH &+ CH_3 OH
\end{align*}
\]

Reaction (1) converts the SBA into a WBA, producing methanol as a by-product, and reaction (2) converts the ammonium group to an alcohol, which has no ion exchange capability, and produces trimethylamine as a by-product.

In reaction (1) the SBA resin loses strongly basic capacity, but the total capacity remains the same, whilst in reaction (2) all exchange capacity (for that particular functional group) is lost.

In practice, both reactions happen approximately to the same extent (see graph included in the Resin life section below). Hofmann’s reaction is catalyzed by OH\(^-\) ions. When the resin is constantly in salt form (e.g. in sugar decolorizing applications) the degradation is much less severe. Type 2 SBA resins are more sensitive than type 1 because the alcohol function in their active group weakens the bond to the nitrogen atom. The thermal stability of SBA resins declines as follows for different ionic forms:

\[
Cl^- > HCO_3^- > CO_3^{2-} > OH^- 
\]
**Capacity loss**

A type 1 strongly basic anion resin in the OH− form was tested at various temperatures. The remaining strongly basic groups were measured after 140 hours. The graph below shows the degradation profile of this resin.

![Thermal Stability - Type 1 Strong Base Anion Resin](image)

While styrenic type 1 anion exchange resins have the highest resistance to temperature compared to other strong base anion resins, capacity degradation still accelerates as temperature increases. For this reason, increasing operating temperature will always increase resin degradation rate.

**Resin life**

The following graph shows the estimated capacity degradation of type 1 and type 2 styrenic SBA resins regeneratated with caustic soda at 40°C.

![Percent of initial capacity](image)

A faster degradation of the type 2 resin is clearly visible. For this reason, type 2 SBA resins should only be regenerated at ambient temperature.
**Condensate polishing**

Tech Fact

Thermal degradation is one of the most common issues with condensate polishing anion resin because:

- In power stations, the temperature of condensate is usually between 30°C and 45°C. In some cases (air-cooled stations) it can reach 60°C or higher for a limited time.

- Condensate polishing anion resin spends most of its time in the OH⁻ form.

The next graph shows the half-life time of SBA resins used in power stations at various temperatures:

![Graph showing half-life time of SBA resins](image)

The half-life time is the time during which the resin loses half of its capacity. Condensates from municipal heating stations have often much higher temperatures, up to 90°C, and cannot be treated with mixed bed resins. Instead, they are treated on cation resins only in the sodium or ammonium cycle.
Recommended temperature limits

Operating conditions for all resins produced by Dow are shown in individual data sheets. Most cation exchange resins can withstand at least 100°C without problem. The table below summarizes the maximum recommended operating temperature for anion exchange resins.

<table>
<thead>
<tr>
<th>Resin type</th>
<th>OH⁻ or free base form</th>
<th>Cl⁻ form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrenic SBA type 1</td>
<td>70°C (158°F)</td>
<td>100°C (212°F)</td>
</tr>
<tr>
<td>Styrenic SBA type 2</td>
<td>35°C (95°F)</td>
<td>70°C (160°F)</td>
</tr>
<tr>
<td>Acrylic SBA</td>
<td>35°C (95°F)</td>
<td>80°C (175°F)</td>
</tr>
<tr>
<td>Styrenic WBA</td>
<td>100°C (212°F)</td>
<td></td>
</tr>
<tr>
<td>Acrylic WBA</td>
<td>90°C (200°F)</td>
<td></td>
</tr>
</tbody>
</table>

1 WBA resins operate in the free base form.

General note

All estimations and recommendations in this document are based on normal operating conditions. The presence of oxidants, metals or other impurities in the water to be treated and in the regenerant solutions may accelerate the degradation and shorten the life of the resins.

The choice of the operating temperature is mainly an economical decision based on resin life time or operating performance and cooling or energy savings.

The time of operation at high temperature is also an important factor that will affect resin long term performance. In many cases, a resin can be exposed to high temperature for a short period of time (less than 24 hours), like a heat sanitation process, without being damaged.