

Ion exchange resins can theoretically last for several years, but in practice their performance can degrade due to various factors, leading to a decrease in yield and deterioration in treated water quality. The performance degradation of ion exchange resins can be caused by chemical changes such as oxidation of the ion exchange resin, decomposition of the functional group, physical issues like contamination or fracturing of the ion exchange resin with foreign substance accumulation, fines formation due to cyclical swelling & reversible swelling from repeated Service-Regeneration cycles, and compaction during the service cycle.

### 1. Oxidative degradation of Strong Acid Cation Exchange Resins

Styrene-based strong acid cation exchange resins are chemically very stable and have strong heat resistance. However, they are prone to oxidation. When strong acid cation exchange resins are oxidized, the cross-linked structure of the ion exchange resin is destroyed, causing the resin to swell in volume, which is irreversible. The portion where the crosslink is cut has a weak acid functional group containing carboxyl groups.

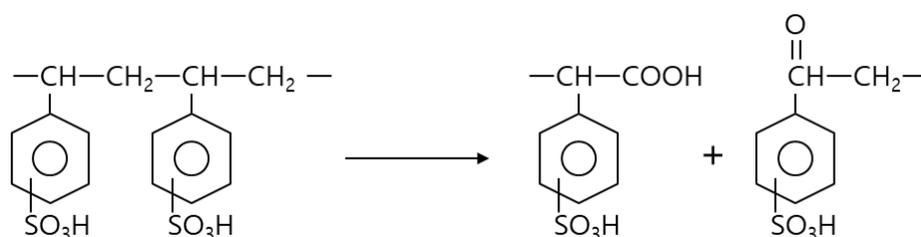


Figure 1) Irreversible swelling of functional group in strong acid cation exchange resin

Low cross-linked ion exchange resins are easily oxidized and are more likely to undergo irreversible swelling. Irreversible swelling reduces the exchange capacity per unit volume, but the overall exchange capacity does not decrease (as the functional group is not decomposed or transformed). As oxidation progresses, the resin becomes a low cross-linked resin, which may lead to an increase in yield due to improved regeneration efficiency.

In general water treatment processes, oxidizing agents like free chlorine are often present in the raw water. Even trace amounts of these can oxidize the ion exchange resin over prolonged use. Ions like Fe and Cu can act as catalysts for oxidation. Extensive oxidation of ion exchange resins can weaken the strength of the resin, making it impossible to service. Therefore, the feed free chlorine and Fe should be restricted. Preferably, Activated Carbon Filter for removal of oxidizing agents & Iron/Mn removal filters should be considered as pre-treatment in case presence is detected or anticipated.

Please refer the resin data sheet for allowable free Chlorine and Iron in feed water.

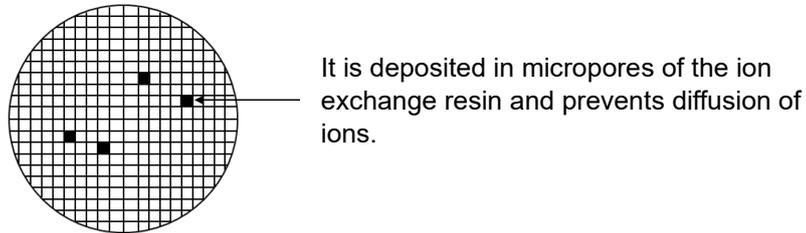
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## Performance Deterioration

### 2. Fouling of Strong Acid Cation Exchange Resins

Ion exchange resins, during service cycle, tend to accumulate Suspended Solids (SS) from the raw water. Regular backwash will help in removing the accumulated suspended solids from the Resin Bed.

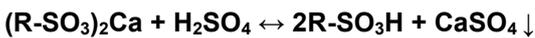
In water softening units, Fe and Mn readily accumulate on cation exchange resins and cause contamination. Iron exists as divalent or trivalent inorganic salts or a part of separated organic complexes. Divalent iron is exchanged on the ion exchange resin, but trivalent iron cannot be exchanged and is insoluble. Trivalent iron deposits on the cation exchange resin, causing performance degradation. To remove deposited iron, acid cleaning or strong reducing agents should be used. The contamination mechanism for manganese is similar to that of iron.



It is deposited in micropores of the ion exchange resin and prevents diffusion of ions.

Figure 2) Cation exchange resin contaminated with iron

In addition to SS, attention should be paid to substances that precipitate and accumulate on the ion exchange resin. When regenerating with sulfuric acid at a high concentration, the hardness components such as Ca, Mg, Ba bound to the ion exchange resin react with the sulfate ions, forming precipitates like CaSO<sub>4</sub>.



These precipitates accumulate in the resin bed, gradually dissolving during operation, affecting the treated water hardness and hindering ion diffusion. To prevent precipitation of calcium sulfate, the concentration of sulfuric acid is typically controlled at 1~4%, and a stepwise regeneration (injection divided into 3 stages) is adopted. If the resin bed is contaminated with CaSO<sub>4</sub>, it is necessary to clean with HCl.

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### 3. Thermal Degradation of Strong Acid Cation Exchange Resins

Strong acid cation exchange resins are chemically very stable. They are also very heat-resistant, but when heated above a certain temperature, the functional group starts to decompose slowly. The following figures illustrate the thermal decomposition mechanism of functional group in strong acid cation exchange resins.

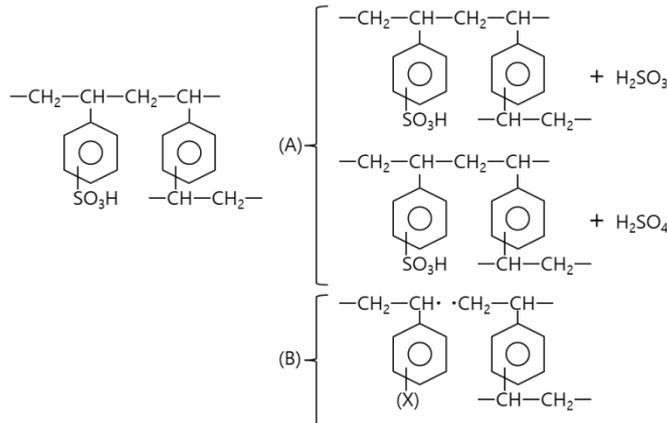


Figure 3) Thermal decomposition of functional group in strong acid cation exchange resin

#### 3.1 H-Form

Standard cross-linked ion exchange resins can be used at temperatures of 120°C or higher for a significant period. However, they become somewhat unstable above 150°C, which may lead to a reduction in exchange capacity during use.

#### 3.2 Na-Form

More stable than the H form, it can be used not only at 120°C but also at 150°C for a significant period. However, above 180°C, it becomes unstable, which may lead to a reduction in exchange capacity during use.

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### 4. Thermal Degradation of Strong Base Anion Exchange Resins

Strong base anion exchange resins use tertiary or quaternary amines as functional groups, which can easily decompose with heat.

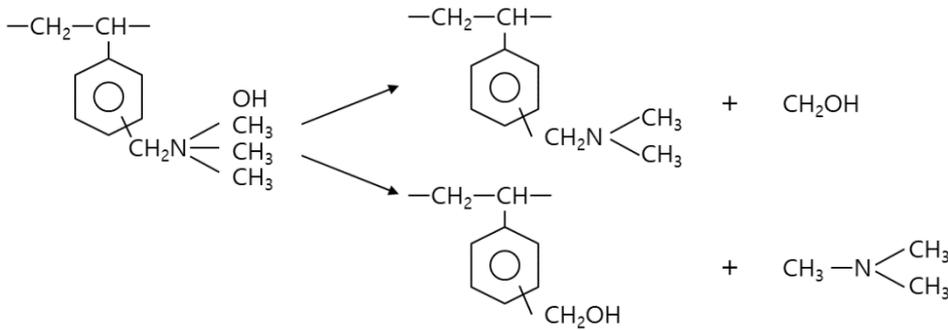


Figure 4) Thermal decomposition of functional group in strong base anion exchange resin

The thermal decomposition mentioned above is due to the self-decomposition of amine groups caused by heat. Especially in the OH-Form, the OH ion, being highly nucleophilic, attacks the C-N bond, making the functional group decomposition easier. Functional group decomposition leads to a decrease in exchange capacity and causes partial weak-base formation.

Type II resins decompose more easily than Type I, which is due to their instability. Typically, the limits are as follows: Type I resin (OH-Form): 60°C, Type I resin (Cl-Form): 80°C, Type II resin (OH-Form): 40°C, Type II resin (Cl-Form): 60°C. These limits are inferred from experimental results, and it does not mean that using the resin below these temperatures will prevent any performance deterioration.

The OH-Form decomposes quickly, so long-term storage in this form leads to rapid decomposition. Therefore, for long-term storage of strong base anion exchange resins, it is advantageous to convert them to the Cl-Form, and the general commercial form is the Cl-Form.

### 5. Oxidative Degradation of Strong Base Anion Exchange Resins

The functional groups of strong base anion exchange resins are tertiary or quaternary amines, which are easily oxidized by dissolved oxygen in water. Oxidation leads to a reduction in exchange capacity since the functional group transforms from a strong base to a weak base.

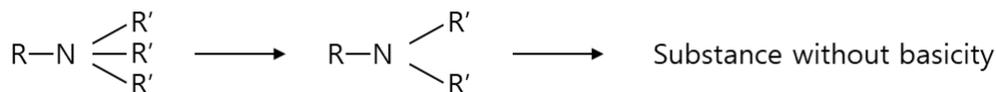


Figure 5) Weakening of base due to oxidation of strong base anion exchange resin

While oxidation affects only the resin matrix of strong acid cation exchange resins, it affects both the matrix and the functional group of strong base anion exchange resins. This indicates the chemical instability of the exchangers in anion exchange resins.

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## Performance Deterioration

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### 6. Organic Contamination of Anion Exchange Resins

When using strong base anion exchange resins for water treatment, after many cycles, the purity of the treated water may decrease. This may be due to organic matter being absorbed on to the resin, blocking the micropores and hindering ion diffusion. This phenomenon is called organic contamination. Organic contaminants change into polymers at a certain pH and become fixed within the anion exchange resin. Generally, low cross-linked resins are more resistant to organic contamination than standard cross-linked resins.

Organic matter in raw water can be categorized into two types:

- 1) Insoluble organic matter - Particulates of plant and animal origin, microorganisms, plant and mineral oils
- 2) Soluble organic matter - Humic and fulvic acids, sugars, amino acids, proteins

Insoluble organic matter in raw water can be removed by methods such as sedimentation and filtration, leaving soluble organic matter. Among soluble organic matter, the key substances affecting ion exchange resins are humic and fulvic acids. Humic and fulvic acids exist in raw water as acids or salts, and their structures are known to be very complex.

Humic and fulvic acids can adsorb onto anion exchange resins, acting as potential sources of organic contamination. They can also bind with heavy metal ions, forming even more complex structures that contaminate anion exchange resins.

The process of anion exchange resin contamination involves both ion exchange and physical adsorption via Van der Waals forces. Anion exchange resins not only undergo ion exchange reactions with inorganic ions during the service process but also adsorption and exchange reactions with organic matter. Organic matter adsorbed during the service process is desorbed outside the resin during the regeneration process using caustic soda, but the rate is slow. Since the regeneration process is generally shorter than the service process, organic matter continues to accumulate inside the resin.

The typical discharge rate of contaminants during regeneration is as follows:

- (1) Strong base anion exchange resin (Gel type, Type I): 30~70%
- (2) Strong base anion exchange resin (Gel type, Type II): 60~95%

When organic matter deposits on the ion exchange resin, the following phenomena are observed:

- (1) Reduction in the purity of the treated water
- (2) Decrease in yield (reduction in the operational exchange capacity of the ion exchange resin)
- (3) Increase in the amount of rinsing water

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