Technical Report

Defluorization of Drinking Water with Strongly Basic Anion Exchange Resin

TRILITE SAR20

Samyang Corporation Ion exchange resin
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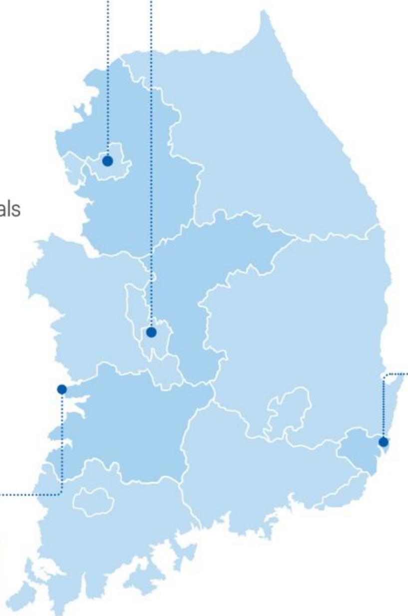
Samyang Corporation is the history of Ion Exchange Resin in Korea.

In 1976, Samyang Corporation successfully initiated localized production of IER in South Korea by technical cooperation with Mitsubishi Chemical Corporation, Japan. In 2011, with the successful development of UPW (Ultrapure water grade) resins, we are contributing to enhancing national competitiveness in semiconductor/LCD industries.
In 2016, Asia's largest UPS (Uniform Particle Sized) specialized IER (Ion Exchange Resin) plant; Samyang Fine Technology Corporation was founded. TRILITE is being supplied to the global market and is receiving rave reviews from the users.



Seoul(Head Office)

- **Technical sales force in 3 fields**
  - Demineralization/Ultrapure water /Condensate polishing/Catalyst
  - Food/Amino acids/Pharmaceuticals
  - Wastewater/Chelating resins /Purification
- **One Stop Service**
  - Analysis of IER
  - Equipment diagnosis and design support
  - Technical seminars and trouble shooting guides

Gusan(UPS Resin Plant)

- **Samyang Fine Technology (Joint venture with Mitsubishi Chemicals)**
- **Largest manufacturing capaicty for UPS resins in Asia**
- **Annual production capacity**
  - Cation 13,000kℓ, Anion 7,000kℓ
- **Product lines**
  - Uniform particle sized resins
  - Chromatography resins
  - Ultrapure water grade resins (OLED, LCD application)

Daejeon(R&D Center)

- **Analysis of IER**
- **Recipe improvement of IER**
- **New product development**
  - Tailored/Specialty resins
- **Application process development**
  - Pilot test
  - Engineering data gathering
  - Process proposal

Ulsan (UPW/Tailored/Specialty Resin Plant)

- **Technology licensed by Mitsubishi Chemicals & Self-development**
- **Specialized production of tailored resins**
- **Production capacity**
  - Cation 3,500kℓ, Anion 2,500kℓ
- **Product line**
  - Ultrapure water grade for semiconductor
  - Tailored resins : food, catalyst, pharmaceuticals
  - Specialty resins: chelating resins, synthetic adsorbents, refining of chemicals

No.1 Total Solution Provider

Samyang Corporation presents the full line-up of TRILITE Ion Exchange Resins from water teratement up to specialty applications. Samynag devlops Tailored resins optimized for customer needs and provoides differentiated technical services such as on-site visti for troubleshooting, technical seminars, process and design consulting, etc. Also, Samyang R&D center offers various analysis services for IERs and develops advanced application technologies.

1. Introduction

The existence of fluoride (F^-) in drinking water is very hazardous to human health, even can cause a disease. In general, water containing fluoride is not appropriate as a drinking water. As fluoride exists in the form of the anion in water, Strongly Basic Anion Exchange Resin can be used to eliminate them. In this case, the use of SBAERs in Cl-form is recommended as the use of OH-form resin increases the pH level of water which becomes inappropriate to drink.

In regard to Fluoride, it shows very low elimination efficiency due to the lowest electronegativity (theory of selectivity order with SBAERs) and also the feature that it is affected by the existence of other anions. However, Type 2 SBAERs show higher efficiency than the Type 1 SBAERs.

For a drinking water process, the water treatment facilities are run to reduce the level of fluoride ions in drinking water to meet the standard which is limited to 1.5ppm or less for drinking water. Fluoride removal efficiency is closely related to the composition of total anions in water hence it is important to examine the water analysis date.

2. Selectivity of Strongly Basic Anion Exchange Resins

Different types of resins have the own selectivity toward each ion. This principle of selectivity is applied to separate a specific ion out of solution where different ions exist in mixed status. Without the understanding on this principle, an operator may cause a decline in the efficiency of the facility.

Selectivity coefficient shows the relation between the ion exchange resins and the selectivity, higher the selectivity coefficient, more selectivity towards the specific ion. However, even for an ion with a very low selectivity coefficient, the adsorption efficiency increases as ionic concentration increases.

The selectivity order of SBAERs is as below:

$$\text{Citrate} > SO_4^{2-} > \text{Oxalate} > I^- > NO_3^- > CrO_4^{2-} > Br^- > SCN^- > Cl^- > \text{Formate} > \text{Acetate} > \mathbf{F^-}$$

The representative selectivity coefficients for anions are summarized in below table.

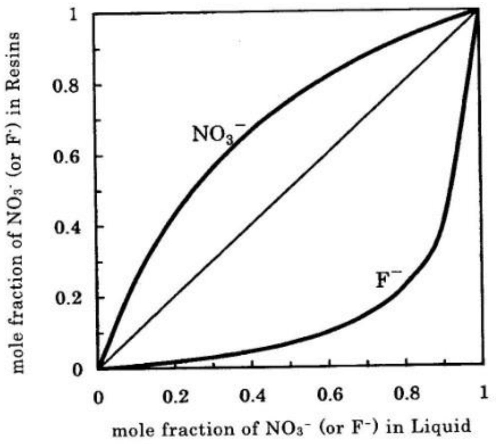
Type of Ion	Selectivity Coefficient		Type of Ion	Selectivity Coefficient	
	Type 1	Type 2		Type 1	Type 2
Hydroxide	1.0	1.0	Cyanide	28	3
“Lignosulfonate”	800	120	Bisulfite	27	3
Benzenesulfonate	500	75	Bromate	27	3
Salicylate	450	65	Nitrite	24	3
Citrate	220	23	Chloride	22	2.3
Iodide	175	17	Bicarbonate	6.0	1.2
Phenate	110	27	Iodate	5.5	0.5
Bisulfate	85	15	Formate	4.6	0.5
Chlorate	74	12	Acetate	3.2	0.5
Nitrate	65	8	Propionate	2.6	0.3
Bromide	50	6	Fluoride	1.6	0.3

Treating Fluoride (F^-) ions involves a mechanism, considering the other anions composition and the competition, due to its very low selectivity.

3. Defluorization with SBAERs

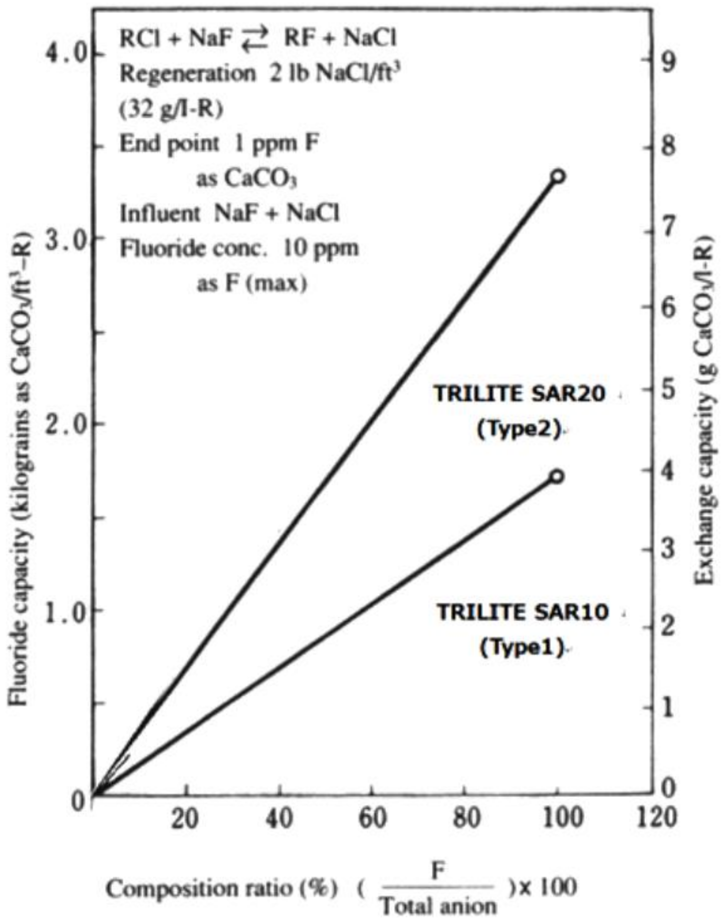
$$R\text{-}N^+Cl^- + NaF \leftrightarrow R\text{-}N^+F^- + NaCl$$

In the Defluorization process, the SBAERs are used in Cl-form with regenerant NaCl.



Defluorization capacity changes with respect to fluoride concentration (molar fraction) to raw water composition. The graph on the left represents the ion exchange equilibrium curve, calculated by the selectivity coefficient of Cl^-, NO_3^-, F^- and HCO_3^- of SBAERs.

Below figure compares fluoride exchange capacity of Type 1 and Type 2 SBAERs according to fluoride concentration to total anions in raw water.



4. Case Study: Defluorization with TRILITE SAR20

Raw water analysis is described as below given that the treated volume is 300ton/day, the regeneration cycle is 1 time/day.

Cl^-	25.0ppm as $CaCO_3$
SO_4^{2-}	4.0ppm as $CaCO_3$
HCO_3^-	10.0ppm as $CaCO_3$
F^-	2.5ppm as $CaCO_3$
NO_3^-	0.3ppm as $CaCO_3$
Total Anion	41.8ppm as $CaCO_3$

From the above figure, the fluoride removal efficiency can be obtained, approximately 0.5g $CaCO_3$/ℓ-Resin) The fluoride concentration is 2.5ppm (Fluoride proportion takes 6% from total anions of raw water).

The treated water amount is 300ton/day×1day/cycle=300ton/cycle, hence the required volume of ion exchange resin can be calculated as below.

$$\textbf{Resin Volume} = \frac{\textbf{Total fluoride}(\text{ppm as } CaCO_3) \times \textbf{Treated water amount}(\text{m}^3/\text{cycle}) \times \textbf{Annual supplementary}}{\textbf{Exchange capacity}(\text{g } CaCO_3/\ell\text{-R})}$$

Total fluoride : 2.5ppm

Treated water amount : 300㎥/day , Service time per cycle =22hr, Regeneration time : 2hr

Total fluoride from treated water : 1.0ppm↓

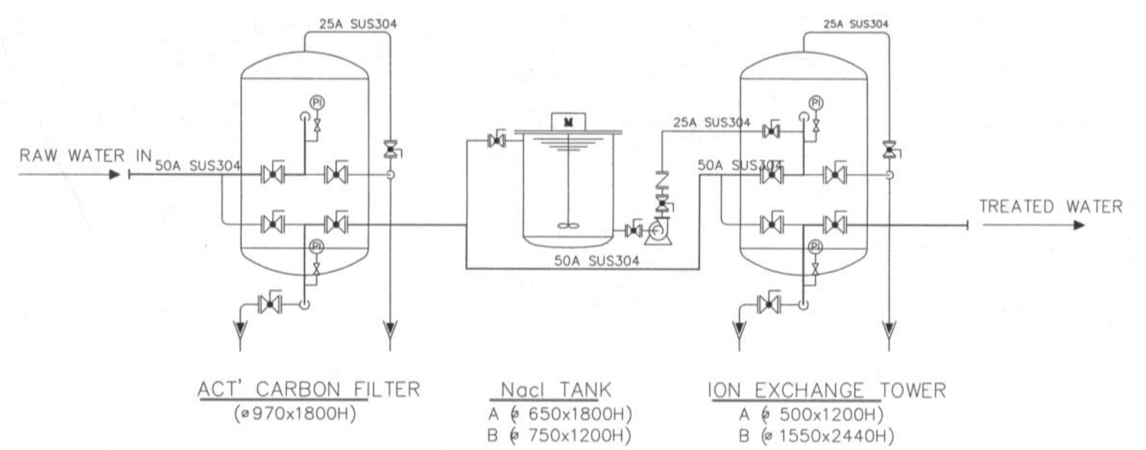
Exchange capacity : 0.5 g $CaCO_3$/ℓ-Resin

Resin volume (TRILITE SAR20) = 2.5 x 300 x 1.20(Safety factor) / 0.5 ≒ 1,800ℓ

Regeneration level : 50g as 100% NaCl/ℓ-Resin

Quantity of regenerant used : 90kg as 100% NaCl/cycle

In general, the Defluorization facility is installed for the pre-treatment combined with activated carbon tower. Below diagram describes a large scale facility as an example.

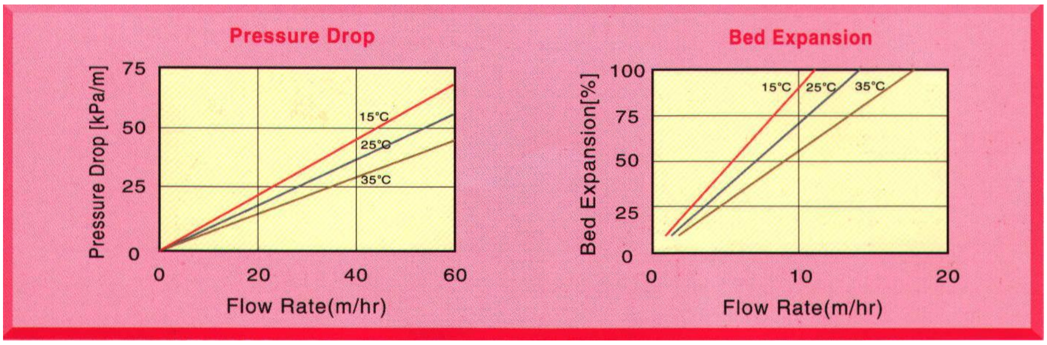


5. Operation Procedure: Defluorization with TRILITE SAR20

Operation	Flow rate	Input	Time	Volume
Service	SV 10～40	Raw water	Cycle time	Same as input volume
Backwash	Bed expansion 50%	Raw water	10～20min	Refer to below diagram
Settling	Until completed	-	5min	-
Regeneration	SV 2～6	10% NaCl	20～40min	Refer to regeneration level
Displacement	SV 2～6	Raw water	20～40min	3～5BV
Rinse	SV 10～40	Raw water	10～20min	1～2BV

Minimum bed depth : 500mm

<Pressure drop and bed expansion of TRILITE SAR20>



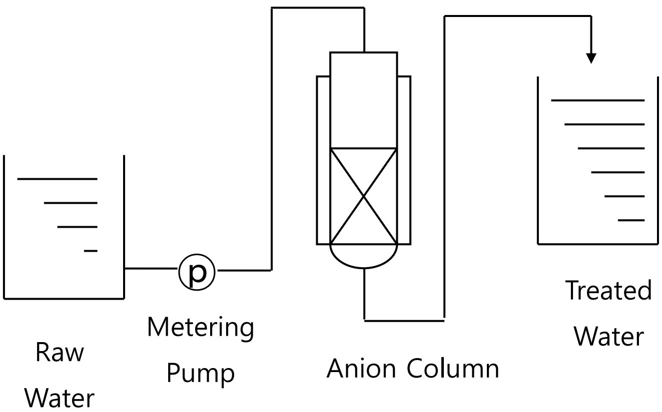
6. Pilot Test: Defluorization with TRILITE SAR20

Type of ion exchange resin: TRILITE SAR20

Quantity per column : 50ml

Type of regenerant : NaCl

Type of regeneration : Co-current Regeneration



Procedure	Service direction
① Operation 1^{st} cycle : Service flow rate, SV 5 After servicing approximately 50BV(Bed volume), collect the sample for every 5BV and check the quantity of fluoride. End the service after servicing approximately 100BV.	↓
② 1^{st} Regeneration : 50g as 100% NaCl/ℓ-Resin, Concentration 10%, Flow rate : SV 2~3	↓
③ Rinse(Flow rate: SV 2~4), Rinse volume approximately 5BV with pure water	↓
④ Operation 2^{nd} cycle : Service flow rate, SV 5 After servicing approximately 50BV(Bed volume), collet the sample for every 5BV and check the quantity of fluoride. End the service after servicing approximately 100BV.	↓
⑤ 2^{nd} Regeneration : 50g as 100% NaCl/ℓ-Resin, Concentration 10%, Flow rate : SV 2~3	↓
⑥ Rinse (Flow rate: SV 2~4), Rinse volume approximately 5BV with pure water	↓
⑦ Operation 3^{rd} cycle : Service flow rate, SV 5 After servicing approximately 50BV(Bed volume), collet the sample for every 5BV and check the quantity of fluoride. End the service after servicing approximately 100BV.	↓