Technical Report

Samyang Packed Bed System

(3rd Edition)

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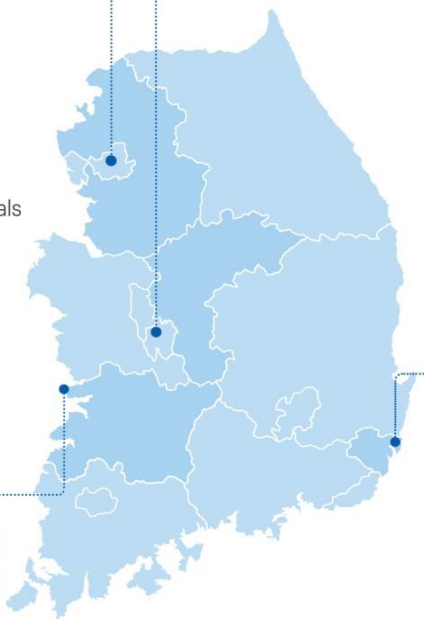
Samyang Corporation is the history of Ion Exchange Resin in Korea.

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



⬡ 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

⬡ Gusan(UPS Resin Plant)

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

⬡ Ulsan (UPW/Tailored/Specialty Resin Plant)

- **Technology licensed by Mitsubishi Chemicals & Self-development**
- **Specialized production of tailored resins**
- **Production capacity**
  - Cation 3,500㎘, Anion 2,500㎘
- **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.

■ Classification by IER layer

SAC	**Strongly Acidic Cation Resin : MC-08, MC-10, ...**
WAC	**Weakly Acidic Cation Resin : WCA10, ...**
SBA	**Strongly Basic Anion Resin : MA-12, MA-10, ...**
WBA	**Weakly Basic Anion Resin : AW30, AW90, ...**

(Classification by IER layer)

Single Bed	SAC WAC SBA WBA
Layered Bed	WAC / SAC WBA / SBA
Mixed Bed	SBA / SAC

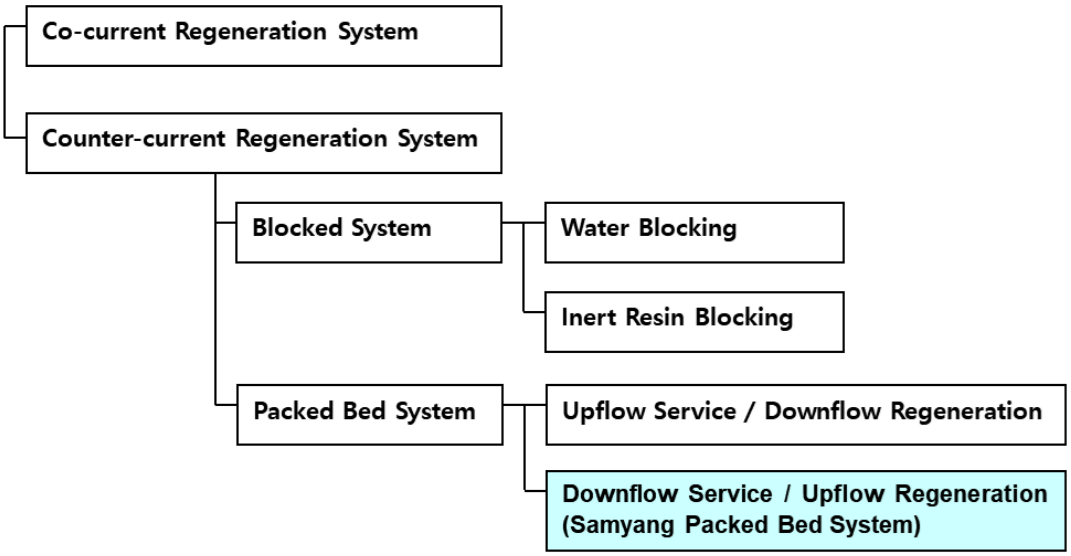
■ Various combinations by Raw water and treated water quality

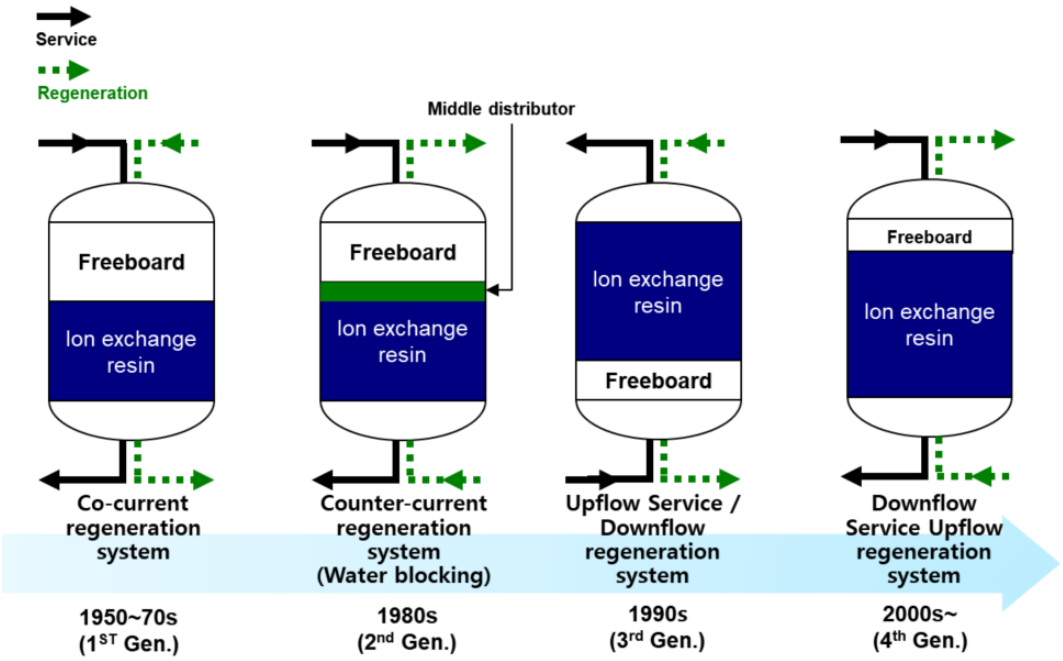
(Demineralization system and IER selection)

2B2T (2Bed 2Tower) Cation Exchanger + Anion Exchanger	SAC → SBA →	MC-08 MC-10	MA-12 MA-20		
2B3T Cation Exchanger + Degasifier + Anion Exchanger	SAC → Degasi-fier → SBA →	MC-08 MC-10	MA-12 MA-20		
Working MB (Mixed Bed)	SBA / SAC →	MA-12(P) MA-20(P) MC-08 MC-10			
2B2T+MBP (Mixed Bed Polisher)	SAC → SBA → SBA / SAC →	MC-08 MC-10	MA-12 MA-20	MA-12(P) MA-10(P) MC-08 MC-10	
2B3T+MBP	SAC → Degasi-fier → SBA → SBA / SAC →	MC-08 MC-10	MA-12 MA-20	MA-12(P) MA-10(P) MC-08 MC-10	
3B3T+MBP	SAC → Degasi-fier → WBA / SBA → SBA / SAC →	MC-08 MC-10	AW90 AW30L MA-12 MA-10	MA-12(P) MA-10(P) MC-08 MC-10	
4B3T+MBP	WAC / SAC → Degasi-fier → WBA / SBA → SBA / SAC →	WCA10L MC-08 MC-10	AW90 AW30L MA-12 MA-10	MA-12(P) MA-10(P) MC-08 MC-10	
4B3T+MBP+CPP (Condensate Polisher)	WAC / SAC → Degasi-fier → WBA / SBA → SBA / SAC → Conden-ser → SBA / SAC →	WCA10L MC-08 MC-10	AW90 AW30L MA-12 MA-10	MA-12(P) MA-10(P) MC-08 MC-10	MA-10OH MA-15OH MC-10H MC-14H

■ Development of Demineralizer Using Ion Exchange Resin

Demineralizers using ion exchange resins are classified according to the regeneration method, and new technologies are being developed as water treatment technology develops.
It is classified into co-current regeneration method and counter-current regeneration method according to the regeneration method, and counter-current regeneration method is distinguished by blocking system and packed bed system again. In recent technological and economic aspects, downflow packed bed system is attracting attention, and Samyang develops, sells and constructs ion exchange resins and systems suitable for this.

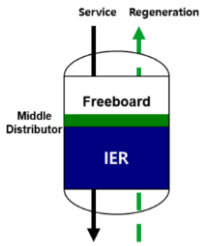


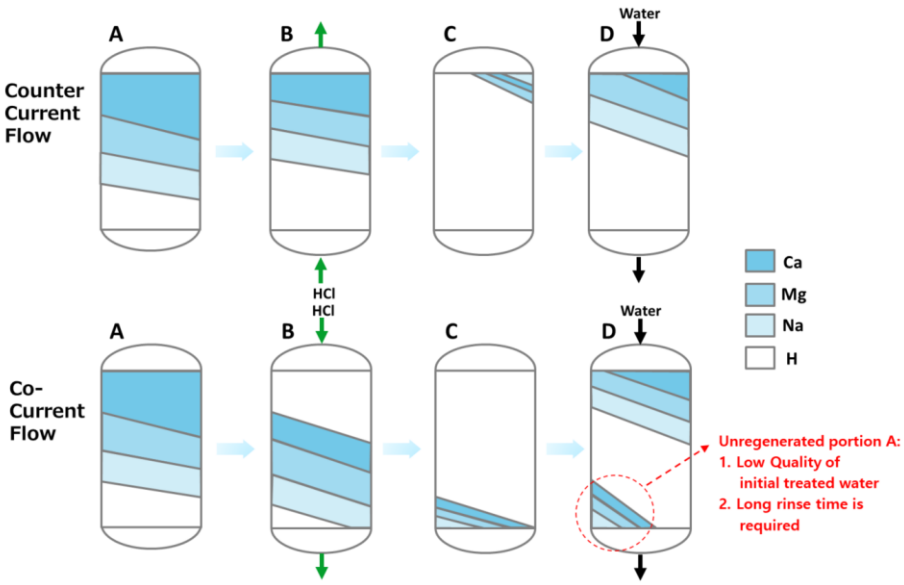


As shown in the above figure, the demineralizer using ion exchange resin has continued to develop, and the Samyang Packed Bed System has recently developed as a system using a uniform particle sized ion exchange resin and has developed its application to layered bed (SBA + WBA).

■ Comparison of Co-Current Regeneration and Counter-Current Regeneration

The demineralizer using the ion exchange resin is distinguished by the co-current regeneration method and the counter-current regeneration method according to the regeneration method. Their characteristics are as follows:

	Co-current regeneration	Counter-current regeneration
Type		
Equipment Summary	The regeneration method by passing the regenerant in same direction as the service flow; generally service and regeneration direction is downflow.	The method by passing the regenerant in opposite direction of treated water flow. There are two cases: service is downflow and regenerant is upflow; and service is upflow and regenerant is downflow.
Strong Point	1. The regeneration process is simple thus stable. 2. The device inside the resin tower is simple. 3. Construction cost is low.	1. The regenerating agent is saved (reduced running cost). 2. High-purity treated water can be obtained. 3. Regeneration time is shortened. 4. Resistant to fluctuations of raw water flow rate and quality. 5. The amount of rinse water is reduced. 6. Disposal of regeneration wastewater is easy.
Weak Point	1. Operation cost is high due to high chemical use. 2. Purity of treated water is low.	1. The inside of the resin tower is complicated (for water blocking system). 2. Construction cost is high (for water blocking system). 3. Regeneration process is unstable compared to the co-current flow.



■ Strong points of Counter-current Regeneration

1. Regenerating agent is saved (running cost is reduced).

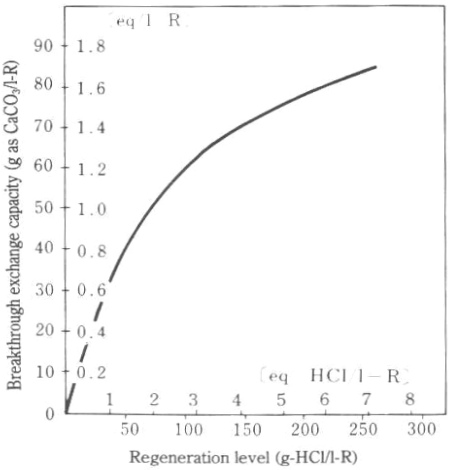
① Effective utilization of ion exchange resin is possible.

In the co-current regeneration method, unused portion remains at the bottom of the resin layer at the service end point, but this can effectively be utilized in the counter-current regeneration method.

② Regeneration with low regeneration level is possible.

As shown in the graph of the regeneration efficiency of the **TRILITE SCR-B**, the lower the regeneration level is, the higher the regeneration efficiency is. Since the counter-current regeneration method leaves unregenerated portion on the top of resin layer, regeneration is possible at a low regeneration level because high-purity treated water can be obtained regardless of the regeneration level.

However, since the unregenerated portion remains at the bottom of the resin layer, the co-current method cannot guarantee the purity of treated water without high regeneration level.



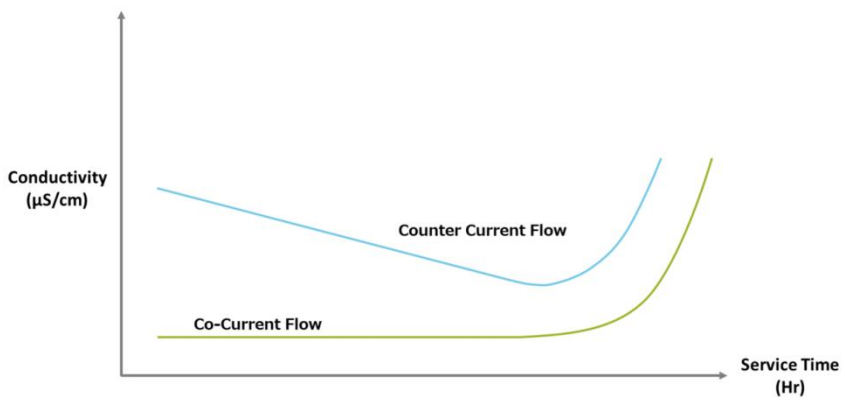
③ Effective regeneration (self-cleaning) by desorption ion is possible.

The ion selectivity for cation exchange resin during service is as follows:

When the concentration of ions is thin	When the concentration of ions is thick
$Ca^{2+} > Mg^{2+} > NH_4^+ > Na^+ > H^+$	$Ca^{2+} < Mg^{2+} < K^+ < NH_4^+ < Na^+ < H^+$

Looking at the cation exchange resin layer during service, it can be seen that adsorption is carried out in the order of Ca^{2+}, Mg^{2+}, and Na_+ from the top to the bottom due to the selectivity of ions. However, a few percent of HCl is used during regeneration, so the selectivity is opposite as explained above.

In the counter-current regeneration method, HCl only needs to push Na+, and at this time Na+ pushes Mg^{2+} and Mg^{2+} pushes Ca^{2+}, allowing effective regeneration by desorption ions. However, in co-current regeneration method, HCl needs to push all Ca^{2+}, Mg^{2+} and Na^+, so effective regeneration cannot be done with desorption ions.



3. Regeneration time is shortened.

The co-current regeneration method requires about 4 hours of regeneration, but the counter-current regeneration method can regenerate within about 2 hours. Therefore, the pure water storage tank is reduced by more than 1/2 compared with the co-current.

4. It is resistant to fluctuation of raw water flow rate and raw water quality.

In the counter-current regeneration method, since the service direction is downflow, the same as the co-current regeneration method, the ion exchange resin layer always has a close layer. Therefore, stable high purity water can always be obtained for rapid flow fluctuation or raw water quality.

5. The amount of rinse water is reduced.

In the co-current regeneration method, the required amount of rinse water is 10X the resin layer, but in the counter current, about 1~2X is enough.

6. Disposal of regeneration wastewater is easy.

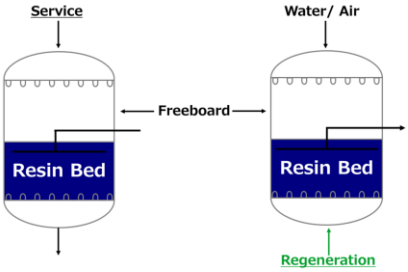
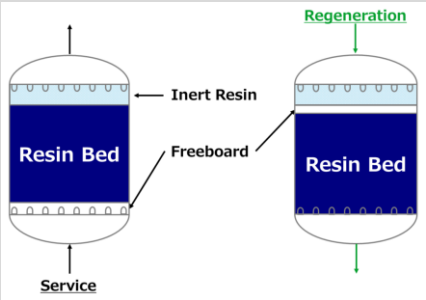
Because the rinse water volume is less than the co-current regeneration method, the quantity of regeneration wastewater is also small. Thus, disposal of regeneration wastewater is easy. Also, since the regenerating agent almost effectively contributes to the regeneration, the amount of the liberated regenerant remaining in the regeneration wastewater is small. Therefore, it is almost not necessary to use agent for neutralization of regeneration wastewater.

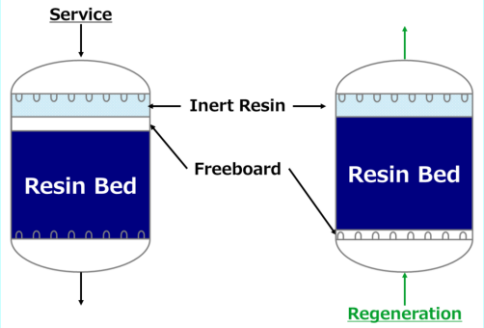
7. Treated water quality comparison

Type			Co-current	**Counter-current**
2B3T	Cation exchanger outlet condition	pH	2.5~3.5	**2.5~3.5**
	Anion exchanger outlet condition	pH	7.0~9.5	**7.0~9.5**
		Conductivity	10 μs/㎝ ↓	**2 μs/㎝ ↓**
		Silica	0.2ppm ↓	**0.1ppm ↓**
MBP		Conductivity	1 μs/㎝ ↓	**0.2 μs/㎝ ↓**
		Silica	0.02ppm ↓	

■ Comparison of Water Blocking Counter-current Regeneration Demineralizer and Packed Bed System

Water blocking counter-current regeneration demineralizer is a system that has proven to be stable and economic enough to be continuously built even recently, but it has disadvantages compared with the packed bed system. In the case of the packed bed system, the comparison between the upflow method (during service) and the downflow method (during service) is as follows:

Type	Comparison	
Water Blocking Counter-current Regeneration System 	**Equipment Summary**	There is a collector in the resin tower where regeneration wastewater is drained. The blocking water from the top and the regenerant from the bottom meet at the collector, become regeneration wastewater, and are drained. About 30~50% of free freeboard exists.
	Strong Point	1. Regeneration efficiency and purity of treated water are excellent. 2. Service process is stable.
	Weak Point	1. Structure of resin tower is complicated and construction cost is high. 2. There is a high possibility of trouble during regeneration process. 3. Due to large freeboard, resin tower cannot be used efficiently, and large installation space is required. 4. A support layer is required, so there are less effective layers. 5. Intermediate collector is easily damaged during contraction and expansion of ion exchange resin.
Upflow Service / Downflow Regeneration Counter-current Regeneration System 	**Equipment Summary**	This is a system that regeneration process is performed by downflow with regenerant and that service process is performed by upflow; about 10% or less freeboard is present.
	Strong Point	1. Excellent regeneration efficiency and purity of treated water 2. Resin tower can efficiently be used. 3. Regeneration process is stable.
	Weak Point	1. Sensitive to fluctuation during flow rate change and service process. (service process cannot be stopped, and unstable) 2. SS (Suspended Solids) are easy to accumulate. 3. Backwash tower is required. 4. Installation of resin trap is essential. 5. Intermediate nozzle plate is needed when designing layered bed.
Downflow Service / Upflow Regeneration Counter-current Regeneration System (Samyang Packed Bed System)	**Equipment Summary**	This is a system that regeneration process is performed by upflow with regenerant and that service process is performed by downflow; about 10% or less freeboard is present.

	**Strong Point**	1. Regeneration efficiency and purity of treated water are excellent. 2. Service process is stable. 3. Resin tower can be used efficiently. 4. Retrofit of existing equipment is easy. 5. It can cope flexibly with raw water flow rate fluctuation (Can be stopped during service process). 6. When changing to layered bed, intermediate nozzle pate is not necessary and easy to apply. 7. Pollutant discharge is easy during regeneration, so backwashing tower is not needed, and system can be constructed economically.
	Weak Point	1. The regeneration process is an upflow, so if there is a change in the injection flow rate, the regeneration failure may occur. 2. It is difficult to design Upper distributor.

■ Comparison of Upflow Service Method and Samyang Packed Bed System

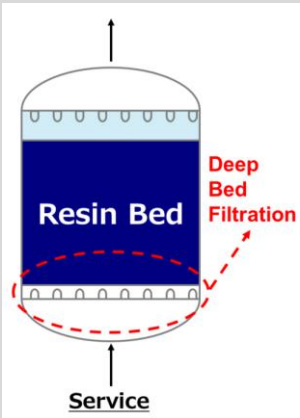
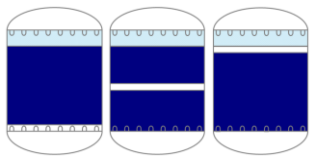
As described above, even the packed bed system has characteristics according to the service direction; when compared technically and economically, the downflow system (Samyang Packed Bed System) is advantageous. Details are described below.

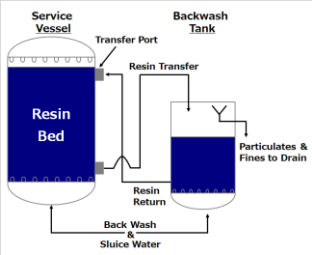
1. Strong points of Samyang Packed Bed System according to service direction

① Self-Cleaning

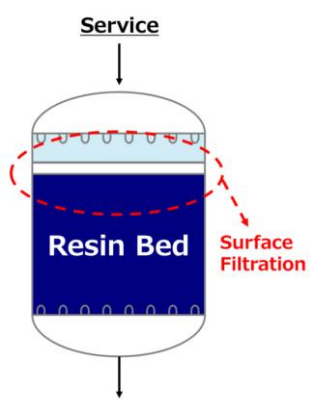
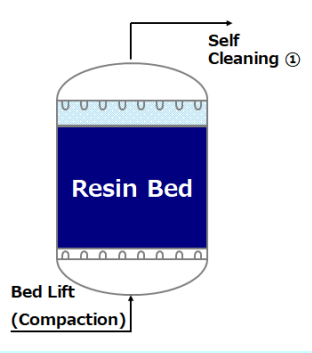
In Samyang packed system, cleaning is performed at the same time as regeneration, thus it can be used under raw water condition where organic load is high. It is also economical since backwash tower is not needed.

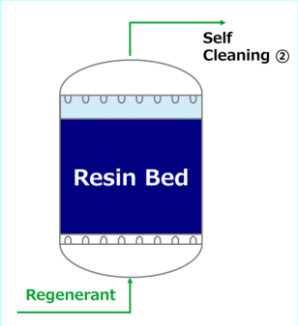
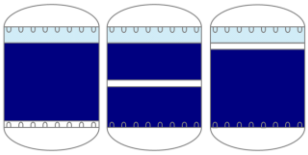
The upflow service method operates the service process by upflow, so organic matter is suspended within ion exchange resin layer. The process is divided into the following processes:

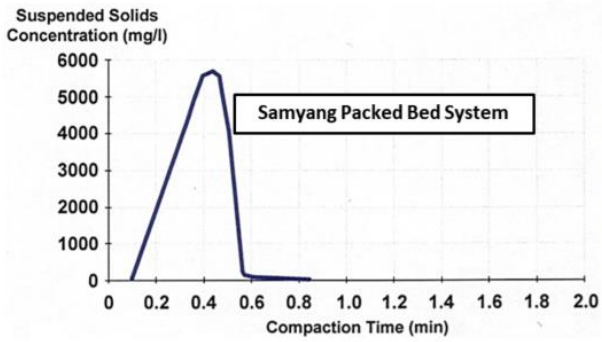
Process	Flow Direction	**Picture**	Description
Service	↑		After the regeneration and rinse are finished, service is performed in upflow by bed lifting the ion exchange resin layer. At this time, the organic matter and SS (Suspended Solids) contained in the raw water enter from the bottom and are suspended into the ion exchange resin layer. (Deep bed filtration) The flow rate change during service causes the resin layer to shake resulting in deterioration of the water quality and loss of attainable water. Thus, flexible operation is impossible.
Settling	↓		The organic matter and SS deposited during settling process have low density, tending to move upward and causing the contamination of the whole ion exchange layer.

Backwash	⇔		In the packed bed system, bed expansion is not possible, thus backwash is performed after moving to backwash tower to clean the ion exchange resin layer contaminated from the bottom. During the transfer, the ion exchange resin breaks due to physical impact; and it requires high construction cost because a backwash tower is needed.
Regeneration (Injection)	↓		The regeneration process is downflow thus stable, but the cleaning effect during regeneration process is lower than that of upflow regeneration, so backwashing must be carried out regularly using backwash tower.
Regeneration (Displacement)	↓		
Rinse	↓		

Samyang Packed Bed System has a structure that the organic material and SS exist on the top of ion exchange resin layer because the service process is downflow. This allows cleaning during the regeneration process, preventing contamination of ion exchange resin, not needing backwash tower, and being applied to raw water with high organic load.

Process	Flow Direction	Picture	Description
Service	↓		After regeneration and rinse are finished, service is performed by downflow. At this case, the organic matter and SS (Suspended Solid) contained in the raw water enter from the top and remain in the upper layer of the ion exchange resin. **(Surface filtration)** Service process is stable, and the operation is flexible because there is no deterioration of water quality and amount of attainable water even if flow rate changes or the process restarts after stopping.
Compaction	↑		Service is performed by fast upflow with soft water or pure water for bed lift and resins layer compaction. At the same time, organic matter and SS existing at the top are discharge smoothly because the slit of upper strainer is wide(0.5 ㎜) and inert resin is filled. (**Self Cleaning ①**)

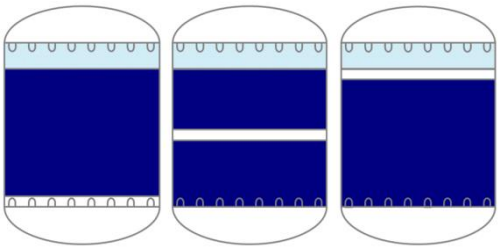
Regeneration (Injection)	↑		When the regenerant is added, the ion exchange resin is swelled and the pollutants and organic acids deposited inside are eluted and discharged smoothly. (**Self Cleaning②**) During displacement, rinsing is done, so the ion exchange resin layer is cleaned without a regular backwash process.
Regeneration (Displacement)	↑		
Settling	↓		The freeboard moves up and traces of contaminants and ion exchange resin particulates, which may be present in the resin layer, move up and are discharged during the next regeneration process. During the settling process, the ion exchange resin layer relaxes to prevent channeling.
Rinse	↓		After the settling process, rinse is performed until the specified water quality is reached.



In Samyang Packed Bed System, organic matter and SS causing organic contamination are surface filtered and remain at the upper part of ion exchange resin layer, so they are discharged during compaction (Bed Lift) process. Thus, backwash tower is not required, and stable system can be formed. The figure on the left shows the amount of organic matter discharged during the compaction process, illustrating that most of it is removed within 1 minute.

② Service reliability

Samyang Packed Bed System is stable because service direction is downflow; and flexible operation is possible because it is free to stop and start during service.



Since the upflow service method carries out the service process by upflow, ion exchange resin layer shaking occurs similar to settling process during service stop and flow rate change. This causes ion exchange resin absorbent bed to be unstable, resulting in water quality deterioration and reduced yield of attainable water when the service resumes again. Therefore, it is necessary to make a larger pure water storage tank to reduce fluctuation of flow rate during service, and this

leads to the increase of investment cost and facility inefficiency. That is, the service process is unstable.

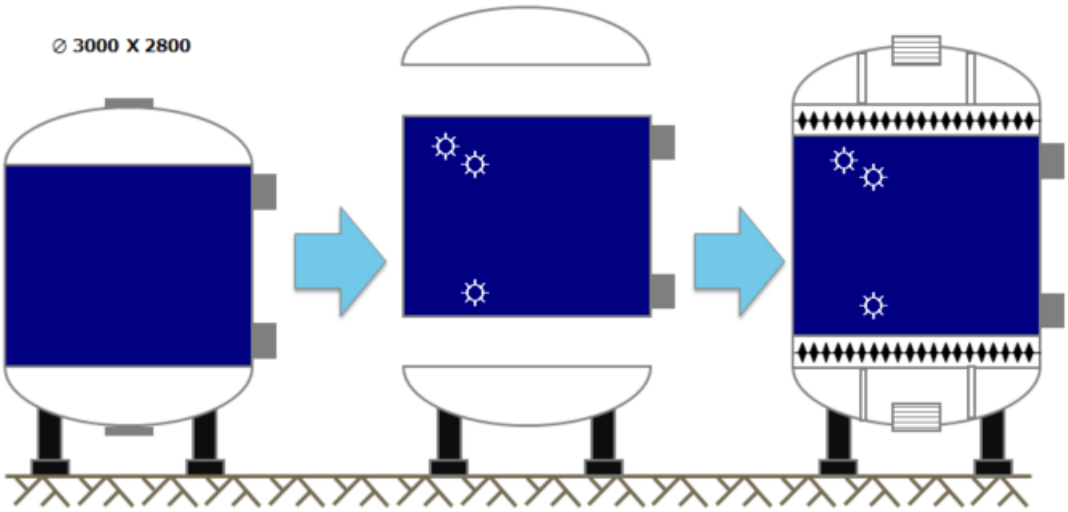
Samyang Packed Bed System allows stable service process and flexible operation because there is no deterioration of the water quality and yield of attainable water even after changing the flow rate and restarting after stopping.

2. Strong points of Samyang Packed Bed System according to system construction

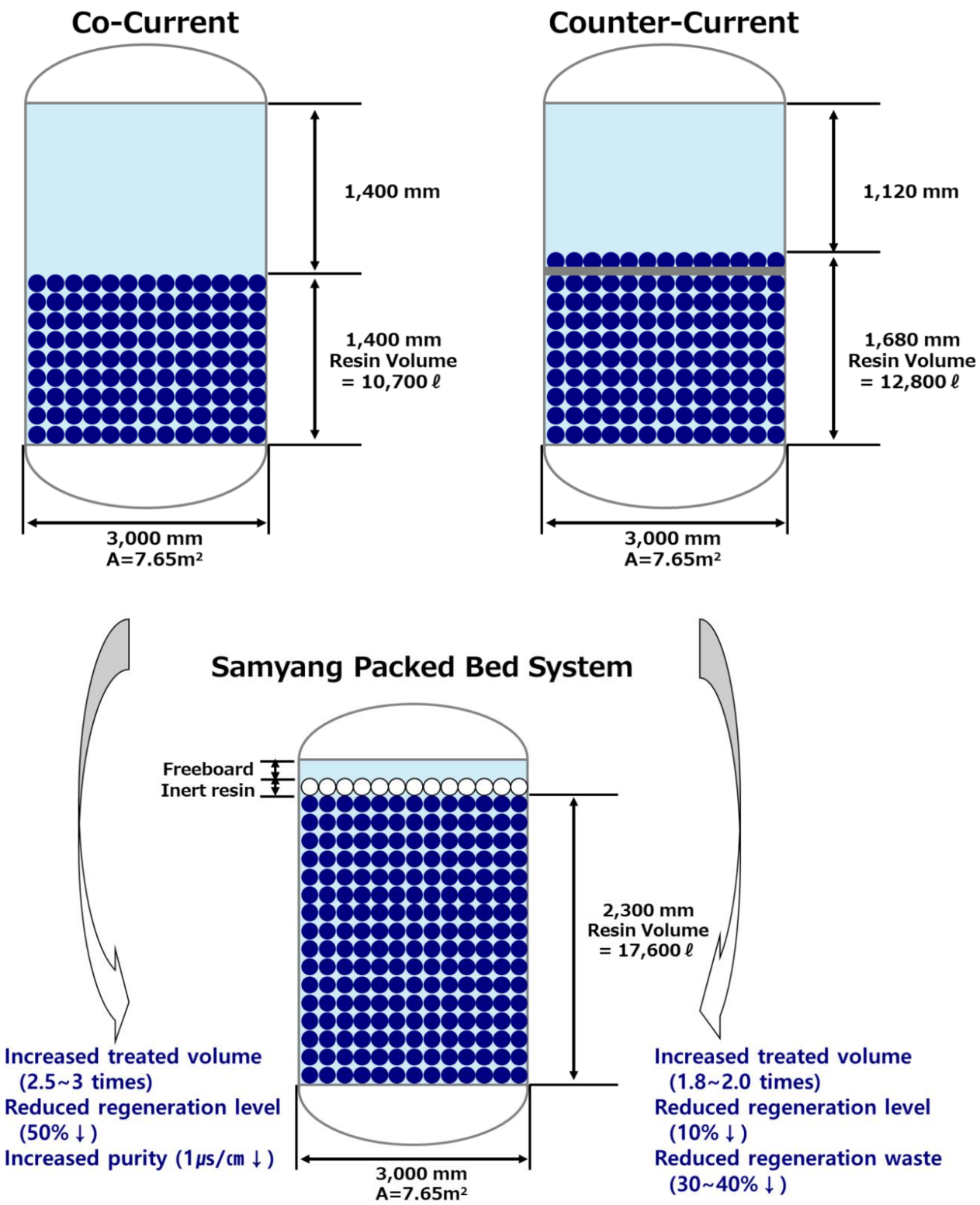
Samyang Packed Bed System does not require a backwash tower, so the installation area is reduced when the system is constructed. When the existing equipment (especially water block type counter-current regeneration method demineralizer) is retrofitted, the cost is reduced and economical.

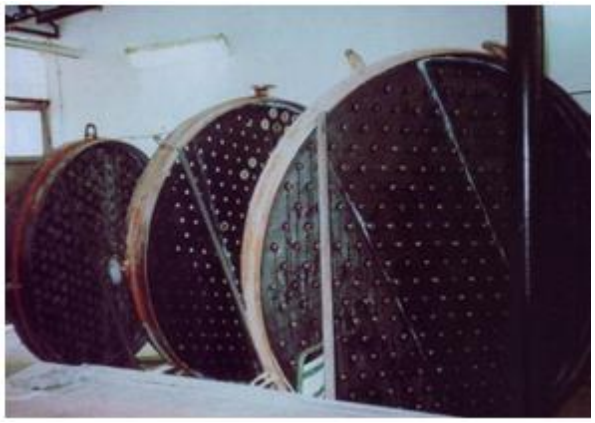
In Samyang Packed Bed System, the resin tower is simple in structure and can be manufactured at economical cost. So, the existing co-current regeneration demineralizer and water block counter-current regeneration demineralizer can be retrofitted at a minimal cost.

It is economical because the existing freeboard in co-current and counter-current regeneration facilities can almost be eliminated, increasing the fill of ion exchange resin. Thus it is economical because the capacity is increased at the existing site and existing vessel can be used. Examples of retrofit by changing existing equipment are as follows:

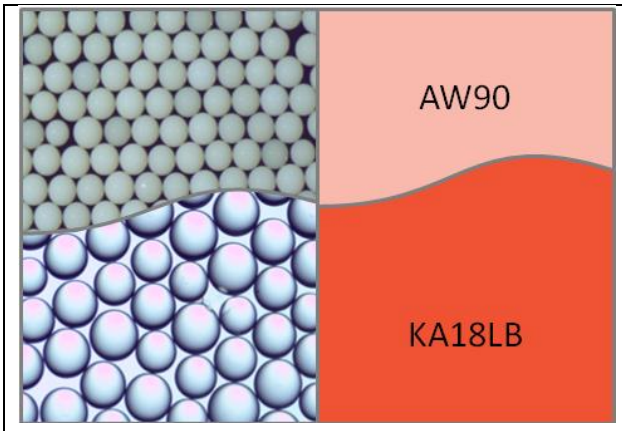


If an existing co-current regeneration demineralizer of Φ3,000 × 2,800H is retrofitted to the Samyang Packed Bed System, the upper and lower distributors should be re-installed. In this case, the existing vessel can be reused and the amount of attainable water is doubled. In the case of counter-current regeneration demineralizer, it is possible to retrofit the equipment more economically than co-current by removing the intermediate collector and re-building the upper distributor.

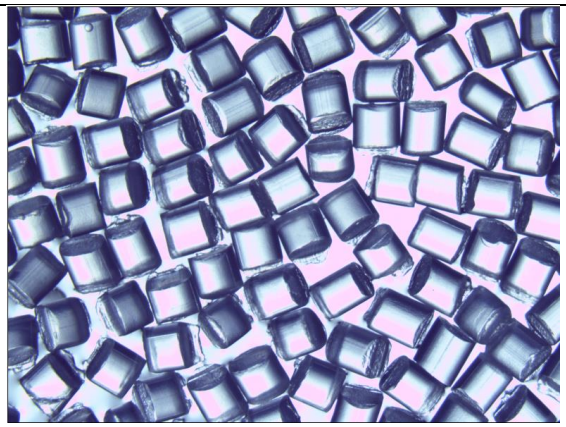




As shown in the figure above, it can be retrofitted by using existing ion exchange resin tower; and if necessary, the upper and lower plates need to be retrofitted.



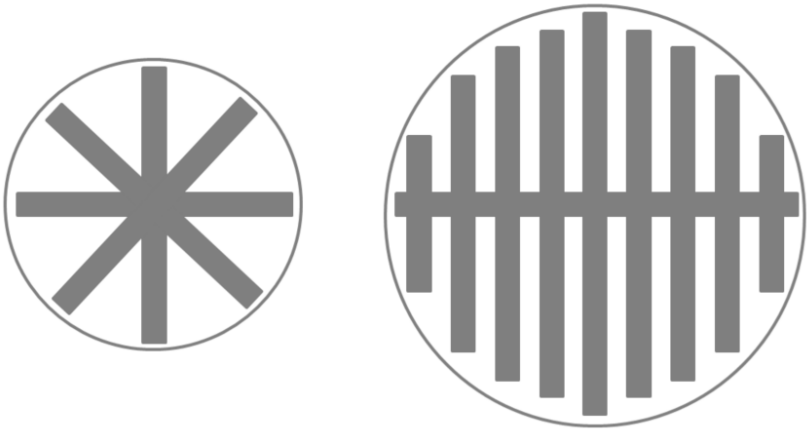
Anion resin (Weakly/Strongly Basic)



Inert resin (TRILITE TR70)

Since the Samyang Packed Bed System is an upflow regeneration system, inert resin is present above the ion exchange resin layer, and the density of the inert resin should be less than ion exchange resin to be able to float at the upper part of resin layer. And the particle size should relatively be large for the passage of fine particles or accumulated suspended solids (SS) during regeneration. Samyang TRILITE TR70 (upper right figure) is suitable for Samyang Packed Bed System with particle size of 1.2-1.8mm and apparent density of 500g/ℓ. The amount of inert resin should be sufficient to cover the upper distributor. By using inert resin, it is possible to prevent the loss of ion exchange resin even if the slit width of the nozzle of the upper distributor is up to 0.5mm and the discharge of pollutants and fine particles of ion exchange resin can be smooth

For Samyang Packed Bed System, design of the upper distributor is important because it requires efficient service from top to bottom during the service, and because it should discharge regenerated waste, organic matter and SS during regeneration. If the diameter of ion exchange resin tower is small, the distributor of the type shown in the upper left figure is used; and if the diameter is large, the type shown in the right is used.

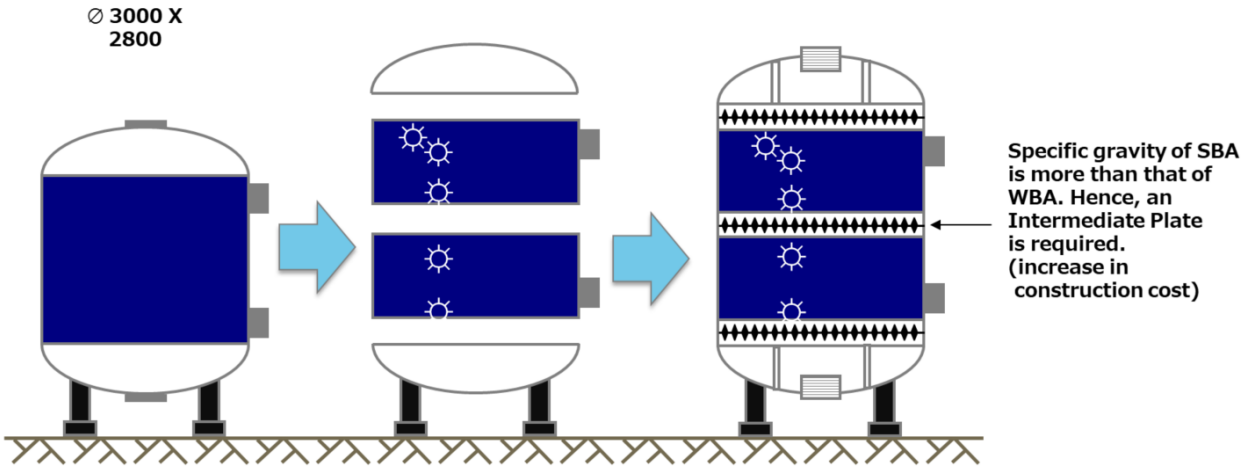


For the lower distributor, the type shown below is used.

When layered bed demineralizer is designed or changed, the intermediate plate is not required, so the construction cost is reduced and the design of ion exchange resin tower becomes simple. Generally, the life cycle of layered bed demineralizer is shorter than the cation tower due to larger generation of organic contamination. It is a method applied to anion tower which is expensive to maintain, and it combines WBA (weakly basic anion) exchange resin, which has strong resistance to organic contamination and high regeneration efficiency, and WBA (weakly basic anion) exchange resin type 1, which has excellent chemical stability and treated water quality. It is a system with high regeneration efficiency and good treated water quality.

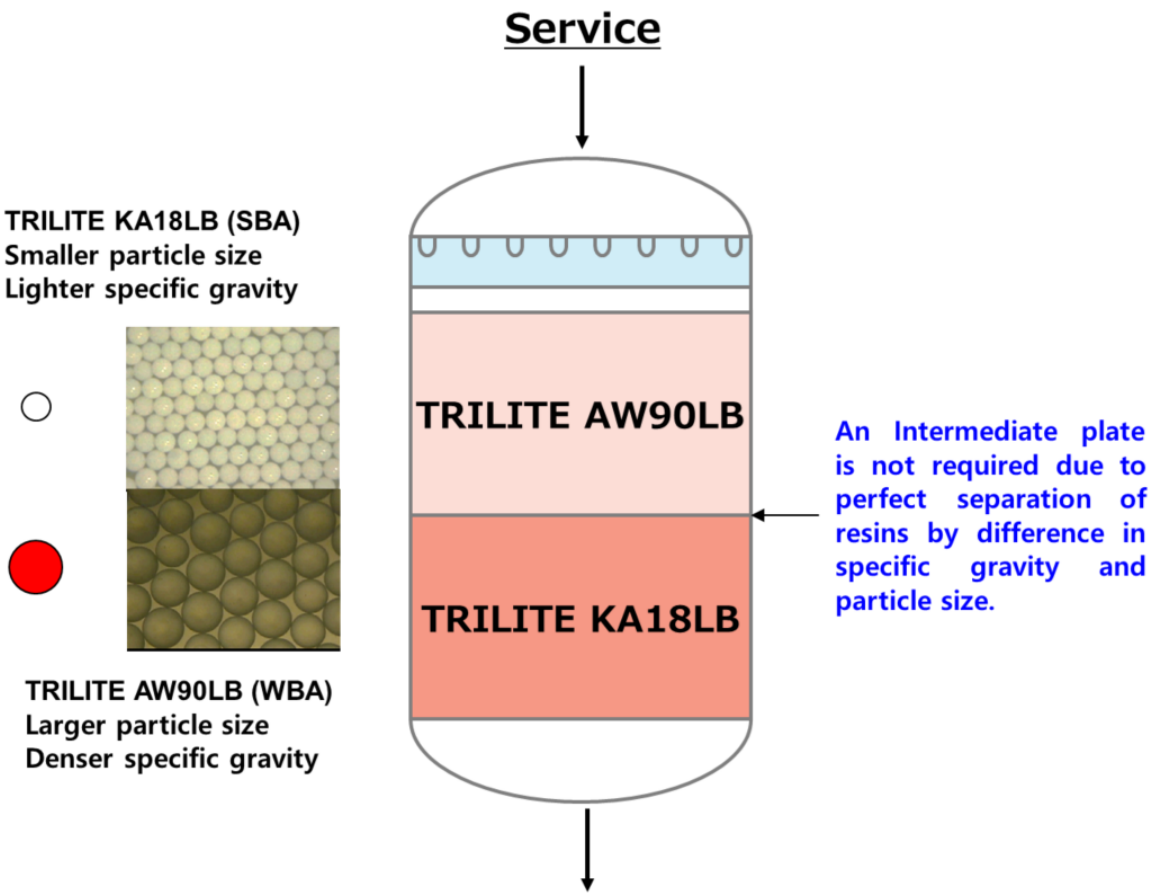
The cation tower outlet water must pass WBA before SBA; however, in case of upflow service type demineralizer, true specific gravity of WBA is less than that of SBA. Therefore, two chambers should

be built using the intermediate plate to charge SBA in the upper chamber and WAB in the lower chamber. This method increases the cost for producing the intermediate plate, which is also to increase the cost when the existing equipment is retrofitted.



However, in the case of Samyang Packed Bed System layered bed demineralizer, the ion exchange resin can be charged in the order of true specific gravity because the service direction is top to bottom. Because the intermediate plate is not required, the construction cost is reduced and the resin tower structure is simplified. In addition, recently developed resin for layered bed demineralizer boasts perfect separation performance by adjusting particle size as well as true specific gravity.

Grade	**TRILITE KA18LB (SBA)**	**TRILITE AW90LB (WBA)**
Type	Strongly Basic Anion Exchange Resin (Gel type)	Weakly Basic Anion Exchange Resin (Porous type)
Matrix	Styrene-Divinylbenzene Copolymer	
Functional group	Trimethylammonium (Type1)	Dimethylammonium
Ionic form	Cl	OH
Physical form	Beige translucent spherical beads	Ivory opaque spherical beads
Specific gravity	**1.11g/㎖**	**1.04g/㎖**
Moisture retention(%)	43~47%	40~50%
Total capacity	1.3meq/㎖	1.5meq/㎖
Swelling rate	OH / Cl = 1.24	Cl / OH = 1.30
Uniformity coefficient	1.4 ↓	1.1 ↓
Particle size	**0.6~1.2mm**	**0.5~0.6mm**
Operating temperature	60℃(OH form) 80℃(Cl form)	100℃ ↓
Operating pH range	0~14	0~9

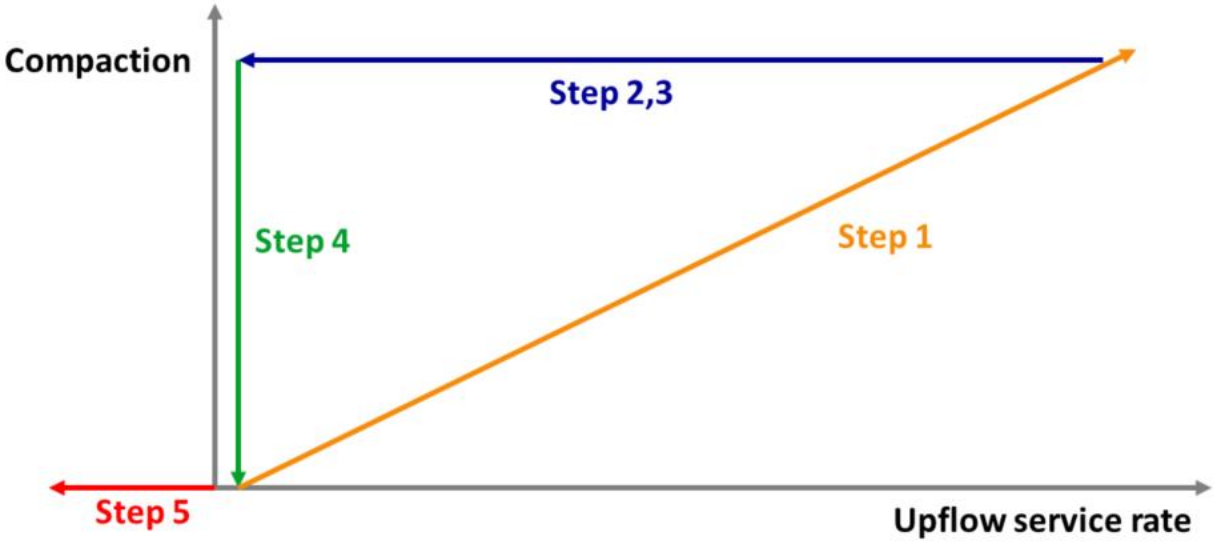

Service
TRILITE KA18LB (SBA)
Smaller particle size
Lighter specific gravity
TRILITE AW90LB
TRILITE KA18LB
TRILITE AW90LB (WBA)
Larger particle size
Denser specific gravity
An Intermediate plate is not required due to perfect separation of resins by difference in specific gravity and particle size.

■ Comparison of Upflow Service System and Samyang Packed Bed System (Conclusion)

Samyang Packed Bed System and Upflow Service System are comprehensively compared as follows. When considering the economical construction cost, flexibility of equipment operation and applicability to existing equipment, it shows that Samyang Packed System is the most excellent equipment.

Type	Samyang Packed Bed System	Upflow Service System
System		
1. Water Quality	+ + (Better)	+ + (Better)
2. Chemical Efficiency	+ + Better	+ + Better
3. Construction simplicity	+ + Better	+ Good
4. Retrofit suitability	+ + Better	- Normal
5. Layered Bed without Intermediate Plate	+ + Better	- Normal
6. Control / Automation	+ + Better	- Normal
7. Fines removal	+ + Better	- Normal

■ Samyang Packed Bed System Process



Step 1	:	Resin layer compaction
Step 2	:	Injection
Step 3	:	Displacement
Step 4	:	Settling
Step 5	:	Rinse

The detailed process of Samyang Packed Bed System is as follows:

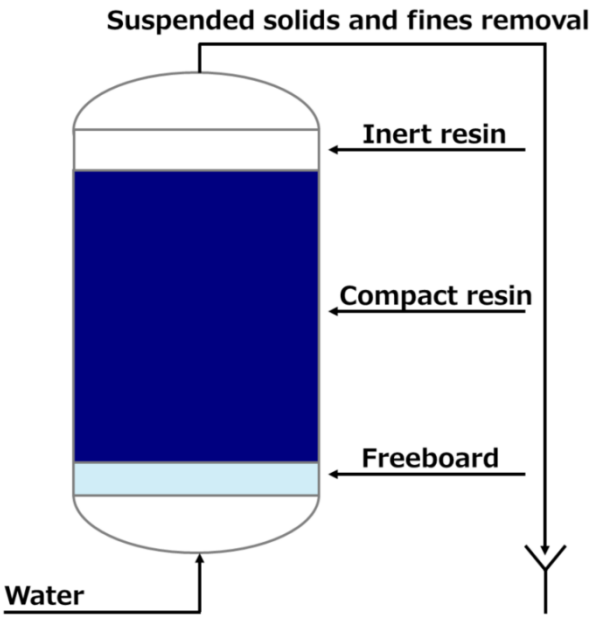
① Service

The raw water is injected into the upper part and is served downflow to produce pure water.

② Resin layer compaction

Service the regeneration water upflow before the injection and displacement process. At a fast flow rate, the resin layer is compacted on top of the resin bed with the absorbent bed maintained.

The flow rate required for the resin layer compaction is affected by the particle size distribution, density, degree of freeboard, and water temperature of the ion exchange resin. It takes only a few minutes for the resin layer to be fully compacted. The top inert resin prevents the ion exchange resin from being lost out of



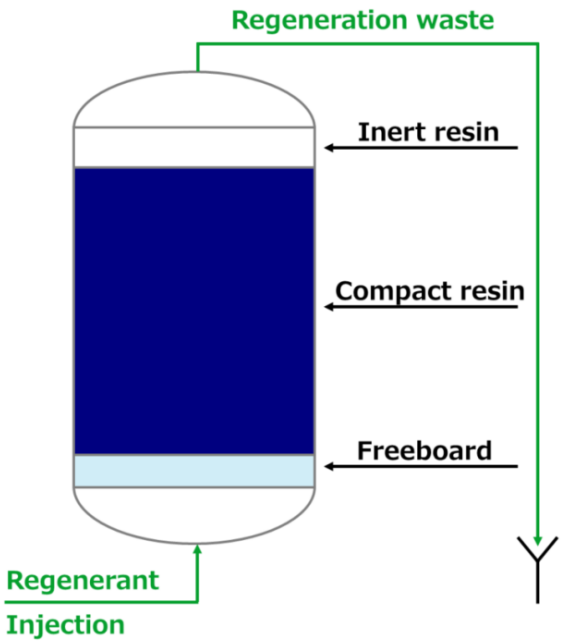
the system and assists in the discharge of SS and particulates.

③ Injection / Displacement

When the resin layer is compacted, the regenerant is injected, but the flow rate is lower than the resin layer compaction process. (See figure at right).

Even if the flow rate decreases, the resin layer remains compacted at the top, which is called hysteresis. The regenerant maintains its ideal contact time, concentration and flow rate, while the resin layer maintaining compacted.

After the injection, compaction process is carried out to help the reaction of unreacted regenerant and lead discharge of regeneration wastewater.

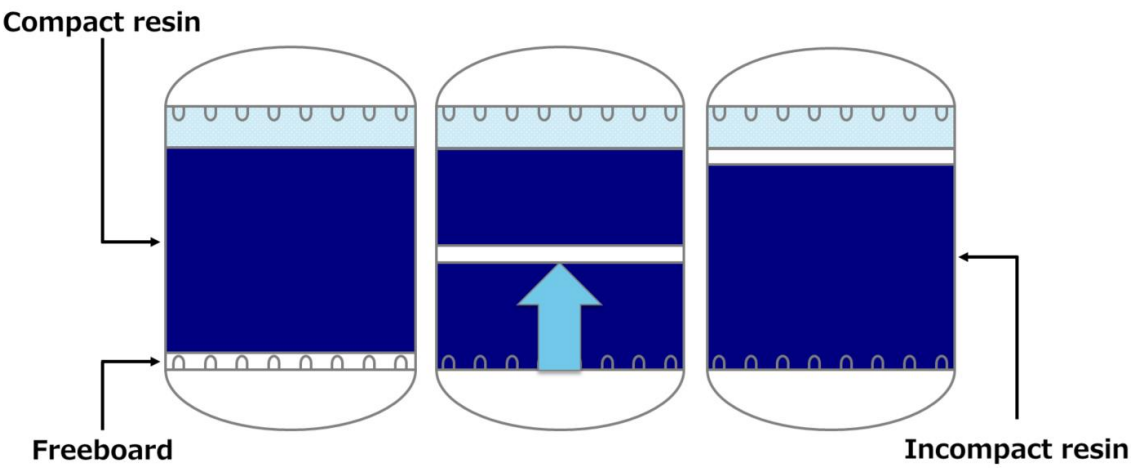


Note) Hysteresis

Hysteresis becomes evident in magnetization of ferromagnetic material and deformations of elasticity: these are referred to as magnetic hysteresis and elastic hysteresis, respectively. For a state change in which a hysteresis appears, a curve -a loop - represents the relationship between the state change and physical quantities that cause the state change, for example, magnetization intensity, external magnetic field, deformation and external force. This is called the hysteresis curve.

④ Settling

At the end of the displacement process, the upflow stops and the resin layer free-falls to accumulate at the bottom of the resin tower. At this time, since the absorbent bed of the resin layer is maintained, it is possible to collect treated water of high purity to efficiently use ion exchange resin. In addition, the resin layers is released during settling process; the fine particles and SS in the resin layer move to the upper part of the resin layer and are discharged during the next regeneration process.



⑤ Rinse

After the regeneration process is finished, rinsing is performed to ensure the desired treated water quality. It is common practice to operate at the same flow rate as the service flow rate and circulate from the cation exchanger to the anion exchanger in order to reduce the water consumption.