

Acid Recovery Technology By TRILITE MA-23F
Chromatography Ion Exchange Resins (Ver. 1)

Technical information



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Samyang Corporation Ion exchange resin

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숫자로 보는 삼양트리라이트

1

First & Only



대한민국 유일의
이온교환수지 메이커입니다

+2

Factories



한국 울산, 군산에 자체 공장,
해외 OEM공장

+200

Products



발전소, 초순수, 식품, 의약,
축매 등 제품 200종

+400

Partners



전세계 400개
파트너사와 함께 합니다

+50

Sales
networks



전세계 50개국에
판매하고 있습니다

1.1↓

Uniformity
coefficient



균일계수 1.1 이하
고품질 균일계이온교환수지

Locations (본사, 공장, 테크센터)

Seoul (Headquarter)

- 3개 분야 전문기술영업 인력 보유
 - 수처리/초순수/응축수처리 (Condensate polishing)/축매
 - 전분당/핵산/아미노산/의약
 - 폐수처리/킬레이트/특수정제
- 원스톱 토탈솔루션 제공
 - 이온교환수지 분석
 - 설비 진단
 - 설계 지원
 - 기술 세미나
 - Trouble shooting

Gunsan (UPS Resin Plant)

- Uniform particle sized resins
- 삼양화인테크놀로지 (Since 2016)
- 일본 미쓰비시케미칼과의 합작법인
- 아시아 최대 규모 균일계 이온교환수지 전용 공장
- Product line
 - 균일계 이온교환수지
 - 초순수수지(OLED, LCD)
 - 크로마토그래피 수지

Daejeon (Technical Center)

- 이온교환수지 분석
- 이온교환수지 생산 Recipe 개선
- 신제품 개발
 - 주문품 / 특수품
- 응용기술 개발
 - Pilot test
 - Engineering data gathering
 - Process proposal

Ulsan (UPW/Tailored/Specialty Resin Plant)

- 삼양사 울산공장 (Since 1976)
- 다양한 고객 맞춤형 이온교환수지 (Tailored resin) 생산
- Product line
 - 초순수수지(반도체)
 - 주문품 수지(전분당, 핵산, 축매 등)
 - 특수 수지(킬레이트, 합성흡착제 등)



1. Acid recovery process

In practice, there are two conventional ways for acid recovery process; one using diffusion dialysis method through an ion exchange membrane and the second using the chromatography acid recovery principle using an ion exchange resin. Of the two technologies, the chromatography method is more widely applied because of its high processing capacity and initial cost of equipment installation.

General principle of the chromatography method is the separation of acid and salts as the acid(H_2SO_4) is adsorbed to the ion exchange resin charged in acid form(SO_4), and the metal salts ($\text{Al}_2(\text{SO}_4)_3$) are not adsorbed but pass through the ion exchange resin beds.

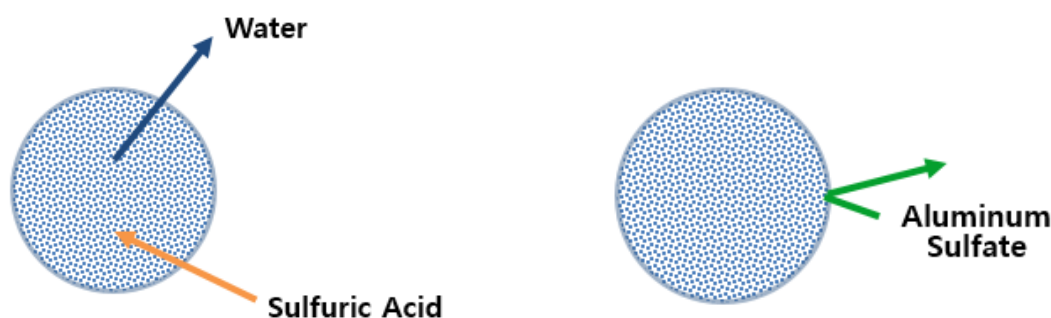


Figure.1 Sorption Resin Bead

This principle is experimentally proven in the separation of hydrochloric acid and iron chloride, sulfuric acid and iron sulfate, and sulfuric acid and aluminum sulfate. Below Figure. 2 shows a typical example of sulfuric acid and aluminum sulfate separation.

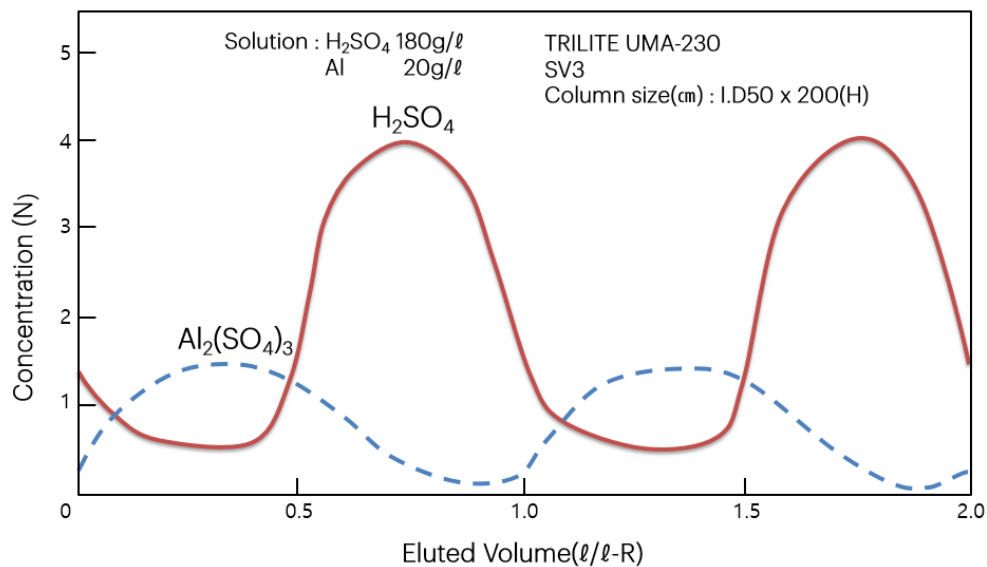


Figure.2 Sulfuric acid and aluminum sulfate separation

This technology is used for recovery and separation of sulfuric acid and aluminum sulfate generated in the cathode oxidation line of aluminum factories. When an aluminum product is electrolyzed in a cathode oxidation tank (sulfuric acid tank), aluminum is dissolved in the sulfuric acid tank and the solution in the sulfuric acid tank gradually deteriorates.

In general, the concentration of the sulfuric acid solution is controlled such that H_2SO_4 at 10 to 30 w/v% and Al not more than 20 grams per liter of sulfuric acid.

The sulfuric acid solution is discharged when the aluminum concentration reaches 18 grams per liter and is replaced with fresh sulfuric acid. After neutralization, the discharged solution is discarded or reused as a coagulant. At this time, utility cost is increases due to the neutralization or replacement of new sulfuric acid. It is also a burden from the environmental management perspective.

1. Acid purification unit (APU)

The acid purification unit using ion exchange resins consists of a suspended matter removing filter and a separation tower filled with chromatography resin; TRILITE MA-23F is the premium grade acid recovery resin developed by Samyang Corporation.

In general, APU operation is conducted for four to five minutes and is divided into an upstream process and a downstream process as shown in Figure.3 below. During the upstream process, the feed solution flows through the pump toward the upside of APU resin tower. In this process, metal salts are excluded by the ion exchange resin and flow out before the acid and collected to the by-products line.

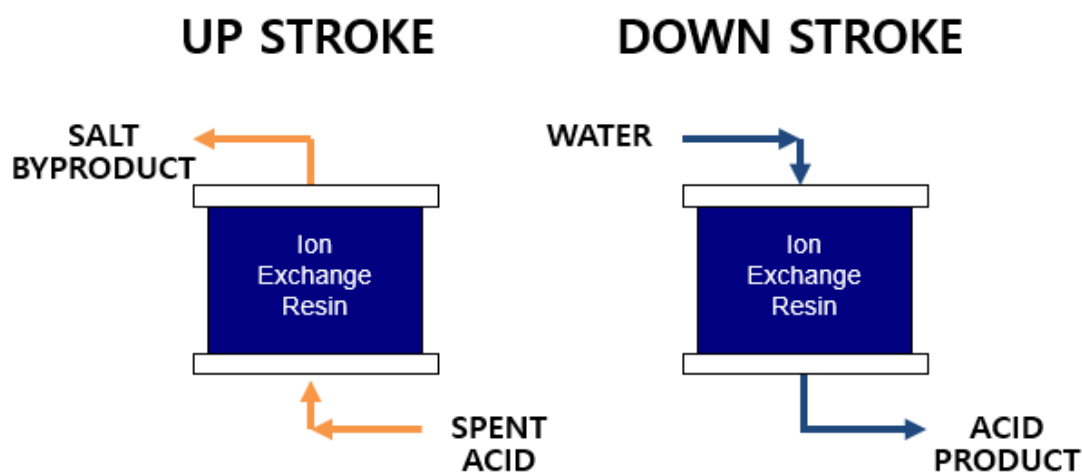


Figure.3 APU Operating Cycle

In a down flow process, water flows downwards through the resin tower. As water continues to service through the resin tower, most of the metals are displaced and the purified acid removed during the upstream process is desorbed and collected as a product.

The concentration of purified acid product ranges from 50 to 110% of the feed value, depending on the operating conditions and feed concentration. By adjusting the volume and flow rate of these operating process, the performance of APU can be optimized according to the targets. Typical process capabilities are 70 to 90% acid recovery and 50 to 60% metal recovery efficiency.



2. Short bed Ion Exchange

The performance of APU system can be optimized by the short bed ion exchange technology due to significant advantages over conventional ion exchange.

1) Fine mesh resins

TRILITE Chromatography resins are produced by one of the leading production technology (uniformity coefficient less than 1.1). The much smaller diameters than conventional ion exchange systems (approximately 20%) greatly improves the exchange kinetics. It allows operation at higher flow rates and reduces the length of the mass transfer zone. Particularly the exchange rate is inversely proportional to the square of the particle diameter of ion exchange resin. Thus, halving the particle size increases the exchange rate by 400%. As a result, with the use of fine mesh resins, the APU can operate with smaller quantity of resins at higher flow rates compared to the widely used conventional ion exchange resins.

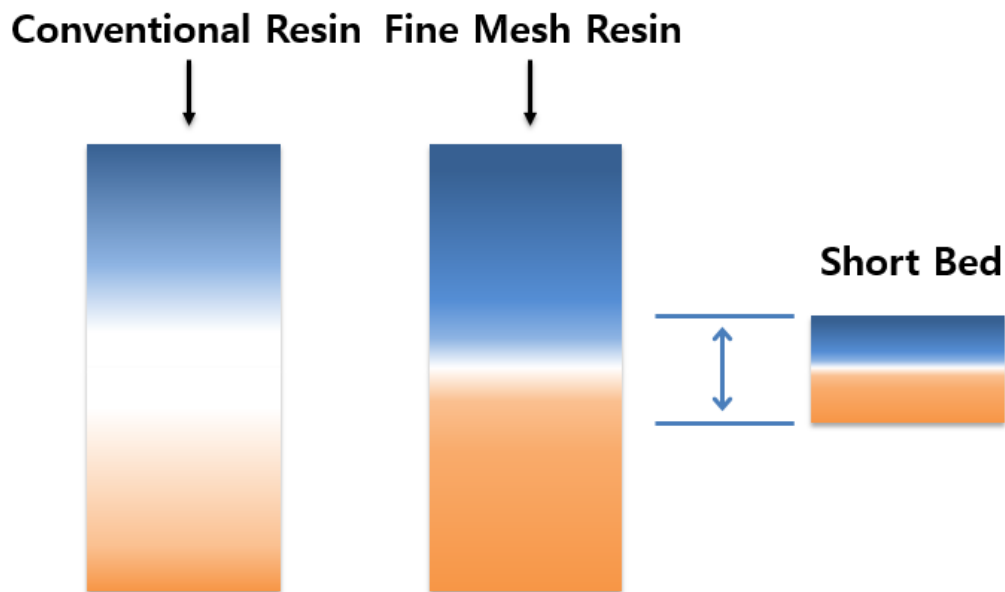
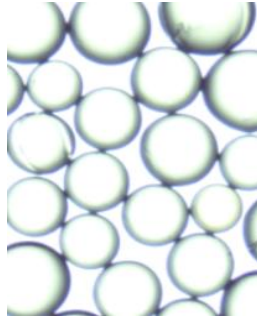
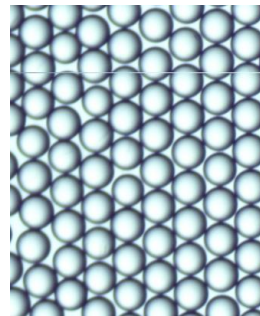


Figure.4.1 Short Bed System

**(a) Conventional****(b) Fine Mesh resin****Figure.4.2 Conventional / Fine Mesh resin**

2) Short depth resin beds

During the fixed bed operation process, only in the fraction of the bed is involved for ion exchange. Upstream resins has been exhausted and downstream resins remain in the regenerated form. Hence, there are inactive resins in conventional type APU. Short bed process reduces the depths of these inactive resins and contribute to more effective utilization of remaining resins. Hence, the ion exchange capacity is fully consumed.

3) Counter current regeneration

As approved in general water treatment, counter current regeneration system (the direction of service and regeneration is to the reverse direction) features higher regeneration efficiency as well as reducing the regenerant consumption.

4) Packed bed system to prevent channeling phenomenon

Packed bed system (which maximize the loading of ion exchange resin to the volume of vessel) optimized the performance of APU, without any dilution of solutions and contributes to maintain



the resin layers within the vessel. It is also related to the regeneration optimization using counter current regeneration method.

Packed bed system also minimized the chance of channeling (phenomenon that solutions passes more through the resin bed with higher voids, causing rapid exhaustion of ion exchange capacity). The resins should be properly packed into the APU, and APU should be designed to evenly spread the acid solution and regenerant to maximize the performance of packed bed system.

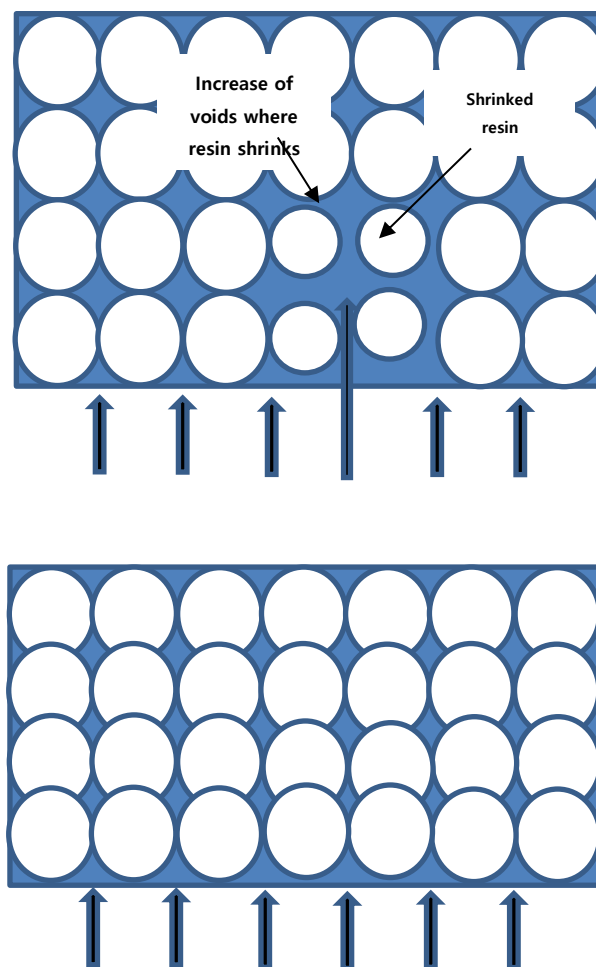


Figure.4.3 Short Bed System



Below Table.1, is the experimental data to achieve acid recovery rate more than 87% by the APU system. There may be practical difference depending on the characteristics of each application, it is found feasible to remove more than 70% of metal components on average. With the presence of contaminants such as antimony and bismuth, the removing efficiency drops to about 50%.

Table1. APU Performance for Separation of metals

Stream	H2SO4 Product			An Nodizing			HCl Product		
	H2SO4 (g/l)	Ni (g/l)	Cu (g/l)	HNO3 (g/l)	HF (g/l)	Metal (g/l)	HCl (eq/l)	Co (g/l)	Zn (g/l)
Feed	275	15	5	107	19.3	45	3.3	8.4	1.13
Product	240	3.75	1.25	104	18.5	12.6	3.2	7	0.03
by Product	35	11.25	3.75	0.3	0.3	30.4		1.4	1
Removal	-	75.0%	75.0%	0.3%	1.6%	67.6%	-	16.7%	88.5%

Source: Michael sheedy, Paul pajunen (Eco-Tec Inc)



5) TRILITE MA-23F

TRILITE MA-23F is a specially developed APU resin by Samyang Corporation. It is a gel type, strongly basic anion exchange resin type 2 and features styrene-divinylbenzen matrix and has functional group of DMEA(Dimethyl Ethanol Ammonium).

Produced by the state-of-the-art polymerization technology, the particle distribution is extremely even and features the uniformity coefficient less than 1.1. It also features excellent physical, chemical stability for long term use of the resins. Especially, the particle sizes ranges between $230 \pm 10 \mu\text{m}$ contributing to the excellent chromatographic separation efficiency. Due to excellent osmotic attrition feature, it features very low crush rate even after long-term use. It is supplied in Cl form and can also be applied as a catalyst for bio-diesel production and others.

<Specification>

Grade name	TRILITE MA-23F
Ionic form	Cl form
Shipping weights	715 g/l(approx.)
Specific gravity	1.1 (approx.)
Whole bead count	Min. 95%
Moisture content	42~46%
Exchange capacity	Min. 1.4eq/l
Average diameter	220~240 μm
Uniformity coefficient	1.1
Swelling rate	Cl / OH = 1.20 (approx.)
Operating temperature	40°C(OH form) 60°C(Cl form)
Operating pH range	0~14

SAMYANG

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