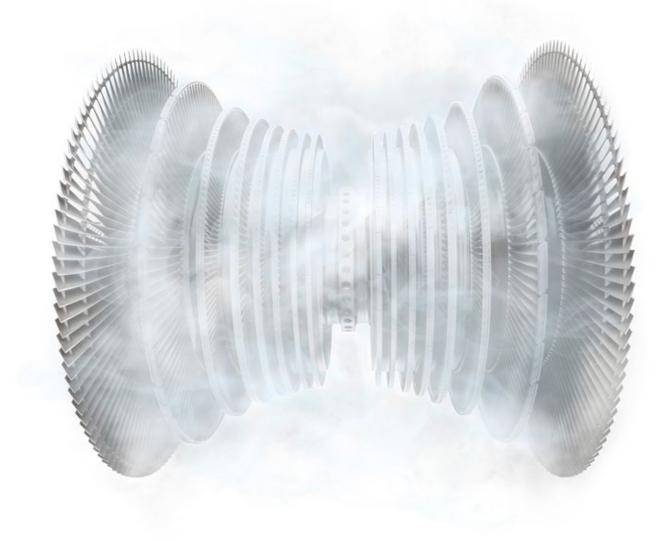
QUALITY ENERGIZES.



Ion Exchange Resins for Condensate Polishing in Power Plants and General Process Industry







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INTRODUCTION



LANXESS is a major global manufacturer of ion exchange resins for almost any application. This brochure will give you an introduction to LANXESS' portfolio with an emphasis on its use for condensate polishing within water-steam circuits. The latter are of crucial importance in power plants of various kinds, but also in the process industry in general. On the basis of decades of experience in research and development and thanks to its in-depth and comprehensive application know-how, LANXESS is a first-choice partner for ion exchange resins with its Lewatit[®] product portfolio. Lewatit[®] resins are approved by numerous major power companies, both fossil and nuclear, throughout the world.

Resins from LANXESS are an excellent fit for many water treatment plants and at the cutting edge of technology due to continuous research and development. LANXESS developed and implemented resins of uniform particle size (monodisperse resins) based on polystyrene and divinyl-benzene for use in fluidized bed systems about 30 years ago. Many of these Lewatit[®] resins have proved their excellent performance and reliability over a long period of time in many industrial applications. This is primarily due to the outstanding property profile of these ion exchange resins. The uniformity in particle size is key to producing ion exchange resins with highly homogeneous properties, e.g., equally distributed functionalization. Specially developed advanced production processes also make it possible, for example, to produce anion exchange resins with a very low content of covalently bound chlorine, which contributes to exceptionally low chloride content and very low chloride leakage.

In addition, LANXESS's calculation and design software LewaPlus[®] provides value for customers. It enables the modeling, dimensioning, and optimizing of diverse ion exchange systems in a variety of configurations. One of its numerous modules specifically addresses condensate polishing. With the aim of creating sustainable processes, LewaPlus[®] will help find the ideal system configuration to maximize productivity while also saving resources at the same time.



KEY REQUIREMENTS FOR CONDENSATE POLISHING

Water-steam circuits are a key component of almost any power plant, bridging the gap between heat generation and electricity generation. Moreover, in other sectors of the process industry they facilitate steam-based energy transport. Initially generated heat is employed to produce steam in boiler vessels. This steam is used to propel turbines or other machinery or to transfer heat, e.g., for heating reaction vessels or remote buildings. After energy transfer, the condensate is reused – eventually in combination with make-up water from external sources – as boiler feed water.

In order to prevent metal parts from corroding, e.g., piping or vessels, coming into contact with this water at elevated temperatures and pressures, condensate needs to undergo demineralization and condensate polishing by ion exchange. The condensate polishing unit removes "crud" – solid corrosion products consisting mostly of oxides of iron, copper, or nickel and dissolved substances – mostly sodium, chloride, silica, and carbon dioxide. Even very low quantities of dissolved salts or other contaminants can be removed from the circulating water to avoid problems such as the formation of incrustations. Otherwise, this scale could precipitate inside pipes or within devices such as boilers, steam generators, condensers, heat exchangers, steam turbines, and cooling towers.

Specific requirements for specific applications

Depending on the specific process (see fig. 1), boiler feed water has to meet various requirements at various levels, such as the maximum tolerable concentration of particles, ions, and organics or specific pH values. By means of ion exchange, pure water with conductivities of less than 0.1 μ S/cm can easily be obtained.

Apart from overall conductivity, polishing setups may vary depending on a variety of parameters. Among these are the total organic carbon (TOC) load of the feed water or specific pH values or ion concentrations as required, e.g., in the Chemical and Volume Control Systems (CVCS) of nuclear power plants. Depending on the application, non-regenerable or regenerable mixed-bed resins consisting of an anionic and a cationic component may be employed and the latter may be regenerated internally or externally.

Most often, state-of-the-art polishing of the condensate stream is realized by mixed beds to remove all kinds of ionic impurities from the water. The cycle time is between several weeks and several months before the resins need regeneration.

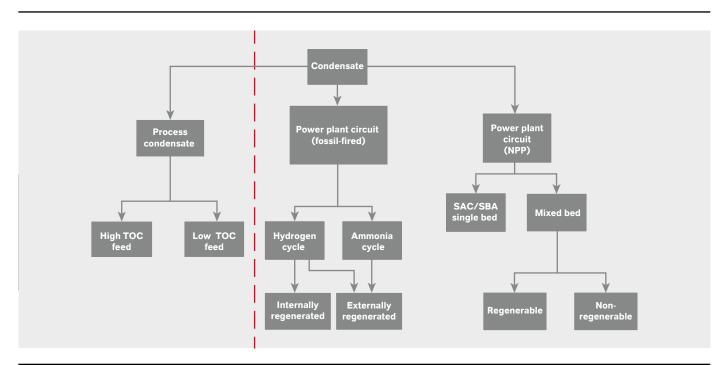


Fig. 1 Different operation conditions in condensate polishing applications



Additionally, a deaerator removes dissolved air from the water, further reducing its corrosiveness. Furthermore, a corrosion inhibitor is typically added in ppm concentrations. It is dosed with pH control agents such as ammonia to keep the residual acidity low. Lewatit[®] cation and anion exchange resins, as well as mixed beds, are widely and very successfully used for the polishing of condensates. Due to their monodispersity, high capacity, and purity, they offer many advantages to the operator:

Lewatit[®] ion exchange resins – up to the challenge

- Virtually linear pressure drop gradient across the entire bed depth, allowing operation with higher bed depths.
- High operating capacities at low consumption of regenerants and rinse water.
- High flow rates during operation and regeneration.
- Homogeneous throughput, resulting in better capacity utilization.
- High resistance to oxidative stress, leading to lower TOC emissions.
- Very good separation of components for mixed bed regeneration.

Key characteristics of the resins employed include their capacity, stability, selectivity, leakage, kinetics, and – eventually – regenerability (see fig. 2). LANXESS offers strongly acidic and basic ion exchange resins with the grade identifier KR. They are monodisperse, highly regenerated, and purified to meet the specifications and requirements of the nuclear industry. Lewatit[®] KR resins are noted for their outstanding stability. Their excellent hydrodynamic properties allow for particularly high flow rates. The high grade of monodispersity – maximum uniformity coefficient UC 1.1 – and a very small content of fines result in especially low pressure losses compared to standard resins. Premium resins such as Lewatit[®] MonoPlus S 200 KR (SAC, strongly acidic cation exchange resin) or Lewatit[®] MonoPlus M 800 KR I (SBA, strongly basic anion exchange resin) are particularly suitable for use with radioactively contaminated water, e.g.:

- Removal of radioactives from circuits in nuclear power plants (decontamination).
- Treatment of primary coolants, e.g., for Chemical and Volume Control Systems (CVCS) in Pressurized Water Reactors (PWRs).
- Purification of steam generator blowdown, irrespective of conditioning.
- Polishing in primary and secondary circuits as a mixed bed component.

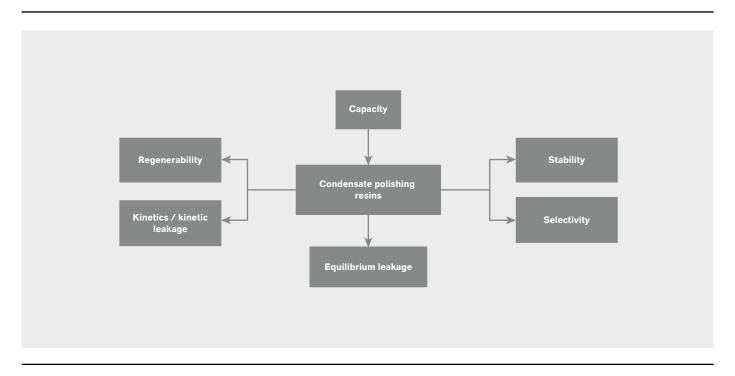


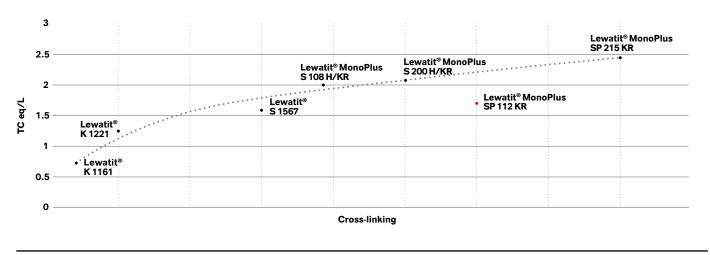
Fig. 2 Key parameters in condensate polishing

ENHANCING PERFORMANCE AND ENDURANCE – CAPACITY AND STABILITY

In order to achieve long service lives, resins with high total capacities are preferentially employed. Such high total capacities are usually realized by the enhanced cross-linking of the polymer matrix. The KR series of highly cross-linked Lewatit[®] resins has been developed to specifically meet the needs of the power industry.



Fig. 3 Total capacity v cross-linking for different SAC resins (black – gel-type; red – macroporous)



Source: LANXESS product data sheet and own data

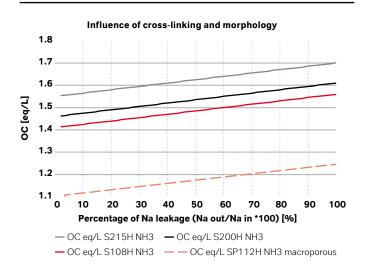
However, total capacity is not everything. Operating capacity is what counts during everyday operations and additionally depends on the excess of chemicals employed during regeneration. As a result, an SBA such as Lewatit[®] MonoPlus M 500 could be superior to Lewatit[®] MonoPlus M 800 in terms of operating capacity at a low excess of regenerant, although the latter resin exhibits the higher total capacity.

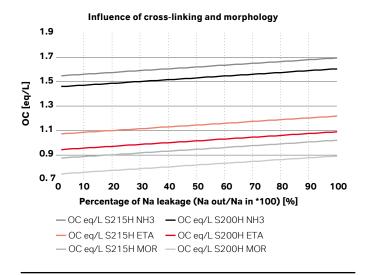
Generally, gel-type resins (Lewatit[®] MonoPlus S 108 H, 200 H or 215 H) offer higher capacities than macroporous resins (e.g., Lewatit[®] MonoPlus SP 112 H) (see fig. 3). Due to the macropores, the macroporous resins have a higher water content and a smaller number of functional groups per volume. However, in the case of high organic loads in the feed, the macropores mitigate the negative impact on the performance. Due to the high density of functional groups on the bead surface, a large part of the resin's capacity is even available with favorable kinetics. On the other hand, gel-type SACs with polishing resins are usually initially operated in the "hydrogen cycle" in which the cation resin is in hydrogen form and the anion resin is in hydroxide form.

The operating capacity for SACs is often determined by the tolerable sodium leakage. This leakage is also markedly influenced by the choice of conditioning agents other than ammonia, such as ethanolamine or morpholine. The latter additive especially leads to a pronounced decrease in operating capacity (see fig. 4).



Fig. 4 Operating capacity of SAC resins of varying morphologies (left) and in the presence of different conditioning agents (right)





Source: LANXESS LPT lab data

Polishing resins are usually initially operated in the "hydrogen cycle" in which the cation resin is in hydrogen form and the anion resin is in hydroxide form. After several days of operation the cation resin gets converted into a loaded form and requires regeneration if operation is to be continued in a hydrogen cycle. This mode of operation can almost always produce condensate of the required quality with ease. Also advantageous is a reasonable capacity for the removal of silica. As an alternative, the polisher can be run in an "ammonia cycle," i.e., with an ammonium-loaded SAC. Sodium leakage then needs to be monitored ion-selectively instead of simply measuring conductivity. Additionally, the SBA has to be in a highly regenerated state in order to prevent unacceptably high chloride leakage (see fig. 6).

Alongside enhanced cross-linking, the mechanical stability of the resin beads increases, as indicated by friability tests (see fig. 5). SACs as well as SBAs from the Lewatit[®] product portfolio exhibit superior properties when compared with competitor products. Thermal and oxidative stability also increase. However, highly cross-linked resins are usually more brittle and show lower osmotic stability. Lewatit[®] MonoPlus S 200 KR and S 215 KR both exhibit high mechanical stability. This makes them especially suitable for external regeneration. Despite its only medium to high cross-linking ratio, Lewatit[®] MonoPlus S 200 KR shows identical or even slightly higher operating capacities compared with highly cross-linked (13–16%) resins.

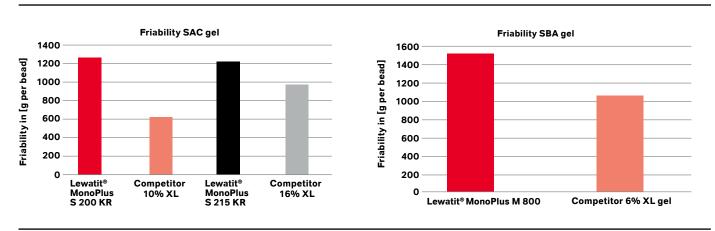


Fig. 5 Friability tests of two gel-type SACs and one SBA, compared to competitor products

Source: LANXESS lab data

PRODUCT QUALITY AND EXPERTISE – SELECTIVITY AND LEAKAGE

lon selectivity is another key property of ion exchange resins. As shown below for sulfonated SACs, selectivity coefficients increase for resins with higher degrees of cross-linking. Generally, this effect is even more pronounced for divalent cations.

Leakage (see table 1) of ions generally occurs at the end of a cycle of the ion exchange system. The higher the concentration of an elutable ion on the resin, the more likely the leakage of that ion. Additionally, factors such as temperature or pH value may influence the tendency toward leakage.

Tab. 1 Relative selectivity coefficients (H⁺ = 1) of SACs as a function of the degree of cross-linking

DVB	4%	8%	12%	16%
H⁺	1	1	1	1
Na ⁺	1.3	1.5	1.7	1.9
NH_4^+	1.6	1.95	2.3	2.5
Mg ²⁺	2.4	2.5	2.6	2.8
Ca ²⁺	3.4	3.9	4.6	5.8
Sr ²⁺	3.85	4.95	6.25	8.1
Ba ²⁺	6.15	8.7	11.6	16.5

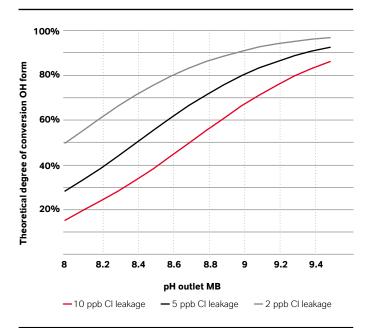
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¹ WAC = weakly acidic cation exchange resin

² WBA = weakly basic anion exchange resin

For example, as is obvious from the law of mass action, any pH increase will shift the equilibrium between resin-bound chloride and a basic liquid phase towards resin-bound hydroxide, whereby chloride is liberated (see fig. 6).

Fig. 6 Theoretical minimum degree of conversion into hydroxide form to achieve a required maximum of chloride leakage



Source: LANXESS' own calculation based on law of mass balance and selectivity coefficients

Low chloride leakage is often required as a precaution against corrosion, especially in nuclear power plants, and especially PWRs, where the liquid phase contains high amounts of boric acid for neutron moderation purposes. To achieve such low chloride leakage, it is crucial to start with an SBA predominantly in hydroxide form.

In order to provide such high degrees of conversion into hydroxide form, LANXESS employs special regeneration techniques and air-tight packaging of the resins. In order to maintain this high hydroxide loading for a long time during transport and storage, carbon dioxide from the ambient air must be kept away from the anion exchange resin to avoid bicarbonate formation.

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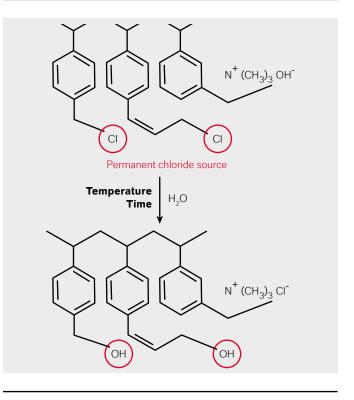


Minimizing covalently bound chlorine from the start

In addition to the elutable chloride, an SBA contains covalently bound chlorine in the form of allyl chloride residues resulting from the chloromethylation of an unreacted vinyl group. Over time and especially at elevated temperatures, these residues are hydrolyzed and chloride is liberated (see fig. 7). Therefore, in order to avoid chloride leakage above the required threshold concentrations, the total chlorine content of the resin has to be taken into account. To meet this requirement, LANXESS has developed an advanced functionalization process for the basic polymer.

As a result, SBAs with an approximately tenfold lower content of total chlorine can be obtained (see fig. 8). For CVCS of nuclear power plants, in order to establish the required balance between 7Li concentration for neutron moderation and added boric acid as a neutron absorber (so-called "coordinated boron/lithium mode of operation"), resins preloaded with 7Li are available. These are the mixed bed resins Lewatit[®] MonoPlus SM 1000 KR 7Li and SM 1015 KR 7Li. By alternating between the two mixed bed types, lithium can be either released into the feed or removed from the feed. That makes it possible to control the pH without introducing potentially corrosive ions into the circuit.





Source: LANXESS

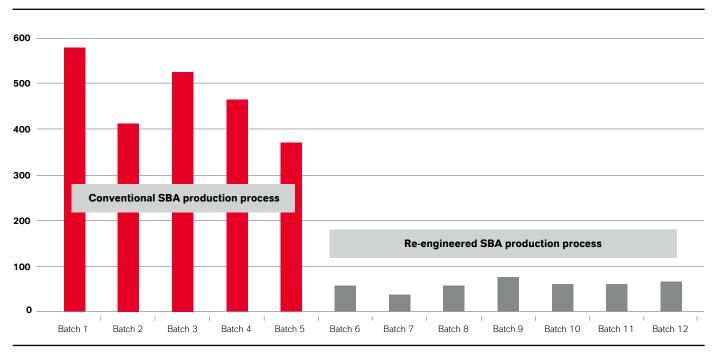


Fig. 8 Total chlorine content [mg/kg] in dry resin (SBA Cl form) of standard and advanced SBA resins

Source: LANXESS lab data

EXPERIMENTAL EXCELLENCE – DEVELOPMENT OF A PROPER KINETIC TEST

The mass transfer coefficient (MTC) is an important and widely employed property that defines acceptable resin performance, most importantly for the SBA resin component of mixed bed systems. The MTC is measured by a simple column test with a known feed concentration of ions at a sufficient flow rate to achieve kinetic leakage out of the bed. However, the standard measuring method (ASTM D6302-98(2017), Standard Practice for Evaluating the Kinetic Behavior of Ion Exchange Resins) exhibits several drawbacks, i.e.: The higher the MTC the better. However, according to ASTM guidelines, even at MTC values between 1.5 and 2.0 x 10-4 m/s, the tested resins are considered to be satisfactory for normal operation, as stated by the ASTM standard. SBA resins from the Lewatit[®] product range easily achieve superior values between 2 and 3 x 10-4 m/s. This is especially true for Lewatit[®] MonoPlus M 800 KR I (see fig. 9).

- The test setup is rather complex.
- Only one component of the mixed bed can be tested at a time.
- Sulfate leakage needs to be determined at ppb level, most often requiring calibration curves.

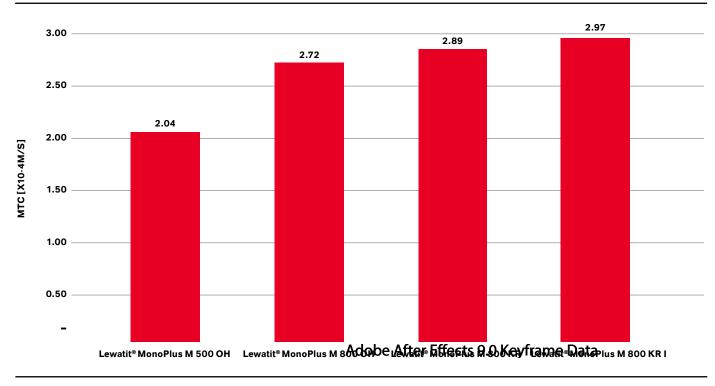


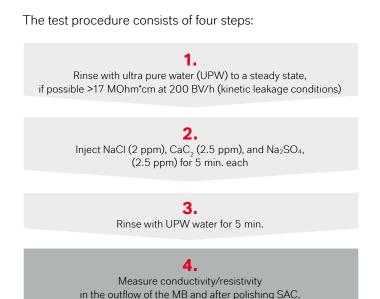
Fig. 9 MTC values of gel-type SBAs from the Lewatit[®] product range as determined according to ASTM D6302-98(2017)

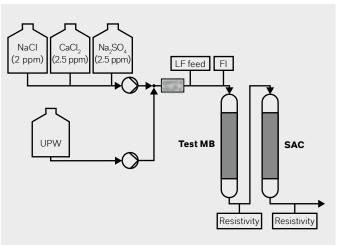
Source: LANXESS lab data



In order to determine both the SAC and the SBA performance of a mixed bed in only one test, LANXESS has developed an advanced testing procedure based on conductivity/ resistivity measurement (see fig. 10)¹.

Fig. 10 Setup for resistivity-based performance test developed by LANXESS





¹ See also: "Ion Exchange Resins Quality Features in Thermal Power Plants", S. Hilger, H.-J. Wedemeyer (LANXESS Deutschland GmbH), IEX2022 - A Vision for the Future, online conference, Society of Chemical Industry, Sept. 7, 2022.

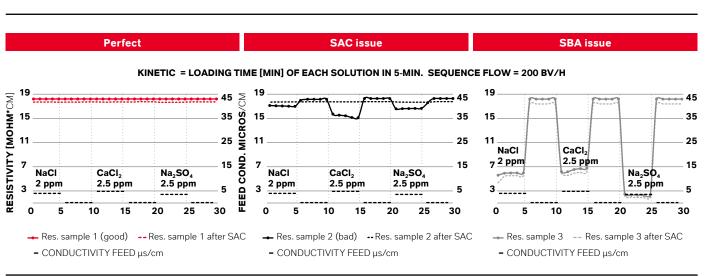


Fig. 11 Examples of resistivity-based performance tests

Source: LANXESS lab data

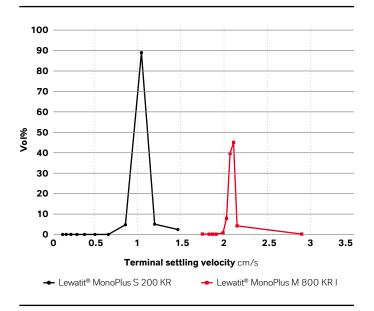
The kinetic leakage resistivity drop of sodium chloride, calcium chloride, and sodium sulfate injection are measured subsequently and thus immediately indicate if there are any issues with the SAC or SBA of a mixed bed respectively. This kind of test can therefore also be used to establish predictive maintenance.

COST SAVINGS BY IMPROVING THE REGENERABILITY

For regenerable ion exchange resins, mechanical stability (see fig. 5), especially resistance against fracture and abrasion, is a crucial requirement. This is even more important when they are regenerated externally, which most often is the case. Especially the degree of cross-linking has to be chosen carefully in order to find the best compromise between mechanical and oxidative stability and the ease of regenerability.

For regenerable mixed bed systems, SAC and SBA need to be separated completely before regeneration chemicals are applied in order to prevent charging the SAC with cations and the SBA with anions from the respective regenerants. Optimum separation can be achieved by carefully adjusting the particle size with respect to the different individual densities of the SAC and the SBA. As a result, the respective particles exhibit a markedly different settling velocity (see fig. 12).

Fig. 12 Terminal settling velocity of SAC (Lewatit[®] MonoPlus S 200 KR) and SBA (Lewatit[®] MonoPlus M 800 KR I) components of a regenerable mixed bed system



Source: LANXESS' own calculation based on bead size distribution data

When beads of SAC and SBA are of clearly different colors, as is the case for all gel-type resins in the Lewatit[®] portfolio, the quality of the separation (see fig. 7) can easily be checked visually (see fig. 13).

On the other hand, the requirement may be contrary in order to prevent the segregation of SAC and SBA during normal operation, for example in closed cycles containing radioactive ions, where the mixed bed should last for more than 6 months. Behavior of this type is in the focus for non-regenerable mixed bed systems (see fig. 14).

Fig. 13 Bad (imperfect) versus perfect pre-regeneration separation of SAC (dark) and SBA (light) of a mixed bed in a transparent column

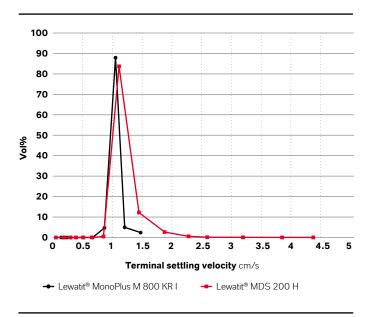


Perfectly separated mixed bed

Badly separated mixed bed



Fig. 14 Terminal settling velocities of SAC (Lewatit[®] MDS 200 H, not sold separately) and SBA (Lewatit[®] MonoPlus M 800 KR I) optimized to prevent separation



Source: LANXESS' own calculation based on bead size distribution data

A recently introduced new module of LewaPlus[®] specifically allows calculations involving ready-to-use mixed bed ion exchange systems. Its main purpose is the hydraulic design of the filter. It also makes it possible to simulate the performance with different water sources and different endpoints.



Summary

Due to the usually expected high specific flow rates, the low expected ionic leakage in the ppb range condensate polishing applications presents a challenge to the performance of the ion exchange resins. Due to our long-term experience in those applications and our state-of-the-art production assets, Lewatit[®] resins present the best answer to those challenges.

OUR COMPREHENSIVE LEWATIT® PORTFOLIO – EXCEPTIONAL QUALITY FOR CONDENSATE POLISHING

Lewatit® strongly acidic cation exchanger (SAC), uniform particle size

Lewatit [®] MonoPlus	lonic form	Туре	тс	Water retention	Mean bead size	Major application
			[eq/L]	[%]	[mm]	
S 200 H	Н	gel	2.1	45-50	0.60 (<u>+</u> 0.05)	Polishing MB, CP
S 215 H	Н	gel	2.4	40-45	0.60 (<u>+</u> 0.05)	Polishing MB, CP ammonia cycle
SP 112 H	Н	mp	1.6	56-60	0.67 (<u>+</u> 0.05)	DM, MB, CP

Lewatit® strongly basic anion exchanger (SBA), uniform particle size

Lewatit® MonoPlus	lonic form	Туре	тс	Water retention	Mean bead size	Major application
			[eq/L]	[%]	[mm]	
M 800	CI	gel	1.4	43–48	0.59 (<u>+</u> 0.05)	DM, MB, CP
M 800 OH	OH	gel	1.2	57-62	0.64 (<u>+</u> 0.05)	DM, MB, CP
MP 800	CI	mp	1.0	63–68	0.62 (<u>+</u> 0.05)	DM, MB, CP
MP 800 OH	OH	mp	0.8	70–76	0.65 (<u>+</u> 0.05)	DM, MB, CP
MP 500	CI	mp	1.1	60–65	0.62 (<u>+</u> 0.05)	DM, MB, CP
MP 500 OH	ОН	mp	0.9	70–77	0.65 (<u>+</u> 0.05)	DM, MB, CP

Lewatit® strongly acidic cation exchanger (SAC), uniform particle size – nuclear grade

Lewatit® MonoPlus	lonic form	Туре	тс	Water retention	Mean bead size	H conver- sion	Major application
			[eq/L]	[%]	[mm]		
S 200 KR	Н	gel	2.1	45-50	0.60 (<u>+</u> 0.05)	99.9	CP, CVCS, rad waste
S 215 KR	Н	gel	2.4	40-45	0.60 (<u>+</u> 0.05)	99.9	CP in amine conditioned cycles, CVCS, rad waste
SP 112 KR	Н	mp	1.7	52–61	0.67 (<u>+</u> 0.05)	99.9	Decontamination, remov- al of activated cleavage or corrosion products
S 300 KR	Н	gel	2.1	45–50	0.55 (<u>+</u> 0.05)	99.9	CP, CVCS

All resins listed are monodisperse with a maximum uniformity coefficient of 1.1. At LANXESS, resins exhibiting uniformity coefficients above 1.1 are not considered monodisperse at all.



Lewatit® MonoPlus	lonic Type form		тс	OH (SBA)	CO₂ (SBA)	CI (SBA)	SO₄ (SBA)	Major application
			[eq/L]	[min. eq%]	[max. eq%]	[max. eq%]	[max. eq%]	
M 500 KR	ОН	gel	1.1	95	5	0.5	0.5	CP, CVCS, rad waste
M 800 KR	OH	gel	1.2	95	5	0.5	0.5	CP, CVCS, rad waste
M 800 KR I	ОН	gel	1.2	95	5	0.2	0.3	CP, CVCS, rad waste
MP 800 KR	ОН	mp	0.8	95	5			CP, CVCS, rad waste

Lewatit® strongly basic anion exchanger (SBA), uniform particle size – nuclear grade

Lewatit® mixed bed, uniform particle size - nuclear grade

Lewatit [®] MonoPlus	lonic form	Туре	TC (SAC)	TC (SBA)	H (SAC)	OH (SBA)	CO ₂ (SBA)	CI (SBA)	SO₄ (SBA)	Ratio SAC:SBA	Major application
			[eq/L]	[eq/L]	[min. eq%]	[min. eq%]	[max. eq%]	[max. eq%]	[max. eq%]	[%]	
SM 1000 KR	H/OH	gel	2.1	1.2	99.9	95	5	0.2	0.3	33:67	NGP
SM 1015 KR	Н/ОН	gel	2.4	1.2	99.9	95	5	0.2	0.3	33:67	NGP for amine conditioned water
SMP 1000 KR	Н/ОН	mp	1.7	0.8	99.9	95	5	0.3	0.3	33:67	NGP with colloidal content
SM 1001 KR	H/OH	gel	2.1	1.2	99.9	95	5	0.2	0.3	67:33	NGP
SM 1000 KR Li	Li/OH	gel	2.1	1.2	99.9 (Li)	95	5	0.2	0.3	33:67	NGP lithiated, for amine con- ditioned water
SM 1015 KR Li	Li/OH	gel	2.4	1.2	99.9 (Li)	95	5	0.2	0.3	33:67	NGP, lithiated
UP 1297	Н/ОН	gel	2.1	1.1	99.9	95	5	0.5	0.5	40:60	NGP, reduced separation during opera- tion

CP – Condensate Polishing

CVCS – Chemical and Volume Control System

DM – Demineralization

MB – Mixed Bed

md-monodisperse

mp – macroporous

NGP – Nuclear Grade Polishing

TC – Total Capacity



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