# QUALITY PROTECTS.

Ion Exchange Resins for the Power Industry

**X** Lewatit<sup>®</sup>

QUALITY WORKS.



# LEWATIT® HIGH-PERFORMANCE MONODISPERSE RESINS

LANXESS is one of the world's most important manufacturers of ion exchange resins for almost any application. This brochure intends to give an introduction to LANXESS' portfolio with an emphasis on the use in power stations. More specifically, its focus is on condensate polishing within water-steam circuits. On the basis of decades of experience in research and development and application know-how, LANXESS is a first-choice partner for all kinds of ion exchange resin usage in power stations. This is illustrated by several referential examples from well-known industry partners and some scenario-type cases which are presented in this brochure.

Resins from LANXESS are an excellent fit to many water treatment plants and are at the cutting edge of technology. LANXESS developed and implemented monodisperse resins based on polystyrene and divinylbenzene about fifteen years ago for use in fluidised bed process filters, and many resin fillings even of that first generation are running very well in industrial applications. LANXESS's monodisperse resins have both excellent chemical and osmotic stabilities. They have got uniformity coefficients of 1.1 at maximum, so the share of fines and resulting pressure losses are very low. The resin's total capacity is well utilized, and the requirement of rinse water is reduced. Another advantage is the homogenous throughput of regenerants, water and solutions which leads to a homogenous operating zone. The pressure drop gradient is virtually linear across the entire bed depth, and components can be separated very well in mixed bed applications.

Gel-type resins are employed in most cases, but sometimes it is necessary to get larger quantities of naturally occurring organic material absorbed. This can effectively be achieved by the use of macroporous resins.

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# WATER-STEAM CIRCUITS IN DIFFERENT TYPES OF POWER STATIONS

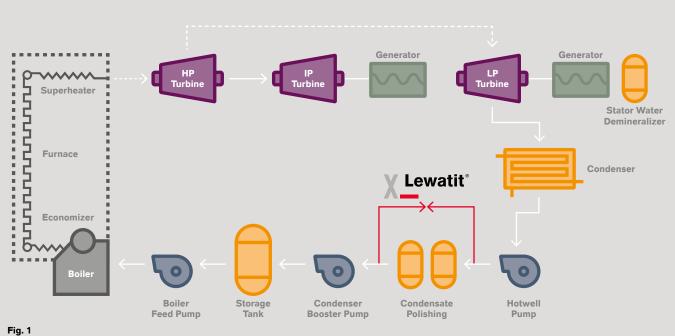
#### **Fossil-fuelled power stations**

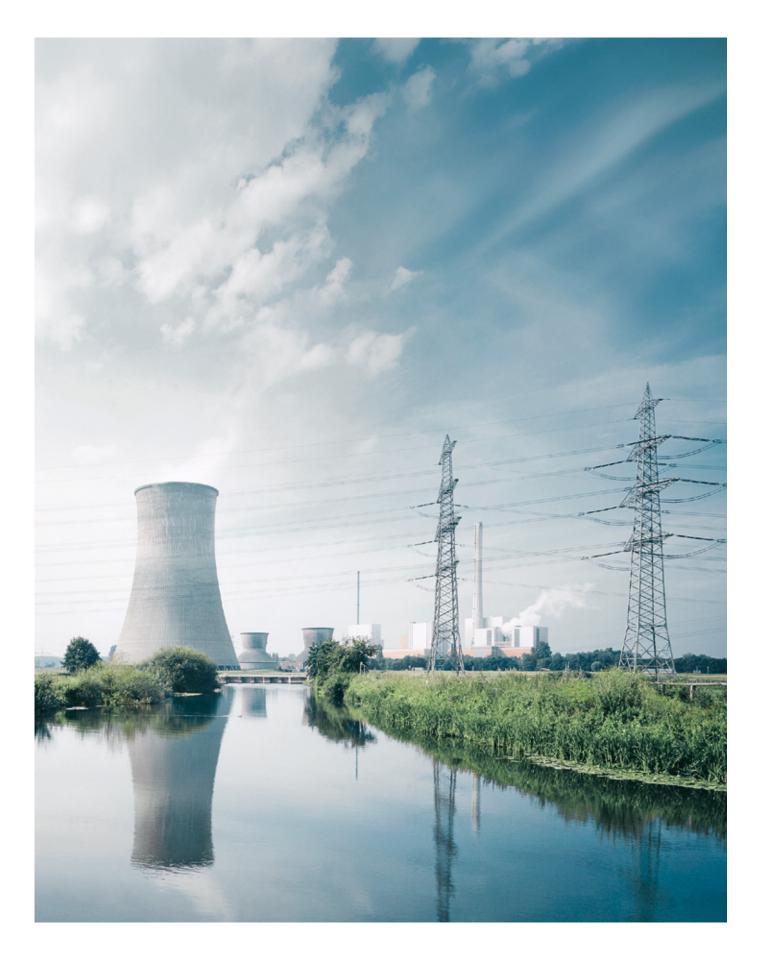
Fossil-fuelled power stations, e.g. the coal-fired one shown schematically in Fig. 1, convert the combustion heat into mechanical and ultimately electrical energy by means of a turbine and an electrical generator, respectively. The prime mover is a steam or a gas turbine, or, in small plants, a reciprocating internal combustion engine. Ion exchange resins are mainly used for demineralizing make-up water, for polishing condensates, and sometimes in the cleaning of waste water. The heat generated by burning fossil fuels is transferred to water boilers in which water steam is produced. This steam is used to propel the turbines. The water which is fed to the boilers – so-called make-up water – has to be fully demineralized before use.

The production of make-up water is not covered by this brochure. Further information about this has been collected in numerous leaflets issued by LANXESS.

Recycled condensate – another major component of boiler feed water – also has to be purified before its reuse. This is to avoid corrosion of metal parts coming into contact with this water at elevated temperatures and pressures. Demineralization and condensate polishing by ion exchange can easily produce pure water with conductivities of less than 0.1  $\mu$ S/cm.

### FOSSIL PLANT – FOSSIL FUEL BOILER





#### **Nuclear power stations**

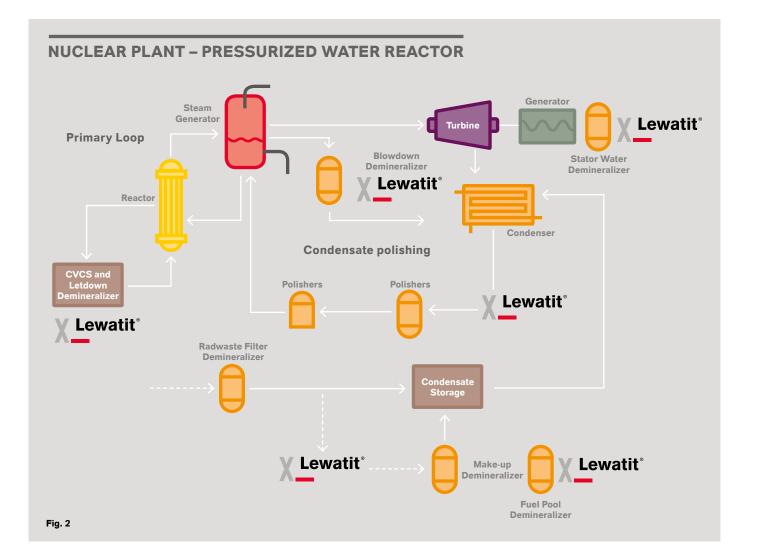
There are different types of nuclear reactors. In most countries, pressurized or boiling water reactors (PWR, BWR) represent the segment of light water ( $H_2O$ ) reactors. In both PWRs and BWRs, ordinary (light) water serves as moderator fluid and as coolant for the reactor core as well.

Water treatment in nuclear power plants may considerably differ from that in fossil-fuelled ones. Ion exchange resins are applied for making up raw water, for all kinds of treating water in the primary and secondary cooling loops, for condensate polishing and for treating waste water.

In <u>PRESSURIZED WATER REACTORS PWR</u> (Fig. 2), pressure vessels contain the nuclear fuel, control rods, moderator, and coolant. They are moderated and cooled by liquid water held under high pressure. The hot radioactive water leaving the pressure vessel is led through a steam generator, which in turn heats a secondary (non-radioactive) circuit of water to produce steam being able to run turbines. The majority of current reactors work by this principle. The fission material is 235U-enriched uranium oxide.

BOILING WATER REACTORS (BWR) are cooled and moderated by water like a PWR, but at a lower pressure, which allows the water to boil inside the pressure vessel producing steam that runs the turbines. Hence, it only requires one cooling loop (Fig. 3).

Water circuits installed in nuclear power stations often contain traces of radioactive materials. This applies, for example, to the primary circuits of BWRs and PWRs, but even to the secondary circuits in PWRs, and to spent fuel pools, of course, as well.



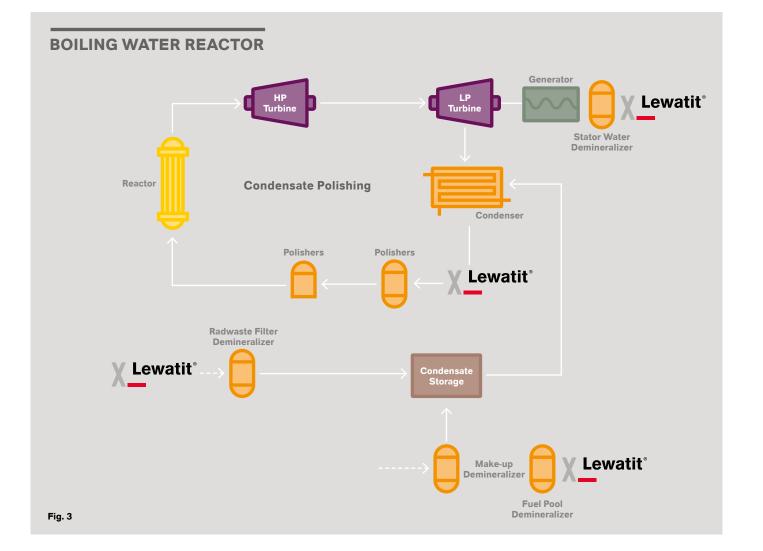
<u>SPENT FUEL POOLS</u> are used for storing spent fuel rods from nuclear reactors. They are approx. 12 m deep. Their bottom is equipped with storage racks designed to hold fuel assemblies after they have been removed from the reactor. This kind of pool is situated at the reactor site. After a usage time of three to six years in the reactor, spent fuel rods are often kept underwater for another 10 to 20 years before they get either reprocessed or are sent for their final storage in special casks. The water in the spent fuel pools cools the fuel and also provides efficient shielding from radiation.

A <u>PRESSURIZED HEAVY WATER REACTOR (PHWR)</u> like the CANDU Qinshan Nuclear Power Plant developed in Canada uses non-enriched uranium as its fuel, and heavy water as a moderator (deuterium oxide,  $D_2O$ ). The heavy water is kept under pressure to be able to carry more heat out of the reactor core. Though heavy water is expensive, cost is moderate since a PRWR does not require fuel enrichment. Heavy water is kept in a large tank (calandria) which is penetrated by pressure tubes containing the nuclear fuel. As in a PWR, the primary coolant generates steam in a secondary circuit to drive the turbines. The reactor is very efficient in its demand for uranium and it allows for precise flux control in the core.

Ion exchange resins are used in both:

- Low-pressure/low-temperature moderator circuit
- High-pressure/high-temperature primary heat transport circuit (PHT)

Especially the performance of mixed bed resins in removing gadolinium nitrate from moderator water is an important requirement. Gadolinium salts (Gd3+) are used in the range from 0.05 to 0.20 mg/kg as soluble neutron adsorbers in the moderator systems of many PHWRs. A pH in the range of 5–5.5 has to be maintained as Gd3+ is water-soluble only under acidic pH conditions.



# EMPLOYING LEWATIT® RESINS IN INTERNAL WATER CIRCUITS

#### **General remarks**

Condensate polishers are employed in systems using steam generation to transport thermal energy both in fossil-fuelled and in nuclear power plants. By using a technology similar to that of a water softener, very low quantities of dissolved salts or other contaminants are removed from the circulating water to omit problems such as the formation of incrustations. Otherwise this scale could precipitate inside pipes, or, in the worst case, within devices such as boilers, steam generators, condensers, heat exchangers, steam turbines, and cooling towers. Malfunctions including leakages of sodium, high pressure losses, leaching of TOC, etc. may then occur.

The removal of minerals has a secondary beneficial effect of maintaining the pH balance of the water at or near neutral by removing ions that would tend to make the water more acidic. This reduces the rate of corrosion where water comes in contact with metal.

The necessary type of condensate treatment for boilers depends on various factors:

- Condensate quality, e.g. conductivity, corrosion products, hardness, silica content, hydrocarbons, pollutants due to ingresses of product
- Amount and quality of condensate return in the boiler feed water
- Requirements to the boiler feed water and boiler water, depending e.g. on boiler type, boiler pressure, maximum heat transfer
- Requirements on the steam produced, e.g. super-heater/ turbine operation, high-quality steam for production processes
- Economic and ecologic requirements, e.g. blow down rate, effluent requirements



Basically, condensate treatment consists of mechanical filtration and/or demineralization by means of ion exchanger units of different designs.

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

Also in the course of condensate treatment, a deaerator removes dissolved air from the water, further reducing its corrosiveness. Furthermore, a corrosion inhibitor like hydrazine is added in ppm concentrations. It is dosed with pH control agents like ammonia to keep the residual acidity low. Typically the cooling water causes the steam to condense at a temperature of about 35°C (95°F).

#### Advantages of LEWATIT® in condensate polishing

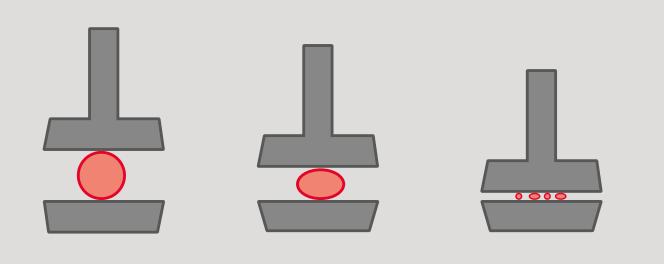
LEWATIT<sup>®</sup> cation and anion exchange resins, as well as mixed beds, are widely and very successfully used for the polishing of condensates. Most of these resins are monodisperse, hence offering many advantages to the operator:

- High flow rates during regeneration and loading
- High operating capacity at a low consumption of regenerants
- Low demand for rinse water
- Homogeneous throughput of regenerants, water and solutions, resulting in a homogeneous operating zone
- Virtually linear pressure drop gradient across the entire bed depth, allowing operation with higher bed depths
- Lower TOC emission and high resistance to oxidative stress
- Very good separation of components in mixed bed applications

Of vital importance is the retention of undesired components such as crud, corrosion products, remainders of hardness constituents, and silica by ion exchange resins selected for polishing condensates. Of these, retained solid constituents in the condensate have to be removed in regular intervals (blow down).

LANXESS developed some new resins both for polishing and ultra pure water applications. One of them is the LEWATIT<sup>®</sup> MonoPlus S 215 KR which is strongly crosslinked. This resin has got a very low tendency to leach, and, at the same time, a rather high total capacity of 2.4 eq/l at least.

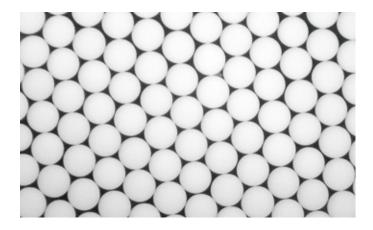
#### HIGH FRIABILITY



#### Ion exchange resins for non-radioactive water circuits of PWRs

Nuclear power plants equipped with a PWR have got two separate cooling systems that must be monitored to ensure a compliance with the guidelines, namely the reactor and the steam circuits. Modern, monodisperse ion exchange resins such as LEWATIT<sup>®</sup> MonoPlus excellently perform in both segments and thus safeguard a compliance with the specifications.

The design of the condensate polishing stage is the same as for modern high-pressure power plants using fossil fuels. The long-time experience LANXESS has had with macroporous, monodisperse resins, e.g. LEWATIT<sup>®</sup> MonoPlus SP 112 KR and LEWATIT<sup>®</sup> MonoPlus MP 500 KR or MP 800 KR, is a great advantage for customers.



% 100 50 0 0.40 0.55 0.60 Bead size [mm]

#### Monodisperse bead size distribution (Schema)

The use of macroporous resins compared to standard geltype resins offers complementary advantages:

- Lower risk of organic fouling
- High stability to oxidants compared to gel-type resins
- Longer life expectancy
- SAC with highest oxidative stability of the matrix to reduce sulfate leakage
- Very effective rinsing behavior due to a lower risk of organic fouling on the anion resin as well as outstanding kinetics, reduced amount of waste
- Low pressure drop due to outstanding monodispersity and absence of fine resin beads (<0.315 mm: max. 0.1%)</p>
- SAC with a lower demand for chemicals in comparison with highly cross-linked gel-type cation exchange resins
- Outstanding separation behavior in mixed bed systems due to their high degree of monodispersity, i.e. a maximum uniformity coefficient of 1.1, and appropriate bead diameters
- Low inherent leaching

Due to this, highly cross-linked gel-type LEWATIT<sup>®</sup> resins have been developed which are at least equivalent regarding the above-mentioned aspects, while offering enhanced capacity.

#### **Osmotic stability SAC H-Form**

M+	S 108	B H								98%
Co	mpetit	or 1								90%
Co	mpetit	or 2								67%
Competitor 3										56%
50	55	60	65	70 Perfe	75 ct bea	80 ds [%]	85	90	95	100

Numerous factors govern the decision for an appropriate resin or resin combination, such as:

- Cycle chemistry and length
- Temperature: Condensate return flow temperature
- Regeneration: Internal or external, types of regenerants and their qualities
- Filter columns: Arrangement and geometry
- Impurities: Organics and their concentration, expected silica concentrations
- Water quality in general: During start-up phase (iron oxides)
- Corrosion rate

In each case, the decision is if macroporous or gel-type ion exchange resins or even a mixture of them, i.e. gel-type cation and macroporous anion, should be used in mixed bed condensate polisher units. Operating capacities of macroporous resins are usually lower than those of gel-type resins. Moreover, gel-type cation exchange resins with enhanced cross-linking ratios have weaker regeneration efficiencies and exchange kinetics.

For this reason, highly cross-linked (13–16%) gel-type cation exchange resins have specific advantages for use in nonregenerable single beds or mixed beds, e.g. in PWR primary circuit condensate polishing.

Compared to those highly cross-linked cation exchange resins, identical or even slightly higher operating capacities are achieved by resins such as LEWATIT<sup>®</sup> MonoPlus S 200 KR. This is due to their monodisperse polymer matrix (uniformity coefficient max. 1.1), also providing better kinetics if the water-steam cycle is conditioned with amines, and sulfuric acid is applied for regeneration in co-current operation. In external regeneration, the high mechanical stability of LEWATIT<sup>®</sup> MonoPlus S 200 KR is a great advantage.

If amines are used as corrosion inhibitors, the concentration of organic substances in the water-steam cycle drastically rises. In this case, macroporous anion exchange resins, e.g. the LEWATIT<sup>®</sup> MonoPlus MP 800 KR, in mixed bed units are recommended in combination with highly cross-linked (10 to 12%) cation exchange resins such as LEWATIT<sup>®</sup> MonoPlus S 200 KR. This is the better alternative to using a purely gel-type LEWATIT® MonoPlus S 200 KR/M 800 KR variant. The latter should be preferred in case of moderate organic fouling, and if higher operating capacities are required, occasionally with higher silica loads.

Mixed bed filters used for the polishing of condensate do not only remove common cations from the water, but also ammonia which is used as a volatile alkalizer. This usually results in a reduced time of operation. However, it is possible to extend the operation time beyond the breakthrough of ammonium ions the so-called "ammonium operation". The authors showed that, during this kind of operation, the leakage levels for sodium issued by the VGB for boiler feed water are not exceeded. Furthermore, the measured uptake capacity for sodium has been higher than expected compared to theoretically calculated examples quoted in the literature. The "ammonium operation" is, therefore, an economically attractive mode of running a power plant.

Much higher absorption and desorption capacities of macroporous LEWATIT® MonoPlus MP 800 KR, particularly for organic substances of high molecular weight, result in lower organic fouling, especially after longer service cycles. These resins are less susceptible to kinetic impairment when compared to gel-type anionic exchange resins.



# Ion exchange resins for water circuits in radioactive environments

#### Chemical & Volume Control System (CVCS)

CVCS for reactor waters are used both in light and heavy water reactor designs and consist of mixed beds containing both a cation and an anion exchange resin operating under pressure. To prevent contamination of heat transfer surfaces, and to limit radioactivity in the water and in the anticorrosion layers, CVCS clean-up removes the following substances from the cooling water:

- Inactive and radioactive corrosion products
- Undesirable positively and negatively
- charged species Fission products

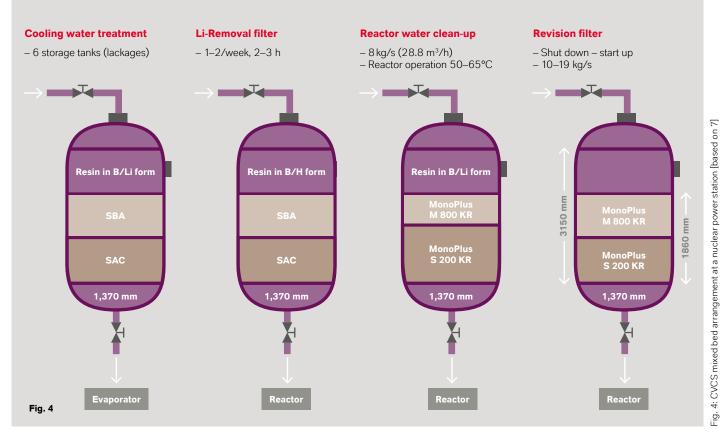
Reactor cooling circuits (primary cooling circuits) of PWR (see Fig. 3, page 7) are operated by the alkaline method. Lithium hydroxide (containing isotopically pure <sup>7</sup>Li as neutron moderator) is usually used as the alkalizing agent. Boric acid is added to the reactor coolant as a neutron absorber,

too. Due to its reaction with thermal neutrons, more <sup>7</sup>Li is formed during operation of the power plant according to:

$$^{10}B$$
 +  $^{1}nth \rightarrow [^{11}B] \rightarrow ^{7}Li + \alpha + 2.31$  MeV.

By the specific dosage of lithium hydroxide or the removal of lithium, it is possible to adapt the service conditions in a way that the amount of suspended corrosion product approaches a minimum. This is called the coordinated boron/ lithium method.

Fig. 4 explains the use of a CVCS mixed bed arrangement at a nuclear power station. Lab tests applying several resin combinations (macroporous/macroporous, gel/gel, macroporous/gel) as well as resins with different cross-link rates during normal operation have been carried out on site. The service water is original reactor cooling water bypassed for treatment in CVCS service mixed bed column filled with standard gel-type resins. For example, a combination of LEWATIT® MonoPlus S 200 KR and M 800 KR is very effective in cleaning up reactor water.



# Tab. 1: Decontamination factors of downstream CVCS mixed bed filter during shutdown for various radioactive contaminants (activities in Bq/m<sup>3</sup>)

Cross-link rate	Feed	<b>Gel/Gel</b> <u>S 200 KR/</u> <u>M 800 KR</u>	DF	Macro/Gel <u>12%</u>	DF	Macro/Gel <u>16%</u>	DF	
Fission products								
Cs-134	<1,2E+05	< 1,0E + 04		< 1,7E+04		<2,4E+04		
Cs-137	1,50E+05	<1,2E+04	> 12,5	<1,9E+04	> 7,8	<2,6E+04	> 5,8	
J-131	< 1,0 + 05	<9,1E+03		< 1,4E+04		< 2,0E + 04		
Np-239	<1,3E+05	<1,2E+04		< 2,0E + 04		<2,6E+04		
Rb-88	<3,9E+05	<7,0E+05		<1,4E+07		<1,9E+08		
Ru-103	< 1,1E + 05	<9,2E+03		< 1,7E+04		<2,1E+04		
Ru-106	< 1,1E+06	<9,7E+04		< 1,7E+05		<2,2E+05		
Activation products								
Ag-110m	3,50E+06	< 1,4E + 04	>250	<2,5E+04	>140	< 3,1E + 04	> 112	
Mo-99	<4,1E+04	<3,6E+03		<6,3E+03		< 7,9E + 03		
Na-24	1,20E+05	<8,5E+03	> 14,1	<9,7E+03	>12,4	< 1,3E+04	>9,2	
Nb-95	8,20E+06	1,60E+05	51,3	6,00E+05	13,7	1,00E+06	8,2	
Sb-122	3,20E+06	<1,4E+04	>229	<2,6E+04	>123	<3,6E+04	>88,9	
Sb-124	4,70E+06	<1,1E+04	>427	<1,7E+04	>276	<2,6E+04	> 181	
Sb-125	<3,5E+05	<2,1E+04		<4,3e+04		< 6,0E + 04		
Tc-99m	<4,4E+04	<4,4E+03		< 8,4E + 03		< 1,2E+04		
Te-123m	5,10E+05	<4,3E+03	> 119	<7,7E+03	>66,2	<9,6E+03	> 53.1	
Te-125m	<1,3E+07	<1,3E+06		<1,8E+06		<2,5E+06		
W-187	<3,9E+05	<3,8E+04		< 6,7E + 04		< 8,9E + 04		
Zn-65	2,60E+05	<9,5E+03	>27,4	<2,0E+04	> 13	<2,7E+04	>9,6	
Zn-69m	<3,7E+04	< 3,1E+03		< 7,4E+03		< 1,1E+04		
Zr-95	6,30E+06	1,10E+05	57,3	4,50E+05	14	7,80E+05	8,1	
Zr-97	2,50E+05	< 1,0E + 03	>250	<2,1E+04	> 11,9	< 3,0E + 04	>8.3	
Corrosion products								
Co-58	7,50E+07	1,10E+05	682	4,80E+05	156	1,20E+06	62,5	
Co-60	4,30E+07	3,50E+05	123	1,80E+06	24	3,40E+06	12,6	
Cr-51	3,30E+06	2,60E+05	13	1,90E+06	2	3,30E+06	1,0	
Fe-59	<4,9E+04	<6,7E+03		3,30E+04		4,10E+04		
Mn-54	1,20E+06	8,10E+03	148	5,10E+04	24	1,10E+05	10,9	
Mn-56	< 1,3E+05	< 1,5E+04		<5,5E+04		< 1,4E+05		

Tab. 1 quotes decontamination factors for typical reactor waters in typical nuclear power stations during shutdown in CVCS mixed bed for different resin combinations. Numerous different radioactive nuclides, including fission products, are shown to be efficiently captured and retained.

#### Application in cooling circuits

LANXESS offers some strongly acidic and basic ion exchange resins with the grade identifier KR (refer to section 5.2 for details). They are monodisperse, highly regenerated purified to meet specifications and requirements of the nuclear industry.

LEWATIT® KR resins are noted for their outstanding mechanical, chemical and osmotic stabilities. Because of their excellent hydrodynamic properties, they allow for particularly high flow rates. The high grade of monodispersity and a very small content of fines, i.e. max. 0.1 vol. % for particles smaller than 0.315 mm, result in especially low pressure losses compared to standard resins. When used in radioactively contaminated water circuits, they provide a number of special features, as shown below.

Resins such as LEWATIT<sup>®</sup> MonoPlus S 200 KR (SAC, strongly acidic cationic) or MonoPlus M 800 KR (SBA, strongly basic anionic), respectively, are particularly suitable for:

- Decontamination of circuits in nuclear power plants;
- Removal of radioactive cations. The MonoPlus S 200 KR, for example, is very selective for capturing 137Cs, and it also removes an excess of <sup>7</sup>Li;
- Treatment of primary coolants, e.g. in PWRs;
- Purification of steam generator blow down irrespective of a previous conditioning with Levoxin<sup>®</sup> (hydrazine hydrate), ethanolamine or morpholine;
- Polishing in the primary and secondary circuits as a mixed bed component with a matching KR resin. Very effective combinations are e.g. LEWATIT<sup>®</sup> MonoPlus S 200 KR and MonoPlus M 800 KR, LEWATIT<sup>®</sup> Mono-Plus S 200 KR and MonoPlus M 880 KR, or LEWATIT<sup>®</sup> MonoPlus SP 112 KR and MonoPlus M 800 KR.

If hydrazine, hydroxylamine, morpholine, ethanolamine, or ammonia is applied to prevent corrosion, the feed water – and later on the condensate – will always contain several ppm of ammonia. If ammonia gets in contact with the cationic exchange resins of the condensate polishing unit, they will hold it back, and the majority of absorbed cations will be ammonium. As a consequence, regeneration cycles get shorter. This can be avoided to a certain degree if the level of exhaustion is not determined by the leakage of conductivity, but if it is, in contrast, coupled to the leakage of sodium. However, if a leakage of sodium is finally measured, there is the threat of a chloride leakage on the anionic side. Regeneration has to be performed immediately in this case. Anion polishers should always be used in their OH grades, otherwise the output of chloride will quickly attain a critical level.

A few ion exchange resins are doped with <sup>7</sup>Li since this isotope has a very small neutron cross-section of approx. 45 millibarns. A controlled release of <sup>7</sup>Li enables the operators to steer the flux of neutrons within the aqueous phase and, therefore, to either accelerate or slow down the nuclear chain reaction. <sup>7</sup>Li hydroxide is used for alkalizing the coolant in pressurized water reactors.

#### Cleaning up spent fuel pool process water

Spent fuel pools are used for storing spent fuel rods from nuclear reactors. A water column of approx. 2.4 m height is already sufficient to keep the level of radiation below critical levels. The large extra depth provides a safety buffer. This enables operators to work with the assemblies without protective shielding.

Every year, about a quarter of the whole fuel load of a reactor is removed from the core and replaced with fresh fuel. Spent fuel rods generate a substantial amount of heat and dangerous radiation that must be thoroughly controlled. The fuel bundles freshly removed from the reactor core are usually segregated for several months for initial cooling before being put in the pool.

Metal racks keep the fuel elements in fixed positions at reasonable distance to each other in order to prevent nuclear chain reactions. The water quality is strictly controlled to prevent the fuel elements or the surrounding mechanical equipment from degrading. Within the first two to four years, the surface temperature of the spent fuel bundles decreases significantly. In the course of time, the speed of the cooling process decreases.

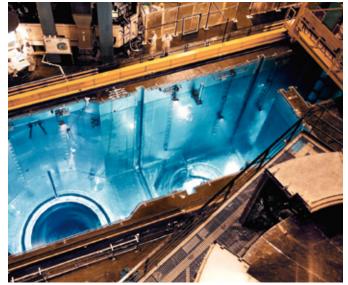
The fuel pool water is continuously cooled to remove the heat produced by the spent fuel assemblies. Pumps circulate water from the spent fuel pool to heat exchangers and back to the spent fuel pool. The temperature of the water is kept below 50°C.

lon exchange resins help to remove any ionic particles. It is very important to tightly check radiolysis occurring in the

pool which may not only cause a generation of hydrogen, but also of hydrogen peroxide.

From time to time, the ion exchange resins employed either need regeneration, or they have to be disposed of in case they are designed for a single use. In both cases, either the aqueous phase or the resin itself has to be stored in steel cylinders after their vitrification. The external surface of the cylinders is afterwards decontaminated; finally, the steel cylinders are stored, usually in underground repositories.





## **CASE STUDY 01** ENHANCING CONDENSATE POLISHING CAPACITY AT E.ON'S POWER STATION IN WILHELMSHAVEN

#### The power plant

E.ON's hard coal power station in Wilhelmshaven was inaugurated in 1976 and has an energy output of 756 MW. It was the first one in Germany having been equipped with a flue gas desulfurization unit as early as 1978. Carbon dioxide emissions of this power station have dramatically been reduced while significantly enhancing the energy output at the same time.



#### The project:

In May 2010, the condensate polishing system in the Wilhelmshaven power station was equipped with new gel-type ion exchange resins in a mixed-bed setup to enhance operation capacity and improve overall operational parameters.

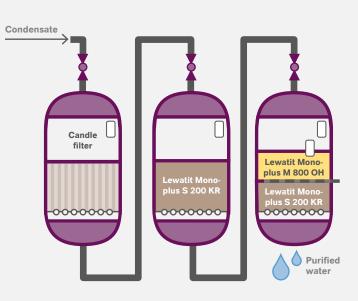
The water-steam cycle is equipped with two ion exchange units of a capacity of up to 250 m<sup>3</sup>/h each for condensate polishing and two units of 25 m<sup>3</sup>/h capacity for demineralization. In the course of the project, the plant's old condensate polishing mixed bed consisting of macroporous cation and anion exchange resins was replaced. It suffered from drawbacks such as bad separation, cross-contamination, leakage of sodium ions, and, as a consequence, a badly utilized capacity in combination with a relatively high consumption of regeneration chemicals.

Newly introduced during normal operation of the power station were gel-type resins, namely LEWATIT<sup>®</sup> MonoPlus S 200 KR and LEWATIT<sup>®</sup> MonoPlus M 800 OH resins.

#### **Results:**

Thanks to the outstanding separation capabilities of these gel-type resins, a drastically reduced tendency to cross-contamination and ionic leaching has been observed. As a result, the operators have been able to enhance the polishing capacity by at least 50%. Therefore, less frequent regeneration and less regeneration chemicals are needed with the new resins. At the same time, the content of fines could be reduced, leading to decreased pressure loss, and, as a consequence, a lower consumption of electrical energy. "I would like to recommend products and expertise of manufacturers of ion exchange resins such as LANXESS in the field of condensate polishing also to other operators of fossil-fuelled power stations. I am impressed by the improvements we have been able to realize."

Ingo Mai, Laboratory Manager Provision and Discharge Chemistry, E.ON Kraftwerke GmbH, is equally content with LANXESS's project management as well as with the installed solution.



#### **Products involved:**

Lewatit<sup>®</sup> MonoPlus S 200 KR (strong acidic, SAC)
Lewatit<sup>®</sup> MonoPlus M 800 OH (strong basic, SBA)

### **CASE STUDY 02** EFFECTIVE CONDENSATE POLISHING AND TOC REDUCTION AT THE GKM AG (GROSSKRAFTWERK MANNHEIM AG)



#### The power plant

The GKM AG (Grosskraftwerk Mannheim AG, "large-scale power station") has been providing electrical power generated from steam since 1923. Its current nameplate output is 1,675 MW, including 190 MW for providing the railway catenaries.

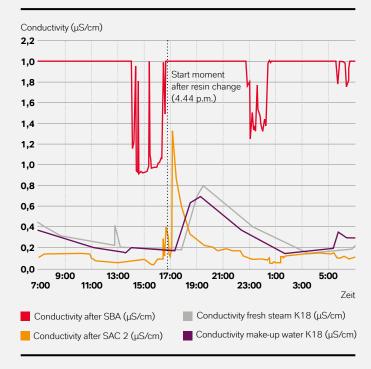
#### The project:

Over years, the GKM operates its condensate treatment units by using cation and anion exchange resins in the form of single filter systems. In the past, challenges have been the enhancement of electrical conductivity in the steam during the ramp-up phase after replacement of the ion exchange resin. The reason for this was organic material (TOC, total organic carbon) released by the standard strongly basic anion exchange resin (SBA) in its chloride form. This quantity of TOC was later on degraded in the hot steam upon which the conductivity increased.

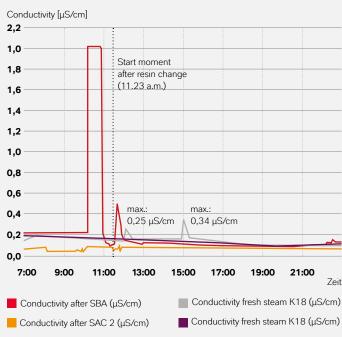
#### **Results:**

By introducing the gel-type, highly regenerated LEWATIT<sup>®</sup> MonoPlus M 800 OH resin into the plant's single bed anion exchange filter in December 2009 during operation, the generation of TOC could be omitted almost completely. As a consequence, the electrical conductivity in the condensate circuit has significantly been reduced (see Fig. 7).

#### Resin change KRA SBA filter column Str.1/ (15.10.2009) using CI- Form







#### Resin change KRA SBA filter column Str.2/ (17.12.2009) using M+ M800 OH<sup>-</sup> Form

#### **Products involved:**

■ Lewatit<sup>®</sup> MonoPlus M 800 OH (strong basic, SBA)

### **CASE STUDY 03** WATER TREATMENT IN THE SPENT FUEL POOL MAKE-UP SYSTEM OF THE NUCLEAR POWER PLANT EMSLAND (NPP EMSLAND)

#### The power plant

The Emsland NPP (nuclear power plant) in Germany belongs to the RWE group, a large power supply company in Germany. The power plant, a PWR of the KONVOI design from Siemens, came into operation in 1988. The reactor contains 193 fuel elements with a total thermal power output of 3,800 MW. The total electrical power output is 1,400 MW.



#### The project:

The mixed bed filter of the spent fuel pool make-up system had a shorter running life than comparable filters due to blocked downstream candle filters by degradation products of the exchange resins. The make-up system, as a consequence, had to be turned off quite frequently for a short time span and the resin had to be exchanged. It was assumed that the reason for this was the chemical effect of hydrogen peroxide having been generated by radiolysis in the spent fuel pool.

#### **Results:**

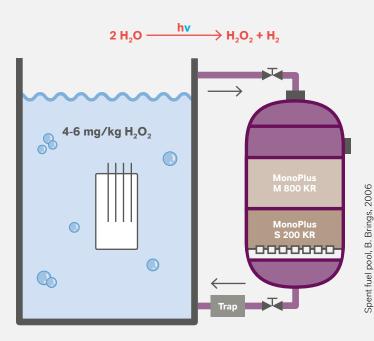
KR resins with a high share of cross-links were introduced in spring of 2010. Due to the more robust backbone structure of the resin molecules, the beads are stabilized to efficiently prevent a possible degradation effectuated by hydrogen peroxide. Moreover, KR resins have got high capacities to effectively bind even traces of cations and anions in the corresponding aqueous system.

By using a new mixed bed resin composition, consisting of the gel-type LEWATIT<sup>®</sup> MonoPlus S 200 KR and the LEWATIT<sup>®</sup> MonoPlus M 800 KR resins, it became possible to establish longer operation spans of the corresponding system.



"On the whole, the operation lifetime of the mixed bed filter is no longer governed by the blocking of filters but only by the ion capacity of the resin. This is also highly beneficial for minimizing radioactive waste."

Dr. Timo Stoll, Head of Chemistry, NPP Emsland, 49811 Lingen/Germany



#### Products involved:

Lewatit<sup>®</sup> MonoPlus S 200 KR (strong cationic, SAC)
Lewatit<sup>®</sup> MonoPlus M 800 OH (strong basic, SBA)

### **CASE STUDY 04** EFFICIENT REMOVAL OF IONS FROM REVERSE OSMOSIS PERMEATE AT SORFERT ALGÉRIE NITROGEN FERTILIZER COMPLEX ARZEW, ALGERIA

#### The power plant

In 2012, Sorfert Algérie built a new fertilizer plant in Arzew (Algeria), close to Oran and 350 km southwest of Algiers. The US\$2 billion investment consists of an industrial complex with two ammonia plants, each with a total production capacity of 2,200 tons/day, and a urea plant with a production capacity of 3,450 tons/day.

The plant has got a water-steam circuit. A reverse osmosis (RO) plant is fed with seawater, and the resulting permeate is led into a cation and anion exchange unit. Finally, the condensate is treated in a condensate polishing mixed bed.



#### The project:

The electric conductivity of the permeate is higher than 500  $\mu$ S/cm, and the permeate contains approx. 0.6 meq/l of calcium, 1 meq/l of magnesium, 5 meq/l of sodium, and low concentrations of potassium and ammonium ions leading to a total cationic concentration of 7 meq/l. The chloride concentration of the permeate amounts to approx. 6.5 meq/l, other anions occur in only minor amounts. In addition to water from RO, condensates from the process are also treated in cation and anion exchange. Waters with low concentration of minerals, e.g. condensate from the turbines or the product of thermal desalination, are treated in the mixed bed units.

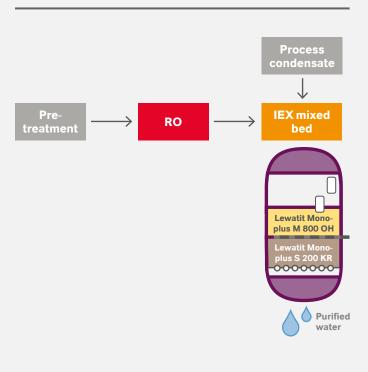
#### **Results:**

Both the demineralization and the mixed bed units of this fertilizer plant have been equipped with LEWATIT<sup>®</sup> ion exchange resins. These are working very reliably regarding the removal of cations and anions from the permeate (feed water) and the condensate as well.

By installing LEWATIT<sup>®</sup> MonoPlus S 200 KR and LEWATIT<sup>®</sup> MonoPlus M 800 both in the demineralization unit and in the mixed bed unit, a very effective removal of ions could be achieved.

"The fertilizer plant including off-sites and utility systems needs up to 1,200 m<sup>3</sup>/h of polished water. This alone is a remarkable requirement which can only be satisfied by a sophisticated combination of reverse osmosis and ion exchange resins as LANXESS provides it."

Lothar Grum, Senior Package Unit Engineer at ThyssenKrupp Uhde GmbH



#### **Products involved:**

Lewatit<sup>®</sup> MonoPlus S 200 KR (strong cationic, SAC)
Lewatit<sup>®</sup> MonoPlus M 800 (strong basic, SBA)



### **CASE STUDY 05** USE OF MACROPOROUS RESINS IN A NEW POWER PLANT AT POČERADY POWER STATION, CZECH REPUBLIC



#### The power plant

The Czech power stations owned by the large supplier CEZ have extensively been adapted to an ecologically friendly production as of the mid 1990s. In all, 28 desulfurization units and seven fluid vessels have been installed, and the handling systems have been improved. Emissions of sulfur dioxide and ash could be reduced by 90%, that of nitrogen oxides by 50%. Overall, 6,462 MW of electrical output capacity have been desulfurized by gas scrubbing or wet calcium hydroxide wash in that way.

The five 200 MW blocks of Počerady power station were equipped with a wet calcium hydroxide washing system between 1994 and 1996. At present, new gas and steam turbine power generation units are either under construction or have recently come onstream, with an additional output of 840 MW.

#### The project:

A new plant of the Počerady complex has been equipped with mixed beds based on macroporous LEWATIT<sup>®</sup> MonoPlus resins. The operators attached high value to mechanical and osmotic stability since the mixed beds are regenerated externally.

The plant's condensate polishing system is characterized by a throughput of  $2 \times 250 \text{ m}^3$ /h with a projected extension to  $2 \times 320 \text{ m}^3$ /h. The typical temperature of the water is 40°C. The central quality requirement for the treated condensate is a conductivity of less than or equal to 0.3 µS/cm.

#### **Results:**

The practical experience with macroporous LEWATIT<sup>®</sup> resins is very good.

In the case of the cation exchange resin, the end of the cycle is governed by the maximum allowed conductivity being reached. Its length lies between 150,000 and 400,000 m<sup>3</sup>, depending on the quality of the condensate.

For the mixed bed system, the criterion for the length of a cycle had been the breakthrough of silica in past times – before the project started. These cycles were very long, usually more than half a year passed between two regenerations. Nowadays, the frequency of regeneration is mainly determined by conductivity data. As a result, the operators usually decide to regenerate every two months, even when the water analysis is still sufficient.



#### **Products involved:**

Lewatit<sup>®</sup> MonoPlus SP 112 (strong cationic, SAC)
Lewatit<sup>®</sup> MonoPlus MP 500 (strong basic, SBA)

## PRODUCT OVERVIEW: SELECTING THE RIGHT LEWATIT<sup>®</sup> RESIN



Different grades of LEWATIT<sup>®</sup> are tailored to meet all sorts of customer requirements:

Usually, **normal grades** of our LEWATIT<sup>®</sup> resins already meet most of the requirements even in critical conditions of operation.

**MB grades** are specially manufactured for their application in mixed beds. The share of cross-links is exactly applied to attain best results. They have high regeneration efficiency and, at the same time, consumption of rinse water is low. The anionic forms are miscible with the cationic ones without problems, and their separation and regeneration is easy due to differences in color and density.

LANXESS offers some strongly basic, monodisperse anion exchange resins in highly regenerated forms (min. 80% of OH) which are designed for all polishing applications. Both gel-type and macroporous resins are available in their OH forms. These **OH grades** are especially useful for polishing processes conducted in the LEWATIT<sup>®</sup> Multistep System or in conventional mixed bed arrangements, and they are preferably used in combination with the corresponding H grades, e.g. LEWATIT<sup>®</sup> MonoPlus SP 112 H or LEWATIT<sup>®</sup> MonoPlus S 108 H. **KR grades**, e.g. LEWATIT<sup>®</sup> MonoPlus M 500 KR, are specially purified and highly regenerated, and have, as a rule, a share of at least 95% of OH groups. KR resins are very stable to mechanical, chemical and osmotic impacts. Due to their excellent hydrodynamic behavior they allow high flow rates. In addition, they are monodisperse, combined with a low content of fines, and the pressure losses are lower than for standard grades. If they are used in water circuits containing radioactive materials, they safeguard a water quality fully meeting the requirements of the nuclear power industry.

# 5.1 TREATMENT OF CONDENSATES

The resins have to thoroughly remove all traces of hardness constituents and other ionic impurities occurring in the con-

densate. LEWATIT<sup>®</sup> resins, both strongly acidic and basic ones, have been successfully in use for many years for this purpose.

#### Ion exchange resins for treatment of non-radioactive condensates

Product	Product Matrix	Total Capacity (eq/l) min.	Bead Size (mm): <u>Monodisperse</u> (MD, mean val.) <u>Heterodisperse:</u> HD, Share >90%	Uniformity Coefficient max.	Applications
SAC					
ewatit MonoPlus® Styrene/DVB gel 5 108 H		2.0	MD: 0.65 (+/- 0.05)	1.1	Demineralization Make-up water Mixed bed component
Lewatit MonoPlus® SP 112	Styrene/DVB, macroporous	1.7	MD: 0.65 (+/- 0.05)	1.1	Condensate polishing Demineralization Make-up water
Lewatit MonoPlus® SP 112 H	Styrene/DVB, macroporous	1.6	MD: 0.67 (+/- 0.05)	1.1	Condensate polishing Demineralization Make-up water Mixed bed component
Lewatit MonoPlus® S 200 H	Styrene/DVB gel	2.1	MD: 0.60 (+/- 0.05)	1.1	Condensate polishing Demineralization Make-up water
SBA					
Lewatit MonoPlus® M 500 OH	Styrene/DVB gel	1.1	MD: 0.64 (+/- 0.05)	1.1	Condensate polishing Mixed bed component
Lewatit MonoPlus® MP 500	Styrene/DVB macroporous	1.1	MD: 0.62 (+/- 0.05)	1.1	Condensate polishing Demineralization Make-up water Mixed bed component
Lewatit MonoPlus® MP 500 OH	Styrene/DVB macroporous	0.9	MD: 0.65 (+/- 0.05)	1.1	Condensate polishing Mixed bed component
Lewatit MonoPlus® M 800	Styrene/DVB gel	1.4	MD: 0.59 (+/- 0.05)	1.1	Condensate polishing Mixed bed component
Lewatit MonoPlus® M 800 OH	Styrene/DVB gel	1.2	MD: 0.64 (+/- 0.05)	1.1	Condensate polishing Mixed bed component
Lewatit MonoPlus® MP 800	Styrene/DVB macroporous	1.0	MD: 0.62 (+/- 0.05)	1.1	Condensate polishing Demineralization Make-up water Mixed bed component
Lewatit MonoPlus® MP 800 OH	Styrene/DVB macroporous	0.8	MD: 0.65 (+/- 0.05)	1.1	Condensate polishing Mixed bed component

# **5.2 TREATMENT OF RADIOACTIVELY CONTAMINATED WATER**

#### Ion exchange resins for treatment of radioactively contaminated water

Product	Product Matrix	Total Capacity (eq∕l) min.	Bead Size (mm): <u>Monodisperse</u> (MD, mean val.) <u>Heterodisperse:</u> HD, Share >90%	Uniformity Coefficient max.	Main Applications
SAC					
Lewatit MonoPlus® S 108 KR	Styrene/DVB gel	2.0	MD: 0.65 (+/- 0.05)	1.1	Condensate polishing
Lewatit MonoPlus® SP 112 KR	Styrene/DVB, macroporous	1.6	MD: 0.67 (+/- 0.05)	1.1	Condensate polishing
Lewatit MonoPlus® S 200 KR	Styrene/DVB gel	2.1	MD: 0.60 (+/- 0.05)	1.1	Condensate polishing
Lewatit MonoPlus® S 200 KR Li	Styrene/DVB gel	2.1	MD: 0.60 (+/- 0.05)	1.1	Condensate polishing primary loop
Lewatit MonoPlus® S 215 KR	Styrene/DVB gel	2.4	MD: 0.60 (+/- 0.05)	1.1	Condensate polishing Permanganate acid production
Anion Exchange Resi	ns				
Lewatit® A 8075 KR	Polyacrylate macroporous	3.5	HD: 0.4 -1.6	1.7	Clean-up of radioactive waste
Lewatit MonoPlus® M 500 KR	Styrene/DVB gel	1.1	MD: 0.64 (+/- 0.05)	1.1	Condensate polishing
Lewatit MonoPlus® M 800 KR	Styrene/DVB gel	1.2	MD: 0.64 (+/- 0.05)	1.1	Condensate polishing
Lewatit MonoPlus® MP 500 KR	Styrene/DVB gel	0.9	MD: 0.65 (+/- 0.05)	1.1	Condensate polishing
Lewatit MonoPlus® MP 800 KR	Styrene/DVB gel	0.8	MD: 0.65 (+/- 0.05)	1.1	Condensate polishing
Mixed Bed Systems					
Lewatit MonoPlus® SM 1000 KR	Styrene/DVB gel	2.1 C/1.2 A	MD: 0.60 +/- 0.05 C 0.64 +/- 0.05 A	1.1 C/1.1 A	Condensate polishing/ Spent fuel treatment
Lewatit MonoPlus® SM 1015 KR	Styrene/DVB gel	2.4 C/1.2 A	MD: 0.60 +/- 0.05 C 0.64 +/- 0.05 A	1.1 C/1.1 A	Condensate polishing, particular suitable for amine conditioned systems
Lewatit MonoPlus® SM 1000 KR <sup>7</sup> Li	Styrene/DVB gel	2.1 C/1.2 A	MD: 0.60 +/- 0.05 C 0.64 +/- 0.05 A	1.1 C/1.1 A	Condensate polishing primary loop
Lewatit MonoPlus® SMP 1000 KR	Styrene/DVB gel	1.6 C/0.8 A	MD: 0.67 +/- 0.05 C 0.65 +/- 0.05 A	1.1 C/1.1 A	Demineralization, decontamination and elimination of rad. waste: Decon- tamination of circuits in nuclear reac- tor plants. Removal of activated cleav- age or corrosion products, including mechanical filtration of suspended impurities. Treatment of waste water in e.g. TEU-systems.

\*fb – free base



# PHOTOGRAPHY

Page 2 Voith Hydro Holding GmbH & Co. KG

Page 5 Corbis GmbH

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Page 18–19 Grosskraftwerk Mannheim Aktiengesellschaft, Mannheim Page 20–21 KKW Lippe-Ems, Lingen

Page 22–23 ThyssenKrupp Uhde GmbH, Algeria

Page 24–25 Počerady Power station, Czech Republic

All other photo subjects: LANXESS Deutschland GmbH

# CONTACT

#### Headquarter:

LANXESS Deutschland GmbH Kennedyplatz 1 50569 Cologne, Germany lewatit@lanxess.com www.lpt.lanxess.com

#### NAFTA:

LANXESS Sybron Chemicals Inc., Birmingham, NJ, US, Fax: +1 609 894 8641 ionexchange@sybronchemicals.com www.lpt.lanxess.com

#### **ASIA PACIFIC:**

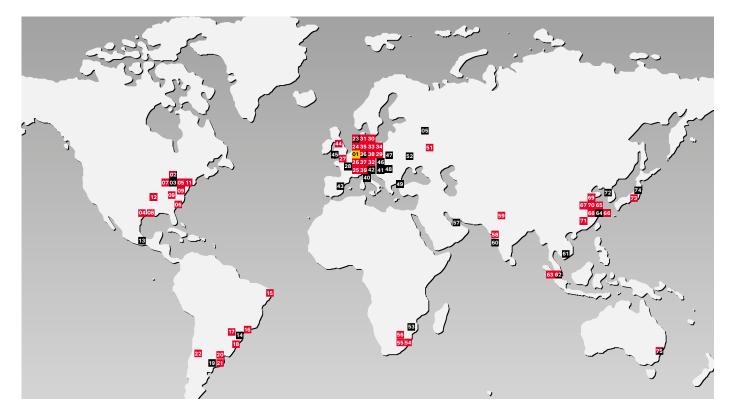
LANXESS Pte. Ltd., Singapore Fax: +65 6 2666959 lewatit.sg@lanxess.com

#### **JAPAN & SOUTH KOREA:**

LANXESS K.K., Minato-ku, Tokyo, Japan Fax: +81 3 3280 9869 lewatit.jp@lanxess.com

#### SOUTH AMERICA:

LANXESS Industria de Productos Quimicos e Plasticos Ltda, Sâo Paulo, Brazil Fax: +55 11 3741-2555 lewatit.br@lanxess.com



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LANXESS Deutschland GmbH Liquid Purification Technologies Kennedyplatz 1 50569 Cologne, Germany

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