

CLEAN



WASTE WATER

**Keeping Waste Water Clean
with Lewatit® Ion Exchangers**

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X LEWATIT®
ION EXCHANGE RESINS

LANXESS
Energizing Chemistry

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1. INTRODUCTION

1.1 THE WORLD OF WASTE WATER

In this world, there are as many types of waste waters as there are industrially produced goods and manufacturing processes. Waste waters are a natural consequence of human activity. Where people live and work, waste waters will always be found.

Waste water from industrial production can contain an unspeakable variety of different inorganic and organic chemicals, in all combinations and concentration levels. The whole spectra of synthetic and natural chemicals can be found in these streams.



figure 1: Waste water is a natural consequence of human activity

Waste waters vary in composition in step with their related production processes. The concentration levels of these ingredients, however, are not always so clearly defined. They vary in ranges according to the fluctuations in the production processes and are normally characterized by average, minimum or by peak values.

There are waste waters that occur only in small quantities per day. These can easily be collected and disposed of over time. In contrast, there are remarkably huge waste water streams of several thousand cubic-meters per hour. They can only be handled with continuously operating large scale plants, often the same size as the production units.

Waste water streams are often combined in networks and can influence one another. In between they are stored, treated, mixed, further treated, etc. Usually they are running through several pipelines, tanks and treatment units before they are finally discharged into the environment.

Waste waters are discharged into a variety of environments with different geological and ecological characteristics. In addition to their scientific characteristics, these environments have different political systems, with different regulations, and different levels of infra-structure sophistication. As a result, the significance of a individual waste water, independent of composition, is different, depending on the location where it appears. For all of these reasons, each waste water is unique. Unique in its composition, in the way it changes its properties, and in its relation to its environment.

Getting a clear picture of a waste water is not an easy job. One has to go through a thorough analysis to clarify its nature. Thereby a chemical analysis is just the first step of a much more work intensive project.



figure 2: Before waste water is legally discharged into the environment, it runs through a network of storage-, control- and treatment steps before

1.2 THE TOOLBOX OF A WASTE WATER TECHNICIAN

As a consequence of their unique character, every measure to keep waste waters clean is individual and has to be adjusted to the specific environment of the distinct waste water. There rarely are solutions off-the-shelf. Efficient solutions can only be obtained by specialists with a solid knowledge of all the relevant chemical, physical, biological and economical backgrounds.

To find these solutions, waste water specialists require a well-equipped tool-box, containing different unit-operations, based on a variety of operating principles. Typically, each one of these unit-operations is so complex, that dealing with one alone is already a specialty in itself. Having a full overview of them all is nearly impossible, but there are a few waste water technicians that come very close.

Mechanic Treatment

- screening
- sedimentation
- flotation
- filtration
- microfiltration
- ultrafiltration
- nanofiltration
- reverse osmosis

Physical Treatment

- adsorption by solid adsorbers
- extraction with liquid extractants
- flocculation / coagulation

Chemical Treatment

- precipitation
- wet oxidation
 - fenton
 - ozonolysis
 - oxygen
- autoclave-hydrolysis
- reduction
- ion-exchange
- chemisorption
- incineration

Thermal Treatment

- evaporation
- distillation
- steam-stripping

Biological Treatment

- aerobic biological degradation
- anaerobic biological degradation
- degradation by immobilized and specialized microorganisms

figure 3: The toolbox of a waste water technician. There is a variety of unit operations available. Each has to be used and combined in the most efficient possible way to achieve a technically, economically and ecologically useful solution. The unit operations marked in red can be realized with the LANXESS-Products that are described in this paper.

Individual waste waters can theoretically be cleaned by different methods. Looking at a specific case, it is often possible to name several methods at first glance. For instance, in the case of a water stream polluted with the toxic organic compound phenol, the following methods can be applied to remove it from the water:

1. adsorption with activated carbon
2. steam stripping or distillation
3. wet oxidation
4. reverse osmosis
5. extraction with organic liquid/liquid extractants
6. adsorption with ion exchangers
7. biologic degradation

The challenge now is to choose the most effective, inexpensive, and most ecologically relevant method under the given frame conditions. This task almost always involves laboratory testing, and often pilot testing. Only by means of laboratory testing can the interested parties be sure that the planned treatment process will work at the end of the day. At the same time it is possible to generate useful data for the design of a full-scale unit.



figure 4: It does not take much to test ion exchange resins in laboratory scale. A pump and a glass-column are most important. The rest is standard equipment.

2. TO FIND THE OPTIMUM WASTE WATER TREATMENT CONCEPT

2.1 QUESTIONS TO BE ANSWERED WITHIN A WASTE WATER TREATMENT PROJECT

During the development-phase for a suitable waste water treatment concept, the following questions have to be answered:

- Where does the water come from and how is it generated? Is it a mixture of different waste waters? Does the composition change with time? Is there a buffer tank in between that helps to equalize fluctuations?
- Where is the waste water sent to after the treatment? Is there a buffer tank where it is further diluted? Is there a chance to adjust the pH before it is discharged?
- What is the ideal form of a secondary waste stream resulting from the waste water treatment? How should the secondary waste stream look like so that it can be re-used in the production process or sent to a downstream waste treatment process?
- Who will operate the waste water treatment unit? Which level of education is required? Who maintains the process control equipment? Is it better to have manual process control or full automation?
- What kinds of energies (electric power, steam, water, and chemicals) are available and which of these would be advantageous to use?
- What are the relevant local regulations? Which ingredients of the waste water are especially critical and which one can be neglected?
- Which unit operation is especially efficient to treat the waste water and can eventually remove more than one of the critical ingredients at the same time?
- How can different unit operations be combined and which order has the most advantages. How do the different steps mutually influence each others? How have the steps to be tuned to allow the best fit and also the highest level of usage.
- What are the most effective operating supply items (types of ion-exchangers, types of activated carbon, and other adsorbers), consumer item qualities (steam, process water, agents), separating medias (e.g. types of membranes and filter cloth, ...)?

- What are the most effective operating conditions (dosing rates, residence times, contact times, flow velocities, ...)?
- Are there any negative effects that can disturb the regular operation (e.g. plugging of nozzles, and other sensitive parts by fouling or crystallisation processes, intoxication of activated bio-mass, irreversible adsorption, ...)
- Are there any toxic products resulting from side reactions (chlorinated hydrocarbons, metabolites of bacterial degradation) ?
- What is the basic design (sizing) of the relevant units (sizing of filter-beds, membrane surface, volume of agitated tanks, ...)?
- What are the appropriate materials of construction?
- What are the available foot-print and the height of the building? Is a separate building necessary?
- ...

With all the assorted questions, it is clear that many different aspects must be considered, and much information collected, before a suitable concept can be developed. The task requires the care of one or more specialists. Different parties must cooperate: the “producer” of the waste water, the original equipment manufacturer (OEM), the future operator of the waste water treatment plant, the equipment provider, local authorities, etc. Combining the information and coming to a viable solution is often like working on a puzzle or playing a game of chess.

In many waste water projects, the application of ion exchange is warranted. In these cases there are suitable specialists available at LANXESS. We are eager to help find solutions by supplying relevant data from our files, and in some cases generating the required data through testing in our laboratories.

3. PRINCIPLE OF ION EXCHANGE AND OVERVIEW OVER DIFFERENT TYPES OF RESINS

3.1 CONSTITUTION AND OPERATING PRINCIPLES

Synthetic and industrially produced ion exchange resins consist of small, porous beads that are insoluble in water and organic solvents. The most widely used base-materials are polystyrene and polyacrylate. The diameter of the beads is in a range of 0.3 to 1.3 mm. The beads contain around 50% of water, which is dispersed in the gel-structured compartments of the material.

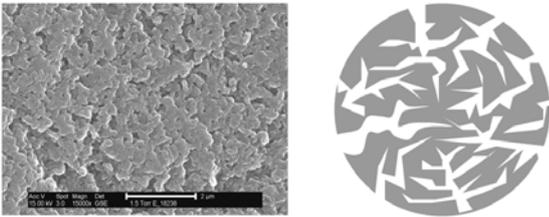


figure 5: Ion exchange resin beads contain many fine pores that fill with water. The water content of some types is up to 70%.

Since water is dispersed homogenously through the bead, water soluble materials can move freely, in and out.

To each of the monomer units of the polymer, so called “functional groups” are attached. These functional groups can interact with water soluble species, especially with ions. Ions are either positively (cations) or negatively (anions) charged. Since the functional groups are also charged, the interaction between ions and functional groups is exhibited via electrostatic forces. Positively charged functional groups (e.g. a quarternary amine) interact with anions and negatively charged functional group (e.g. a sulfonic-, phosphonic- or carboxylic acid group) will interact with cations.

The binding force between the functional group and the attached ion is relatively loose. The exchange can be reversed by another ion passing across the functional group. Then another exchange reaction can take place and so on and so on. One exchange reaction can follow another.

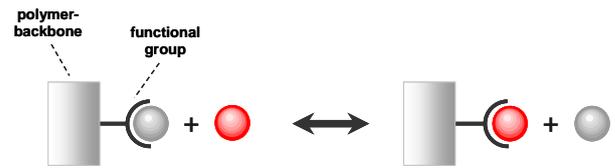


figure 6: a fixed and a mobile ion are changing places in a so-called ion exchange reaction. This simple reaction scheme is the base for more than 500 applications involved in the purification of water and other fluid media.

3.2 THE PRINCIPLE OF SELECTIVITY

There is a huge variety of existing ions. Let us especially have a look at the different types of cations. We distinguish different types of alkali-cations (sodium, potassium, ...), of earth- and rare-earth-alkali-cations (magnesium, calcium, strontium, barium, lanthanum, iridium, ...), heavy metal ions (lead, cobalt, nickel, mercury, ...), light metal cations (aluminium, beryllium, titanium, ...), semi-metal-cations (germanium, gallium, indium, ..), noble metal cations (gold, silver, platinum, palladium, ...).

By investigating the adsorption of different kinds of cations on ion exchange materials, it is found that different ions do interact differently with the functional groups of ion exchangers. Some are strongly bound, some are less strongly bound.

This results in the fact, that a weakly bound ion can preferably be displaced by a stronger binding ion. This effect is called the principle of “selectivity”. A more selective ion binds more strongly than a less selective ion.

The effect of selectivity can be used to remove distinct ions from water and to replace them with others. Applications are found not only in industry, but also in household, where the use of ion exchangers for water softening is well known. In water softening applications the hardness causing calcium-cations are bound and exchange the weaker binding sodium or hydrogen cations.

Especially for waste water applications so called “chelating resins” have been developed, which have a high selectivity for toxic heavy metal ions. These materials selectively adsorb the toxic components from the waste stream and leave the less toxic components, such earth alkali and alkali metals untouched.

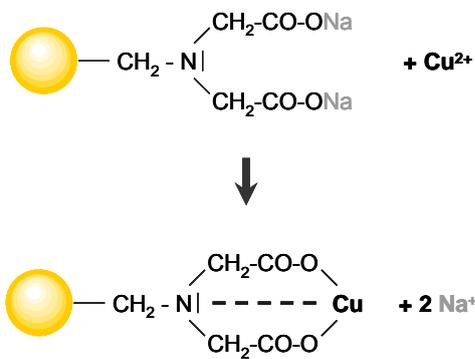


figure 7: Mechanism of binding of a copper-ation to the functional group of an imino-di-aceticacid-resin (IDA-resin). A so called “coordinative complex binding” of especially high stability is formed. The electrostatic interaction between functional group and cation is supported by the interaction of the free electron pair of the amine-group.

The high affinity of chelating resins towards heavy metal ions is accomplished via the formation of a so called “complex – bonding”. In this special type of bonding the functional group and the ion do not only interact via electrostatic forces. Additionally there is a so called “coordinative bonding” which supports and strengthens the interaction, making it tighter than a usual binding. In **figure 7** there is an example of this type. The exchange of sodium ions by a copper ion is shown. The copper is bound via two electrostatic types of bonds and by the interaction of the sole electron pair of the nitrogen atom of the functional - group.

The selectivity of ion exchange resins is expressed via the so-called selectivity series. **Figure 8** shows the selectivity series for an IDA resin. As can be seen, the heavy metal ions bind more strongly than the alkali earth ions and these bind more strongly than alkali metals.

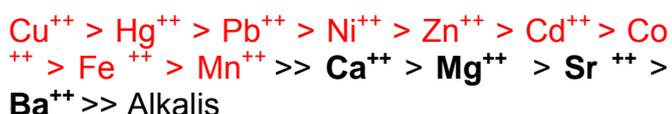


figure 8: Selectivity series of an imino-di-acetic acid (IDA)-resin. Only a selection of ions (mainly divalent ones) is given. Heavy metal ions are preferably bound.

3.3 THE PRINCIPLE OF EQUILIBRIUM AND MASS ACTION

Selective ions displace less selective ions as mentioned previously. The exchange continues as long as there are enough selective ions available for the resin to exchange and/or until the functional groups are saturated with the selective ions.

In some cases this means that all of the functional groups have lost the less selective ion and have taken up a selective ion. It can also mean that the exchanger reaches a certain level of loading with a certain ratio of functional groups that remain un-exchanged and still carry the less selective ions. This effect is called the effect of equilibrium or in other words the effect of mass action.

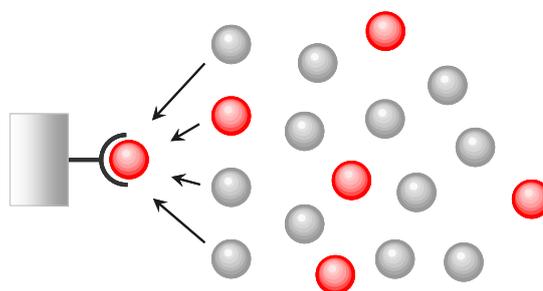


figure 8.1: Binding of ions to functional groups involves continuous competition. Which type of ion is adsorbed and how long it stays fixed is ruled by the binding forces (selectivity) and the ratio of concentrations. The higher the concentration of an ionic species is, the higher is its effect – which is called the rule of mass action.

This effect comes from the fact that the less selective binding ions still affect the degree of exchange. Due to the weaker interaction force however, its effect is not as great. Even though the attraction forces are weak, the effective force increases with the concentration of the less selective ions. For example, if the attraction force is 100 times weaker but the concentration is 100 times higher; the less selective ions can equal the higher selective species in the final reaction. This is called the impact of mass action. As a result, to understand the exchange rate in a certain exchange situation, both the binding force and the concentration levels must be considered.

Thus dealing with ion exchange applications in waste water treatment requires full knowledge about water composition to judge competing effects. Once known, a better understanding of the efficiency of the process can be realized. If the ratio of concentrations of less selective to highly selective

ions is low, high operating capacities resins can be expected. If the ratio of concentrations is high, lower operating capacities will be realized. Therefore the efficiency of a waste water treatment process always depends on the water composition which is individual – as already mentioned above.

3.4 REGENERATION OF ION EXCHANGERS

The principle of displacement of selectively binding ions by less selective binding ion is the basis for each regeneration procedure. Most ion exchangers can be regenerated by acids (excess of H⁺-ions), salt-brines (excess of sodium or chloride ions) or by alkali (excess of OH⁻ ions). During regeneration the adsorbed ions are removed and replaced by the ions named above.

The spent regenerant solution contains the formerly adsorbed pollutants in a concentrated form. In some cases the solutions must be treated for disposal. In other cases the solutions can be re-used in the production process where the waste water was generated.

For effective regeneration, the stronger an ion binds on the ion exchanger, the more regenerant solution must typically be applied. Thus a resin with high selectivity may have advantages regarding the efficiency of removal from the waste water, but the regeneration efficiency must also be taken into account to judge the overall value of the process.

3.5 ADSORBER RESINS

Next to ion exchange resins stands a close group of products, the so called adsorber resins. From the outside they look similar: little beads of a porous material. The striking difference is the lack of functional groups.

Even though adsorber resins are not functionalized, they have the potential to remove ingredients from water. Typically organic materials with low solubility in water can be adsorbed. These so called hydrophobic substances tend to get close to lipophilic surfaces. Adsorber resins provide a huge surface of these lipophilic surfaces inside their pores, resulting in a high capacity for hydrophobic molecules.

Adsorber resins adsorb through mechanisms similar to activated carbon. They can be regarded as a kind of “fully synthetic” activated carbon.

The appropriate way to regenerate these materials strongly depends on their physical properties. Those are characterized by their vapour pressure (volatility) or solubility in organic solvents, bases, or acids.

Volatile substances can be removed by steam-stripping, whereas non-volatile substances can be removed by liquid stripping media, in which they are soluble.

In contrast to activated carbon the adsorber resins can be regenerated more than 1000 cycles without thermal reactivation. These materials do not bleed minerals and possess a much higher mechanical stability than activated carbon. They do not form dust or fines by abrasion that plug the filter bed and pollute the regenerant or the treated water with suspended solids.

3.6 EQUIPMENT CONSIDERATIONS

Ion exchangers are typically applied in pressure vessels. They are equipped with appropriate internal plumbing that has two purposes: first it prevents the ion exchange resin from being washed out of the vessel and secondly it provides the appropriate distribution of liquid flow through the ion exchange bed.

In the simplest case the internal system is a screen, mounted above a porous backing plate. More commonly, slit nozzles (strainers), mounted in star- or so called fishbone piping, or fixed in equal distances directly onto the base- or cover plate are found.

The slit width in these strainers is 0,2 to 0,3 mm, which is fine enough to effectively restrain the ion exchange or adsorber resin beads. At the same time pressure drop is low.

Usually the pressure vessel is filled to only half of its volume. The empty space above the ion exchanger bed is called “freeboard”. The freeboard has several functions: First of all it allows the ion exchanger bed to “breathe”. This is necessary because the exchangers often shrink or swell during operations of exhaustion, regeneration and conditioning. The specific volume of the resin can change by up to 70% of its original volume.

Secondly the freeboard is used for backwashing the ion exchanger bed. Thereby the backwashing water is flowing through the resin bed in upflow mode and fluidizes the bed. Depending on the linear velocity the bed expands by a certain ratio

and the beads leave their fixed positions and roam around. Backwashing loosens the bed, breaks up clumps, and destroys larger channels that have been established. At the same time entrapped suspended particles or broken beads are removed. When backwashing is finished the bed lays down in a homogenised package that permits uniform flow in following operating steps.

If an empty pressure vessel is to be filled with ion exchange beads these can easily be filled in by hydraulic transportation. In the same way a pressure vessel can be emptied by washing out the beads. In the planning of an ion exchange plant for this procedure dedicated pipelines have to be considered.

It is very useful to provide sight glasses in the walls of the pressure vessels to permit observing the condition of the filter bed during operation. Especially the larger filters should be equipped with windows. The windows should be arranged in a manner that the bottom window tracks the bulk of the filter bed, the medium window tracks the surface, and the top window tracks the freeboard.

The most practicable way to connect the pressure vessel to the piping is to only have one connection at the top and one connection at the bottom with different connections realised by T-connectors.

Figure 9 gives an example for the construction of an ion exchange column with its basic constituents.

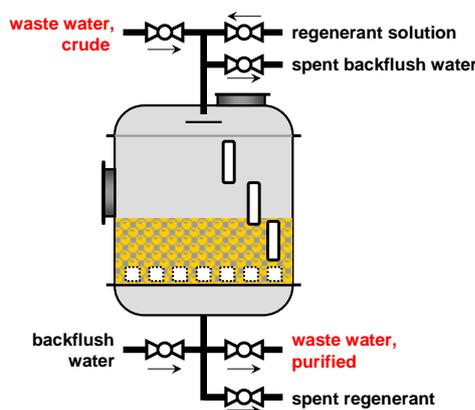


figure 9: basic constituents of an ion exchange column

In technical installations ion exchange columns are rarely stand-alone units. Usually they are installed as twins in series (Lead/Lag - concept) or triplets (Merry go round-concept). Having more

than one filter unit permits continuous operation with one filter on-line and the other one in the regeneration cycle. It is sometimes useful to have two filters in series whereby the lag-one serves as a polisher or a police filter for the first one.

3.7 SPECIAL ADVANTAGES AND FIELDS OF APPLICATIONS FOR ION EXCHANGERS

The application of ion exchangers is particular advantageous if the pollutant that has to be removed from waste water binds with especially high selectivity. Then the filters capacity is mainly used up to adsorb the pollutant only and is not consumed by other, non-critical components.

Simultaneously a second advantage is realized, particularly if the pollutant is already in a low concentration. The results are long cycle times and high concentration factors in comparing the concentration of the pollutant in the spent regenerant and in the original waste water. Concentration factors of > 10 already are advantageous but in some practical cases concentration factors of 1000 and higher can be achieved. As a rule of thumb the concentration of a pollutant in waste water should not extend 300 ppm to allow efficient operation.

A third advantage is realized when waste water streams are relatively large and alternate treatment methods simply exceed the size of the regular equipment. As an example, site space does not permit the installation of evaporation ponds or precipitation tanks. In this case an ion exchange filter unit can be used to change a large waste water stream into a small concentrated spent regenerant stream that is more convenient to be treated further in smaller conventional processes.

In **box 1** the advantages and disadvantages of competing waste water treatment methods are discussed in a case study. Similar trains of thought are passing through the head of a waste water engineer while he is planning a waste water treatment concept.

In this case the advantages clearly lay on the side of the ion exchange technology when it is combined with post-treatment of the spent regenerant by precipitation or electro winning. The same advantages can also be found in other cases, particularly, when the spent regenerant solution is reused in the related production process. This case is often found in applications at metal finishing, in the winning and refining of metals, in the production of organic materials as well as in the production of batteries.

box 1:

Case Study: Evaluation of Different Waste Water Treatment Methods in a Particular Case		
Frame Conditions		Flow rate: 100 m ³ /h , c Cu 100 mg/L, c NaCl: 10 g/L, rest concentration c Cu: 0,5 mg/L
Reverse Osmosis	Disadvantages	<ul style="list-style-type: none"> • high specific energy consumption • no selectivity, salt is accumulating in retentate • concentration factor in maximum $f = 30$, otherwise over saturation of NaCl • electro winning of Cu not possible due to chloride in concentrate
Nanofiltration	Disadvantages	<ul style="list-style-type: none"> • low selectivity, salt partially accumulates in retentate • no sufficient rejection of Cu; limits difficult to reach
Evaporation	Disadvantages	<ul style="list-style-type: none"> • same disadvantages as with reverse osmosis • at flow rate of 100 m³/h extremely large invest costs
Precipitation	Disadvantages	<ul style="list-style-type: none"> • to provide 0.5 h of residence time agitated vessels of 50 m³ volume need to be installed. Also precipitation tanks of the same size and a filter press • to reach rest concentrations of less than 0.5 ppm toxic and expensive sulfidic precipitants have to be used (additionally flocculants and polyelectrolytes) • electro winning from precipitate not possible • a precipitation with lime and/or caustic alone will not allow to reach rest concentrations below 0.5 ppm
Selective Ion Exchange	Advantages	<ul style="list-style-type: none"> • small footprint and low installation costs • rest concentrations of < 0,5 ppm are secured • concentration factor of $f > 200$ possible • with sulfuric acid as regenerant solution copper can be directly recovered by electro winning. At the same time the regenerant acid is recovered • in case no electro winning is provided the spent regenerant has to be treated by precipitation but in much smaller vessels than in the case of precipitation as a stand alone treatment step

box 2:

Example of Plant Design	
Flow rate	q = 100 m ³ /h
Copper concentration in crude waste water	c Cu 100 mg/L
Target rest concentration in waste water	c Cu: 0,5 mg/L
Further waste water ingredients	c NaCl: 10 g/L
Resin type	Lewatit® Monoplus TP 207
Bed volume per filter	5 m ³
Resin volume in total	10 m ³
Number of filter units	2 (for lead lag-operating mode)
Specific velocity	20 BV/h
Cycle time	15 hours
Filtered volume per cycle	300 BV equalling 1500 m ³
Operating capacity of resin	30 g/L
Efficiency	under the given frame conditions the operating capacity is 48% of the total capacity
Regenerant	H ₂ SO ₄
Concentration of regenerant	10%
Volume of regenerant per cycle	2 BV = 10 m ³
Concentration of copper in spent regenerant	15 g/L (in case of connected electro winning step even higher concentrations can be accomplished)
Rinse water demand per cycle	2 BV = 10 m ³ (rinse water can be used to prepare regenerant solution)

3.8. DESIGN OF ION EXCHANGE UNITS

As an example for the case study discussed in **box 1**, a design is presented in box 2. The waste water stream in this example is relatively big. For smaller flow rates the dimensioning of the filter bed size is reduced proportionally. This means if the flow rate is ten times smaller, the resin bed volume is ten times smaller too.

3.9 OVERVIEW ON DIFFERENT TYPES OF ION EXCHANGE RESINS

Ion exchangers are no magic bullets. In another case study similar to the example explained in box 1, frame conditions can be presented in a way that other treatment methods are favourable and the ion exchanger loses its competitive advantages. Clearly the applicability of ion exchangers has to be checked for each individual case. Not only the ion exchange technology itself has to be evaluated, but also the different types of ion exchange resins have to be put on the scales.

An overview of the different types of ion exchange resins, distinguished by their functional groups, is given in **box 3**. Besides the chemical formula and the general chemical denomination of the resin type, the Lewatit-brand name can be found here too.

There are many more types of functional groups that have been synthesized in laboratories. Not all of them have been commercialized in large scale. The ones given here are all commercially available. In **box 4** on the next page the special selectivities of these resin types are listed.

Overall, ion exchange resins and adsorber resins are powerful and efficient tools for the waste water engineers' toolboxes. They have been well established in a large number of applications. In many cases they are the only reasonable alternative for water treatment, making them indispensable in these applications. Whenever waste water treatment concepts are evaluated, ion exchange resins should always be considered in the feasibility studies. Chapter 4 will further highlight this thesis with several examples.

box 3: Overview of different types of ion exchange resins, their functional groups, and their Lewatit® brand name.

 $\text{— SO}_3\text{Na}$ strongly acidic IX (SAC) (e.g. Lewatit® SP 112)
 $\text{— CO}_2\text{H}$ weakly acidic IX (WAC) (e.g. Lewatit® CNP 80)
 $\text{— CH}_2 - \text{N}(\text{CH}_3)_2\text{H Cl}$ weakly basic IX (WBA) (e.g. Lewatit® MP 62)
 $\text{— CH}_2 - \text{N}(\text{CH}_3)_3\text{Cl}$ strongly basic IX type 1 (SBA1) (e.g. Lewatit® K 6362)
 $\text{— CH}_2 - \text{N}(\text{CH}_3)_2\text{CH}_2\text{-CH}_2\text{-OH Cl}$ strongly basic IX type 2 (SBA2) (e.g. Lewatit® K 6363)
 $\text{— CH}_2 - \text{N}(\text{CH}_2\text{-CH}_2\text{-CH}_3)_3\text{Cl}$ strongly basic IX type 3 (e.g. Lewatit® Monoplus SR 7)
 $\text{— CH}_2 - \text{N} \begin{cases} \text{CH}_2\text{-CO-O Na} \\ \text{CH}_2\text{-CO-O Na} \end{cases}$ IDA-chelating resin (e.g. Lewatit® TP 207)
 $\text{— CH}_2 - \text{N} \begin{cases} \text{CH}_2\text{-P(=O)(O Na)}_2 \\ \text{H} \end{cases}$ AMPA-chelating resin (e.g. Lewatit® TP 260)
 $\text{— CH}_2 - \text{N} \begin{cases} \text{SH} \\ \text{C=NH} \\ \text{H} \end{cases} \leftrightarrow \dots$ thiourea chelating resin (e.g. Lewatit® Monoplus TP 214)
 $\text{— CH}_2 - \text{N} \begin{cases} \text{CH}_3 \\ \text{OH} \\ \text{H} \end{cases} - \text{CH}_2 - \text{C} \begin{cases} \text{OH} \\ \text{H} \end{cases} - \text{C} \begin{cases} \text{OH} \\ \text{H} \end{cases} - \text{C} \begin{cases} \text{OH} \\ \text{H} \end{cases} - \text{CH}_2\text{OH}$ methyl-glucamine-IX (e.g. Lewatit® MK 51)
 $\text{— CH}_2 - \text{N}(\text{CH}_3)_2 / \text{FeO}(\text{OH})$ hybrid adsorber (e.g. Lewatit® FO36)
 adsorber resin (e.g. Lewatit® VP OC 1064 PH)

box 4: Overview of diverse waste water contaminants and resin types, used for selective removal

Waste Water Ingredient	Appropriate Resin Type
Cu ²⁺ , Pb ²⁺ , Cd ²⁺ , Pb ²⁺ , UO ₂ ⁴⁺ , Al ³⁺ , Ti ⁴⁺ , Co ²⁺ , Ni ²⁺ , VO ²⁺ ...	Lewatit® TP 207 or Lewatit® TP 260
Hg ²⁺ , Ag ⁺ , Pd ²⁺ , Pt ²⁺ , ...	Lewatit® TP 214 or Lewatit® TP 240
[Fe(CN) ₆] ³⁻ , [Cu(CN) ₄] ²⁻ , [Zn(CN) ₆] ⁴⁻ , [AgCN ₂] ⁻ , CN ⁻ ...	Lewatit® MP 62 or Lewatit® K 6362
[FeCl ₄], [ZnCl ₃], [HgCl ₄] ²⁻ , [RdCl ₄] ²⁻	Lewatit® MP 62 or Lewatit® K 6362
Br ⁻ , BrO ₃ ⁻ , I ⁻ , ClO ₄ ⁻	Lewatit® MonoPlus SR 7
CrO ₄ ²⁻ , HCrO ₄ ⁻ , MoO ₄ ⁻ .WO ₃ ⁻	Lewatit® MP 62 and Lewatit® K 6263
NO ₃ ⁻ , NO ₂ ⁻	Lewatit® MonoPlus SR 7
HAsO ₄ ²⁻ , HPO ₄ ²⁻ , As(OH) ₃ , SCN ⁻ , CN ⁻	Lewatit® FO 36
B(OH) ₃ , [B(OH) ₄] ⁻ , HAsO ₄ ²⁻ , HSbO ₄ ²⁻	Lewatit® Monoplus MK 51
NH ₃ , NRH ₂ , ...	Lewatit® CNP 80, Cu-doped
F ⁻	Lewatit® TP 260, Al-doped
Ba ²⁺ , Ra ²⁺	Lewatit® SP 112
Zn ²⁺ , In ³⁺ , Ga ³⁺ , Fe ³⁺ , ...	Lewatit® OC 1026
Detergents, Phenoles, Anilines, Pesticides, AOX, ...	Lewatit® VP OC 1064 or Lewatit® AF 5
Salt, Conductivity, TDS, ...	Lewatit® SP 112 and Lewatit® MP 64
Acetic Acid, Propionic Acid, Citric Acid, Oxalic Acid, ...	Lewatit® K 6362
Organic Amines, NH ₄ ⁺	Lewatit® SP 112
Radioactivity	Lewatit® SP 112 or Lewatit® TP 207

3.10 WHAT ELSE HAS TO BE CONSIDERED

In planning and operating ion exchange units the following items must be avoided to maintain effective performance:

- contamination of the ion exchange beads with droplets of oil, grease or slime that plugs the pores of the polymer beads
- feeding of molecular or ionic species that irreversibly bind to the functional groups
- feeding the filter with suspended solid containing liquids that will plug the bed in short time (TSS > 2 ppm)
- strong variations of pH and salt content of the feed solution
- feeding with fluids of critical temperatures
- back flushing and taking back into service before the filter is completely exhausted without another filter in lag position
- permanently feeding strong oxidizing chemicals (e.g. Cl₂ > 0.1 ppm)
- permanently operating the unit at high pressure drops (> 1.5 bar)
- using a density of strainers in base plates of less than 80 entry points per square meter
- providing not enough free-board in the use of resins, that undergo intensive (>30%) changes in volume throughout the cycles
- regeneration with concentrated nitric acid without special safety precautions (danger of explosion)
- Use of sulfuric acid as a regenerant solution in case the resin is highly loaded with calcium (danger of gypsum precipitation)
- to cut down regular backwashing
- plug pipelines for the release of backwashing water with slit nozzles or screens
- use bed depth less than 0.8 meters
- carry out neutralization reactions on resin with highly concentrated solutions (e.g. feed H⁺ into a resin that is in the OH⁻ or free base form or vice versa).
- transportation of resin suspensions with centrifugal pumps
- feed a column without distribution systems
- feed with linear velocities of less than 5 m/h

4. CONCEPTS TO USE ION EXCHANGERS IN ENVIRONMENTAL PROTECTION

4.1 GENERAL OVERVIEW

As shown in **figure 10**, ion exchangers can be used in five different concepts to keep waste water clean.

The **first concept** is the “direct filtration” of the waste water. Without any pre-treatment than except pH-adjustment, the water is directly filtered over the ion exchange resin. After filtration, it is directly discharged into the environment.

In the **second concept** the ion exchanger is used as a polishing or “police” filter. Here the ion exchanger is placed downstream of another waste water treatment unit that removes the major amount of pollutants. The ion exchanger removes the normal residual leakage of pollutants coming from the heavy load primary treatment unit, or the entire load should an operational failure occur. Regardless, the ion exchanger is there to assure that the concentration levels of pollutants are safely below the emission limits.

Police filters are compulsory when the waste water is treated continuously and/or the heavy load treatment step alone can not reach the emission limits.

Both the direct filtration – as well as the polishing concept are categorised as “end of the pipe” waste water treatment or as “additive environmental protection”.

Concept number 3 simply refers to water recycling. It is mainly applied to dilute process streams that can reasonably be desalinated and converted into demineralised water. Within this approach the main idea is to reduce the amount of discharged waste water while preserving fresh water resources.

The **fourth concept** is back-integrated into the production process. It entails recycling of process streams. If these streams are simply disposed after exhaustion, they create heavy loads to the waste treatment plant. Examples are the mineral acids used to pickle metals and electrolyte solutions applied for surface plating. During use, these process streams get enriched with impurities due to corrosion of metal surfaces or to the generation of side products. If the concentration of impurities exceeds a certain critical level, these process solutions become exhausted and must be renewed or disposed.

The generated waste waters will not only be charged with the impurities, they will also be heavily loaded with the active component used in the process stream.

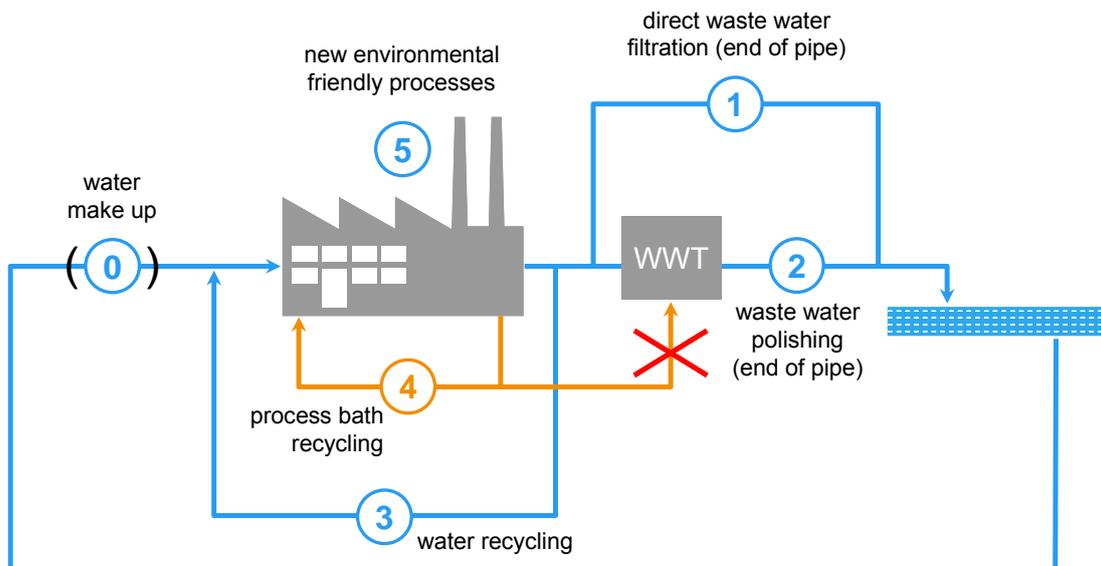


figure 10: Different concepts to keep waste water clean with ion exchangers

Ion exchangers often can be used to selectively filter the impurities from the process bath while keeping the active ingredient in solution. In this manner, the generation of heavy load waste water is reduced and valuable chemicals are saved. There also are advantages on the product quality. Permanent cleaning of the process bath reduces disturbing effects of the pollutants and helps to keep quality under control.

The **fifth concept** is complete process integration. For existing processes it requires an extensive rearrangement – a so called re-engineering – of the entire production process. Often it is employed to replace hazardous chemicals with less hazardous chemicals and/or to drastically reduce the consumption of water and save energy-resources.

Unlike end-of-pipe strategies, the fifth concept makes use of ion exchangers not simply to improve environmental protection measures. It can advance new sophisticated approaches that are completely process integrated. For this reason the brochure was given the name “keeping waste waters clean” and not “cleaning waste waters”.

The hazardous component is removed by means of a selective ion exchanger. If more than one hazardous species is present, two cases can be distinguished. First, in an ideal case, all pollutants can be adsorbed on the same ion exchanger. If, for example, all the contaminants are heavy metal cations, they can be adsorbed by means of an IDA-resin (Lewatit® TP207).

In a second, more challenging case, species with different chemistries, e.g. a mixture of cationic and anionic pollutants require treatment. In this case, for each group of ions, separate adsorbers must be provided for the different classes of contaminants. Here, a selective cation exchanger must be combined with a selective anion exchanger in series. Anionic heavy metal containing ions are metal-cyanide-complexes or oxo anions of chromium, molybdenum, tungsten, vanadium, arsenate, and antimonate.

Under optimal operating conditions ion exchangers can reduce the concentration of pollutants to less than 0.1 ppm. There are special cases known, where residual concentrations of less than 0.01 ppm can be achieved.

After exhausting the ion exchange filters require regeneration. The next very important question is what to do with the spent regenerant solution.

4.2 THE CONCEPT OF “DIRECT FILTRATION”

The principle of direct filtration is illustrated in **figure 11**. It is applicable to water that is slightly contaminated from a production process. It may contain one or more pollutants. To allow economic operation the concentration level of pollutants in sum should not exceed 300 ppm.

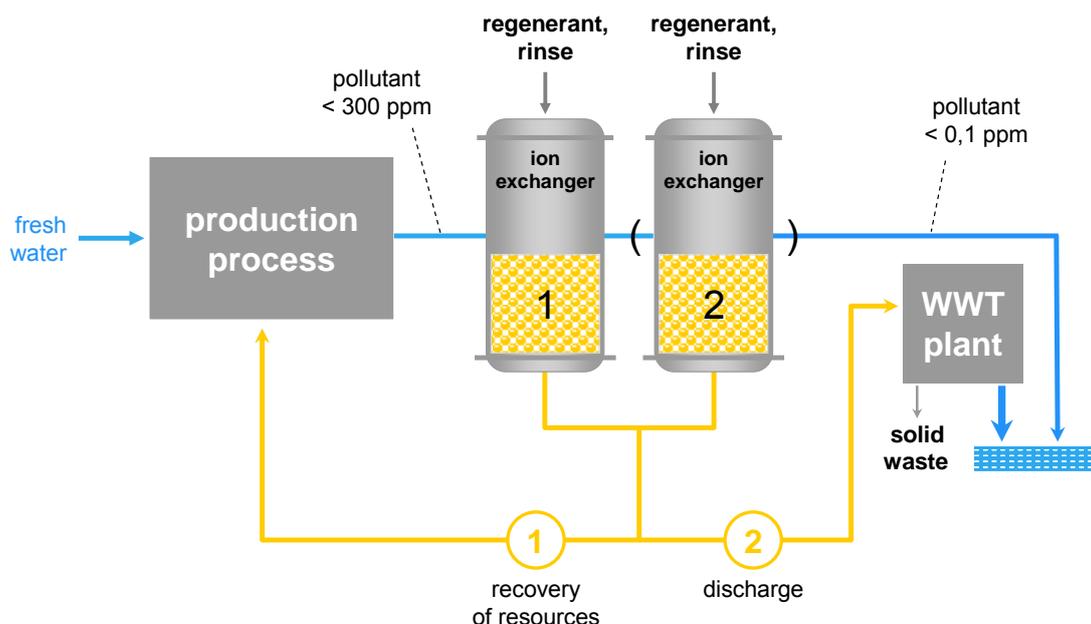


figure 11: principle of “direct filtration”

The most favourable way is to reuse the spent regenerant in the production process. (**figure 11**, pathway (1)). To allow this kind of solution, the regeneration method has to be adapted to the production process through the proper selection of the regenerant chemistry and concentration.

If reusing is not possible, the spent regenerant solution must be treated. (**figure 11**, pathway (2)). In many cases this is a precipitation reaction, where the pollutant is chemically converted into a water-insoluble solid that can be incinerated, disposed of in a landfill, or used as a raw material in metal-winning.

The concept of direct filtration with treatment of the spent regenerant only makes sense in case the process delivers a significant reduction of the waste stream. This typically means that the spent regenerant stream is about 10 times smaller than the original waste stream.

Box 5 contains some examples of this application type. The applicable Lewatit-product and the potential for reuse of the spent regenerant are indicated.

Overall there are two aims for the concept of “direct filtration”. One is compliance with waste water regulations; the second is to recover valuable material.

4.3 THE POLISHING-FILTER-CONCEPT

The concept of polishing or “police- filters” is illustrated in **figure 12** and uses the example of heavy metals as described previously.

Grossly contaminated water (as a rule of thumb the pollutant concentration is in a range of > 1 g/L) first is treated in a heavy-load-treatment step. In this case, precipitation of the metal ions through the dosage of milk of lime and/or caustic is employed. The metal ions are converted into sparingly soluble hydroxides and can be removed by filtration.

Usually a precipitation process removes 99% of the pollutant from the waste water. With a starting concentration of 1000 ppm, a 99% removal rate means that a residual concentration of 10 mg/L is present, which is normally too high for direct discharge.

To assure that the waste water is in compliance with regulations for emission into the environment, the water is conveniently treated with an ion exchange unit to take care of the final purification of the water.

In this step, the ion exchange filter further reduces the pollutant concentration with an efficacy of 99%. In sum the combination of heavy load and fine purification treatment steps yields a degree of removal of 99,99% with residual concentrations typically less than 0.1 ppm.

box 5: examples for direct filtration applications

Impurity	Application	Type of IX	Reuse of spent regenerant
NH ₄ ⁺ /NO ₃ ⁻	Fertilizer production	Lewatit® K 2629 / S 4428	X
Cu ²⁺	Printed wiring board	Lewatit® TP 207	
Cu ²⁺ , Ni ²⁺	Mining waste water	Lewatit® TP 207	X
Co ²⁺ , Mn ²⁺	Phtalic acid production	Lewatit® TP 207	X
Cu ²⁺ , Zn ²⁺	Cooling water blowdown	Lewatit® TP 207	
CrO ₄ ²⁻ , VO ₄ ²⁻	Cooling water blowdown	Lewatit® K 6362	
[HgCl ₄] ²⁻ , Hg ²⁺	Chlorine plants (Hg-cell)	Lewatit® MP 64 / TP 214	X
Pb ²⁺	Battery producers	Lewatit® TP 207	X
Co ²⁺	Lacquer producers	Lewatit® TP 207	X
Au, Ag, Pd, Pt	Gold smiths, jewelers	Lewatit® MP 64 / TP 214	
Ag ⁺	Solar cell – industry	Lewatit® TP 240	

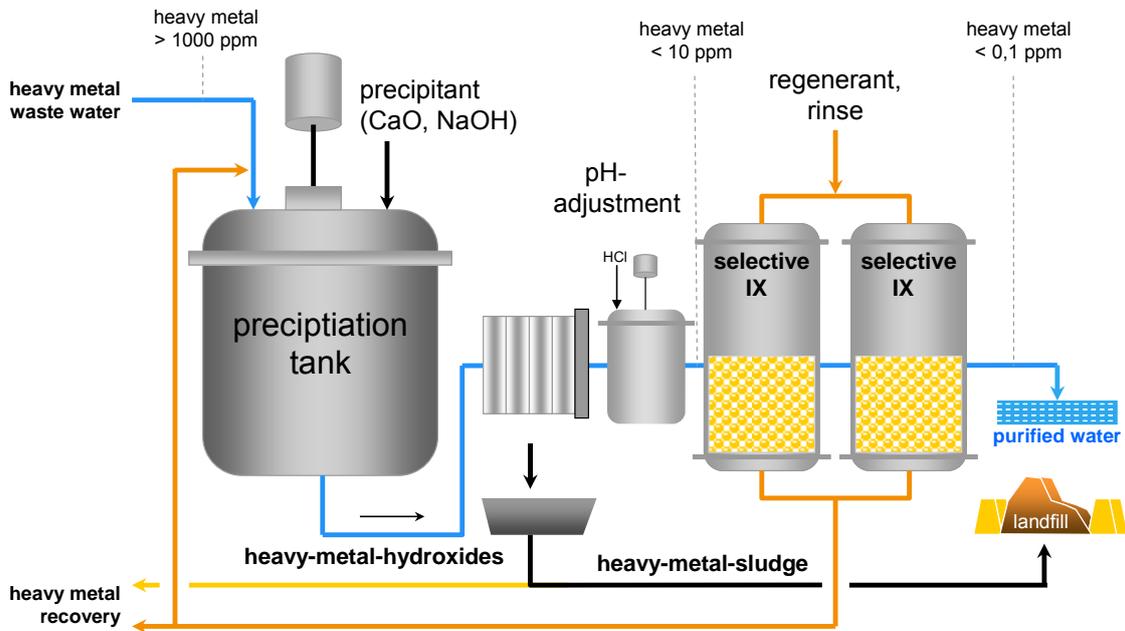


figure 12: principle of a "polishing-filter"

The spent regenerant solution usually is passed back into the heavy load treatment step. In the case depicted in **figure 12** this means into the precipitation tank. As a result, there is only one secondary waste discharge. In **figure 12** this is the filter press. No other method to treat and dispose of the spent regenerant is required. The heavy metal containing sludge is discharged to a landfill. If it contains exclusively one kind of heavy metal (mono-sludge) it can often be used in smelters as a raw material.

The concept to combine a heavy load purification unit with a polishing step is not confined to heavy metal removal. The same concept can be applied to the removal of toxic anions such as chromate, borate, arsenate, etc. It is also applicable to the removal of organic impurities. For example, phenol can first be removed by steam stripping with polishing by adsorber resins. The adsorber resin is regenerated with steam and the condensate is passed back into the steam stripper. Examples for the practical use of the polisher-concept are given in **box 6**.

box 6: examples for fine polishing applications

Pollutant	Application	IX-type
Cu ²⁺	Printed wiring board	Lewatit® TP 207
Ni ²⁺	Automotive industry	Lewatit® TP 207
Ni ²⁺	Machine building	Lewatit® TP 207
Cd ²⁺ , Ni ²⁺ , Pb ²⁺ , Hg ²⁺	Hazardous waste incineration	Lewatit® TP 207 / Lewatit® TP 214
HAsO ₄ ²⁻	Copper refining	Lewatit® FO 36
B(OH) ₃	Glass- and ceramics	Lewatit® MK 51
CrO ₄ ²⁻	Chrome plating workshops	Lewatit® K 6362
HAsO ₄ ²⁻	Chemical weapon destruction	Lewatit® FO 36
F ⁻	Glass workshops	Lewatit® TP 260 / AlCl ₃
Cd ²⁺	CdSe-photovoltaic cells	Lewatit® TP 207

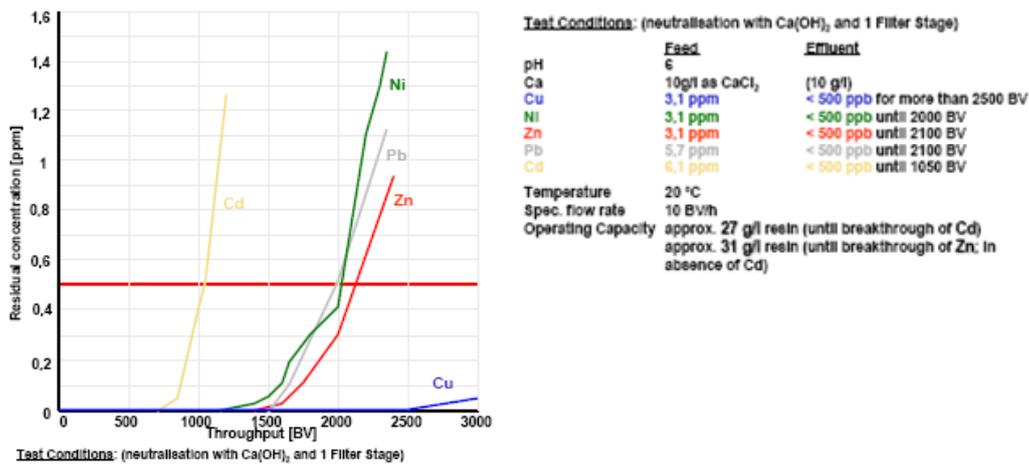


figure 13: Break through curves of different heavy metal ions. The water comes from a lime precipitation step. Lewatit® TP 207 is used.

The polishing filter type ion-exchange applications usually employ selective ion exchange reactions. The main reason for this is that these types of waste waters contain large amounts of neutral salts that are added in the heavy load treatment step. For example, in precipitation circuits, large amounts of lime and caustic are added to adjust the pH. As a result, high concentrations of calcium and sodium are generated. Because both of these cations compete with heavy metals in ion exchange reactions, selective ion exchangers are most effective.

An example of filtration curves (break through curves) of different heavy metals found in one type of waste water is presented in **figure 13**. The effluent concentration of the metal ions is plotted against the filtered volume. Due to the pre-treatment by precipitation, the water has an extraordinarily high content of calcium (10 g/L as CaCl₂).

Despite the high calcium concentration, the heavy metal ions are efficiently removed by Lewatit® TP207, an IDA-resin. In the first phase of the filtration the residual concentrations are below 0.1 ppm. This is usually in compliance with environmental legislation.

After a certain point, the residual concentrations of metals suddenly increase. Note that the ions do not break through all at the same time. In this example cadmium breaks through first and copper is the last. The break-through of metals more or less follows the order of selectivity.

It can be seen from the selectivity series in **figure 8** that cadmium has the lowest selectivity of all the metal ions, resulting in the early break through of cadmium.

Returning to the polishing concept, it is important to mention that pH adjustment may be required after the heavy load treatment step. For example, after precipitation, the pH may be too high to efficiently use an ion exchange resin. This is because at high pH heavy metals may be in an inappropriate form that does not interact with the functional groups. This may be negatively charged hydroxyl-complexes (e.g. zinc, lead, cadmium and aluminium) or it may be that at high pH metals are present as hydroxide-particles in colloidal form. Since both forms cannot be adsorbed by cation exchangers, the pH must be reduced to a value between pH = 5 and pH = 7. This will re-dissolve colloids and/or transform metals back into the cationic form.

Another critical performance issue is the presence of complexing agents such as EDTA, NTA, and cyanide in the waste water stream. These complexing agents should be destroyed (i.e. oxidation) upstream of the ion exchanger.

In addition, sulphide precipitation (sulphides, thioles, thiazoles, thiocarbamates) should be avoided in combination with ion exchanger polishers. Not only are these chemicals toxic in excess, they also produce an ugly smell when the ion exchanger is regenerated with acid.

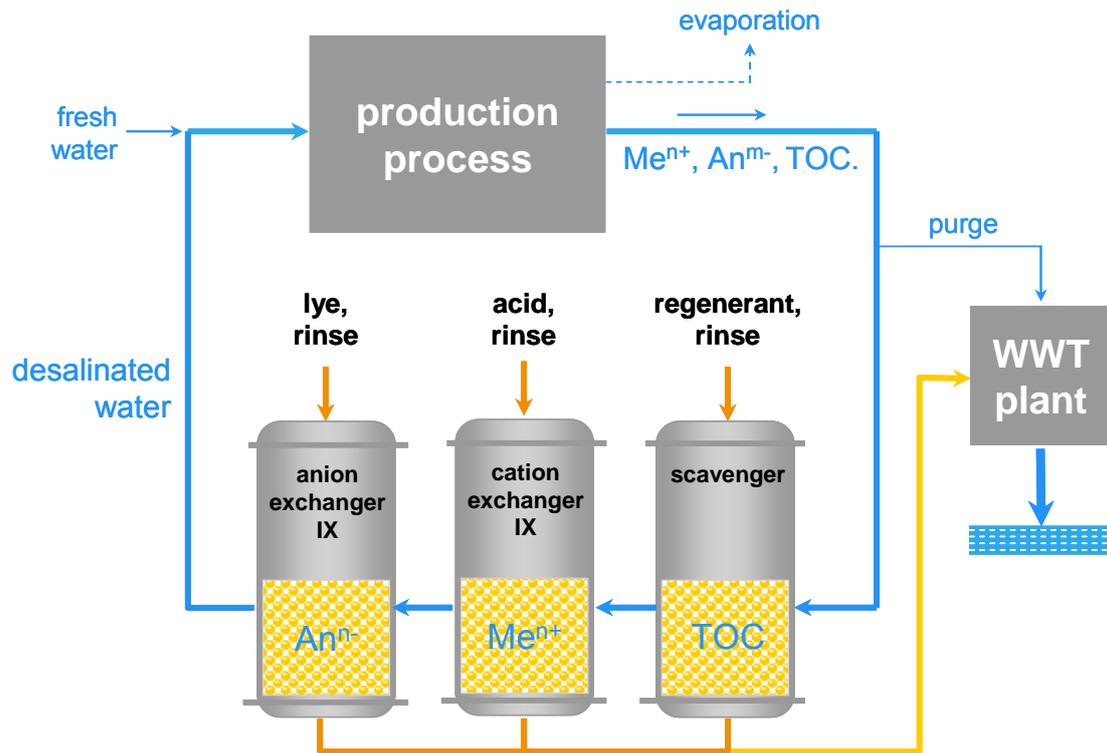


figure 14: the operating scheme of a water recycling unit

In addition, hydroxide precipitation in combination with ion exchange resins typically meets the required effluent concentrations. As a result, the use of sulfide precipitation agents in this concept is simply a waste of money, not withstanding their toxic properties and miserable odor. The use of sulfide agents makes sense only within the concept of precipitation as the stand alone treatment step. Here hydroxide precipitation alone is not sufficient to reach heavy metal concentrations in the ppb range.

Finally it is important to mention that regular back flushing is necessary, especially for ion exchangers used to polish effluents from filter presses. This is because filter presses always release suspended solids, particular at the beginning of the new filtration cycle. The solids are captured inside the ion exchange bed. Furthermore, there are post-precipitation and crystallisation effects that produce solids inside the resin bed.

If these particles are not thoroughly removed they may disturb the process and also reduce the life of the resin.

4.4 WATER RECYCLING CONCEPT

In some processes, mainly in the rinsing of manufactured products, only slightly contaminated water with low salt content is produced. The resulting salt content may even be lower than that of the raw water. In such cases water recycling through an ion exchange process is useful. The produced demineralised water can be reused in the production process.

The process scheme is shown in **figure 14**. The plant consists of a cation and an anion exchanger. Cations are exchanged by protons (H^+) and anions are exchanged by hydroxyl ions (OH^-). Protons and hydroxyl ions react to form water. Downstream of the ion exchange unit, salt concentrations are remarkably low and the conductivity can easily be less than $5 \mu S/cm$. Should even lower conductivity be required, a mixed bed ($>18 M\Omega \cdot cm$) can be added. Ultra pure water quality can be prepared by means of the mixed bed product Lewatit® SM 1000 KR.

If the rinse water also contains ionic detergents (wetting agents), the use of a scavenger filter is necessary. In these cases activated carbon or an adsorber resin is used.

Without the scavenger, cationic detergents will irreversibly foul cation resins. Likewise, anionic detergents block strongly basic ion exchangers. Therefore, these substances must be removed ahead of the ion exchange filters.

The normal products used in water recycling units are macroporous strongly acidic resin (e.g. Lewatit® SP112) in combination with a weakly basic resin (Lewatit® MP64). If the rinse water contains high concentrations of weakly acidic anions such as CN^- , H_2BO_3^- , HSiO_3^- or HCO_3^- , a third ion exchange filter should be considered. This filter contains a strongly basic resin like Lewatit® K 6362. A weakly basic resin can not capture these specific ions alone.

If a strongly basic resin is employed, the weakly basic filter should never be over-run. Otherwise there is the danger of irreversible binding of special ions such as metal-cyanide-complexes, chromate and other components. They cannot be removed from the strongly basic sites. Complexing agents based on carboxylic acids, amine- or phosphonic acid, can also be irreversibly adsorbed by ion exchangers.

If the water contains suspended solids, droplets of oil or emulsified oil, these substances should be removed before contacting the ion exchanger. An appropriate pre-treatment by emulsion break down, phase separation or filtration should be provided.

Strong oxidants, such as free chlorine or peroxides should not come in contact with the ion exchangers. These agents harm the ion exchangers by oxidizing the functional groups as well as the polymer backbone of the beads.

Another frequently occurring problem in water recycling units is growth of bacteria and algae. Algae growth in tanks can be reduced by the use of wall material that is impervious to light. Other measures include the use of disinfection by UV-lamps in tanks. Bacteria growth can be reduced by non oxidising disinfecting agents.

Once an ion exchanger is contaminated by bacteria a treatment with caustic followed by a thorough backwash delivers good results. In cases of strong bacterial contamination a short time treatment with more aggressive disinfecting agents can be applied.

box 7: examples in the field of water recycling

Pollutant	Application	Type of IX
Salt/ Cu^{2+}	Printed wiring board rinse water	Lewatit® SP 112 / MP 64
Salt/ CrO_4^{2-}	Chrome plating bath rinse water	Lewatit® SP 112 / MP 64
Salt	Electronic chip rins water	Lewatit® SP 112 / MP 64
Salt	Semi conductor rinse water	Lewatit® SP 112 / MP 64
NO_3^-	Fish farming water	Lewatit® Monoplus SR 7
$\text{Ca}^{2+}/\text{Mg}^{2+}$	Produced water from oil fields	Lewatit® CNP 80
Salt	Monoethylglycol-solutions in photovoltaic cell production	Lewatit® SP 112 / K 6363

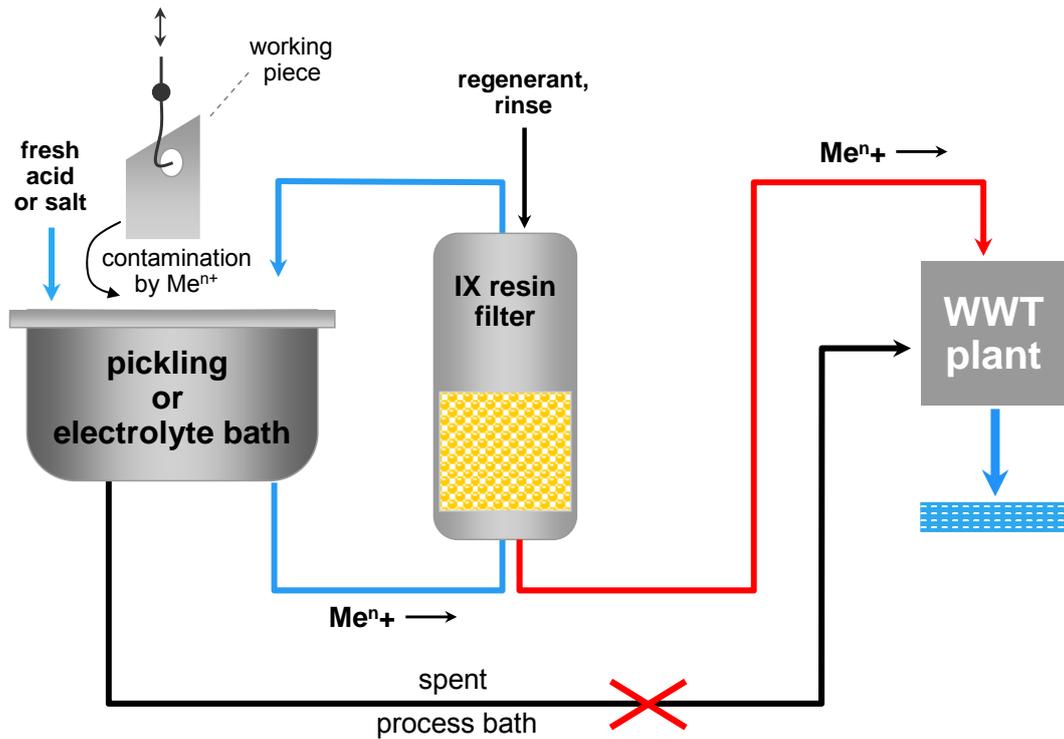


figure 15: process scheme for the recycling of process bath solutions

4.5 RECYCLING OF PROCESS STREAMS

A process stream in this brochure is defined as an aqueous liquid that contains a dissolved active chemical in a relatively high concentration. The active chemical has a certain function in a related production process. There it is deposited, or may react on a surface, or serve as an educt in a chemical synthesis. Examples of this kind of processes are:

- Pickling or etching of surfaces by means of acids or brines (e.g. passivation of aluminium in sulphuric acid baths, pickling or de-rusting of steel in hydrochloric acid)
- passivation of metal surfaces by salt solutions (e.g. phosphatizing),
- electrochemical plating of surfaces (plating of zinc, nickel, copper, chromium)
- chemical and mechanical polishing of silica wafers
- synthesis of organic product by means of hydrazinium hydrate

In all of these processes the process bath ultimately requires treatment for a couple of reasons:

- the active chemical is consumed
- side products are generated and get enriched due to corrosion processes on the surface of the working pieces

Consumed active chemicals can be replaced. For example, consumed acid in a pickling bath can be replaced with fresh acid. Zinc, copper, nickel, chromium etc. used for the plating of metal surfaces can be replaced by mounting fresh anode material or adding chemicals.

Side-products and corrosion products are enriched over time. Once they reach a critical concentration, the quality of the surface treatment process is affected. This can be noticed as a spot on the surface or by reduced corrosion inhibition of the surface layer.

If the impurities cannot be removed from the process bath the bath must be replaced after a certain time has passed. Replacement results in the following environmental and cost issues:

- the active chemical contained in the process bath (acid, salt, agent) are lost and requires replacement
- a relatively large volume of spent process bath has to be treated in a relatively large waste water treatment unit
- a relatively large amount of secondary waste (e.g. heavy metal containing sludge) is formed at one time and has to be discharged.

Ion exchangers can be used to selectively remove side products and other impurities from certain process baths. As a result, only a tiny amount of active chemicals is lost. There are several known unique processes of this type.

a) Recycling of Chromic Acid Baths

Chromating baths contain chromic acid and are used for plating steel with chrome surfaces. In chrome VI baths, chrome is present in an anionic form. By corrosion, the chromating bath is contaminated with iron and other metals cations like nickel and copper. Additionally, chrome III is formed in a side reaction. When the concentrations of iron and other impurities reach critical levels, plating quality decreases. The critical concentration for iron and chrome III for instance is around 5 g/L for both.

To remove the impurities by an ion exchanger the bath first must be diluted to a concentration of 100 g/L CrO_3 and the temperature cooled to room temperature. Otherwise the resin will be damaged by oxidation.

To remove the metal cations, a strongly acidic resin Lewatit® SP112 is used. It can be loaded with up to 20 g/L of metal cations under the given conditions. It leaves the chrome VI ions untouched, because the cation exchanger cannot adsorb anions.

Before pumping the purified chrome(VI) electrolyte back into the bath, it is concentrated by evaporation to achieve the original concentration in the bath.

b) Recycling of Hydrochloric Acid

In the pickling of steel surfaces with hydrochloric acid, iron (II) ions are dissolved in the acid. By dosing H_2O_2 , the iron (II) can be oxidized to form iron (III) that forms a dark coloured $[\text{FeCl}_4]^-$ – chloro-complex. This complex binds strongly to strongly basic anion exchangers like Lewatit® K6362. By percolating the acid over an ion exchange bed, residual concentrations of iron of less than 1 ppm can be reached. The regeneration is conveniently effected by rinsing water through the bed. Because of the low concentration of chloride in the regenerant water, the negatively charged chloro-complex is destabilised. As a result the positively charged iron cation is released and subsequently washed out from the resin. The process is very efficient for both primary rough cleaning and fine purification.

c) Recycling of Sulfuric Acid by Retardation

Sulfuric acid is used in large amounts for anodising aluminium surfaces by the so-called “Eloxal” process. Aluminium gets enriched in the process bath by corrosion and is tolerated up to a certain concentration.

The purification of acid in the bath is effected by the so-called “acid retardation” process. The principle of this process is the absorption of acid by a strongly basic anion exchanger. The cationic impurity Al^{3+} is repelled by the resin (so called “Donnan-Effect”) and thereby separated from the acid.

Usually the acid is pumped into the slim filter bed filled with a special resin. At the outlet of the column, different fractions exit, one after the other. The first fraction is pure water remaining from the previous cycle. It can be stored in a buffer tank and used in other process steps. After the water, the next fraction contains the impurities, in this case the Al^{3+} ions together with its counter ion sulphate. This fraction is released into the waste water treatment unit. Finally the fraction containing the retarded acid exits the column. At the moment this fraction arrives at the outlet, the column feed is interrupted to prevent acid loss. At this point, the column is regenerated and the adsorbed acid is washed out with pure water. The water is fed in counter current flow to the acid feed. As a result, high concentrated acid exits the column hydraulically and is pumped back into the bath.

To keep the volume of the acid bath constant, the volume of acid pumped out of the bath and the volume of water to regenerate the column has to be exactly equal.

The process is called acid retardation because the acid is coming out later than the salt. The flow of acid is retarded by the absorption in the resin bed.

In service as well as in the regeneration the flow rates are kept relatively low. The breakthrough of acid appears after roughly 1 bed volume of acid has been fed. One cycle containing service and regeneration lasts roughly 1 hour.

The efficiency of the process is highest at acid concentrations between 10 and 20 percent. The concentration of metal cations in the process bath can be kept constant at a level of 5 g/L to 10 g/L. The method is not appropriate for a fine purification of acid.

LANXESS has developed a special acid retardation resin with the brand name Lewatit® K 6387. Since the beads are very fine (0.35 mm in diameter) it possesses an especially sharp separating effect, comparable to a chromatographic material. Thereby impurities and acid can be sharply separated from each other, with reduced losses of acid.

d) Recycling of Hydrazine-Hydrate

In the synthesis of active organic substances, e.g. pesticides or pharmaceuticals, hydrazine-hydrate in a 30% aqueous solution is often used. During the reaction, hydrochloric acid is produced and built in the solution. After the reaction the aqueous hydrazine hydrate solution can be separated from the organic phase and recycled when hydrochloric acid is removed.

The removal of the hydrochloric acid can be carried out by means of a strongly basic ion exchange resin (e.g. Lewatit® K 6362) in OH-form. In this process, the OH-reacts with the H⁺ of the hydrochloric acid, and the remaining chloride ion binds to the functional group. The resin can easily be regenerated with caustic.

The spent regenerant from the ion exchanger has only a minor effect on the environment in comparison to the disposal of the complete process bath. In addition, the spent regenerant stream is a nearly continuous release that can easily be handled by a small waste water treatment unit. The user profits from a simplified waste water treatment and savings for buying new chemicals. A remarkable advantage is the continuous quality of the process bath. This results in improved product quality and consistency throughout the plant.

Beyond these just described, there are several more examples where process baths are purified and recycled, resulting in significantly longer life cycles. An overview over the most important processes is given in **box 8**.

box 8: Examples of applications for recycling process streams and process baths.

Pollutant	Application	Type of IX
Fe ³⁺	HCl pickling bath	Lewatit® K 6362
Al ³⁺	Aluminium-passivation (H ₂ SO ₄)	Lewatit® K 6387
TOC	H ₂ SO ₄ from cellulose digest	Lewatit® K 6387
Co ²⁺	H ₂ SO ₄ from ore digest	Lewatit® K 6387
Ti ⁴⁺	Spent battery acid	Lewatit® TP 260
Zn ²⁺ , Fe ²⁺	Cr(III) passivation bath	Lewatit® OC1026
Zn ²⁺	Ni-plating bath	Lewatit® OC1026
Fe ²⁺	Zn-plating bath	Lewatit® TP 207
Fe ²⁺ , Cr ³⁺	Cr(VI)-plating bath	Lewatit® SP 112
TOC	Cr(III)-passivating bath	Lewatit® OC 1064 / AF 5
HCl	Hydrazin-hydrate	Lewatit® K 6362

4.6 RE-ENGINEERING OF PROCESSES

Particular products, chemicals or other goods typically can be produced with different manufacturing approaches. Different materials, additives, solvents, sources of energy etc. can be chosen. Depending on these choices, the industrial activity can have a significant affect on the quality of the environment.

With a systematic re-engineering of production processes, the impact on the environment can be driven in a more environmentally friendly and less dangerous direction. Toxic chemicals can be replaced by less toxic chemicals. Energy consuming processes can be replaced by energy saving processes. The use and contamination of water can be reduced by use of alternative media.

The re-engineering of processes is the most sensuous approach among all activities in protecting the environment. It can also be the one connected with the most effort and expense. This is because changing one step in the production chain can lead to serious consequences in the other steps too. As a result, in many cases, the whole process has to be changed completely. It is understandable, then, that changes in production processes are typically realised in new grass-roots plants. In most cases it is simply too expensive to change installations at existing plants that have not yet been depreciated.

Three examples of re-engineered processes are described below.

a) New Process for Chlorine Production

Maybe the most precious example of successful re-engineering is the development of the membrane-electrolysis-cell for chlorine production.

In former times and in some areas still, the so-called mercury-cell process was widely used. Mercury was used as a cathode material and pumped in circuits through the plant in large streams. Not only were tons of dangerous mercury in use, exposing humans and their environment to serious threats; the specific energy consumption was relatively high.

In the 1960s, particularly in Japan, there arose a particular awareness of the danger on mercury and its compounds. This was due to an incident in the Bay of Minamata that seriously affected hundreds of fishermen and their families.

From this experience, there were strong efforts expended in the re-engineering of the mercury processes for chlorine and caustic production. The result was the membrane-cell-process that completely excludes the use of mercury and additionally has a higher efficiency in converting electrical energy into chlorine.

The crux of this process is the separation of the cathode and the anode chamber by an ion exchange membrane. This membrane is a high tech product and costs several thousand dollars per square meter. In addition to its cost, this membrane is also very sensitive to fouling from impurities that are contained in the electrolyser feed-brine.

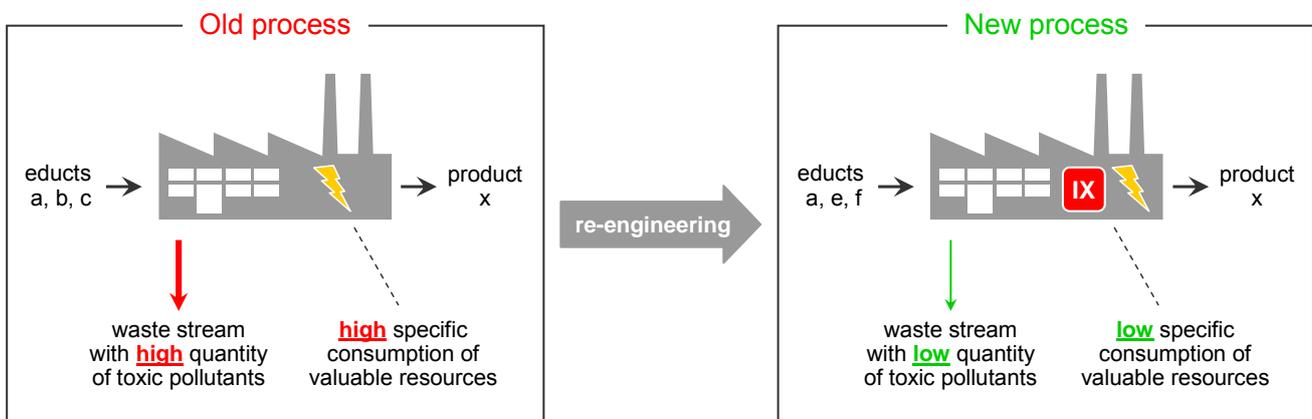


figure 16: re-engineering of production processes to make them environmentally friendly

The critical impurities are calcium and magnesium salts contained in the raw material used for the chlorine production; rock-salt or salt from salines. Only a few ppb of hardness are allowed in the feed of the membrane electrolyser. If the concentration of calcium and magnesium regularly exceeds 20 ppb, irreversible damage can occur at the membrane surface and it must be replaced.

The feasibility of the membrane cell process in large scale was mainly dependant on the availability of technical methods to remove trace hardness from a solution containing 30% alkaline salt. During the research and development work, it was found that selective ion exchange resins of the IDA- and AMPA type (see chapter 3) could handle that challenging task.

Today several hundred plants are operating worldwide based on the membrane-cell process. In most of these plants the brine is first purified by precipitation and then undergoes fine purification with selective ion exchange resins. It is not an over-exaggeration to say that this ecological and economical technology would not have been realized without the appropriate ion exchange resin.

b) New Methods for Metal Winning

One more interesting example for a successful re-engineering is taking place in the field of metal winning. Here ion exchangers can replace liquid/liquid extractants (LX); chemicals that have several ecologic and economic disadvantages. These are such as:

- LX are toxic
- LX are diluted with kerosene, therefore inflammable and explosive
- LX are partially water soluble and are released in waste water
- different LX used in serial treatment steps are contaminated over time losing their efficacy
- LX get spoiled by suspended solids
- LX are highly expensive

In contrast to that, ion exchangers (IX) have the following properties:

- IX are not poisonous
- IX are not explosive
- IX are not water soluble and do not contaminate water
- IX can easily be kept separate by screens and do not cross-contaminate
- IX can be easily be cleaned by back washing
- IX can be purchased at reasonable prices

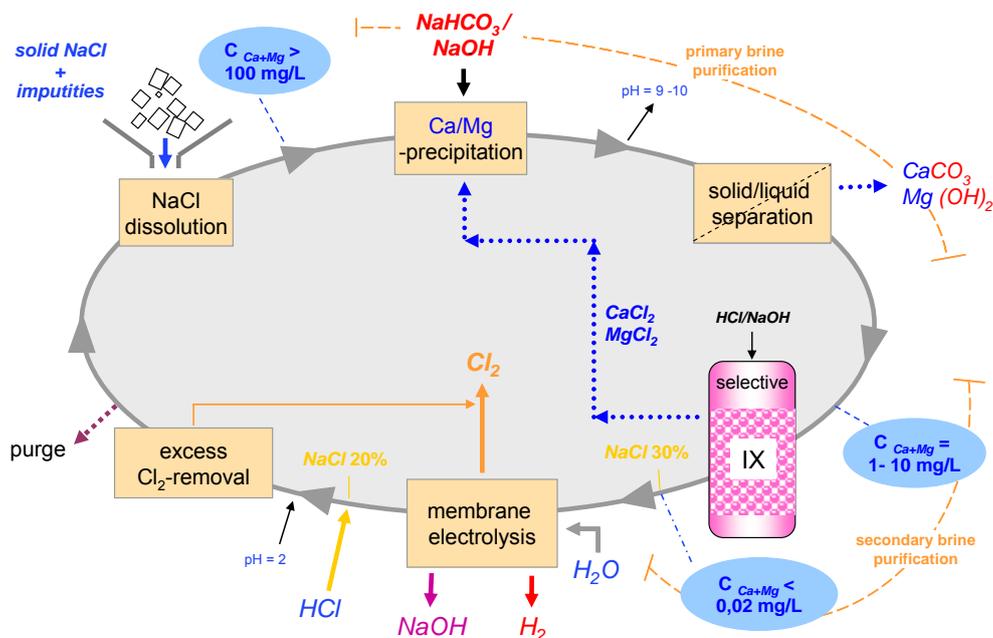


figure 17: A successful example of re-engineering of a process: The production of chlorine can be realised now without any use of the toxic mercury. This was made possible due to the availability of selective ion exchangers that purify salt brine in a way that sensitive membranes can be used for the construction of electrolyser cells.

In metal winning processes ion exchangers can be applied in normal filtration columns. Here they extract the metals from ore digests (pregnant liquors). Additional technology is also applicable. This process is called “Resin in Pulp“ or RIP. It mixes the ion exchange resin beads with the already digested and unfiltered pulp of ores. The resin extracts the valuable metals from the solution and from the pores of the ore particles.

After the extraction the saturated beads are separated from the pulp by screens. Due to the small pulp size, it is advantageous to use resin beads with larger particle sizes than usual. For this purpose, LANXESS has developed a special monodispersed resin type with particle diameters of 0.8 mm. One example of this type is the so called “Mining Resin”, “Lewatit® TP207 XL“.

Due to the huge flow rates of this process streams and the small particles encountered, any solid/liquid separation process is extremely difficult, time consuming, and expensive. The RIP-process has the very significant advantage that no solid/liquid separation is required before the extraction. A further advantage is a higher yield of metal, because the metal ions in the pores of the particles are also extracted. This also means less release of heavy metals into the environment, because the ore residues usually are deposited on land fields (tailings-dams).

Today there are pilot plants running with this technology. Due to the listed advantages, it is expected that soon more and more ion exchangers will take over the place of liquid/liquid extractants.

c) Fine Purification of Biodiesel

For the purification of biodiesel, glycerine has to be removed to residual concentration of only a few ppm. Otherwise glycerine would decompose the alloys of the motor-block.

Due to the fact that glycerine is highly soluble in water, an earlier process was based on washing the biodiesel with water.

After the washing there is not only the non-trivial problem of phase separation of biodiesel and washing water. There is also the problem of what to do with the washing water which is highly contaminated with organics (TOC and BOD). The water can be purified in a biological treatment unit or treated by a distillation unit. Both treatment measures are inconvenient. The first requires large space and the second has relatively high energy consumption. Alternatively, glycerine can be purified by means of strongly acidic cation exchangers (Lewatit® GF 202). In this process, the cation exchanger acts more as an adsorber for hydrophilic compounds than an ion-exchanger. This is because of the polarity of the functional group can adsorb hydrophilic substances via hydrogen-bridging.

As a result, the adsorber not only adsorbs glycerine, it also adsorbs other impurities such as traces of salt, of soaps etc.

The regeneration is carried out with water free methanol that removes the impurities and keeps the resin free of water.

The crux of this process is the fact, that the spent regenerant methanol can be used in another process step of the bio-diesel production. This means that there is no waste stream from the ion exchanger. Methanol is used twice and consumed.

These three are examples of complete process re-engineering. All the other processes for process stream recycling can be regarded as partial process re-engineering.

box 9: examples for successful re-engineering of processes by means of ion-exchangers

Application	Type of IX
Chloroalkali electrolysis with membrane-cell technology	Lewatit® TP 208 / TP 260
Metal winning by RIP-process	Lewatit® TP 207 XL et al.
Purification of bio-diesel by dry adsorbers	Lewatit® GF 202 et al.

5. EPILOGUE

The examples in this brochure demonstrate that ion exchangers can be used in different ways to keep waste waters clean from hazardous compounds. Ion exchangers are powerful tools on the top shelf of the waste water engineer's toolbox. They can be used alone or in combination with other treatment methods.

Water treatment concepts involving ion exchangers can be designed in different ways, like the easy to install additive "end-of pipe" process. Process-integrated measures that directly operate on process streams in the heart of the process can be employed too.

In the preceding examples, ion exchangers deliver economic solutions to problems because the principle of selectivity can be put into action. Selectivity is economical because the consumption of chemicals and energy targets the treatment of one trace component, and keeps other non-hazardous components untouched.

Given this selectivity advantage it is very important that different types of ion exchangers and adsorber resins are available. Multiple types allow the engineer to select the most suitable resin for a given application.

It is important to mention that the development of special adsorbers is not finished. LANXESS is always eager to further improve their products and to create new products for new fields of application. In this way, LANXESS is helping to insure that tailor-made products for the purification of waste water are available both now and will be in future times; for the sake of our environment and for the sake of all of us.

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