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Anion Exchangers: Ion Exchange

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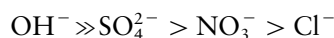
Introduction

Anion exchange resins consist of a polymeric matrix to which different functional groups are attached. Most weakly basic anion exchangers contain tertiary amino groups; in a few cases primary and secondary groups are also encountered. In many cases weakly basic anion exchangers are not monofunctional but possess a variety of amino groups. Strongly basic resins contain quaternary ammonium groups. Standard commercially available exchangers contain either $-N^+(\text{CH}_3)_3$ groups (type 1 resins) or $-N^+(\text{CH}_3)_2\text{C}_2\text{H}_4\text{OH}$ groups (type 2 resins). Both weakly and strongly basic exchange resins are available in gel-type or macroporous modifications.

Properties and fields of application mainly depend on the dissociation properties of the functional groups in which dissociation plays the most important role. By means of the mass action law, dissociation constants of the protonated amino and ammonium groups can be estimated. The respective numerical values are in the range of $\text{p}K_a > 13$ for strongly basic resins and 5–8 for weakly basic resins. Therefore, strongly basic resins are protonated over the entire pH range but weakly basic exchangers are protonated at pH values below 5–8, depending on the type. As a consequence, strongly basic resins will exchange anions in both acid and alkaline solutions. In addition, these exchangers can adsorb weak acids and even ionize very weakly dissociated acids. Weakly basic resins, however, can operate only in acidic media and are unable to convert neutral salts to the respective hydroxides (e.g. NaCl to NaOH). Furthermore, they cannot normally adsorb weak acids.

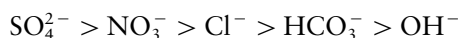
The uptake of anions by resins is subject to specific interactions between counterions and co-ions and the distribution of exchangeable ions depends on the properties of both the exchanger and the ions. Consequently, a favoured sorption of certain types of anions occurs. The sequence of affinities is given either qualitatively by the selectivity series or quantitatively by, for example, separation factors. For weakly basic anion exchangers the sequence of most common anions in fresh water is:

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Due to the dissociation properties of the functional groups, hydroxyl ions are strongly preferred. This is important for the conversion of these resins to the hydroxyl (or free base) form in the regeneration step, in which only slightly more than the stoichiometric amount of OH^- bearing solutions is required.

For strongly basic anion exchangers the selectivity series is:



For these resins hydroxyl ions are the least preferred among the standard anions. Conversion of the resins to the hydroxyl form therefore requires comparatively large excess amounts of sodium hydroxide.

For elimination of nitrate anions from drinking water the preferred sorption of sulfate ions causes considerable disadvantages. Extensive research during the 1980s has shown that this drawback can be overcome by introducing functional groups which are more hydrophobic and bulkier. By these means, the ability to adsorb sulfate ions is considerably decreased. The so-called nitrate-selective resins which are now commercially available contain triethyl instead of trimethyl groups and, therefore, exhibit a reversed preference for nitrate and sulfate ions.

The rate of exchange depends mainly on the internal interdiffusion of exchanging ions. On the completely ionized strong base resins this diffusion is rather quick and the overall rate of exchange mainly depends on the particle size distribution. With weakly basic exchangers, however, the poor dissociation and further specific interactions between functional sites and diffusing ions considerably slow the rate of exchange. For these resins, both the uptake of acids and conversion to the free base form by means of sodium hydroxide strongly depend on the concentration of the liquid phases.

Strongly basic anion exchangers in the hydroxyl form are subject to considerable degradation of

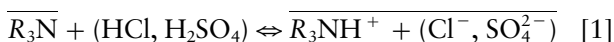
functional groups at temperatures above 40°C, leading to a loss of strongly basic functionality. Weakly basic exchangers are very stable.

Applications

Water Demineralization

The most important application of anion exchangers in water treatment has been in demineralization processes. Demineralization consists of the subsequent cation exchange for hydrogen ions as the first step and either adsorption of acids by a weakly basic exchanger or real anion exchange for hydroxyl ions on a strongly basic exchanger as the second step. As a result, demineralized water is produced: this may be used for various purposes, such as boiler feed water.

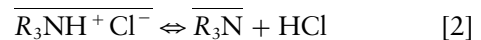
The effluent from the preceding cation exchange step consists of a mixture of strong mineral acids and carbonic acid; this is equivalent to the cations originally dissolved. Furthermore it contains silica and dissolved organic compounds, neither of which are retained by the cation exchangers. If no silica removal is needed, weakly basic anion exchangers in their free base form are used to remove strong mineral acids. This process develops as the uptake of acids:



(Parantheses are used to express the stoichiometry of the exchange; R_3 denotes the matrix of the weakly basic exchanger.) In technical filter columns the uptake of sulfuric and hydrochloric acid results in the development of zones with different predominant loadings: firstly, a sulfate-rich zone close to the inlet; secondly, a chloride zone; and finally, a zone in which the resin is still in the free base form. During the filter run the sulfate and chloride zones become larger and the boundaries between the zones are shifted towards the column outlet. Consequently, chloride ions are the first to appear in the column effluent.

Theoretically, the strong acids should be completely eliminated. In practical installations, however, the leakage of sodium from the strongly acidic cation exchanger cannot be avoided and it is in the range of 2–50 $\mu\text{g L}^{-1}$, depending on the level of regeneration. By this means, the feed solution for the anion exchanger contains some neutral salt which cannot be eliminated. Consequently, an equivalent amount of chloride ions remains in the effluent. Apart from this sodium leakage-caused 'slip', the presence of chloride

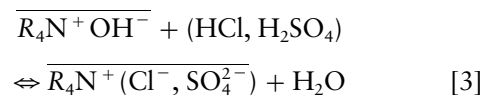
ions may also be due to the hydrolysis of the hydrochloride form of weak base resins:



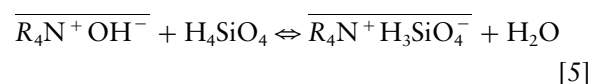
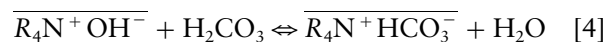
Weak acids like carbonic acid are only adsorbed to a small extent and hydrogen carbonate ions are rapidly replaced by anions of strong acids. Carbonic acid or CO_2 is therefore eliminated either by physical degassing or by means of a strongly basic exchanger. Since the capacity of weakly basic resin increases with increasing total ionic concentration (to which carbonic acid contributes), degassing of CO_2 is often placed after the weakly basic exchanger filter.

Regeneration of weakly basic anion exchangers is usually carried out by means of sodium hydroxide, although other chemicals like $\text{Ca}(\text{OH})_2$ or ammonium hydroxide have also been proposed. To avoid the precipitation of calcium sulfate, the regenerant solutions of anion exchangers generally require calcium-free water. Since the strong acids are easily neutralized, regeneration is efficient. The operating capacity depends on the composition of the raw water and the resulting loading of the anion exchanger. If equal amounts of caustic are applied in the regeneration step, the effective capacity decreases by about 10% if the raw water contains exclusively sulfate instead of only chloride ions.

Unlike with weakly basic resins, the removal of acids by a strongly basic resin develops as a neutralization reaction:



(R_4 denotes the matrix of the strong base resin.) Because of the high pH value in the resin phase, strongly basic exchangers can ionize and adsorb ions from carbonic acid and even from silica:



For boiler feed water, for example, the removal of both carbonic acid and silica is of great interest. Usually, most of the carbonic acid is removed by physically degassing. By this means a large part of the capacity of the strongly basic anion exchanger is saved and the resin has to eliminate only the remaining traces of carbonic acid. The removal of silica is far more complicated than shown in eqn [5] above.

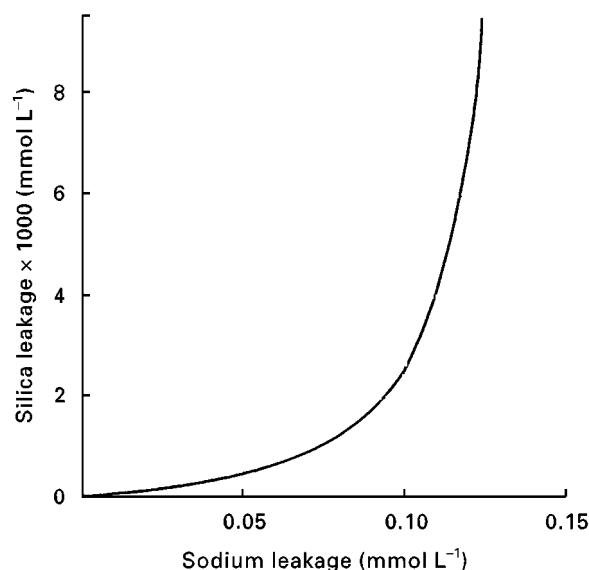


Figure 1 Interdependence of sodium and silica leakage.

During the accumulation in the resin phase, silica starts to polymerize. This is favoured by long cycles as well as by high concentrations in the feed water. Regeneration using NaOH may, therefore, become a dissolution rather than a true ion exchange process. Warm solutions (approximately 50°C) are considerably more effective than solutions at ambient temperature. In addition, regeneration may be adversely influenced by the mode of regeneration and the possible displacement of hydrogen carbonate ions. The leakage of silica is closely related to the leakage of sodium in the preceding cation exchanger (**Figure 1**).

Regeneration of strongly basic resins is generally carried out by means of NaOH at concentrations between 1 and 5%. As with weakly basic exchangers, the resulting operating capacity depends on the composition of the feed water, the relative amount of NaOH, temperature and, to a certain extent, the rate of filtration during regeneration. The relative quantity of NaOH required is considerably higher than for weak base resins and lies between 150 and 250% of the stoichiometric amount. For the slightly weaker basic resins of type 2, the operating capacities are higher than for type 1 resins.

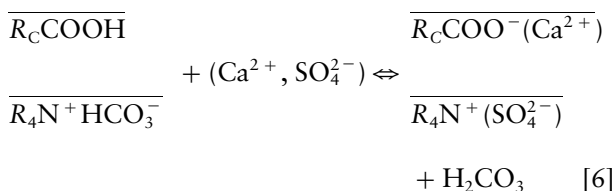
There can therefore be savings in chemicals and cost if the anion exchange step is split into two stages. In the first stage a weakly basic resin is applied for the elimination of strong acids. After physical degassing to remove carbon dioxide, the strongly basic exchanger is exclusively used to eliminate the remainder of the carbonic acid and silica. Both resins are regenerated together: the NaOH solution first passes through the strongly basic resin which requires a concentrated regenerant without impurities. The effluent

then passes the weakly basic resin. Due to the strong preference for hydroxyl ions, considerable levels of impurities can be tolerated.

Demineralization of water by subsequent or simultaneous cation/anion exchange has been realized in countless installations for both fresh and waste water treatment. It has become extremely important for boiler feed water and for ultrapure water for the electronics and pharmaceutical industries. Typical conditions to be met are conductivities below 0.2 $\mu\text{S cm}^{-1}$ and silica concentrations < 5 mg L^{-1} .

Partial Demineralization of Drinking Water

In Europe numerous water supplies distribute drinking water with elevated total hardness caused by the presence of sulfate and calcium ions. Treatment of such water, therefore, requires the elimination of sulfate ions parallel to diminishing hardness. In such applications complete demineralization is not required. Consequently, considerable leakage of the ion exchangers can be tolerated. The condition of simultaneously diminishing the concentrations of alkaline earth and sulfate ions is met by the carbon dioxide regenerated ion exchange (CARIX) process. This process uses a mixed bed consisting of a weakly acidic resin in the free acid form and a strongly basic resin in the hydrogen carbonate form. In contact with calcium- and sulfate-bearing raw water, both kinds of ions are replaced by carbonic acid:



The advantage of this process is its reversibility: for regeneration, carbon dioxide is dissolved in untreated raw water under a pressure of typically 0.4–0.5 MPa. The carbonic acid solution is pumped across the mixed bed and simultaneously regenerates both resins. Although carbon dioxide is applied in large excess, this does not contribute to the salt content of the waste water which exclusively contains the ions removed during the service cycle. Carbonic acid is a weakly effective regenerant for both resins and generates an effective capacity of $\approx 50\%$ of the total capacity on the cation exchanger and only 20% on the anion exchanger. As a consequence, complete demineralization is not possible and considerable leakage is observed. The possible throughput between two regenerations is small. Within certain limits the

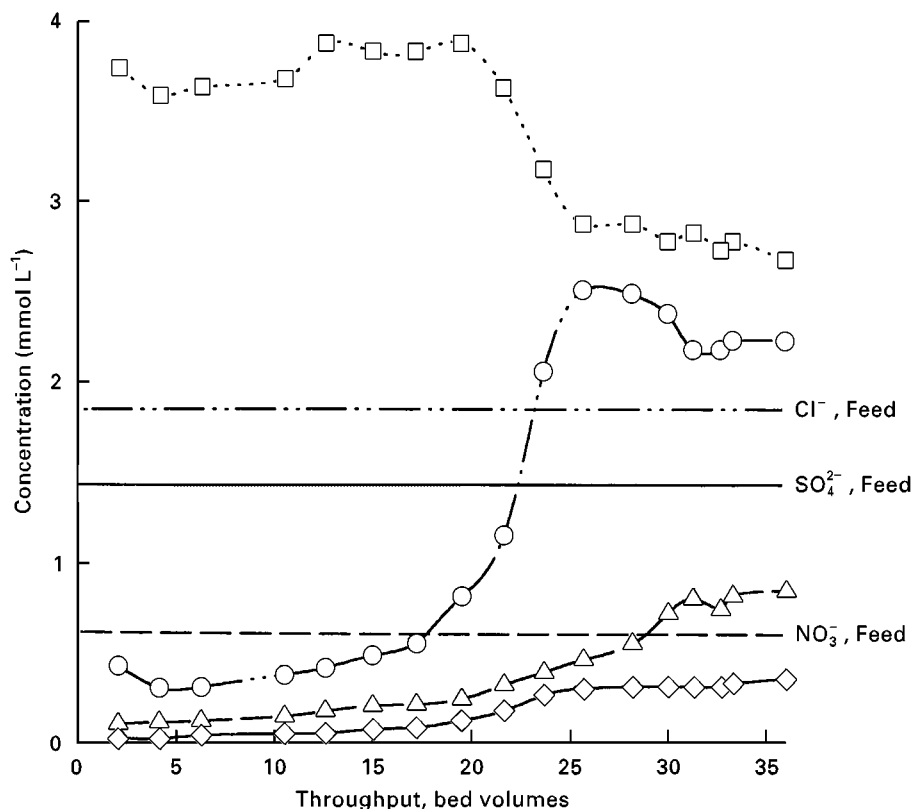


Figure 2 Concentration histories of chloride, nitrate and sulfate in the Carix process. Feed alkalinity (HCO_3^-): 6.5 mmol L^{-1} . Circles, Cl^- ; triangles, NO_3^- ; diamonds, SO_4^{2-} ; squares, HCO_3^- .

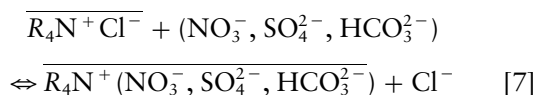
CARIX process can be adapted to the objective of treatment by adjusting the volume ratio $V_{\text{anion}} : V_{\text{cation}}$ of the two resins in the range of 3 : 1 to 1 : 3. With respect to both the removal of sulfate and regeneration by means of carbonic acid, type 2 and acrylic anion exchangers show the best results.

So far, the process has been realized in three full-scale plants in water works in Germany. Each of these plants consists of one or two sets of three filters which operate in a merry-go-round mode. The total throughput for each filter between two regenerations is 35–50 bed volumes. After half of the total throughput, a second filter starts its service cycle. After the full throughput, the filter is regenerated and waits for the next service cycle while the third one is started. The product water is the mixed effluent of the two operating filters. Typically, about 10% of the raw water is needed for regeneration. From the waste water, 90% of the unspent carbon dioxide is recovered. Thus, the consumption of CO_2 amounts to $0.4\text{--}0.45 \text{ kg m}^{-3}$.

Figure 2 shows a typical breakthrough history for standard anions. Average product water concentrations are listed in Table 1.

Nitrate Removal

For many drinking water supplies the presence of nitrate in ground and surface water at elevated concentrations has become a serious problem because of its health effects. As the simplest possibility, nitrate can be eliminated from water by means of strong base anion exchangers in the chloride form:



Using conventional strong-base anion exchangers, the main difficulty of this method arises from the

Table 1 Partial demineralization by means of the CARIX process

Parameter	Raw water	Product water
Total hardness	5.4 mmol L^{-1}	2.3 mmol L^{-1}
Hydrogen carbonate	6.6 mmol L^{-1}	3.4 mmol L^{-1}
Sulfate	1.6 mmol L^{-1}	0.35 mmol L^{-1}
Nitrate	0.6 mmol L^{-1}	0.45 mmol L^{-1}
Chloride	1.5 mmol L^{-1}	1.3 mmol L^{-1}
Conductivity	$930 \mu\text{S cm}^{-1}$	$470 \mu\text{S cm}^{-1}$
pH Value	7.30	7.80

preferred uptake of sulfate ions. Consequently, the nitrate uptake capacity strongly depends on the sulfate/nitrate concentration ratio in the raw water. As an example, for a type 2 resin the nitrate uptake capacity decreases by 60% if the sulfate concentration in the feed increases from 50 to 220 mg L⁻¹.

During the uptake of sulfate, nitrate and hydrogen carbonate by a chloride-loaded conventional anion exchanger, loading zones develop in the filter column: a sulfate-rich zone, a nitrate-rich section and a mixed chloride/hydrogen carbonate zone followed by the resin in its original chloride form.

Due to the development of the zones and the displacement of less preferred anions, continuous change occurs in the effluent composition. When the hydrogen carbonate-rich zone has reached the outlet there is still removal of nitrate species, but an increase in the concentration of hydrogen carbonate and a corresponding increase in the pH in the effluent occur. The column run has to be stopped when the nitrate-rich zone reaches the filter outlet.

Regeneration is carried out using brine solutions of 2–10% NaCl:



The total quantity of NaCl used depends on the tolerable nitrate leakage in the service cycle. To achieve effluent concentrations ≤ 2 mg L⁻¹, the required amount is ≥ 200 g L⁻¹ resin. With smaller quantities the leakage becomes larger.

The operating capacity of conventional anion exchangers depends on both the nitrate and sulfate concentrations of the feed water. Figure 3 shows the respective interdependence for a commercially available type 2 resin.

The objective of treatment normally does not consist of the complete elimination of nitrate but only of its reduction below the maximum permitted concentration. A tolerable nitrate concentration in the product water can therefore be achieved by two different methods: the first uses an exchanger which has been regenerated with a large amount of NaCl. Since the leakage of the column is small, only part of the water has to be treated and can be blended with a by-pass of untreated water.

This kind of nitrate removal process was first realized in 1975 in Long Island in a pseudo-continuous installation. This plant consisted of a closed-loop tube including sections for back-washing, regeneration

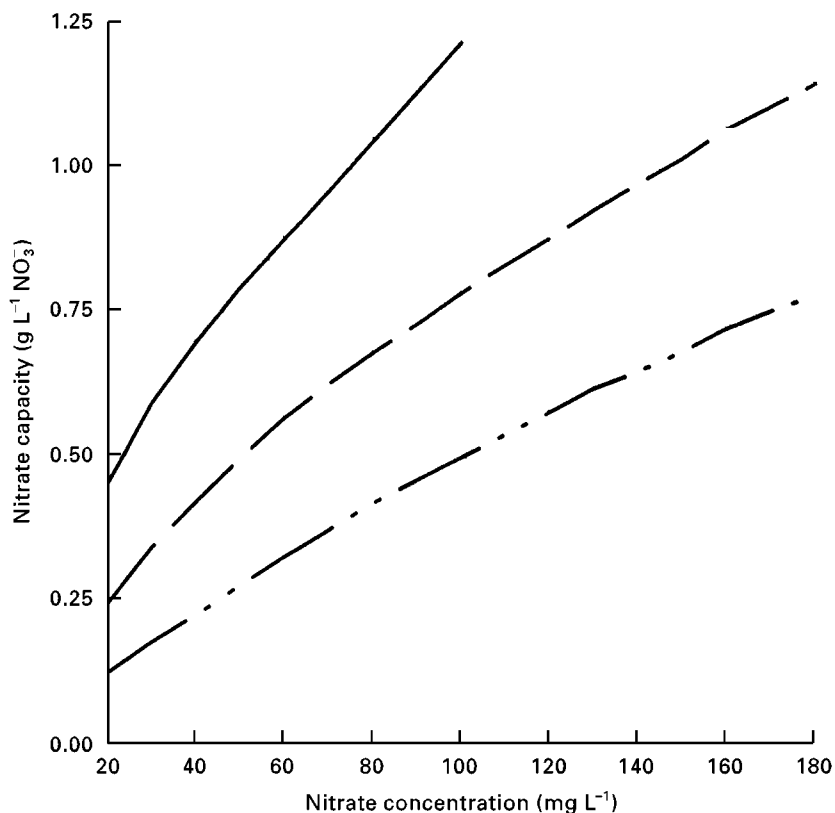


Figure 3 Operating capacity of a type 2 strongly basic anion exchanger depending on the concentrations of nitrate and sulfate in the raw water. Continuous line, 0.36 mmol L⁻¹; dashed line, 0.72 mmol L⁻¹; dotted and dashed line, 2.1 mmol L⁻¹. Resin: Lewatit M600.

Table 2 Data of operation of Ecodenit plant

Parameter	Feed water concentration (mg L ⁻¹)	Product water concentration (mg L ⁻¹)	Waste water concentration (g L ⁻¹)
Nitrate	70	25	25
Sulfate	50	10	10
Hydrogen carbonate	65	55	55
Chloride	50	120	120

and rinsing of the exhausted resin. After exhaustion the resin material in the contacting section is pulsed into the back-wash part, whereas regenerated and rinsed resin material enters the contacting section. The plant was designed for a maximum throughput of 277 m³ h⁻¹. The nitrate concentration was diminished from 100 to 43 mg L⁻¹ as the tolerable maximum.

In the second possibility the amount of NaCl required during regeneration is smaller. As a consequence, the regeneration is less efficient and the nitrate leakage becomes larger. Thus, all the water has to be treated. This principle is shown in the Ecodenit process developed in France. This process operates with NaCl quantities of ≤ 100 g L⁻¹ of resin and uses co-flow regeneration. The first full-scale plant for the treatment of 160 m³ h⁻¹ is in service in northern France. This plant consists of three filters operating in a merry-go-round mode. Each filter contains 8 m³ of a strongly basic resin. Results of the operation of the full-scale plant are summarized in Table 2.

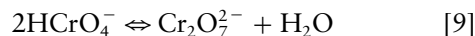
Both principles are combined in a third modification. Such a plant went into service in 1983 in California. The plant was to treat 115 m³ h⁻¹ blended with 45 m³ h⁻¹ raw water. It consists of three columns which are also operated in a merry-go-round mode. For each filter the throughput between two regenerations amounts to 250 bed volumes. The nitrate concentration is decreased from 71 to 11.5 mg L⁻¹ in the mixed effluent of the service filters and to 27–36.5 mg L⁻¹ in the blended product water. Since 1983, numerous nitrate elimination plants have come into service: most apply nitrate-selective exchangers.

Chromate Removal

Chromic acid and chromates are widely used in many applications. Anion exchange offers an ideal opportunity for the removal and recovery of chromates. Both strongly and weakly base resins can be applied.

In aqueous solutions chromate ions exist in different ionic forms. The speciation mainly depends on the pH value. In the acidic region (1 < pH < 6.5) and for

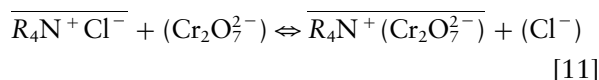
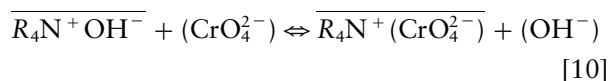
dilute solutions, HCrO₄⁻ is the predominant species. Above pH 6.5 mostly CrO₄²⁻ is found. With respect to ion exchange processes it is important that dimerization occurs at elevated concentrations:



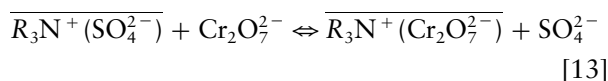
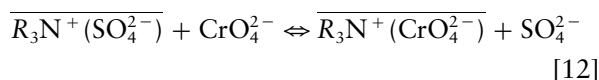
The respective pH conditions may exist in the anion exchanger phase. Therefore, the resins can be considered to be at least partly loaded with Cr₂O₇²⁻ species.

Chromate species are strongly preferred over chloride and sulfate ions under normal conditions. However, at acidic pH this preference vanishes for both weakly and strongly basic anion exchangers when chromate is the trace component. Consequently, fixed-bed experiments using standard acidic chromate-bearing waste waters exhibit a gradual increase in the effluent concentration. An increase in the concentration of competing sulfate ions yields only a negligible decrease in chromate capacity. In contrast to this, an increase in the chloride concentration leads to a considerable decrease in chromate capacity for a given liquid-phase concentration. For weakly basic resins the chromate capacity decreases with increasing pH because of the deprotonation of the functional groups. Below pH 5 the capacity is constant and depends only on the background composition of the solution.

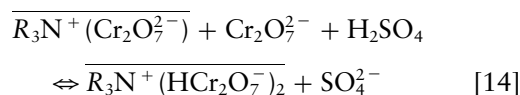
Using strongly basic exchangers chromate can be removed by the following exchange processes:



Weak base anion exchangers are applied, for example in the sulfate form:



Acidification of the feed solution leads to the formation of hydrogen dichromate species, which doubles the capacity of the resins, e.g.:



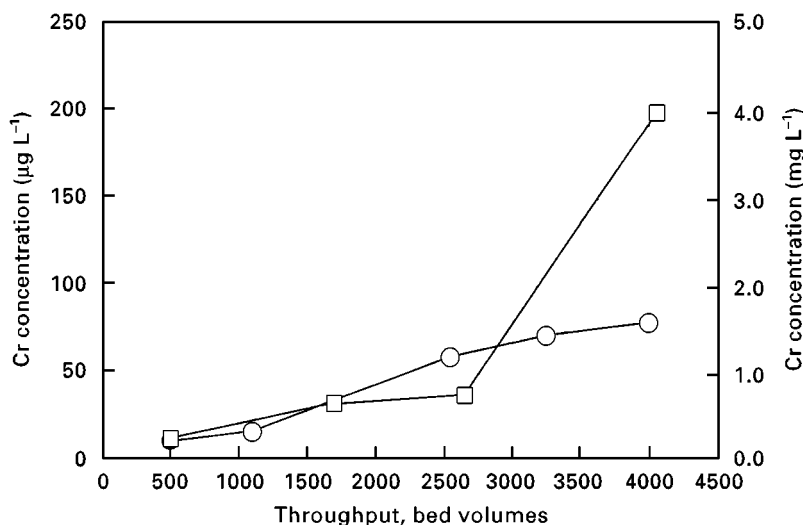
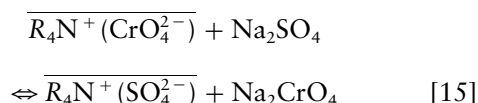
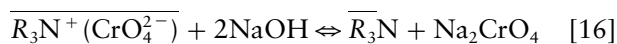


Figure 4 Elimination of Cr(VI) from cooling tower blowdown. Effluent concentration histories of loading (circles) and polishing (squares) columns. Feed water composition: Cl^- (500 mg L^{-1}), SO_4^{2-} (200 mg L^{-1}), Cr(VI) (10 mg L^{-1}), HCO_3^- (100 mg L^{-1}), $\text{Ca}^{2+} + \text{Mg}^{2+}$ (5.5 mmol L^{-1}), Na^+ (250 mg L^{-1}). Resin: Amberlite IRA 94.

After exhaustion, treatment with NaOH will convert hydrogen dichromates to chromates and, subsequently, yield half of the chromate loading on elution. Removal of the remainder of the chromate from the strongly basic exchanger requires concentrated sodium sulfate solutions:



In contrast to strongly basic exchangers, weakly basic ones can be completely regenerated by means of NaOH. However, before the following service cycle, the resins have to be reconverted to the sulfuric acid form:



Chromate species elimination from cooling tower blowdown has been achieved by application of a styrene weakly basic resin in a merry-go-round system with three columns. In the plant, column 1 serves as the crude loading column which eliminates most of the chromate. The relatively low effluent concentrations are further decreased by the second (polisher) column. The third column is regenerated/conditioned or waits for service. When the maximum tolerable effluent concentration of the polisher column is exceeded, the sequence is switched

so that the polisher column now acts as the loading column and the freshly regenerated filter is applied for polishing. The previous loading column is regenerated and conditioned. A typical example is given in Figure 4.

Removal of Organic Substances

Natural organic substances normally have an anionic nature at pH values above neutral. Apart from their elimination in a suitable pretreatment step, they can be adsorbed by both weakly and strongly basic anion exchangers. Uptake of organic substances is due to both ionic and van der Waals forces. They may present a problem for anion exchangers because of a possibly irreversible adsorption by styrene-based gel-type resins.

Both types of exchangers, therefore, can act as scavengers for the removal of organic compounds prior to further ion exchange steps. In general, strongly basic exchangers exhibit a better elimination of humic substances. For demineralization of industrial water they are applied in the chloride form as scavenger units at the head of the deionization train. The basic problems associated with the application of anion exchangers as scavengers in demineralization plants are the additional exchanger unit and the exchange of the organics and hydrogen carbonate ions for chloride. Thus, the effluent composition may be less favourable for the application of weakly acidic exchange resins.

Depending on the total concentration of organic matter in the feed water and to the desired level in the effluent, different resin types are recommended. The combined application of weakly and strongly basic

resins has been successfully applied in the Stratated® concept, in which two layers of the respective resins, both of the polystyrene type, are used. The application of this concept requires the use of exchange resins with a particle size distribution which allows the maintenance of the stratified bed in each column. Since regeneration is carried out using warm NaOH solution, precipitation of silica is avoided. Favourable conditions are met: waters of poor alkalinity and chloride and sulfate are the major part of the anions present. Acrylic anion exchangers allow a reversible uptake of humic acids. Although the capacity of acrylic resins for organics is poorer, they are highly effective. They can be used in all applications except in condensate polishing with extremely high flow rates. Under these conditions the elastic properties of these resins exclude their use.

At low levels of organic matter in the feed water the application of macroporous weakly basic resins in their free base form in the de-ionization train allows an efficient removal. Furthermore, these resins are less susceptible to irreversible fouling.

In drinking water treatment, macroporous styrene-based strong base resins were employed in Hanover in Germany as a single treatment step for the removal of organic matter from ground water. Dissolved organic carbon was to be reduced from 6.5 to about 3 mg L⁻¹. After 5000 bed volumes, the resin was regenerated by means of an alkaline NaCl solution which could be reused seven times. The plant was shut down in 1995.

Apart from the elimination of natural organic matter, anion exchangers may also be applied to the removal of organics from different types of waste water. Weakly basic resins have been used for the removal of phenol. Sorption is carried out at rather low flow rates of 2–8 BV h⁻¹. NaOH or organic solvents are used for regeneration. Macroporous weakly basic resins in the sulfuric acid form are applied for decolorization of kraft bleach liquors. After exhaustion they are regenerated using NaOH and conditioned by means of sulfuric acid.

See also: I/Ion Exchange. III/Water Treatment: Overview: Ion Exchange. Resins as Biosorbents: Ion Exchange.

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WATER-SOLUBLE VITAMINS: THIN-LAYER (PLANAR) CHROMATOGRAPHY

See III/VITAMINS/WATER-SOLUBLE: THIN-LAYER (PLANAR) CHROMATOGRAPHY

WAXES: SUPERCRITICAL FLUID CHROMATOGRAPHY

See III/OILS, FATS AND WAXES: SUPERCRITICAL FLUID CHROMATOGRAPHY