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ION EXCHANGE RESINS: CHARACTERIZATION OF

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Introduction

An ion exchange resin is an insoluble polymer matrix containing labile ions which are capable of exchanging with ions in the surrounding medium without any major physical change taking place in its structure. They are of two basic types, cation and anion exchangers. So-called cation exchange resins are in fact polymeric anions to which the labile cation is bound, and it is this cation which exchanges with other cations in solution. Likewise, anion exchange resins are polymeric cations with a labile, exchangeable anion.

The first synthetic ion exchange resins were developed by Adams and Holmes in 1935, based on a phenol-formaldehyde structure. The next most important development was the introduction of commercial ion exchange resins based on a cross-linked polystyrene matrix, and these resin types today still represent about 90% of the commercial resin market. More recently, polyacrylic resins have been introduced which have widened the scope and versatility of the synthetic ion exchange resins, and these represent most of the remaining 10% of the commercial market.

The development of synthetic polystyrene and polyacrylic resins has enabled these ion exchangers to be produced in spherical bead form, unlike the irregular-shaped particles of the phenol-formaldehyde types. In the majority of applications, the most efficient treatment of a solution is obtained by passing this solution through a bed of ion exchange resin. A spherical bead shape offers optimum contact with the percolating solution without undue pressure drop across the bed, requiring only minimal inlet pressures.

The first polystyrene resins, introduced in 1947, were of what is now known as a *gel* type. Exchange takes place by diffusion of the ions through the resin structure to and from the ion exchange sites. The polymer chains are only separated by molecular distances, and the ease of penetration of the ions is very much influenced by the amount by which the resin structure can be swelled by the contacting solution. In 1956, Mikes and co-workers discovered a means of introducing pores (or holes) into the resin structure, which led to the introduction of *macroporous* resins, which further increased the scope of ion exchange techniques. These resins comprise a continuous polymer matrix interspersed with a continuous pore matrix.

Synthesis

Polymerization

Generally speaking, the synthesis of a modern ion exchange resin is a two-step process. In the first step, the spherical bead is produced by polymerization of styrene (or an acrylic monomer, usually methyl acrylate) plus a cross-linking agent (usually divinylbenzene, DVB) in an aqueous suspension. This technique of suspension polymerization is used extensively in the production of pearl (or bead) polymers, not specifically to make ion exchange resins, and is dependent on the fact that the monomer is essentially insoluble in water. Thus, when stirred with water, the monomer will disperse into spherical droplets. Small quantities of various stabilizing ingredients are added to the water to make this dispersion more permanent.

An initiator is added to the monomer mixture which, on the application of heat, produces free radicals. These start a chain reaction with the monomer in which monomer units are progressively added to the growing polymer chains. Styrene contains just one double bond capable of reacting into the polymer chain. As a consequence, a polymer produced from styrene alone will comprise a large number of unconnected chains, and this hydrophobic polymer will be soluble in organic solvents such as aromatic hydrocarbons. Cross-linking agents, such as DVB, contain two or more reactive double bonds, each of which is capable of reacting in a separate polymer chain, ultimately leading to an ‘infinite’ single polymer chain network. Solvents will still be absorbed by the polymer chain and swell the polymer, but will not be able to dissolve it. The extent of the swelling is dependent on the proportion of DVB in the monomer: the more DVB, the less the polymer will swell.

The invention of macroporous resins has been briefly mentioned. The continuous pore structure within the resin matrix is produced by polymerizing the monomers in the presence of an inert diluent which is miscible with the monomers but essentially immiscible with the growing polymer chains. As the polymerization progresses, the mixture separates into two phases, one phase being the growing polymer, the other being the diluent plus a continuously decreasing amount of monomer. At the end of the polymerization, the diluent, which has not actually polymerized into the structure, is removed by distillation or washing, leaving the interconnecting network of pores.

Activation

The second stage of synthesis is to add a functional group to the polymer, which will contain the labile ion capable of exchange with ions in solution. The effect of this functional group is to make the polymer structure hydrophilic. The resin will now be swollen by water, but again cannot dissolve due to the polymer chain structure. The extent of this swelling by water is an important characteristic of an ion exchange resin, and controls its behaviour in many applications.

The sulfonic acid group of the strong acid cation resins is added by reaction of the polystyrene polymer with sulfuric acid at temperatures between 90 and 140°C. The amino group of the strong and weak base resins is added in two stages, firstly a chloromethylation to add a chloromethyl group to the polystyrene chain followed by addition of an amine to give the final quaternary or tertiary amino functionality. The choice of amine affects the resin properties, which will be discussed shortly.

Polyacrylic resins are produced as either weak acid cation resins with a carboxylic acid functional group (to which there is no polystyrene resin equivalent), or as strong or weak base anion resin whose properties are similar, but not identical, to those produced from polystyrene.

Classification of Ion Exchange Resins

Both cation and anion resins are available with strong and weak functional groups. The strong functional groups are ionized species within which the ionized labile ion can be replaced with an ion in solution. These resins will therefore easily exchange ions with dissolved salts. On the other hand, the weak functional groups are themselves nonionized and will therefore have very little ability to exchange with salts. Weakly functional anion resins will however readily remove anions from acidic solutions, and weakly acidic resins will readily remove calcium and magnesium from solutions of carbonates and bicarbonates.

Strongly basic resins are further subdivided into three categories. The most commonly encountered of these is the *strong base anion Type I* resin (often abbreviated to SBA I). The second most common category is the *strong base anion Type II* (SBA II), which is a weaker base than the Type I but still not weakly basic enough to be categorized as a weakly basic resin. The third category, *strong base anion Type III* (SBA III), is actually intermediate between these two types, and, although not as yet widely used, is being shown to combine useful characteristics of both.

In more recent years, a number of resins with special functional groups have been produced commercially. These are designed for removal of specific ions for special applications. One particular application is the use of a polystyrene resin with an aminophosphonic chelating group – this resin, in the sodium form, is used to remove calcium and other divalent ions from brine prior to the production of caustic soda by the membrane cell process. A conventional cation resin would be completely unable to remove these alkaline earths from concentrated salt solutions.

Resins in each category can be produced in both gel and macroporous forms.

Fundamental Ion Exchange Resin Characteristics

Irrespective of the resin type, there are certain fundamental parameters which characterize ion exchange resins, and determine how that resin will perform in its applications.

Moisture Retention

As mentioned earlier, an ion exchange resin is swollen by water but will not dissolve in it. The extent of this swelling is one factor which controls how the resin will perform in specific applications. A resin will absorb a certain amount of water, depending on the functional group, the ionic form and the amount of cross-linking. For a given resin type in a given ionic form, the swelling is entirely dependent on the amount of cross-linking.

Moisture retention is defined as the amount of water which is in equilibrium with the dry resin matrix. This water can be removed by hot air drying, but will be readsorbed when the resin is put back in contact with excess water. The value of the moisture retention is easily determined by measuring the loss in weight of a fully swollen resin on drying, and expressing the moisture loss as a percentage of the total wet weight.

The importance of moisture retention in the performance of a resin should be fairly obvious. For the resin to operate, the ions in solution must have access to the active sites throughout the polymer structure, just as the ions which are displaced from these sites must be able to pass out of the resin back into solution. The more open the structure (i.e. the higher the moisture retention), the easier this will be.

The labile ion which is attached to the resin influences the hydrophilic nature of the structure, and so the moisture retention. For instance, at a given amount of cross-linking, a strong acid cation resin in the sodium form (i.e. with a Na^+ group attached to each sulfonic acid site on the structure) will have a significantly lower moisture retention than the same resin in the hydrogen form. Therefore, the ionic form must be stated along with the moisture retention.

Resin Capacity

The ability of an ion exchange resin to exchange ions is a function of the number of active groups that have been placed on the resin during the activation process. The overall term for this is the *capacity* of the resin, but this can be expressed and determined in a number of ways.

Dry weight capacity This measures the proportion of active sites in the dry resin matrix, and is expressed as equivalents per kilogram (or milliequivalents per gram, as some workers prefer). It is easily determined by weighing a dry sample of resin, rewetting it and displacing completely from the resin an ion which can be titrated in solution. This gives the total equivalents of sites on the dry resin, and is a direct measure of the extent of activation of the base polymer. For most applications, the figure obtained does not have any direct significance, since the resin is rarely used in its dry state except in certain specialized applications.

Total volume capacity Since resins are normally supplied and used wet (i.e. fully swollen in water), the capacity based on a volume of wet resin is more useful. It is, however, more difficult to measure a wet resin volume as accurately as dry resin weight, but essentially the test method is the same apart from measuring a known volume of resin rather than weight. The data is expressed in terms of equivalents per litre (or milliequivalents per millilitre).

Although the test value can now be related to the volume of resin installed in the resin treatment plant, it will still not tell the plant designer or user the capacity achievable when the unit is in practical operation.

Operating capacity This is the true practical parameter, but unfortunately it cannot be determined by a straightforward laboratory test. Since the operating capacity of a resin depends on many factors, such as the dimensions of the unit, the flow rate and quality of the liquid to be treated, the quality required of the effluent from the unit, the regenerant quantity and the operating temperature, etc., this capacity can only be calculated from data obtained by extensive laboratory testing of a resin type under simulated operating conditions. This data is usually provided in brochures supplied by the resin manufacturers, and more recently a number of these manufacturers have computer programs available to make these calculations quickly on data stored within the software.

Particle Size Distribution

As already described, modern ion exchange resins are in the form of spherical beads. The suspension polymerization technique does not produce beads of a uniform particle size, rather a distribution of sizes to give a resin within the range 0.3–1.2 mm. Most ion exchange applications have been developed around resins of this particle size range, but some special applications do require the particles to be of a more specific size.

In the majority of applications, the ion exchange resin is contained in a vessel which is designed to allow the solution to be treated to pass through the resin bed and subsequently emerge from the unit. The resin has therefore to be retained within this unit by a suitable means, usually nozzles or slats of such an aperture that the solution can freely pass. Depending upon engineering design, these apertures will normally be about 0.2 mm wide, but in some designs can be as large as 0.4 mm. It is therefore essential that the ion exchange resin does not contain beads close to or less than this aperture size.

A number of resin applications require two resins to operate mixed together in the same unit. For regeneration, it is essential that these resins are separated. Strong acid cation resins have a density of about 1.25–1.30 g g^{-1}, whereas anion resins have a density of 1.07–1.10 g g^{-1}. Therefore, by applying backwash to lift and expand the resin bed, the cation resin beads will sink below the anion resin beads. A complete separation is readily achieved if the cation resin contains less coarse beads an the anion resin less fine beads.

Ions obviously have a greater path length to travel to the centre of a large bead compared to that of a small bead. This decreases the efficiency with which a larger bead can complete the ion exchange process. A number of applications have developed today in which beads of a more uniform size distribution, normally in the range 0.4–0.8 mm, are used, thereby eliminating the most coarse beads of the 'standard' size range.

For these reasons, measurement of particle size distribution of resins is important. The classical method is to use standard sieves, but due to limitations of sieve accuracy and availability, they are not best suited to measuring resins with narrower size distributions. Most resin manufacturers and larger users now use an instrumental technique based on a light extinction principle, such as the OMEGA (Fortress Dyamics, UK) or HIAC (Hiac-Rogco, USA).

Resin Volume Change

It was observed earlier that a given ion exchange resin will be in equilibrium with a different volume of water depending on its ionic form. Consequently, when the resin is treating the feed solution, the bed of resin will slowly swell or shrink as the ions are being exchanged. It is important for the plant design engineer to know the extent of this volume change in order to allow sufficient space for any increase in volume to be accommodated. It has been known for poorly designed plants to smash a resin, or even for the plant itself to be damaged, if this swelling factor has not been properly accounted for.

Other Resin Characteristics

There are a number of other parameters which have to be taken into account when designing an ion exchange plant, such as pH range and operating temperature. All resins of a given type will have virtually identical limitations on these parameters. The recommendations given by the resin manufactures should be followed. It is worthy of note that SBA Type II resins are less thermally stable than their Type I counterparts, and that polyacrylic anion resins are less thermally stable than polystyrene ones with the same functionality.

Macroporous versus Gel Resins

In appearance, gel resin beads are usually transparent. Light entering the bead will pass through the homogeneous structure without being diffracted, therefore being visible from the other side of the bead. With a macroporous bead, there are numerous phase boundaries within the bead between the pores and resin matrix, at each of which the entering light will be refracted. Consequently, little or no light will emerge, giving the resin bead an opaque appearance.

Gel resins were in extensive use in ion exchange for many years before the invention of macroporous resins. These macroporous resins were found to have two main advantages over their gel counterparts – they were less susceptible to osmotic shock and less liable to organic fouling.

As just discussed, a resin will change in volume as it changes its ionic form. Moreover its volume will contract when it is in contact with strong electrolyte solutions which it will encounter during regeneration, and will rapidly swell again when this regenerant solution is washed off. These volume changes exert an osmotic stress across the boundary between resin and solution, which in the case of a gel resin is the resin bead boundary itself. These forces can weaken or even smash the resin bead. Although fragments of resin are still just as good as a whole bead in the exchange process, they will certainly impede the flow of liquid through the bed, increasing the pressure drop and decreasing the flow. Also, the small fragments can block the strainers of the unit, and even contaminate the treated solution.

A macroporous resin, by nature of its structure of interconnecting pores and matrix, comprises very many small resin–solute interfaces, so although the osmotic force across the bead as a whole will be the same, it will be dispersed across all these small boundaries. Therefore, the stress on the bead will be much less, and there will be very much less chance of the resin bead being weakened or broken.

Most natural waters, as well as many organic solutions which ion exchange resins are used to treat, contain large and complex organic molecules. These will slowly penetrate a resin bead, particularly if the organic molecule itself contains an ionic charge. Because of their size, these molecules become entangled with the resin structure, and are not easily removed when the resin is regenerated. Consequently, these molecules build up within the resin, blocking access of the ions in solution to the exchange sites, with a resulting drop in resin capacity. This is known as *organic fouling*. The pore structure of macroporous resins allows greater freedom of passage of these organic molecules, so they are more freely released during regeneration. Anion resins based on an acrylic matrix, due to the nature of this matrix, are also less susceptible to organic fouling.

Unfortunately, macroporous resins also have a major disadvantage. Part of the resin bead, the pores, is purely water with no ion exchange properties. In order that the overall number of ion exchange sites within a given volume of resin is similar to a gel resin, the resin matrix itself has to contain less water – it will be more highly cross-linked. With such a matrix having a lower amount of water associated with the structure, ions will be able to move less freely, so causing the resin to exchange ions more slowly. In practical terms, this results in either reducing the rate at which the solution to be treated can be fed to the resin, or reducing the efficiency of the ion exchange process.

Since optimum efficiency of ion exchange (known as ion exchange *kinetics*) is an important factor in the design and operation of a treatment plant, gel resins will normally be preferred except in circumstances where the advantages of macroporous resins outweigh this major disadvantage.

Resin Regeneration

In most resin applications, the resin is used over many treatment cycles. Once the resin has become exhausted (in other words, when it is no longer removing the ions from solution at the threshold level required by the user), it is then regenerated with suitable chemicals to once again attach to the active group the mobile ion which will subsequently be released into the treated solution. In the case of cation resins in demineralization processes, this will be a mineral acid and in the case of anion resins, an alkali, usually sodium hydroxide.

Not only do resins swell in water to a different extent when different ions are attached, they have a different affinity for the various ions, and in the case of treatment of solutions containing a mixture of ions, the resin sites will compete at different rates for the different ions. This is known as *selectivity*. Likewise, if an ion for which the resin has a higher selectivity is already attached to an active group, it will be much more difficult for an ion of a lower selectivity to displace it from the resin.

Consider a solution containing a cation B, and a cation resin in which all the sites are occupied by cation A. As a B ion penetrates through the bead, it will attach to an active site displacing an A ion in the process (**Figure 1**). Initially, since the resin contains only B ions, this released A ion can do nothing but emerge from the resin back into solution. However, as more and more sites within the bead take up B ions, there is a chance that the released A ion could displace another B ion which had already been taken up on a different site. The ease with which this would occur depends on the relative selectivity of ions A and B to the resin – if the resin is significantly more selective for the B ion, then this is less likely than if the resin were more selective for the A ion.

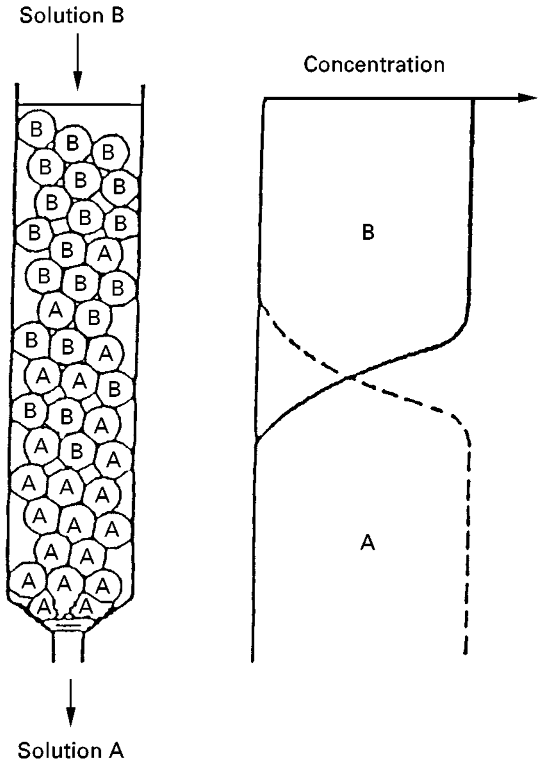


Figure 1 Ion exchange equilibrium.

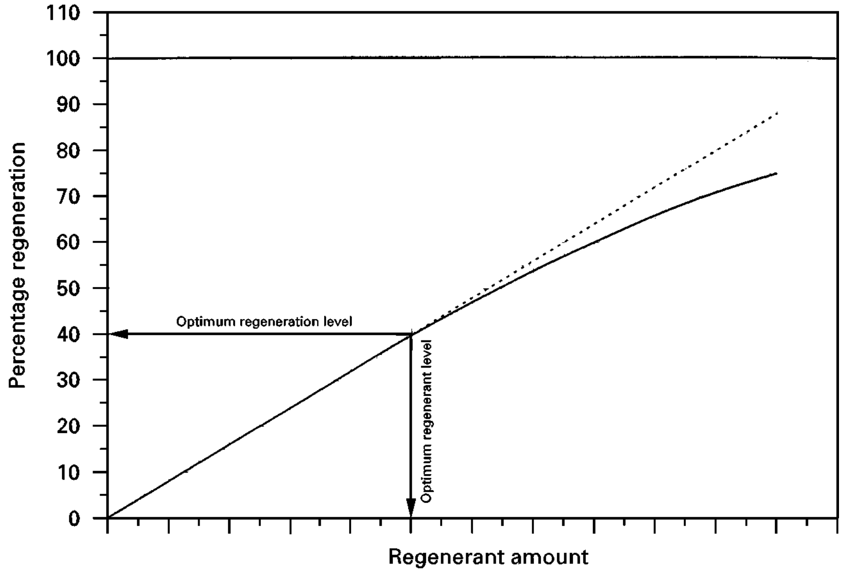


Figure 2 Typical regeneration curve. Dotted line, optimal; continuous line, practical.

When a resin is being regenerated, the more regenerant which is passed, the more completely will the resin be regenerated. However, because of this interchange of ions within the resin, the percentage of resin regenerated is not a linear function of the amount of regenerant (**Figure 2**). In other words, doubling the amount of regenerant used will not necessarily double the number of sites regenerated. Since the operational cost of an ion exchange resin plant is heavily influenced by the regenerant cost, it is not usually practicable to regenerate a resin fully, rather to balance the percentage regeneration to the most economic use of the regenerant. Consequently, a quantity of regenerant much more than the point at which the regeneration curve loses linearity is unlikely to be used.

The shape of this regeneration curve will vary with different resins, depending not only on the nature of the active group and the moisture retention, but also on the structure of the resin matrix itself.

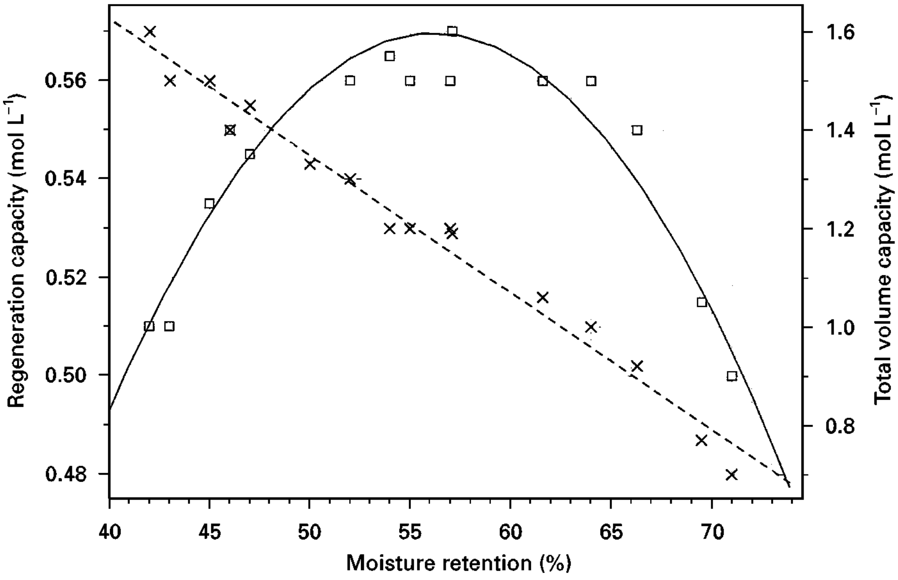


Figure 3 Comparison of regeneration (squares) and volume capacities (crosses) (on the same resin samples). SBA Type I gel resins regenerated with 65 g NaOH per litre resin.

Table 1 Typical regeneration efficiencies of different resin types

Resin	*Regeneration efficiency (%)*
SAC gel	50–60
SAC MP	45–55
WAC gel/MP	80–95
SBA I gel	35–45
SBA I MP	30–35
SBA II gel	60–70
SBA II MP	55-65
SBA III MP	45–55
WBA MP	80–95

Even two resins of the same functionality and total exchange capacity might regenerate differently.

Strongly acidic or strongly basic resins readily exchange ions from neutral salts. The exchange process is therefore an equilibrium, and the ion displaced from a resin site will be capable of exchanging with the ion on another site. In the case of a weakly functional resin, the exchange is more of neutralization reaction, and there is little chance of the released ion exchanging with another site on the resin. For this reason, the regenerability of a resin increases as its acidity or basicity decreases.

Regeneration capacity

In this test, a known volume of fully exhausted resin is put in a column, and a fixed amount of regenerant passed through. The type and quantity of regenerant would be appropriate to the application under consideration. The equivalents of ions displaced or adsorbed by the resin are determined, and the regeneration capacity can be expressed in terms of equivalents per litre of resin, or as a percentage of the total volume capacity of the resin (known as *regeneration efficiency*), which can conveniently be determined on the same measured volume of resin. **Figure 3** clearly shows the significance of moisture retention on the kinetic performance of a resin. As discussed earlier, a gel resin of a given type with a lower moisture retention will have a higher total capacity, but this higher capacity is not reflected by the regeneration capacity, and under many conditions the operating capacity, of the resin.

For the reasons discussed earlier, macroporous resins will generally have a lower regeneration efficiency than their gel counterparts. **Table 1** gives an approximate indication of the regeneration efficiencies of the different categories of resin, using typical regeneration amounts of 60–80 g regenerant per litre of resin.

Conclusions

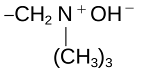
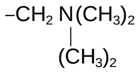
The main characteristics of ion exchange resins are summarized in **Table 2**.

Most current developments in ion exchange resin manufacture have been based on modifying production techniques to give more uniform bead distributions at lower production costs. One exception has been the introduction of a range of highly porous Macronet adsorbent resins which are finding applications in the removal of trace levels of organic contaminants in aqueous, and even gaseous, feed stocks, as well as replacing activated carbon in the removal of coloured bodies from sugar syrups.

There are some new developments of resins as pharmaceutical products or in the extraction of precious metals from spent ores. Newer and more exotic applications are continually being found for ion exchange resins outside the conventional water treatment field, but these generally use existing resin types or only slight modifications thereof.

See also: **II/Ion Exchange:** Historical Development; Inorganic Ion Exchangers; Organic Ion Exchangers; Organic Membranes; Theory of Ion Exchange.

Table 2 Typical characteristics of ion exchange resins

	Strong acid	*Weak acid*	*Strong base*	*Weak base*
Functional group	$-SO_3^-H^+$	$-COOH$	 $-CH_2N^+(CH_3)_3OH^-$	 $-CH_2N(CH_3)_2(CH_3)_2$
Effect of pH on exchange capacity	Largely independent	Negligible in acid solutions	Largely independent	Negligible in alkaline solutions
Resin salts	Stable	Hydrolyse on washing	Stable	Hydrolyse on washing
Regeneration	Excess strong acid required	Readily regenerated	Excess strong base required	Readily regenerated

Further Reading

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ION EXCHANGE: ZEOLITES

See **III / ZEOLITES: ION EXCHANGERS**

ION FLOTATION

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Introduction

Sebba published a paper in 1959 in which he discussed a new method (ion flotation) for recovering solute from dilute solutions by adding surfactant, with subsequent adsorption of the solute onto bubbles. The principles of the process and the characteristics of the solute–surfactant product formed in solution were discussed in his monograph on ion flotation published in 1962. The method rapidly became popular and researchers in several countries have studied various aspects of the separation of metallic ions, trace elements, molecules, inorganic anions and organic matter from aqueous solutions. Many laboratory-scale studies have been carried out, most of them aimed at development, analytical applications, water purification, resource recycling, removing radionuclides from solutions, and recovering metals from sea water.

A comprehensive development of all aspects of the subject was presented in a monograph on adsorptive bubble separation techniques, edited by Lemlich in 1972, in which details and applications of ion and precipitate flotation methods were reported by Pinfold.

The research group directed by Grieves made an important contribution to the theoretical and applied aspects of ion and precipitate flotation during the 1960s, particularly on wastewater treatment. They showed that flotation efficiency of long-chain surfactants was the result of physicochemical aspects of particle growth and dispersion. But the adsorption of surfactant onto the solid and gas phases was identified as a factor limiting bubble-particles attachment in some cases of ion flotation.

The adsorption of the surface-active solutes to the gas–liquid interface was studied by Rubin. An analysis based on the Gibbs and Langmuir isotherm and on an originally developed approach of long-chain ion adsorption in a solution containing several surface-active species was used to determine the effect of their concentrations on the ratio of distribution coefficients. This author also described the kinetic parameters for ion and precipitate flotation.

A detailed review of the precipitate and adsorbing colloid flotation technique with a comprehensive literature review appears in the monograph published in 1983 by Clarke and Wilson.

Golman has given a qualitative description of the chemical and kinetic aspects of ion flotation and some industrial applications, including the removal of molybdenum from solutions of hydrometallurgical flowsheets. He has also given methods for treating foam products and purifying process residual solutions.