



Dow
Liquid Separations

DOWEX™ Ion Exchange Resins

Practical Guidelines

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Disinfection

Disinfection of ion exchange resins must always be operated on a fully exhausted and physically clean bed, in order to avoid undesirable oxidation-reduction reactions induced by residual acidity or basicity of the resins and resulting in disinfecting agent deactivation.

Thorough backwash followed by full exhaustion of resin or bringing to neutral pH effluent is therefore required.

Numerous biocides are available from various manufactures. They essentially differ by their biocidal spectra: fungicides, bacteriacides, sporicides, etc.

Their activity and also their impact on resins integrity are mainly driven by the concentration, temperature and contact time at which they are used. In the case of tight antimicrobial requirements involving special biocides (e.g. in the drinking water, sugar, dairy or pharmaceutical industries), special testing might be required in order to evaluate the chemical impact of the disinfecting agent in the particular conditions of use on both the ion exchanger and on the product resulting from the ion exchange process.

It should be noted that, though well known for their high efficiency as biocides, chemicals featuring a quaternary ammonium group are not compatible with cation exchange resins.

Examples of Disinfecting Compounds

Although it was frequently used, formaldehyde has lately been de-emphasized as an easy-to-use resin disinfection agent.

Commonly used disinfecting agents are sodium hypochlorite and hydrogen peroxide.

Sodium hypochlorite can be applied at a concentration of 0.1-0.25% (pH 9), of which a minimum of 0.5 bed volumes (BV) should be prepared. A contact time of 20 to 30 minutes is appropriate and should not be exceeded, especially for anion exchangers.

After a 2 BV rinse, a double regeneration must be done to convert the resin into the appropriate ionic form.

Hydrogen peroxide can be applied as a solution of 0.2% with a contact time of 15 minutes; 0.05% for 2 hours or 0.05% for 24 hours (0.5 BV minimum). This should be followed by a rinse to eliminate peroxide (detectable by paper re-agents) and then by a double regeneration.

Peracetic acid, stabilized by hydrogen peroxide, can also be a suitable disinfection agent.

Storage and Handling of Ion Exchange Resins

Ion exchange resins are normally shipped in the water-swollen form and should be stored in a sheltered area, and in a manner whereby the moisture within the beads is retained. The resin may be stored in the plastic bag in which it was shipped, provided it is kept tightly sealed, or transferred to a glass container. Although freezing does no harm, repeated freezing and thawing should be avoided.

Resin beads that have dried out become free flowing and some shrinking of the beads is evident. Dry beads will re-swell very rapidly when placed in aqueous or other polar solutions thus causing severe strains, which may lead to bead breakage. Should the beads become dry, they may be hydrated with a saturated sodium chloride solution. The salt is removed by successive dilutions and decantations. It should be emphasized that this re-hydration method will not result in complete elimination of the bead breakage; therefore, it is important that the resin is not allowed to become dry, except for desiccant applications.

The regenerative effect of contact in resin beads that are in other ionic forms (other than sodium or chloride), with a sodium chloride solution should be taken into consideration, and the proper regeneration procedure should be followed to convert the resin to the desired ionic form. Care should be taken to clean up spills of ion exchange resins since the small beads are very slippery when stepped on.

Dyeing Resin

Cation exchange resins (DOWEX™ HCR-W2 (H⁺)) can be dyed with 1.2 grams of 4-phenylazodiphenylamine in 1 liter of ethanol per 28 liters of resin.

Anion exchange resins are dyed with 0.4 grams thymolphthalien in 1 liter of 1:1 ethanol:water, per 28 liters of resin.

The resin is agitated while adding diluted dye solutions in small amounts. Continue agitation for 30 minutes and rinse until all of the excess dye is removed. These resins will, after dyeing, change color when converted from the regenerated to the exhausted form.

Troubleshooting

Problems in the operation of ion exchange systems can be traced to 1) mechanical (operation) faults and/or 2) impaired resin performance.

Mechanical (Operational) Faults

Some commonly occurring operational faults that result in poor water quality, poor capacity or both are:

Improper Backwash

The backwash operation is done to clean the bed of particulate matter which may have been filtered onto and into it during the operating portion of the cycle and to loosen and reclassify the bed, prior to, or subsequent to regeneration. An insufficient backwash flow rate can result in the accumulation of all the suspended and filtered solids on the top of the resin bed without removing them from the ion exchange column. This is likely to result in solution channeling through the resin bed resulting in a lowering of the bed capacity due to non-utilization of a portion of the ion exchange resin present. Excessive flow has the opposite result. Not only are the accumulated solids removed, but ion exchange resin can go with it, resulting in a reduced capacity, due to resin inventory.

If the backwash flow rate is controlled at the backwash inlet, pressure can be released within the ion exchange resin bed and dissolved gas evolution can take place, in and around the resin particles. These gases tend to adhere to the resin particles and float them from the column. Keeping the column under pressure during backwash will prevent the condition.

In locations where water temperature fluctuates seasonally, it is important to note that the change in water viscosity with the temperature can affect the expansion of the resin during the backwash operation. This can result in either insufficient backwash or loss of resin.

Leaking Valves

This seemingly obvious difficulty can nonetheless be the cause of poor water quality if valves controlling the regenerant chemical leak, or if multiport valves separating feed from product water leak.

Insufficient Regenerant

Low capacities can result if the regenerant chemical does not contact the ion exchange resin at the proper concentration for the proper period of time. Various mechanical failures can cause regenerant to be improperly measured or excessively diluted. A specific gravity profile of the effluent from the column during the regeneration step can often pinpoint this difficulty.

Improper Flow Rates

Flow rates different from the design flow rates, particularly excessive flow rates, can sometimes surpass the resins kinetic capabilities, particularly in the case of the weak acid or weak base ion exchange resins. This will result in the production of low quality products.

Plugged Distributors

This can result in unequal distribution of feed across the ion exchange bed and the formation of isolated pockets of incompletely contacted resin. Poor capacity is usually the prime result. This condition will require mechanical cleaning of the distributor system.

Suspended Solids in Feed Water

This condition can result in the fouling of the ion exchange bed with particulate matter, due to the excellent filtration characteristics of an ion exchange bed. The subsequent perforation of the filter cake can result in solution channeling through the bed, causing premature breakthrough and low capacities. This condition can be controlled by better pretreatment of the feed water. The condition may sometimes be controlled by operating for shorter cycles and removing the filtered solids from the resins bed by a sub-surface backwash operation.

Contaminated Regenerant

Ion exchange resin fouling can result from the use of a contaminated regenerant and result in channeling of flow with its attendant problems. Iron contaminant in caustic is a prime example of this difficulty.

Impaired Resin Performance

Operation problems in an ion exchange system which are due to resin instabilities are usually the result of a loss of resin capacity, physical integrity, density or reaction kinetics.

Loss of Capacity

Loss in total ion exchange capacity of a resin will result in a proportionate loss in the ion exchange system capacity. The quality of the product water will not normally be affected. Once lost, the capacity of the resin is not restorable.

Loss of Physical Integrity

Broken beads normally result in increase in pressure loss in a column if the breakage is hemispherical. Finer resin particles are removed regularly with proper backwash operation and the loss of physical particles of resin will eventually show up as a reduction in system capacity. No product quality deterioration would normally be expected.

Loss of Resin Density

This will result in the eventual loss of resin through the backwash operation and reduced system capacity as indicated before.

Loss of Reaction Kinetics

This will lead to ion slippage past the bed and result in poor product quality. If the poor quality does not exceed the breakthrough endpoint, no substantial reduction in capacity would result. However, if this becomes a serious enough reduction in kinetics, the capacity of the system will also be reduced. This problem is particularly apparent in high flow rate mixed beds.

Factors Affecting Resin Stability

In the synthesis of ion exchange resin for commercial applications, resistance to physical and chemical degradation must be a major consideration. Costs of resin replacements must be minimized for maximum economy of operation. Resin life is generally measured by the number of cycles or years of operation before replacement is necessary. Sometimes resin life is expressed in terms of percent loss of operating capacity per year. Resin losses vary widely with application and type of resin. In water softening, losses are frequently less than one percent per year. Many installations still in use have required no resin replacement in over 15 years of continuous operation. In the case of most deionization applications, operating losses on the cation exchange resin generally fall between two and five percent per year; losses in anion exchange resins are usually between five and twenty-five percent per year.

The following six factors affect the resin stability:

- Temperature
- Oxidation
- Fouling
- Osmotic shock
- Mechanical attrition
- Radiation

Temperature

These temperature maxima are offered as guidelines only. Most manufacturers recommend maximum operating temperatures for ion exchange materials. For cation exchange resins, temperature maxima in the range of 248-300°F (120-150°C) have been established for salt forms, and somewhat lower maxima for acid forms. In the case of anion exchange resins, the temperature maxima is in the range of 86-140°F (30-60°C) for resins operating in the hydroxide or free base form; here too the salt forms are more stable.

These temperature maxima are intended only as guides. Thus, a temperature limitation of 212°F (100°C) does not mean that the resin will be unstable above and stable below this temperature. It should also be recognized that thermal degradation is proportional to the product of time and temperature. Thus, an occasional excursion for a brief time to a temperature above the maximum may result in little or no loss in performance. Furthermore, temperature maxima may be exceeded without disastrous effects if the cost of the process permits resin replacement in a relatively short period of time.

Oxidation

Exposure of ion exchange resins to highly oxidate environments can shorten resin life. One of the most common oxidants encountered in water treatment is free chlorine. Hydrogen peroxide, nitric acid¹, chromic acid and chloric acid have also been responsible for resin deterioration. Dissolved oxygen by itself does not usually cause any significant decline in performance, but if oxygen is encountered in combination with heavy metals and/or elevated temperatures, acceleration of losses can be significant, particularly with anion exchange resins.

The decline in operating capacity (salt splitting capacity) may not be seen until more than 25 percent of the capacity has been converted. Weak base resins, particularly those having only tertiary amine groups, have greater stability than strong base resins. Oxidation of weak base resins can result in formation of weak acid groups. When this occurs, the resin tends to retain sodium and requires a large volume of rinse water following regeneration.

Fouling

Irreversible sorption or precipitation within resin particles sometimes causes deterioration in resin performance. Fouling of anion exchange resins due to the irreversible sorption of high molecular weight organic acids is a particularly bothersome problem. Long experience in deionization has demonstrated the advisability of preventing fouling rather than relying on one-off resin cleaning procedures. Proper choice of resin for applications where fouling is likely can result in lower operating costs.

¹ **Warning** Nitric acid and other strong oxidizing agents can cause explosive reactions when mixed with organic materials such as ion exchange resins. In the unlikely event of using strong oxidizing agents, consult sources knowledgeable in handling such materials.

Although fouling rarely occurs with cation exchange resins, difficulties due to the presence of cationic polyelectrolytes in an influent have been known to occur. Precipitation of inorganic materials, e.g. calcium sulfate, can sometimes cause operating difficulties with cation exchange resins. These can be avoided by eliminating contact of the two offending ions and can usually be cured by prolonged acid wash. Iron fouling has occurred in both cation and anion exchange resins; such occurrences can be eliminated by proper treatment of the resins or by prevention, preferably the latter.

Resin clean-up procedures for fouled resins:

1. Organic poisoning can be cleaned up by:
 - a. Warm 10% NaCl
 - b. Warm 10% NaCl – 2% NaOH or,
 - c. 0.2-0.4% NaOCl
2. Silica precipitations, H_2SiO_3 , can be cleaned up by warm (120°F / 49°C) 2-4% NaOH which yields a soluble Na_2SiO_3 .
3. Calcium sulfate precipitate can be cleaned up by contacting with HCl upflow.
4. Oils and greases can be cleaned up by use of low-foaming non-ionic detergents.
5. ABS detergents can be cleaned up by a mixture of alcohols.
6. Iron silicates can be cleaned up by hydrofluoric acid.

Osmotic Shock

Alternate exposure of resins to high and low concentrations of electrolytes can cause cracking and breakage due to alternate contraction and expansion. Eventually there may be significant reduction in particle size, causing increased resistance to flow and subsequent resin losses. Resistance of a given material to osmotic shock can usually be determined by subjecting the resin to cycles of high and low concentrations. For example, alternate treatment of a resin column with 4% NaOH, water, 8% H_2SO_4 and again water, constitutes a very severe but indicative test. Particle size is a most important factor in osmotic shock. Smaller particles, particularly those which pass a number 30 sieve (smaller than about 0.6 mm) are considerably more resistant to breakage than larger particles.

Mechanical Attrition

The physical stability of most currently used ion exchange resins is adequate to prevent attrition losses in column operations. On occasion, losses due to osmotic shock or precipitation within resin pores have been mistakenly reported as mechanical attrition. However, losses due to mechanical attrition can occur when the resin is subjected to unusual mechanical forces. For example, breakage has been encountered in the movement of resin particles from one vessel to another, such as that which occurs in some continuous counter-current equipment. The combination of high flow rate and deep resin beds may also contribute to resin fracture. Large particles are more subject to mechanical attrition than smaller particles.

Radiation

Generally, cation exchange resins are adequately stable for almost all reasonable applications involving radioactivity. Radiation damage shows up as a de-crosslinking of the resin. Anion exchange resins are less stable although generally adequate for use in radiation fields.

Testing of Ion Exchange Resins

Procedures allow determination of the wet volume total (ultimate) capacity, the wet weight total capacity, and the dry weight total capacity as well as the percent moisture of styrenedivinylbenzene resins of the sulphonic acid, quaternary ammonium, or polyamine types presently commercially available. Each of the properties listed above is important in considering chemical stability and each of the properties is inter-related.

The wet volume total capacity is the total number of exchange sites available per unit volume of wet swollen resin. A decrease in the wet volume total capacity after a series of ion exchange cycles may indicate loss of active exchange sites or a breakdown of resin crosslinkage. The determination of the dry weight total capacity allows the calculation of the loss of exchange sites. An increase in moisture content indicates a decrease of crosslinkage in the resin.

A comparison of these properties will allow the determination of a decrease in ion exchange capacity due to loss of exchange sites and/or resin crosslinkage.

Useful Life Remaining on Ion Exchange Resin

The approximate useful life of ion exchange materials may be evaluated by the comparison of water retention capacity of a strong acid cation exchange resin to the original resins; and the comparison of the original salt splitting capacity of a strong base resin with that of a representative sample tested in the laboratory. Figure 1 shows this relationship in a graphical manner. Description of these tests follows.

Water Retention Capacity

The moisture content of a resin furnishes a measure of its water-holding capacity or swelling. This property varies with many factors, principally the composition of the resin matrix (phenolic, polystyrene, etc.) the degree of crosslinking, the nature of the active groups and the ionic form. Determination of the moisture content can give valuable information during the operation of a unit. For example, an increase frequently indicates an attack of some sort of the resin.

Cation exchangers, particularly in the hydrogen cycle, are known to under go oxidation and subsequent de-crosslinking under the influence of strongly oxidative conditions. By keeping a current log of the moisture content, one can soon detect significant increases which should signal an alert. The moisture determination is made by measuring the weight loss of a fully hydrated resin in the appropriate ionic form.

The appropriate ionic form varies with the purpose. Usually comparison is made between the test sample and a new resin of the same type. Moisture determinations should not be made on the OH form of strong base anion exchangers since heat causes gradual decomposition and constant weight is generally not achieved.

Figure 1. Approximation of useful life of in-use ion exchange materials by laboratory

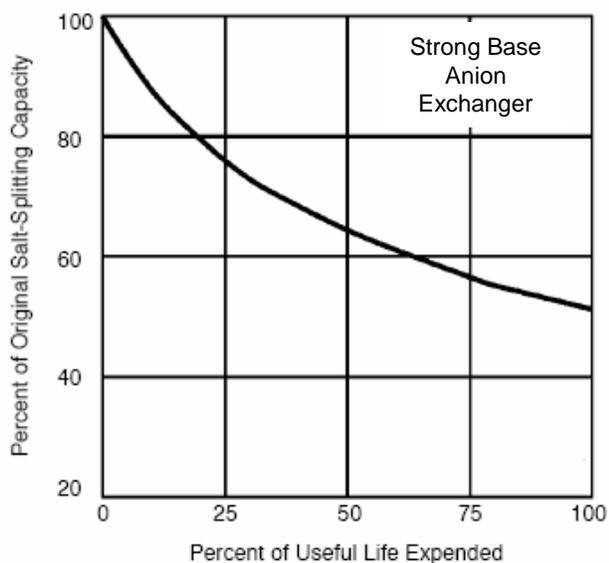
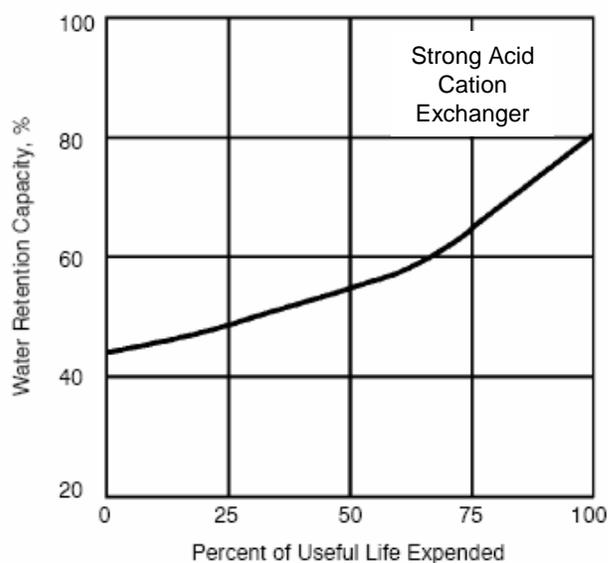


Figure 2. Analysis of a representative sample



Microscopic Examination

Microscopic examination of a resin sample frequently reveals physical properties which are not readily seen with the naked eye. Contamination of resin with foreign material can be readily detected. For most purposes, low power lenses are used in order to see several particles in a single field. The presence of internal cracks and particularly, the nature of the cracks, can be seen. By use of crossed nicol prisms, one can detect the strains which may arise either during manufacture or in subsequent use of a transparent or translucent ion exchange cation exchange bead is only partly sulphonated, examination under crossed-nicols will show the typical interference colors at the site of the strain which exists between the sulphonated and unsulphonated portions.

Rinse Requirements

The rinse requirement is a measure of the volume of water used after regeneration before a resin can be put into service.

The rinse requirement of a resin depends upon its chemical composition and degree of porosity. Any factor which tends to slow diffusion of ions into and out of the resin matrix will tend to prolong the rinse period. In general, weakly ionized groups in a resin tend to prolong rinses because these groups hydrolyze, thus slowly releasing ions to the surrounding solution. Phenolic resins generally have a higher rinse requirement than polystyrene based exchangers.

The rinse requirement of a given resin, as usually supplied by the manufacturer, applies to the new resin after it has been conditioned by a few cycles. Frequently, this requirement increases as the resin ages in service. When this occurs, it is usually found to be due to oxidation or fouling of the resin particles. Anion exchangers are much more susceptible to these effects than cation exchangers because 1) amine groups are chemically less stable than acidic groups and 2) organic foulants (such as those found in surface waters) are often weakly acidic large molecules which may be irreversibly absorbed.

Measurement of the rinse requirement of an anion exchange resin in service often provides a sensitive measure of oxidation or fouling. An increase in the rinse requirement frequently occurs before a capacity decline and thus corrective measures may be taken. These tests may be made either in an existing commercial unit or preferably in the laboratory.

Salt Splitting Capacity

Degradation of a strong base anion exchange resin chemically results in the conversion of the strong base functionality (the resin's capacity to split neutral salts such as NaCl to weak base functional groups). While the total exchange capacity of the resin may remain constant, its ability to perform effectively for the removal of weak acids such as SiO_2 or H_2CO_3 is a function (as shown in Figure 1) of its remaining strong base or salt splitting capacity. Salt splitting capacity may be determined by 1) conversion of the resin to the chloride form by contacting with dilute HCl and rinsing, 2) elution of the HCl sorbed by the weak base functionality using one molar ammonium hydroxide solution and rinsing, 3) elution of the remaining chloride ion held by the salt splitting groups using one molar sodium nitrate solution and analyzing for chloride removed in each case. Weak base capacity is determined from the ammonium hydroxide elution and salt splitting capacity from the sodium nitrate elution; total capacity is the sum.

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Notice: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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