

Understanding Ion-Exchange Resins For Water Treatment Systems

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Part 1 – Preparation techniques, resin characteristics, and terminology

Choosing and using ion-exchange resins for water-treatment systems is often a perplexing procedure. Plant engineers not familiar with such resins encounter a strange array of nomenclature and marketing practices that imply that each product is unique and better than all others.

This article is the first of a series whose purpose is to remove some of the mystery and confusion that surrounds the subject. It discusses preparation techniques, resin characteristics, and terminology. Future articles will deal with ion-exchange reactions, selectivity, and variables, and resin maintenance and life.

How They're Made

Most ion-exchange resins are based on a crosslinked polystyrene or acrylic structure. Except for weak-acid resins that are made in a one-step process, the synthesis of resins is a two or three-step operation involving polymerization, intermediate reactions, and functionalization.

Polymerization

Suspension polymerization is a common method of preparing synthetic ion-exchange resins. First, a base monomer, such as styrene is mixed with a catalyst and a crosslinking monomer such as divinyl benzene (DVB). The resulting organic phase is then suspended in water. The water phase contains suspending agents to ensure that a stable oil-in-water suspension is obtained when the mixture is stirred. (If an acrylic resin is being prepared, the water phase may be a saturated salt solution that minimizes the solubility of the acrylic monomer.)

The suspension is heated to the reaction temperature and held until polymerization is completed. The reaction converts the oil phase droplets to solid spheres of cross-linked polystyrene that are removed from the water phase, washed, and dried. At this point, the copolymer beads of styrene/DVB have no ion-exchange capacity and are resistant to wetting because they possess no ionic functioning capability.

Many of the characteristics of the final ion-exchange resin can be controlled during the polymerization step. For instance, whether the final product is to be a gel or a macro-porous resin is determined. Figures 1 and 2. The amount of crosslinking monomer used affects gel porosity and water retention. The concentration and type of suspending agents in the water phase, coupled with agitator speed and design, influence particle size.



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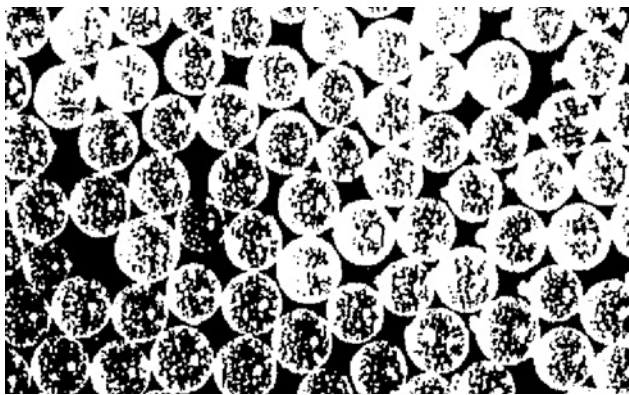


Figure 1: Typical gel, strong-base anion, ion-exchange resin (Courtesy Rohm & Haas Co.)



Figure 2: Typical macroporous strong-acid cation, ion-exchange resin (Courtesy Rohm & Haas Co.)

Intermediate Reactions

Chloromethylation reactions are sometimes required to alter a copolymer's structure to control the final product's functioning capability. Strong and weak-acid resins do not require this intermediate step, but styrene/DVB anion resins do. The additional step is a major reason for the cost differential between anion and cation resins.

In the process, the copolymer is reacted with chloromethylmethyl ether (CME) to produce a chloromethylated copolymer intermediate. Although still nonionic and not yet an ion-exchange resin, the intermediate product is sufficiently active to react with simple amines to form anion-exchange resins.

An unavoidable side reaction occurs during chloromethylation. The reaction, which is referred to as methylene bridging or secondary crosslinking, can be minimized by accurately controlling the reaction temperature and the type and concentration of catalyst. However, some degree of reaction is unavoidable. The problem created is that either too much or too little secondary crosslinking can

adversely affect final resin strength, capacity, and moisture content.

Another disadvantage of chloromethylation is that the starting material, CME, always contains some carcinogenic bis-CME. Because of these problems, acrylic anion resins - which do not require a chloromethylation step - are expected to become more prevalent.

Functionalization

Standard, strong-acid cation resins for water softening, metal removal, and demineralizing applications are prepared by sulfonating preformed crosslinked polystyrene beads. The dried copolymer is slurried in concentrated sulfuric acid, heated to 212°F (100°C), and held at this temperature for several hours until the sulfonation reaction is completed. After cooling, the resin is separated from the acid and slowly hydrated and rinsed with water.

Standard, strong-acid cation resins are kept in a hydrogen (acid) form. However, if the resins are to be used for water-softening applications, the acid-form resins must be converted to a sodium form with caustic soda.

Sulfonated polystyrene resins have good physical stability. But improvements in relative bead strength can be obtained by minimizing sulfonation reaction temperatures or using a solvent to swell the resin before sulfonation.

Standard anion resins based on polystyrene copolymers are prepared by causing amines to react with the chloromethylated copolymer intermediate. The type of amine used determines whether the final product is a weak-base or strong base. Weak-base resins are made by reacting dimethylamine with a chloromethylated intermediate. Type I strong-base resins are prepared from trimethyl amine, type II from dimethylethanol amine. Excess amine remaining after the reaction is distilled and washed from the resin. Weak-base resins are in a free-base form; strong-base resins are in a chloride form.

Anion resin synthesis using the chloromethylated intermediate method is fairly standard for polystyrene resins, regardless of whether they are crosslinked with DVB or an acrylic agent such as ethylene glycol dimethylacrylate (EGDM). However, for anion resins prepared from acrylic monomers, the chloromethylation step is eliminated, and the

functionalization reaction can be performed directly with the copolymer.

Table 1: Comparisons of Gel and Macroporous Ion-Exchange Resins

| | Gel | Macroporous |
|-----------------------|---|--|
| Uses | Standard resin for most water applications | Widely used for special applications |
| Appearance | Transparent | Opaque |
| Porosity | Function of degree of crosslinking | Function of cross-linking and number of discrete pores |
| Crosslinking Levels | Low | High |
| Volume Change | Considerable with high porosity (low cross-linked) resins | Less volume change than gel resins |
| Resistance | Susceptible to oxidizing agents and organic foulants | Good chemical resistance |
| Capacity and Kinetics | High capacity and fast elution kinetics | Reduced capacity and kinetics |

Gel-Macropore Comparisons

As mentioned earlier, whether an ion-exchange resin is to be a gel or macroporous material is determined during the polymerization step. Major differences between the two are listed in the accompanying table.

Gel resins are prepared with the bulk of the organic phase containing the reacting monomers and catalysts. When functionalized, the final product has essentially a continuous gel structure whose water content varies directly with the amount of crosslinking. Without crosslinking, the resins would be completely water-soluble.

Macroporous resins are made by including either a solvent or a solid (such as a linear polymer) in the organic phase. If a solvent is used, it is essential that it dissolves only the monomer, not the final polymer. Once polymerization is completed, the added ingredient is extracted. The removal process creates discrete holes (pores) inside the resin bead. Thus, macroporous resins, in addition to having a gel-phase porosity, have pores whose surface area and size can be predetermined.

Gel resins have historically been the workhorses for water softening and demineralization. However, macroporous resins are preferred for special applications. For example, in cases requiring concentrated regenerants, such as 22% nitric acid used for ammonium nitrate recovery, gel resins deteriorate rapidly because of shrinkage caused by the

osmotic pressure of the regenerant solution. Rapid displacement of the acid with water rehydrates the resin and breakage often occurs. Macroporous resins, which can use higher crosslinking levels and still maintain good reaction kinetics because of their larger surface area, have better ability to withstand such rigorous conditions. It should be noted, however, that high levels of crosslinking are not absolutely required to prepare macroporous resins. They can be produced with identical crosslinking levels as exhibited by gel resins.

Macroporous resins are also more useful in nonaqueous applications. Gel resins must be hydrated to allow ions to diffuse through the resin. No hydration occurs when gel resins are placed in a nonpolar medium, and the resin essentially has no porosity. Thus, no diffusion can occur and the exchange capacity is almost zero. Conversely, macroporous resins maintain their porosity in nonaqueous applications. Their exchange capacity is proportional to the surface area.

Macroporous resins are usually manufactured with high levels of crosslinking. There are, however, macroporous resins produced with crosslinking levels similar to those of gel resins. In either case, the macroporous resins have slightly less capacity than corresponding gel resins. Some resin manufacturers believe that this difference is negligible because the macroporous resins are less susceptible to organic fouling than gel resins. They claim that the porous structure facilitates the removal of organic contaminants when the resin is regenerated. Others claim that the chemical structures of the organic foulant and the ion-exchange resin have more correlation regarding resin fouling than whether the resin is a gel or macropore.

Some equipment manufacturers believe that pretreatment is the proper method for dealing with organic-bearing waters and that the use of a “working ion-exchange resin” to accomplish organic removal is not a satisfactory long-range solution.

Ion Exchange Glossary

The following terms are commonly used in discussions dealing with ion-exchange resins:

Attrition—Breakage and wear of resin particles.

Capacity, Operating—The portion of the total exchange capacity of an ion-exchange resin vol-

ume that is used in a practical ion-exchange operation. Operating capacity is determined both experimentally and empirically under a given set of fixed conditions, such as regenerant dosage and endpoint leakage. Values are usually expressed as kilograms of calcium carbonate (CaCO_3) removed per cubic foot of resin.

Capacity, Total—The ultimate exchange ability of an ion-exchange resin. Total capacity is determined experimentally using large dosages of analytical grade regenerant on small amounts of resin. Results are often expressed in milli-equivalents per milliliter of resin,

Color Throw—The transfer of color from an ion-exchange resin to a liquid. Color throw can be caused by residual manufacturing impurities or attack on the resin structure by oxidants.

Crosslinkage—Binding of the linear polymer chain in the matrix of an ion-exchange resin with a crosslinking agent that produces a three-dimensional, insoluble copolymer.

Elution—Same as regeneration. This term is normally used in special applications, particularly those involving a recoverable product that has been removed from solution by the resin.

Exhaustion (or Service) Cycle - The step in an ion-exchange process in which the undesirable ions are removed from the liquid being processed. When the resin has lost its practical ability to produce the required effluent water purity, the resin is exhausted and must be regenerated.

Fines—Small particles of ion-exchange resin that are undesirable for a particular ion-exchange operation. For example, fines may cause a high pressure drop through the equipment.

Freeboard or Rising Space—The space provided above the resin bed in the column to accommodate the expansion of the resin particles during backwash.

Leakage—Ions that are not fully removed during passage through a regenerated ion-exchange bed. Leakage is caused by incomplete regeneration of the exchanger bed. Ions remaining on the resin after regeneration can enter into solution during subsequent service cycles.

Porosity, Gel Resins—Qualitative term describing property of an ion-exchange resin that allows sol-

utes to diffuse in and out of the resin particle. Gel porosity is directly related to the water content of the particle and, inversely, to the degree of crosslinkage within the copolymer.

Porosity, Macroporous Resins—Quantitative term defining number and size of discrete noncollapsible pores within the ion-exchange bead. Macroporous resin porosity is directly related to bead surface area, and the surface area is inversely related to the size of the discrete pores.

Regenerant—A concentrated solution (commonly 2% to 10%) that is capable of reversing the ion-exchange equilibrium by the principle of mass action. Example of a typical regenerant is a 10% sodium chloride (NaCl) solution used to displace the calcium (Ca^{++}) and magnesium (Mg^{++}) hardness cations picked up in the sodium cycle cation exchanger (water softener) and replace them with sodium (Na^+).

Regeneration—The displacement from the ion-exchange resin of the ions removed from the process water or waste stream.

Salt Splitter—Ion-exchange resin capable of converting neutral salts to their corresponding acids or bases.

Stability, Chemical—The ability of the ion-exchange resin to retain its capacity in the presence of chemical oxidants such as chlorine.

Stability, Physical—The ability of an ion exchanger to resist breakage caused by 'physical manipulation, such as high water flow rates, or by volume changes resulting from osmotic shock.

Stability, Thermal—The ability of the ion-exchange resin to retain its capacity over extended periods at elevated temperatures.

Strong-Acid Cation Exchanger—Ion-exchange resin capable of exchanging hydrogen ions for the metal cations found in water supplies regardless of the anions present. The acid strength of the exchanger is equivalent to that of sulfuric acid.

Strong-Base Anion Exchanger—Ion-exchange resin capable of exchanging hydroxyl ions for the anions of all acids including carbonic and silicic acids. The base strength of the exchanger is equivalent to sodium hydroxide. Type I strong-base resins are the most stable of the normal strongly basic

exchangers and capable of yielding the lowest possible silica leakage at some sacrifice of capacity and regenerant efficiency. Type II strong-base resins have a slightly lower base strength than type I and do not remove silica to the degree possible with type I. Type II resin is less stable than type I, but has higher capacity and regenerant efficiency. Type II resins differ in structure from type I only by the amine used during production.

Swelling, Irreversible—The amount of swelling resulting from a change in ionic form by a new ion-exchange resin. Irreversible swelling is generally 5% greater than the swelling observed for all subsequent exhaustion-regeneration cycles.

Swelling, Reversible—The change in the resin volume that occurs each cycle during the exchange of ionic forms. For example, strong-acid cation resins swell 4% to 6% from the sodium to the hydrogen form; strong-base anion resins swell 15% to 20% from the chloride to the hydroxide form.

Void Volume—The space between the ion-exchange resin beads in a packed column. This volume is generally 35% to 40% of the total volume occupied by a graded resin bed.

Weak-Acid Cation Exchanger—Ion-exchange resin capable of exchanging hydrogen ions for only the cations of the salts of weak acids. For example, the resin will exchange the hydrogen (H^+) ion for the calcium (Ca^{++}) in calcium bicarbonate [$Ca(HCO_3)_2$], but not for the Ca^{++} calcium chloride ($CaCl_2$). The acid strength of the exchanger is similar to that of acetic acid. Weak-acid cation exchangers are commonly called carboxylic resins.

Weak-Base Anion Exchanger—Ion-exchange resin capable of removing strong acids such as hydrochloric (HCl), sulfuric (H_2SO_4), and nitric (HNO_3). True weak-base resins will not adsorb weak acids such as carbonic (H_2CO_3) and silicic (H_2SiO_3). When regenerated with caustic, weak-base resins are converted to the free-base form with a base strength similar to ammonia. When operated in the free-base form, the entire acid molecule is adsorbed.

The following terms apply to the water being treated in ion-exchange systems:

Alkalinity—The total content of bicarbonate (HCO_3^-), carbonate (CO_3^{--}), and hydroxyl (OH^-), ions in the

water. This is always expressed as the alkalinity percent of total anions.

Chloride-Sulfate Ratio—One of many terms used to express the ratio of monovalent strong anions, chloride (Cl^-) and nitrate (NO_3^-), to divalent strong anions, sulfate (SO_4^{--}). Resin manufacturers' data may express this as: chloride percentage of chloride-sulfate, chloride percentage of total mineral anions, chloride percentage of strong anions, or chloride percentage of total acid ions. Nitrates (if present in small quantities) are typically lumped together with chlorides in determining these percentages.

Magnesium-Calcium Ratio—This term may be used to express the magnesium content percent of the divalent cations. Manufacturers may identify these as magnesium percentage of total hardness, magnesium percentage of total cations, or calcium percentage of total cations.

Silica—Amount of this constituent is expressed as a percentage of the total acid ions.

Sodium—Presence of this material is expressed as a percentage of the total cations.

Strong Acids—Acids that are strongly ionized and, therefore, dissociate very readily in water, such as hydrochloric, sulfuric, and nitric. These are usually referred to as free mineral acids (FMA).

Strong Anions—Chloride, sulfate, and nitrate anions that, when combined with hydrogen ions, form strong acids. Strong anions are often called theoretical mineral acidity (ThMA) and total mineral anions (TMA).

Total Acid Ions (TAI)—Total anions plus carbon dioxide (CO_2) and silica (SiO_2).

Total Anions—Total of the bicarbonate (HCO_3^-), carbonate (CO_3^{--}), hydroxide (OH^-), sulfate (SO_4^{--}), chloride (Cl^-), and nitrate (NO_3^-) ions.

Total Cations—Total of the calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), and hydrogen (H^+) ions.

Total Electrolytes (TE)—Total cations or total anions. When expressed as $CaCO_3$ equivalent units, these values are numerically equal.

Total Hardness (TH)—Combined value of calcium (Ca⁺⁺) and magnesium (Mg⁺⁺) cations.

Weak Acids—Acids that are weakly ionized and do not completely dissociate in water, such as carbonic (H₂CO₃) and silicic (H₂SiO₃).

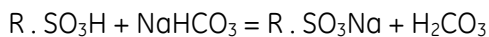
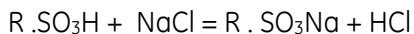
Part II — Ion-exchange reactions, ion selectivity, and variables influencing resin capacity and hardness leakage

No theoretical understanding of how ion-exchange resins are made, how they function, or the variables that affect their performance is sufficient to ensure proper selection of a resin for a given application. However, such knowledge can help eliminate much of the mystery involved in the selection task.

This article covers ion-exchange reactions, ion selectivity, and variables influencing resin capacity and hardness leakage.

Reactions and Selectivity

Some ion-exchange reactions are more efficient than others. For example, the reaction of a hydrogen-form strong-acid (R . SO₃H) resin with sodium chloride (NaCl) is less efficient than if the resin reacts with sodium bicarbonate (NaHCO₃):



With sodium chloride, the strong hydrochloric acid (HCl) produced by the exchange of sodium ions for hydrogen ions is capable of regenerating a strong-acid resin. Thus, an equilibrium is established where by some of the acid can back-regenerate the exchanged sodium off the resin. With sodium bicarbonate, poorly ionized carbonic acid is produced that cannot that does not exert any significant back-regeneration effect.

A simple rule for predicting ion-exchange reactions is that at least one of the reactants must be ionized for an ion-exchange reaction to proceed, and the equilibrium favors the side having the least number of ionized products. When both sides of the reaction have equivalent numbers of ionized products, the relative selectivities of the reacting ions in the influent can be used to predict performance.

In general, at low concentrations, ion-exchange selectivity constants increase for ions having a higher valence. Selectivity rises with increasing atomic weight for ions of the same valence. But factors such as concentration, temperature, non-aqueous media, and resin cross-linking can influence selectivity. Relative selectivity of ions for strong-acid and strong-base exchangers are listed in Table 2.

Table 2: Relative Selectivity of Ions for Strong-Acid and Strong-Based Exchangers

| Standard Strong-Acid Cation | Selectivity Coefficient | |
|--|-------------------------|--------|
| Hydrogen (H ⁺) | 1.0 | |
| Sodium (Na ⁺) | 1.5 | |
| Ammonium (NH ₄ ⁺) | 1.95 | |
| Magnesium (Mg ⁺⁺) | 2.5 | |
| Iron (Fe ⁺⁺) | 2.55 | |
| Calcium (Ca ⁺⁺) | 3.9 | |
| Standard Strong-Base Anion | Type 1 | Type 2 |
| Hydroxide (OH ⁻) | 1.0 | 1.0 |
| Silica (HSiO ₃ ⁻) | NA | NA |
| Bicarbonate (HCO ₃ ⁻) | 6.0 | 1.2 |
| Chloride (Cl ⁻) | 22 | 2.3 |
| Nitrate (NO ₃ ⁻) | 65 | 8 |
| Sulfate (HSO ₄ ⁻) | 85 | 15 |

Ion Exchange Variables

Numerous variables affect resin capacity and Leakage. In water softening, the primary factor determining capacity is the regenerant level (pounds of sodium chloride per cubic foot of cation exchange resin). Regenerant concentration (usually 5% to 15% when introduced) and flow rate and kinetic loading of the resin also influence capacity.

All of the foregoing variables affect leakage from the water softener. In addition, any appreciable amount of sodium salt in the raw water interferes with the resin's ability to retain calcium and magnesium ions and, consequently, increases leakage.

Key variables in a typical two-step demineralizing process involving strong-acid cation exchange followed by strong-base anion exchange, and their effects on capacity and leakage are shown in Table II. The list is incomplete, but the variables are the major ones that affect the process (other than equipment design, mechanical breakdown, and operator expertise). The first eight variables are water-composition factors over which plant engi-

neers have little or no control. But the remaining variables can be controlled.

Temperatures of exhausting water typically range from 59°F to 80°F (15°C to 27°C). Variations do not normally affect resin capacity and leakage significantly, unless the raw water is warmer than 85°F and a stringent silica guarantee is required from the strong-base anion resin. Silica leakage is approximately 50% higher than 85°F (29°C) than at 70°F (21°C).

Bed depth has an appreciable effect on gel cation capacity. Most resin manufacturers' strong-acid cation capacity data are based on conventional regeneration techniques in a laboratory column containing a 30 in. deep resin bed. Assuming that all other factors remain constant, a 24 in. bed has approximately 10% to 15% less capacity than the 30 in. bed, and a 60 in. bed has 5% to 15% more capacity.

Kinetic loading factors refer to the amount of ions that can be removed per unit volume of resin per unit of time. Capacities generally decrease as this factor increases. Resin manufacturers partially recognize this variable by limiting the flow rate per cubic foot of resin. Standard capacities are normally fixed at 2 ppm (mg/L) per cu. ft.; downrating factors are used for higher flows. Anion resins and weak-acid cation resins are more sensitive to kinetic loading factor variations than strong-acid cation resins.

Endpoints and their effects on capacity and leakage are important. Leakage increase to a particular endpoint determines operating capacity. Leakages are normally expressed as average during the service run. To understand a resin manufacturer's capacity data, the amount of leakage increase used to calculate the specified capacity must be known.

Typical strong-acid cation capacity data are based on conventional regeneration techniques with the equipment running until sodium leakage reaches approximately 10 milligrams per liter (mg/L) (as calcium carbonate) higher than the lowest leakage produced during the run. For example, if a resin produced 2 mg/L leakage, the run was ended at 12. Resin capacity is the number of gallons of treated water produced per cubic foot of resin.

Leakage is the average sodium content of the treated water. A strong-base anion resin's capacity and leakage data are typically determined by allowing silica to increase 0.3 to 1.0 ppm (mg/L) above the lowest silica value obtained during the run.

Any change in the foregoing endpoints results in a change in resin capacity and leakage. Lower resin capacity results if the average Leakage value is selected as the endpoint for a two-step demineralization process.

Resin Regeneration

Two important variables not included in Table 3 are strong-acid cation exchange regenerant type and regeneration mode. Neither variable increases or decreases resin capacity and leakage by itself.

Most commercial resin data are based on using sulfuric acid as the regenerant with levels stated as pounds of 66 degree Baumé acid per cubic foot of resin. But hydrochloric acid (usually expressed as pounds of 100% acid per cubic foot of resin) produces a higher exchange capacity and lower average leakage because of its greater available hydrogen-ion content. Hydrochloric acid also eliminates the need to guard against calcium sulfate precipitation during regeneration, as is necessary with sulfuric acid. Nevertheless, sulfuric acid is less expensive than hydrochloric acid and is more commonly used for cation regeneration.

Cocurrent regeneration is the normal regeneration mode because the equipment and controls are relatively simple. Untreated water flows downward through the resin bed in the same direction as the regenerant. A disadvantage of cocurrent regeneration is that leakage is somewhat difficult to control (especially in strong-acid cation exchange processes) because the regenerant becomes diluted as it travels downward through the bed. Thus, the resin at the bottom of the unit, where the treated water exits, is not regenerated as much as the resin at the top, and leakage values are higher.

Table 3: Effects of Ion-Exchange Variables in Typical Two-Stop Water Demineralization Process

| Ion-Exchange Variable | Strong-Acid Cation Exchanger How Increases in Variable Affect | | Strong-Base Anion Exchanger How Increases in Variable Affect | |
|---|--|------------------------|---|------------------------|
| | Capacity | Average Sodium Leakage | Capacity | Average Silica Leakage |
| Sodium (Na ⁺), percent | Higher | Higher | NA | NA |
| Magnesium (Mg ⁺⁺), total hardness | Higher | NA | NA | NA |
| Alkalinity, percent | Higher | Lower | Higher | NA |
| Carbon Dioxide (CO ₂), percent | NA | NA | Higher | NA |
| Silica (SiO ₂), percent | NA | NA | (A) | Higher |
| Chloride (Cl ⁻), percent | NA | NA | Lower | NA |
| Sulfate (SO ₄ ⁻²), percent | NA | NA | Higher | NA |
| Nitrate (NO ₃ ⁻), percent | NA | NA | Lower | NA |
| Temperature of exhausting water | None | None | None | Higher |
| Cation leakage, Na ⁺ | NA | NA | NA | Higher |
| Regenerant level, lb/cu ft. | Higher | Lower | Higher | Lower |
| Regenerant concentration | Higher | Lower | None | None |
| Regenerant temperature | None | None | Higher | Lower |
| Resin bed depth | Higher | None | None | None |
| Kinetic loading | Lower | None | Lower | None |
| Endpoint | Higher | Higher | Higher | Higher |

Less leakage is experienced with countercurrent regeneration in which the regenerant flows in the opposite direction to the water (for example, regenerant flows up, water flows down). With this system, the resin at the bottom of the unit is more highly regenerated than the resin at the top and leakage values are lower. A disadvantage of countercurrent regeneration is that the equipment and controls are more complex and expensive. However, if low leakage at low regenerant levels is required, the additional expenditure is justified.

Different capacity-leakage data must be used for countercurrent systems than for cocurrent systems. For example, resin-beds must be significantly deeper (5 ft or more) than with cocurrent regeneration. Countercurrent regeneration does not lend itself to overrun conditions, so endpoints appreciably higher than specified leakages are not permitted. And the quality of the water used to dilute and displace the regenerants must be considerably higher than that used in cocurrent operation.

Weak-Acid and Base Resins

Variables affecting weak-acid cation exchange and weak-base anion exchange are relatively few compared to those affecting the strong-acid, strong-base exchange processes. In weak-acid cation exchange, temperature of exhausting water has a

significant effect on resin capacity. For example, capacities approximately 20% higher obtained at 75°F (24°C) than at 55°F (13°C). The weak-acid resin has a higher capacity for calcium and magnesium alkalinity waters than for sodium alkalinity waters. Therefore, the ratio of hardness of alkalinity affects capacity. A ratio of 1.0 produces more than double the capacity of a 0.7 ratio. And kinetic loading and endpoint have significant effects on weak-acid cation capacity. Leakage is directly influenced by both endpoint and salt content of the water being treated.

The capacity of a weak-base anion exchanger is affected mainly by kinetic loading and the ratio of monovalent strong anions to divalent strong anions, similar to variables influencing strong-base anion exchangers. Leakage is a function of cation exchanger leakage.

Conclusion

Commercial data for ion-exchange resins are based on laboratory conditions. After all variables have been considered, resin capacities should be down-rated or leakages increased to compensate for the somewhat-less-than optimum conditions that exist in full-scale operations. Actual plant experience with certain resins on equal or similar waters should be used whenever possible.

Ion exchange is a system operation. The ability to produce a certain volume of a particular quality of water is a function of resin selection, operation, and equipment design. Equipment and controls must provide distribution and collection of water and regenerant solutions consistent with required reaction times. Swelling and contracting properties of certain resins must be considered not only in determining column sizes, but also in selecting internal components that have to withstand the mechanical forces created.

Occasionally, ion-exchange resins are referred to as being the most expensive filter media available. This statement illustrates how not to use resins. Suspended matter and organics should be removed from raw water by more appropriate pre-treatment techniques (coagulation, filtration, etc.). Nevertheless, claims continue to be made for “new” resin products that can withstand higher suspended matter or organic content without fouling. Such results can only be achieved by sacrificing ion-

exchange capacity - an undesirable and expensive tradeoff.

Table 4: Commercial Designations of Typical Ion-Exchange Resins

| Resin Type | Manufacturer | | | |
|-------------------------------|------------------------|------------------|----------------------|-------------------|
| | Diamond Shamrock Corp. | Dow Chemical Co. | Ionac Chemical Corp. | Rohm and Haas Co. |
| CATION | | | | |
| Standard Gel | C-20 | HCR-S | C-249 | IR-120 |
| High Crosslinked Gel | C-20X10 | HGR | C-250 | IR-122 |
| Macropore | C-26 | MSC-1 | CFP-110 | IR-200 |
| Weak Acid | C-433 | CCR-2 | CC | IRC-84 |
| ANION | | | | |
| Type I Gel | - | SBR | ASB1 | IRA-400 |
| Type I Gel (less crosslinker) | A-101D | SBR-P | ASB1-P | IRA-402 |
| Type I Macropore | A-161 | MSA-1 | A-641 | IRA-900 |
| Type II Gel | A-102D | SAR | ASB2 | IRA-410 |
| Type II Macropore | A-162 | MSA-2 | A-651 | IRA-910 |
| Weak Base | A-340 | WGR-2 | A-305 | IRA-98 |
| Weak Base Macropore | A-378 | MWA-1 | AFP-329 | IRA-93 |

Commercial designations for some typical ion-exchange resins made by the four major U.S. manufacturers are shown in Table 4. These companies produce over 200 different resin products. In the authors' opinion, this is a staggering number—particularly when 90 percent of the softening and demineralizing applications could be readily handled by no more than five or six products.

The seeming overabundance of resins is attributed to some legitimate requirements in specialized industries, ranging from pharmaceutical to nuclear power. But too many products have been introduced to respond to specifications requiring stronger resins, as measured by laboratory methods that have little or no correlation with field operation. Although some resins with improved strength (as measured by artificial tests) have been developed, such products do not always perform as well chemically in installed equipment as their predecessors. Ion-exchange resin improvements are needed, but the emphasis should be on upgrading the overall product, rather than on producing the strongest resin for a selected application.

Part III—Resin Maintenance, Troubleshooting, and Service Life

Prices of ion-exchange resins, like prices of almost everything else, keep climbing. Increases make it

imperative for plant engineers to know how to get maximum performance and service life out of ion-exchange resins in industrial water treatment systems. This article covers resin maintenance, system troubleshooting, and resin service life.

Performance Guidelines

In simple terms, water softeners use cation exchange resins: demineralizers use both cation and anion exchange resins. Softeners normally are regenerated with salt: demineralizers with acid and caustic. Both types of equipment are subject to the usual hazards of corrosive regenerant chemicals. Cation exchange resins generally retain good efficiency for 5 to 10 years (7 years on the average); anion exchange resins for 3 to 5 years (4 years on the average). Capacity of cation exchangers decreases about 3% a year; anion exchangers may lose as much as 25% in 2 years.

Both operating conditions and procedures influence ion-exchanger resin service life and equipment performance. Several key factors must be controlled:

Raw Water Supply—Typical temperature and chlorine limitations for incoming water are listed in Table 5. In addition, the water should contain no more than 5 ppm turbidity and 0.5 ppm hydrogen sulfide, and no oil. Iron and manganese must be in the dissolved form (water should be clear when first drawn) to avoid fouling the cation exchanger. Oxidizing agents (such as chlorine) must not be added if iron and manganese are present. Air leaks in piping on the suction side of pumps should also be eliminated. The presence of organic matter may cause fouling of the anion exchanger. Pretreatment may be required if organics are present.

Housing—Equipment must be properly housed to protect it against freezing, rain, dust, or other abnormal conditions.

Table 5: Typical Temperature and Chlorine Limitations for Raw Water

| Resin Type (Permutit) | Cation Exchangers | Anion Exchangers | |
|-------------------------|-------------------|------------------|-----------|
| | Standard | Strong Base | Weak Base |
| Maximum Temperature, °F | 250 | 120 | 100 |
| Free Chlorine, ppm | 0.5 | 0.5 | 0.5 |

Temperature—Permissible water temperature is limited by materials of construction and type of ion

exchanger. Temperature of water entering the unit should not exceed that recommended by the manufacturer. If the treated water passes directly into a water heater or other heat-producing apparatus, a swing-check valve must be installed in the line to prevent hot water from backing up into the

overrun does occur, the ion exchanger should be regenerated twice.

Idle Periods—If the equipment is to remain idle for a week or more, the unit should be operated until the effluent indicates that the resin bed is exhausted. The unit should then be drained and the

Table 6: Trouble Shooting Guide for Ion-Exchange Equipment

| Source of Trouble | Possible Cause | Corrective Action |
|----------------------------------|--|--|
| Change in Raw Water Composition | Increase in total electrolytes. A substantial change in percentage of sodium or alkalinity. With anion unit, may indicate inadequate degasifier operation. | Obtain new water analysis. Change meter setting to conform with new capacity. Consult system supplier for new capacity setting. |
| Service Cycle being Exceeded | Flowmeter inaccurate (a) Worn or damaged meter (b) Slippage at low flow rates Conductivity meter inaccurate (a) Meter faulty (weak tubes, damage, etc.) (b) Electrodes worn (c) Electrodes not receiving representative sample. | Repair or replace as necessary. Use higher flow rates or replace with smaller meter. Replace weak tubes and replatinize electrodes as necessary. Check for plugging of sample pipe. For probes in ion-exchanger bed, check bed for channeling in vicinity of probe. |
| Faulty Regeneration | Insufficient chemical dosage. Weak regenerant (too little regenerant or too much dilution water). Poor distribution of regenerant (a) Faulty internal distributor (b) Packed bed Acid too strong or introduction time too slow (cation units), producing calcium sulfate precipitate in bed. | Follow specified regeneration procedure. Repair faulty equipment. For packed bed or calcium sulfate precipitation, give bed an extended backwash to clean. Wash for about 30 min using highest rate possible without washing out ion exchanger. With calcium sulfate precipitation, a white precipitate will also be noted in sump. It causes no permanent damage, but may require several runs to remove from bed. |
| Loss of Ion-Exchange Material | Backwash rate too high (Note that proper backwash rate varies with water temperature). Surges during backwash. Breakdown of ion exchanger (a) Chemical attack by oxidizing agents (chlorine) (b) Excessively high pressure or flow rates Upset supporting bed, or damaged underdrain (check for ion exchanger in effluent). | Check flow rates and water temperature; do not exceed specified rates. Analysis of ion exchanger will confirm suspected chemical attack. If chlorine content is too high, add reducing agent (for example, sodium sulfite) or otherwise remove to prevent further damage. Consult system supplier for recommendations. |
| Fouling of Ion-Exchange Material | Oxidized iron or manganese in raw water (affects cation exchanger). Organic matter in raw water (generally affects anion exchanger, but cation units occasionally fouled). | Prevent oxidation of iron or manganese whenever possible. Air, chlorine, or other oxidizing agents oxidize iron and manganese. Cleaning may restore fouled bed to original condition, or nearly so. Must eliminate cause to prevent recurrence of problem. May require pretreatment of water. |
| Short Circuiting (channeling) | Packed bed (a) Excessive turbidity in inlet water (b) Excessive fines in bed 1. Chemical attack on ion exchanger 2. Excessively high flow rates or opening pressures (c) Inadequate backwash. Damaged underdrain or inlet distributor. | Check for use of specified wash rate and prevent surges or air. Remove turbidity or chlorine from inlet water, if applicable. Use correct wash rates in accordance with water temperature. Give unit an extended backwash (approximately 30 min) to clean bed. Use highest flow rate possible without washing ion exchanger out of unit. |

demineralizing equipment. A pop valve should be between the check valve and heater to protect demineralizer tanks.

Capacity—Ion exchangers should not be operated at flow rates higher than those specified by the manufacturer. Chemical composition of the raw water should be tested periodically to prevent operating units beyond their rated capacities. If an

tanks sealed to prevent the resin from drying out.

If there is danger of freezing, the tanks should be filled with brine. Before startup, the brine should be rinsed from the tanks and the unit should be regenerated several times. If the idle period is to last less than a week, simple shutdown is sufficient. However, before startup, the unit should be rinsed with

water (either recycled or sent to waste) until the effluent quality reaches the required operating level.

Record Keeping—Two basic rules help ensure ion exchange efficiency: (1) Keep records of resin capacity performance (gallons of water softened or demineralized between resin regenerations) and regeneration frequency, and (2) know the condition of the resins.

With good record keeping, most ion-exchange malfunctions can be recognized by these symptoms: reduced capacity or poor effluent quality (occurring gradually or suddenly), increased pressure loss or decreased flow rates (gradual or sudden), or excessive rinse volumes. Each of these symptoms indicates more than one trouble source, and most have more than one possible cause. Table 6 diagnoses common encountered operating difficulties and lists remedies.

Contamination—Resin can be contaminated because the ion-exchange process depends upon ions transferring from an aqueous solution to the insoluble ion-exchange resin and upon the subsequent elution (removal) of these ions from the resin with the regenerant solution. This exchange takes place not only on the surface of the resin particle, but also within the interior of the resin. The pores of the particle serve as routes to the interior exchange sites. If these pores are clogged by deposits, or if the resin surface is coated by inert matter, ion-exchange capacity is reduced and water quality from the ion exchange unit is impaired.

In addition, certain contaminants in the water may adversely react with the resin, breaking down its chemical structure and changing its characteristics so that it is no longer an efficient ion exchanger. A discussion of common contaminants that adversely affect ion-exchange resin performance and how to cope with them, follows.

Suspended Matter in the Influent Water—Suspended or colloidal matter coats the surface of ion-exchange resin particles, thereby blinding the exchange sites on the surface as well as the pores leading to the internal exchange sites. Pretreatment by coagulation or filtration can remove suspended matter before the water reaches the ion-exchange unit. Generally, turbidity above 5 Jackson Turbidity Units causes problems in ion-exchange equipment.

Vigorous backwashing is usually effective in removing dirt that has accumulated in the resin bed and on the particles. The backwash flow rate should be as high as possible without forcing resin from the vessel. The operation may require opening the top of the vessel and mechanically stirring the resin bed to eliminate any resin slumps. The use of an air lance may be helpful too. Backwashing should continue until the wash water is clear.

Precipitates and Oil on Resin Particles—In addition to inorganic silt or dirt, certain chemical precipitates and oil may cause resin-blinding problems:

Iron—This metal precipitate may be present in the raw water, or created by corrosion and picked up from piping, tanks, regenerating vessels, and other equipment.

Iron appears in the divalent (ferrous) and trivalent (ferric) forms. The divalent form is generally soluble and can be removed by ion exchange and eluted from the resin during normal regeneration. However, the trivalent form is quite insoluble.

Unfortunately, the ferrous ion converts to the ferric ion in the presence of oxygen. Well water containing ferrous ions may be initially clear, but rapidly turn turbid or red when exposed to air. Air on the suction side of pumps or the use of hydropneumatic tanks can introduce enough oxygen to cause ferric precipitation.

Treatment with dilute hydrochloric acid dissolves precipitated ferric iron. Usually a corrosion inhibitor (formaldehyde) is used with the acid to protect the metallic parts of the equipment. Fifteen pounds of 20% acid (about 1.5 gallons [6 liters]) mixed with 0.15 gallons [0.6 liters] mixed with 0.15 gal of formaldehyde is recommended per cubic foot of resin.

Before the acid treatment, the ion exchanger should be drained and the acid diluted with water to 5%. The acid is then slowly passed through the resin bed. After the treatment, the bed is rinsed with water for 30 minutes and back-washed until water is clear.

Anion exchangers should be given a double regeneration and the water should be checked to make certain that all acid has been removed. If the treated water is to be used for human consumption,

it should be tested to ensure the absence of formaldehyde.

Aluminum Hydroxide—Alum is used for pretreatment (coagulation) purposes with many water supplies and forms insoluble aluminum hydroxide at a specific pH. However, if the precipitated hydroxide is not removed, or if the pH is improperly adjusted, the precipitate may again dissolve. And subsequent changes in pH will cause the aluminum to again precipitate and coat the cation exchange resin.

Aging rapidly converts the aluminum hydroxide to an insoluble oxide that is difficult to remove. Treatment with hydrochloric acid (similar to that used for iron removal) is frequently beneficial. However, the best way to prevent the problem is to control the pretreatment process.

Oil—Fouling or coating of ion-exchange resin surfaces with oil seriously affects their performance and frequently causes resin clumping. Oil-contaminated resin beds can be reasonably well cleaned by washing them with a warm caustic soda solution mixed with a small amount of detergent. Before treatment, the resin bed must be regenerated with acid to remove cations that may precipitate during the caustic treatment.



Figure 3: Contrast between fresh (left) and fouled (right) resins reveals why clogged surfaces and pores impair ion-exchange capacity. Special lighting was used to show bed depth of fresh resins (courtesy of Ionac Chemical Corp)

Six pounds of sodium hydroxide and 1 oz. (28 grams) of detergent per cubic foot of resin are used to prepare the caustic solution. The solution is then diluted to 5% and heated to 120°F to 130°F (49°C to 54°C). The caustic is fed into the drained ion-exchange unit to a height a few inches above the bed surface and allowed to remain for at least an hour. Mechanical stirring of the bed may be necessary if fouling is severe. The equipment is then drained, rinsed with soft water for at least 30 minutes and backwashed until the wash water is clear.

The unit should be given a double regeneration before being placed into service.

Calcium Sulfate—Cation resins regenerated with sulfuric acid may become fouled with precipitated calcium sulfate if the acid concentration is too high. High-calcium-content waters (>10% calcium) require 2% acid concentration at the beginning of the regeneration step to prevent calcium sulfate precipitation.

Fouled resins can be treated by vigorous backwashing with water followed by exposure to inhibited hydrochloric acid. The procedure is the same as the one outlined for iron removal.

Silica—This precipitation sometimes occurs on anion resins because absorbed or exchanged silica has not been completely removed during regeneration. If the silica buildup is too high, it may polymerize and become insoluble. Silica precipitation can also be a problem in demineralizers using combinations of weak and strong-basic anion resins, when spent caustic from the strong resins is used to regenerate the weak resins. Precipitation may occur in the weak-basic anion unit, causing high silica leakage in the demineralizer effluent.

The solution to the problem is to regenerate the anion exchanger with twice the normal regenerant level. Regeneration should be performed slowly, for at least 1 hour at 120°F to 130°F (49°C to 54°C). Warming the resin bed with 130°F (54°C) water before regeneration is also helpful.

Magnesium Hydroxide—The presence of magnesium in caustic dilution water supplies sometimes causes magnesium hydroxide fouling on anion resins. Precipitation occurs when caustic soda is added to the dilution water. Calcium may also precipitate if it is present in high enough concentrations.

Fouled resins can be treated by regenerating the unit with soft water (5 ppm hardness or less) and vigorously backwashing to remove as much precipitate as possible. After backwashing, the unit should be treated with inhibited hydrochloric acid, as for iron removal, and double regenerated.

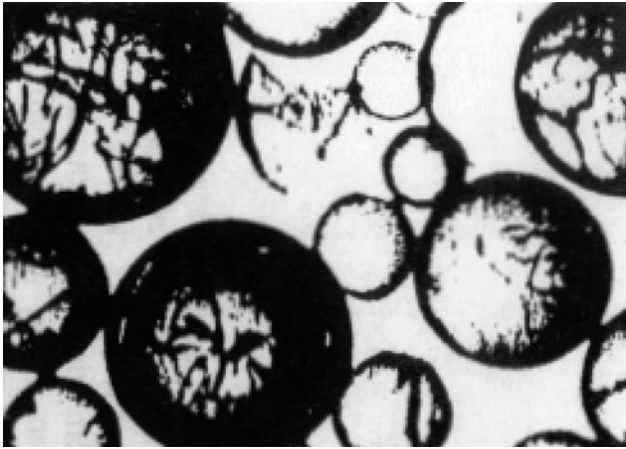


Figure 4: Presence of fractured resins and fines rapidly reduces resin service life and ion-exchange efficiency. (Courtesy of Ionac Chemical Corp.)

Chlorine Problem—Free chlorine in feedwater oxidizes the chemical structure of ion-exchange resins. The rate of degradation is a function of free-chlorine concentration. In general degradation is negligible at concentrations below 0.1 ppm.

Concentrations above 0.1 ppm can be removed by treating the influent water with sodium sulfite or by passing the water through activated carbon filters. Required sodium sulfite concentration is 1.8 ppm for every 1 ppm of free chlorine.

Organic Fouling—Perhaps the most common type of contamination affecting ion exchangers is organic fouling. Organic substances in water supplies normally are the result of wood or leaf decomposition or industrial and municipal wastes. Organic fouling involves a wide range of materials, including organic acids, tannins, phenolic substances and color bodies. Some materials are acidic and have high molecular weights. Anion exchangers—usually strong-base anion resins—are the most susceptible to organic fouling.

Large organic molecules containing anionic groups are captured by the anion exchange resin and cause blockage of the ion-exchange sites. The resin's small pore size prevents the organic molecules from diffusing out of the resin during regeneration. Organic fouling decreases resin capacity, increases rinse water requirements, reduces anion effluent pH, and boosts effluent conductivity.

Organic matter is most easily removed by pretreatment. Such as coagulation, chlorination, filtration, or activated-carbon treatment. If organic content is low and no turbidity exists, chlorination plus activated-carbon treatment (or activated carbon alone) may suffice.

Treatment with hot brine may restore organically fouled anion resins nearly to their original performance. However if the source of contamination is not removed by adequate pretreatment. The effectiveness of each successive treatment decreases. Anion units should be given double regeneration following brine treatment. Cation exchangers may require triple regeneration.

Storage Needs—Improper storage is the most avoidable cause of shortened ion-exchange resin life. Resins must be prevented from drying out, so they should be kept moist during storage. They must also be prevented from freezing, because alternate freezing and thawing fractures the resin particles and creates fines, Fig. 4.

Ion-exchange resins should be in an exhausted condition when equipment is shut down for more than a month, because the resins are stabler in this condition. An easy method of exhausting resins is to flush them with a solution of 8 to 10 lb of sodium chloride per cubic foot of resin. Excess salt must be rinsed from the equipment after the treatment. The unit is then refilled with water and shut down for storage. Double regeneration should be performed on anion units before they are returned to service. Triple regeneration is recommended for hydrogen cation units.