

Essentials of Ion Exchange

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Introduction

Natural water supplies contain dissolved salts, which dissociate in water to form charged particles called ions. These ions are usually present in relatively low concentrations and permit the water to conduct electricity. They are sometimes referred to as electrolytes. These ionic impurities can lead to problems in cooling and heating systems, steam generation, and manufacturing. The common ions that are encountered in most waters include the positively charged cations; calcium and magnesium (hardness forming cations, which make a water "hard") and sodium. The negatively charged anions include alkalinity, sulfate, chloride, and silica.

Ion exchange resins are particularly well suited for the removal of these ionic impurities for several reasons: the resins have high capacities for ions that are found in low concentrations, the resins are stable and readily regenerated, temperature effects are for the most part negligible, and the process is excellent for both large and small installations, for example, from home water softeners to huge utility installations.

Historical Background

There are suggestions found in the Bible, and in writings by the ancient Greeks, that suggest knowledge of desalting brackish waters. It was not until the nineteenth century in England that the first official studies of the phenomenon of ion exchange were documented. In 1850 Harry Thompson and John Way, two agricultural chemists, passed a liquid fertilizer solution containing ammonia through a soil sample. It was noted that the ammonia was retained by the soil and that calcium was thrown off. In their report to the Royal Agricultural Society, they documented a number of important observations that form a foundation for the understanding of the ion exchange process:

1. The exchange of ions in soils involved the exchange of equivalent ions.
2. Some ions were more readily exchanged than others.
3. The aluminum silicates present in the soil gave it exchange characteristics.
4. The exchange of ions was different from true physical adsorption.

The German chemist Eichorn, in 1858, proved that the ion exchange reaction in soil was a reversible one. Lemberg, in 1876, also confirmed the reversibility and calculated the stoichiometry of the process.

The beginning of the twentieth century marked the era when ion exchange was implemented for practical purposes. Another German scientist, Gans, in 1905 developed a process of softening water (trading magnesium and calcium ions for sodium ions) on a commercial basis using cation exchange materials. Gans used synthetic sodium aluminosilicate cation exchangers, which he called zeolites. The term zeolite was first used by a Swedish geologist named Cronstedt about two hundred years ago for naturally occurring siliceous minerals, which became dehydrated when heated. The word zeolite was derived from the Greek words *zein* and *lithos*, which literally mean "boiling rock." The terms zeolite and sodium zeolite softener are still common today, although the true sodium aluminosilicate materials are now rarely used.

The first synthetic zeolites were marketed in America by the Permutit Company in 1913. Sulfonated coal, referred to as carbonaceous zeolite, was used as an ion exchange material in 1935 and was able to be operated in the hydrogen cycle for complete cation removal. That same year, two English chemists, Adams and Holmes, produced two new ion exchangers. The cation exchanger was a phenol formaldehyde condensation product and the anion exchanger

was a condensation product of polyamines and formaldehyde. These products made possible near complete removal of all ions from water, but the early anion exchangers were unable to remove the weak acids of silica or alkalinity.

A result of the research work of an American scientist, D'Alelio, in 1944 helped develop cation exchange resins based on the copolymerization of styrene and divinylbenzene. Anion resins based on the styrene-divinylbenzene copolymer were developed in 1948. These resins could completely demineralize water when run in the hydrogen/hydroxide form respectively. The standard polystyrene-divinylbenzene resins are the most commonly used in the world today and are referred to as being gelular in structure. Many adaptations of the original products have been developed over the years, i.e., differences in porosity, macroporosity, the use of acrylics, etc.

Synthesis

Most ion exchange bead materials are manufactured by a suspension polymerization process using styrene and divinylbenzene (DVB). The styrene and DVB, both liquids at the start, are put into a chemical reactor with roughly the same amount of water. A surfactant is also present to keep everything dispersed. The chemical reactor has an agitator, which begins to mix the water/organic chemical solution. The styrene/DVB begin to form large globules of material, and as the speed of agitation increases, the globules break up into smaller droplets until reaching the size of about a millimeter. At this point, the polymerization reaction is initiated by the addition of benzoyl peroxide, which causes the styrene/DVB molecules to form the resultant small plastic beads. The divinylbenzene is a crosslinking agent that gives the beads their physical strength, and without which the styrene would be water-soluble.

The polystyrene-DVB bead needs to be chemically activated to make it perform as an ion exchange material. Active groups are attached to provide chemical functionality to the bead. Each active group has a fixed electrical charge, which is balanced by an equivalent number of

oppositely charged ions, which are free to exchange with other ions of the same charge. Strong acid cation resins are formed by treating the beads with concentrated sulfuric acid (a process called sulfonation) to form permanent, negatively charged sulfonic-acid groups throughout the beads. Important here is the fact that the exchange sites thus formed are located throughout the bead. The ion exchange process is not a surface phenomenon; more than 99% of the capacity of an ion exchange material is found in the interior of the bead.

Strong base anion resins are activated in a two-step process that consists of chloromethylation followed by amination. The two-step process begins with the same styrene/DVB material as is used for cation resins. The only difference is that the amount of DVB used is less to allow for a more porous bead. The first reaction step is the attachment of a chloromethyl group to each of the benzene rings in the bead structure. This intermediate chloromethylated plastic material needs to be reacted with an amine in a process called amination. The type of amine used determines the functionality of the resin. A common amine used is trimethylamine (TMA), which creates a Type 1 strongly basic anion exchanger. Using dimethylethanolamine (DMEA) will make a Type 2 anion resin.

Physical and Chemical Structure of Resins

The basic material requirements of ion exchange beads are insolubility, bead size, and resistance to fracture. The resin must be insoluble under normal operating conditions. The beads must be in the form of spheres of uniform dimension, normal size range is between 16 and 50 US Mesh. The swelling and contraction of the resin bead during exhaustion and regeneration must not cause the beads to burst. Also, an important property of ion exchange resins is that the active site is permanently attached to the bead.

Ion exchange resins can be manufactured into one of two physical structures, gel or macroporous. Gel resins are homogenous crosslinked polymers and are the most common resins available. They have exchange sites distributed evenly

throughout the bead. The amount of DVB crosslinking used in the synthesis of a bead determines the relative strength of the bead. Standard strong acid cation resin used for softening, which is the most common ion exchange media, is almost always an 8% DVB gelular material. The amount of DVB that this resin contains has proven to be the most economical in terms of resin price and expected operating life.

Resins are available today with a DVB content of from 2 to 20 percent and higher. Higher DVB content gives the bead additional strength, but the additional crosslinking can hinder kinetics by making the bead too resistant to the shrinking and swelling necessary during normal operation.

Macroporous resins were introduced commercially in 1959 and are made with large pores that permit access to interior exchange sites. They are also referred to as macroreticular or fixed-pore resins. Macroporous resins are manufactured by a process that leaves a network of pathways throughout the bead. This sponge like structure allows the active portion of the bead to contain a high level of DVB crosslinking without affecting the exchange kinetics. Unfortunately, it also means that the resin has a lower capacity because the beads contain less exchange sites. The "pores" can take up to 10 to 30% of the polymer. This reduces the ion exchange capacity proportionately.

Gel resins usually have higher operating efficiencies and cost less. A macropore gives better physical stability, primarily because of its sponge like structure, which gives more stress relief. It also eliminates some of the breakage that may occur from osmotic stress. The higher surface area in a macroporous anion resin gives better organic fouling resistance. In a cation resin, the higher crosslinking level gives better oxidation resistance.

There are two basic types of chemical structures, styrene and acrylic. The styrene based materials described above are aromatic hydrocarbons. Acrylic resins are straight chained hydrocarbons based on polyacrylate and polymethacrylate.

DVB is still used as a crosslinker in these resins, but acrylics differ from the styrenics in that the active exchange site is part of the physical structure. This means that their physical and chemical stabilities are intertwined. When an acrylic resin chemically degrades, it is usually at the exchange site, which is the weak link. This destroys the physical structure. As an acrylic resin oxidizes, it will swell and become mushy. Another disadvantage of the acrylic materials is that they are not fully FD&A approved. Therefore, they are usually limited to industrial applications. The acrylics are advantageous in applications where organics are present because they do not foul nearly as much as a styrene based product.

Selectivity of Resins

The selectivity or affinity of ion exchange resins is influenced by properties of the bead, the ions being exchanged, and the solution in which the ions are present.

Water is an essential component of ion exchange resins. For example, strong acid cation resins contain about 50% moisture. The amount of crosslinking of the bead has an impact on the moisture content of the bead, and the moisture content in turn has an impact on the selectivity. A bead with a high moisture content has a high porosity and the active groups are spaced further apart from each other.

Ion exchange resins generally have greater selectivities for ions with increasing valence or charge. Among ions with the same charge, higher affinities are seen for ions with a higher atomic number.

These affinity relationships are reversed in concentrated solutions. This is what makes regeneration of exhausted resins possible. An exhausted cation resin used for softening is predominately in the calcium and magnesium form, both divalent ions. The resin is restored to its regenerated condition, the sodium form, by the introduction of 10% sodium chloride. This sodium chloride solution is concentrated enough (100,000 ppm/) to reverse the selectivity. The

driving force of the monovalent sodium ion then converts the resin back to the sodium form.

Kinetics

The rate of exchange, or kinetics, of ion exchange reactions is governed by several factors. The solution being treated has an effect; higher solution concentrations can speed up the rate of reaction. The amount of DVB crosslinking of the bead determines the porosity of the bead and, in turn, the ionic mobility within the bead. The size of the ions being exchanged also influences the kinetic rate and is somewhat dependent on the size of the pores in the resin structure. Size of the bead also has an effect; smaller beads present a shorter diffusion path to active sites in the interior of the beads.

Resin has a greater affinity for ions with higher valences so a predominance of high valence ions can therefore cause a relatively higher rate of reaction. Other influences include temperature, the ionic form of the exchange sites, and the strength of the exchange sites. Increasing temperature can speed up chemical reactions. The exchange reaction is a diffusion process, so the diffusion rate of the ion on the exchange site has some effect. Also the strength of the exchange site, whether it is strongly or weakly acidic or basic, affects the reaction rate.

Types of Ion Exchange Resins

Strong Acid Cation Resins

Strongly acidic cation resins derive their functionality from the sulfonic acid groups. These strong acid exchangers operate at any pH, split all salts, and require substantial amounts of regenerant. This is the resin of choice for almost all softening applications and as the first unit in a two bed demineralizer or as the cation component of a mixed bed.

Weak Acid Cation Resins

The weakly acidic cation resins have carboxylic groups as the exchange site. The resin is highly efficient, for it is regenerated with nearly 100% stoichiometric amount of acid, as compared to

the 200-300% required for strong acid cations. The weak acid resins are subject to reduced capacity from increasing flow rate, low temperatures, and a hardness-to-alkalinity ratio below 1.0. They are used very effectively in conjunction with a strong acid cation resin operating in the hydrogen form, in either a separate bed or stratified bed configuration. In both cases, the influent water first contacts the weak acid resin where the cations associated with alkalinity are removed. The remaining cations are removed by the strong acid cation resin. The weak acid cation resin is regenerated with the waste acid from the strong acid unit, making for a very economical arrangement.

Strong Base Anion Resins

Strongly basic anion resins derive their functionality from quaternary ammonium exchange sites. The two main groups of strong base anion resins are Type 1 and Type 2, depending on the type of amine used during the chemical activation process. Chemically, the two types differ by the species of quaternary ammonium exchange sites they exhibit: Type 1 sites have three methyl groups; in Type 2 an ethanol group replaces one of the methyl groups.

Type 1 resins are suitable for total anion removal on all waters. They are more difficult to regenerate and they swell more from the chloride form to the hydroxide form than Type 2. They are more resistant to high temperatures and should be used on high alkalinity and high silica waters.

Type 2 resins also feature removal of all anions, but they can be less effective in removing silica and carbon dioxide from waters where these weak acids constitute more than 30% of the total anions. Type 2 anions give best results on waters that predominately contain free mineral acids - chlorides and sulfates - as in the effluent from a cation unit followed by a decarbonator. Type 2 anion resins operating in the chloride form are typically used in dealkalizers.

Weak Base Anion Resins

Weakly basic anion resins contain the polyamine functional group, which acts as an acid adsorber, removing strong acids (free mineral acidity) from the cation effluent stream. This weakly ionized resin is regenerated efficiently by nearly stoichiometric amounts of base - such as sodium hydroxide - which restore the exchange sites to the free base form. The regeneration step is essentially a neutralization of the strong acids that are collected on the resin and it can use waste caustic from a strong base anion unit to enhance economics. Weak base anion resins should be used on waters with high levels of sulfates or chlorides or where removal of alkalinity and silica are not required.

Summary

This presentation has reviewed the history of early resins, described the manufacturing process and the polymers involved, and discussed the importance of DVB crosslinking of the resin structure. The different physical structures, gelular and macroporous were compared, as were the two chemical structures, acrylic and styrenic. The selectivity and kinetics of the different types of exchange sites were also illustrated.

The ion exchange resins described are found in numerous commercial and industrial uses, including softening, dealkalization, demineralization, nitrate removal, condensate polishing, pollution control, and many others. The selection of the appropriate resins for specific applications is determined by the feedwater analysis and desired effluent quality. Contact your resin supplier for detailed engineering information and performance predictions.