

ION EXCHANGE

Water is the universal solvent that is able to dissolve a little bit of everything it touches. It could, therefore, be said that “pure” water does not exist. Even the most highly processed and purified water still contains trace levels of gases, salts or minerals that have been leached from its containment vessel or absorbed from the surrounding air.

Salts are formed naturally when acidic rain water is neutralized by alkaline soil strata. Common salt (also called table salt) is sodium chloride (NaCl), but salt also refers to compounds containing potassium (K), calcium (Ca), iron (Fe), carbonates (CO_3^{2-}), nitrates (NO_3^{1-}) and many other combinations of elements.

When salts dissolve in water, they separate into charged particles called ions. A positively charged particle is a cation and a negative ion is an anion. Calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^{1+}) are examples of cations. Chloride (Cl^{1-}), nitrate (NO_3^{1-}) and sulfate (SO_4^{2-}) are examples of anions. The number of charges on an ion indicates the number of ‘counter-ions’ it will share in any reaction. Calcium ion, for instance requires two ‘counter-ions’ of chloride (CaCl_2) but only one sulfate (CaSO_4) because the final salt molecule must maintain a net neutral charge. Sulfate, for example, would require two sodium ions (Na_2SO_4) to balance the ionic charge for sodium sulfate.

All salts and ions may be considered “contaminants” for some specific water uses. Not all salts (contaminants) are toxic or harmful and therefore do not have to be removed to make water safe to drink. On the other hand, perfectly safe drinking water may not be suitable for many industrial needs because they contain salts that may interfere with the industrial process. Hardness, the salts of calcium and magnesium bicarbonate may precipitate out on heating coils and in boilers and cause scale to form. Yet they are safe to consume in drinking water. Higher pressure boilers may require very “pure” or demineralized water (water from which the minerals have been removed).

To remove unwanted ions (dissolved salts) from a water, a process called “ion exchange” is most often used. Ion Exchange was first observed in the mid-1800s but did not gain wide spread use until the development of modern polymerization technologies developed in the 1940s. With ion exchange, the less desirable or unwanted ions can be exchanged for less objectionable ions to enhance the utility of the water for its intended purpose.

TECHNICAL PROCESS

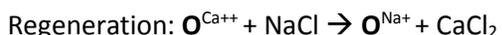
The ion exchange process is widely used for the removal of hardness (as in softening), heavy metals (as in waste treatment), radionuclides (as from power plants) and municipal water feeds (removal of nitrates, arsenic, perchlorate, hexavalent-chrome and others). Since most ion exchange processes are reversible, the ion exchangers can be regenerated (put back into their original ‘salt form’) and used over and over.

Ion exchangers (IEx) are called resins which are plastic beads made from polystyrene or acrylic. They measure 0.5 to 1.0 mm in diameter and are utilized in columns or tanks with resin beds typically about three feet deep. Water passes through the bed of resin where the exchange takes place and when exhausted, they are regenerated with salt, acid or caustic depending upon the process. IEx resins contain functional groups that

dictate which ions can be exchanged. There are four primary types of ion exchangers: strong acid cation, strong base anion, weak acid cation, and weak base anion.

STRONG ACID CATION – SALT REGENERATION

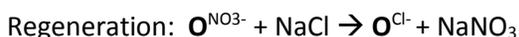
Strong Acid Cation resins (SAC)-typically contain sulfonic acid functionality ($R-SO_3^{1-}$) that can exchange positive ions, such as calcium and magnesium, for sodium or potassium. This resin is commonly used for softening and is regenerated with salt (sodium or potassium chloride). Water hardness is generally associated with bi-carbonate ions (HCO_3^{1-} and is called “temporary hardness”) or chloride or sulfate ions (called “permanent hardness”). It may also contain barium, strontium, iron or other di-valent cations (M^{2+}). Below ‘O’ is the ion exchange resin:



Depending on the level of regeneration, the hardness can be reduced to less than 1 ppm but typically the target is simply less than 17.1 ppm or one grain of hardness per gallon (gpg). One grain is equal to 17.1 ppm of hardness expressed as calcium carbonate. Softeners do not reduce the total dissolved solids (TDS) or dissolved mineral content of water.

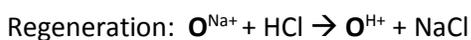
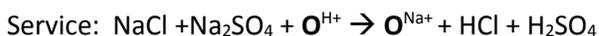
STRONG BASE ANION – SALT REGENERATION

Strong Base Anion (SBA) resins typically contain quaternary (four) amine functionality ($R-N^{1+}(CH_3)$) that can be used to exchange negative ions such as nitrates (NO_3^{1-}) or alkalinity (HCO_3^{1-}) for chloride. These are ideal for residential needs where certain anionic contaminants must be reduced. SBA resins can also be regenerated with salt. In addition to nitrates and alkalinity, SBA resins can also exchange chloride for the ‘oxy-anions’ of hexavalent-chrome, phosphate, uranium or sulfates. Therefore, most of the ‘contaminant’ anions are removed in exchange for chloride ion. During regeneration, the resin is converted back to its original chloride form.



STRONG ACID CATION – ACID REGENERATION

For demineralization applications, Strong Acid Cation resins can also be regenerated with acid to convert the resins to their hydrogen (H^+) form. This form is commonly used to remove **all** cations as part of a demineralizer system. All cations including sodium are exchanged for H^+ ion which converts all the anions to their acid-salt form (decaionization). When exhausted, the resins are regenerated with acid to restore capacity.



The service reaction shows a mixture of sodium chloride and sodium sulfate in the feed water and both are converted to their respective acids as hydrochloric and sulfuric. The pH of decaionized water will be very low (~pH=2-3) when fed with typical city water. CAUTION: This process is not used for treating residential or

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drinking water alone. Caution must be used in making choices for ion exchangers and their regenerants. It is recommended that an ion exchange representative should be consulted to avoid unexpected results.

STRONG BASE ANION – CAUSTIC REGENERATION

Strong base resins can also be regenerated with sodium hydroxide (NaOH) and put into the OH⁻ form which removes the acid from a demineralizer SAC system.

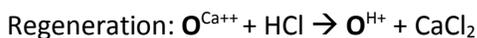
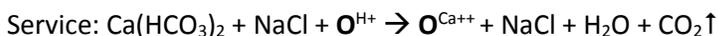


The two bed demineralizer removes up to 99.5% of the dissolved salt content from water and produces a slightly alkaline product at a pH of 9-9.5. When mixed together (**mixed bed** demineralization) they reduce the TDS by 99.99% or more and produce a product water that is so low in mineral content that the only way to measure it is with electrical conductivity measurements. The unit of measure is the micro-siemen, (μS). One μS (also referred to as micro-mho) equals approximately 0.5 ppm of dissolved solids.

The inverse of conductivity is resistivity and the unit of measure is the ohm. Very high resistivity is stated in megohms (one million ohms) and 1 μS converts to 1 megohm (0.1μS = 10 megohm). With very low TDS water, H₂O dissociates into H⁺ and OH⁻ and contributes to conductivity. Therefore, zero conductivity is not possible. The ultimate measure of demineralized water is generally accepted to be 18.3 megohm or 0.055 μS.

WEAK ACID CATION

Weak Acid Cation resins or WACs will have a carboxylic acid group with an exchangeable H⁺ but are very different in function to the SAC. WAC resins do not split neutral salts such as NaCl or Ca(NO₃)₂ but do react with alkaline salts such as Ca(HCO₃)₂. Alkalinity includes HCO₃⁻, CO₃⁼ and OH⁻. Reactivity is limited to the level of the alkalinity present which gives the WAC great utility for single bed softening AND dealkalizing. Only a portion of the cation load is converted to H⁺ (equal to the level of the HCO₃⁻ present. This converts the HCO₃⁻ to CO₂ (carbon dioxide) which can then be off-gassed to soften, dealkalize AND reduce the TDS of the process stream.

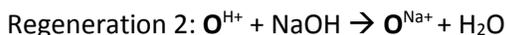
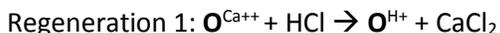


If the total hardness is lower than the alkalinity, some of the sodium will be removed so that the sum of the hardness AND sodium removed will be equal to the level of alkalinity. If the total hardness is higher than the alkalinity, only the amount of hardness equal to the alkalinity will be removed. This is a preferred process used by the carbonated beverage industry to reduce hardness, alkalinity and TDS, all of which can interfere with flavor and carbonation.

Weak Acid Cation resins can also be run in the Na⁺ form to provide softening and/or metals removal. However, they do not regenerate with salt. Regeneration is a two-step process that uses acid to convert back to the H⁺ form and then caustic (sodium hydroxide, NaOH) to convert to the Na⁺ form. WAC resins are highly selective for hardness and di-valent metals when run in Na⁺ form and have the ability to operate in much higher TDS background than do SAC resins. They can be used to soften brackish water ranging up to about 10,000 ppm and

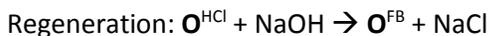
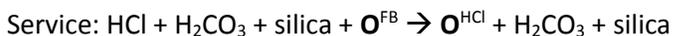
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are often used as metal scavengers in the plating industry and in small cartridges for lead and other heavy metals removal from drinking water. Regeneration is a two-step process done by first regenerating back to the H⁺ form and then converting to the Na⁺ form with NaOH.



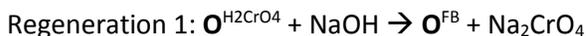
WEAK BASE ANION

Weak Base Anion resins or WBAs are produced by a similar process to SBA except they have tertiary (three) amine functionality and operate in what is called the free base (FB) form. WBAs do not split neutral salts but only react with free acids by sorption. WBAs only react with strong acids such as HCl, HNO₃ and H₂SO₄ so they do not remove CO₂ (carbonic acid) or silica (silicic acid) which are weak acids. WBA resins are often used in two-bed demineralizers to neutralize the acid produced by the SAC unit. Operations such as car wash spotless rinses find great utility in WBA because they have high capacity and very good chemical efficiency. Regeneration is with sodium hydroxide, NaOH.



On drying, the H₂CO₃ evaporates leaving only silica behind. Before employing the SAC/WBA for spotless rinses, the user should check the level of silica. Levels much above 10-15 ppm may leave damaging residue on the surface. In this case, the use of SAC/SBA mixed beds are dictated for true spot free rinsing.

Weak Base Anion resins can also be run in the acid form to remove more strongly selective acid radicals from solution. An example of this is the use of WBAs run in HCl form to remove hexavalent-chrome from well water. Regeneration is a two-step process done by first converting the resin back to the free base form and then converting that to the acid form.



RESIN SELECTIVITY

Ion Exchange operations and the choice of resins to use are highly dependent on the water analysis, what has to be removed and to what level it has to be reduced. The primary driving force is **selectivity**. Selectivity is determined by the ionic charge on the specific ion and the resin type. Typically, resins have a higher selectivity for multiply charged ions than for singly charged ions (see below). Also, this is highly influenced by the other ions in solution that might compete for the reactive sites. No resin is so highly selective that it is exclusive for a specific contaminant.

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Even if the selectivity is low compared to the selectivity of the ionic form the resin, ion exchange can still take place on a **mass action** basis. If the resin is very clean and free from the contaminant, it will react to pick up the contaminant from solution. An example is with the use of a SBA to reduce fluoride. The F^- ion is below the selectivity of the Cl^- ion on the resin and even though the equilibrium may be unfavorable, the SBA resin can be used to remove F^- from the feed. Selectivity dictates that the resin will absorb all other anions as well as the F^- so the capacity is greatly reduced. In general, selectivity for an ion will increase with its molecular weight and ionic charge. For SAC one can expect $Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ and $Al^{3+} > Mg^{2+} > Na^+$. For SBA one can expect $I^- > Br^- > Cl^- > F^-$ and $SO_4^{2-} > Cl^-$.

UNITS OF CONCENTRATION

In order to work with ion exchange systems and design, it is very important to have a complete and accurate water analysis. The water analysis is generally presented in units of weight per unit volume such as ppm or ppb (mg/l or $\mu g/l$). Labs differ in their reporting so one must not confuse the data. The local lab that deals with agricultural issues may report only those constituents that affect plants rather than people. In addition, reports may present data based on how it was generated. For instance the nitrate content as NO_3-N meaning that the analysis is only telling you the nitrogen (N) content and not the nitrate (NO_3) value. Metals are often reported as ppb (parts per billion) rather than ppm (parts per million). Hardness and alkalinity values are frequently reported in units as ppm “as $CaCO_3$ ” even though the sample may contain neither calcium nor carbonate. The unit “calcium carbonate” is not a measure of hardness contained but is a unit of measure based on the number of atomic sites it represents. With ion exchange, we have to work with the number of ions rather than with milligrams of contaminant so there is a need to be familiar with the conversion process.

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