

The Basics of Water Chemistry (Part 2)

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Summary: In this, the second part of a three-part series, we examine the proper use of a water analysis and traps to avoid in deciphering it. In the first part, we discussed basic ionization and the value of the Periodic Table of Elements to the water treatment professional. In Part 3, next month, we'll discuss the use of chemistry and ion exchange selectivity to solve certain water treatment problems. Throughout this series, we try to demystify some of chemistry's complexities to offer readers a good grasp of the fundamentals of filtration and ion exchange.

To properly design a water treatment system, particularly with ion exchange and reverse osmosis, it's necessary to first get both a quantitative and qualitative listing of what the intended feed stream contains. This listing is known as the water analysis, and a proper interpretation is a must to assure good results. Although the purpose of an ion exchange system is to remove only the offending ionic components of a feed stream, other factors such as temperature, total dissolved solids (TDS), pH and trace minerals also play a role and must therefore be considered.

Laboratories usually report a water analysis using certain approved test methods, which give the results in milligrams per liter (mg/L). This is convenient because 1 mg/L is equal to 1 ppm, or part per million. This number, however, is in units of weight. Ion exchangers, on the other hand, don't deal with weight; they deal with ions, which are the real chemical components we are trying to remove. A milligram of magnesium or calcium does not contain the same number of ions or ionic equivalents as does sodium or hydrogen. The convention commonly used is to convert to ppm as CaCO₃—calcium carbonate. Confusion arises because both the mg/L value and the CaCO₃ value can and are often reported as ppm. A good practice would be to refer to elemental components (the analysis) as mg/L and the CaCO₃ equivalents (the conversion) as ppm.

CaCO₃ as ppm

CaCO₃ is an arbitrary name choice. It has a formula or molecular weight (M.W.) of 100 (compared to carbon with a M.W. of 12). Both the calcium (Ca⁺⁺) and carbonate (CO₃⁼) ions are divalent. That is, they have a charge value of +2 and -2, respectively (compared to sodium at +1), and, thus, an equivalent weight of 50.

The equivalent weight (eq. wgt.) of any substance is equal to its M.W. divided by its valence. In the case of CaCO₃, this is 100 ÷ 2 = 50. It should be noted neither Ca⁺⁺ nor CO₃⁼ have an equivalent weight of 50, but the combination does. The eq. wgt. of Ca⁺⁺ is 20 (M.W. = 40 ÷ 2 = 20) and the eq. wgt. of CO₃⁼ is 30 (M.W. = 60 ÷ 2 = 30). We therefore must equate even the Ca⁺⁺ and CO₃⁼ content of water to the eq. wgt. of CaCO₃. We do this by multiplying by a conversion factor (which is derived by dividing the number 50 by the eq. wgt. of the substance). In the case of Ca⁺⁺, this is 50 ÷ 20 = 2.5. For CO₃⁼ it's 50 ÷ 30 = 1.67. We can readily see that most common components of water will have a different M.W., we'll have a variety of conversion factors. Table 1 lists the common elements and their conversion factors.

Table 1
Conversion Factors for Common Water Components

Cations		Anions	
Ca ⁺⁺	2.50	HCO ₃ ⁻	0.82
Mg ⁺⁺	4.10	CO ₃ ⁼	0.83*
Na ⁺	2.18	SO ₄ ⁼	1.04
K ⁺	1.28	Cl ⁻	1.41
Fe ⁺⁺	1.79	NO ₃ ⁻	0.81
Mn ⁺⁺	1.82	SiO ₂	0.83

*For ion exchange purposes, it is assumed that carbonate reacts as the monovalent ion.

A simple water analysis converted from mg/L to ppm as CaCO_3 is shown in Table 2.

While the total dissolved mineral content of this water (residual by evaporation) would measure 435 mg/L, the TDS as CaCO_3 is 273.5 ppm (for deionization or DI purposes). One does not add the cation and anion values together. For anion determinations, the silica is quoted as an afterthought. “I have 273.5 ppm water with 15 ppm of silica.” For mixed bed calculations, this is 288.5 ppm water. For softening calculations, it’s 10 grain water, and for dealkalization, it’s 10.5 grain water. There are 16.0 grains of cations and 16.9 grains of anions for deionization.

Every ion has a partner

Every ion is assumed to have a counter-ion (as a dancing partner, so to speak). It should be noted that with extreme pH conditions (i.e. <4 or >10), there will be an excess of cations or anions, respectively. Normally, every cation has an anion (with the exception of silica) so the total cations should equal the total anions (without silica). Silica, a weakly ionized acid, is presumed to exist (for DI purposes) as H_2SiO_3 (silicic acid) and has H^+ as its partner. It therefore stands alone.

Sometimes the water analysis will be incomplete in that only the offending ions (calcium, magnesium, iron, alkalinity, sulfate and silica) are reported—sodium and chloride are missing. If the analysis appears incomplete, look for the obvious. You can estimate the ppm as CaCO_3 by dividing conductivity (as micromhos, or umhos) by 2.5. In Table 2, we show conductivity as 650 umhos. Dividing by 2.5 gives us a TDS of 260 ppm.

If the totals for cation and anion are not equal, we make them equal by adding to the sodium (Na^+) or chloride (Cl^-) values. For instance, if the cation total were 15 less than the anion, we would add 15 ppm to Na^+ as CaCO_3 to the cation load. Include the ppm as CaCO_3 values for all monovalent cations (K^+ , NH_4^+) as part of the Na^+ total and monovalent anions (NO_3^-) as Cl^- totals. We then add silica value to the anion total to get the “total” anion load. This is done after balancing the cation and anion totals.

For the purposes of capacity calculations, it’s generally safe to ignore any items with values below 0.1 ppm. Dividing these corrected totals by 17.1 converts the ppm as CaCO_3 values to grains per gallon (gpg) values. Since the ion exchange capacity is usually determined in kilograins (Kgr) per cubic foot, (1 Kgr = 1,000 grains), we can now determine the “throughput” capacity in gallons per cubic foot (gal/ft^3) of resin. Simply divide the grains of loading into the capacity of the resin.

Example: Determine the proper size of a DI system that will handle 20 gpm for 12 hours using the above water analysis. Use 6 pounds per cubic foot (lbs/ft^3) of HCl for regeneration of cation and 7 lbs/ft^3 of room temperature caustic (NaOH) for the anion. The literature shows that the cation capacity (at approximately 40 percent Na and 60 percent alkalinity) to be 27.5 Kgr/ ft^3 . Using a 10 percent engineering downgrade, we have a net design capacity of 24.75 Kgr/ ft^3 ($27.5 \times .9 = 24.75$) for the cation. The anion (use a Type II) will have a book capacity of 20.3 Kgr/ ft^3 (with 5 percent silica in the influent) and we will downgrade this by 15 percent

Table 2
Water Analysis Conversions

Cations	mg/L	as CaCO_3	Anions	mg/L	as CaCO_3
Calcium	60	150 ppm	Bicarbonate	220	180ppm
Magnesium	4.9	20 ppm	Carbonate	5	4 ppm
Sodium	45.9	100 ppm	Sulfate	38.5	30 ppm
Potassium	2.3	3 ppm	Chloride	35.5'	50 ppm
Iron (ferrous)	0.3	0.5 ppm	Nitrate	4.3	3.5 ppm
<i>Subtotal</i>	<i>113.4</i>	<i>273.5</i>	<i>Subtotal</i>		<i>303.3</i>
			Silica		15
			<i>Total</i>		<i>321.3</i>
Temp	68°F				
pH	7.6				
Turbidity	.5 NTU				
Color	35 APHA				
Cond	650 umhos				

for design purposes (multiply by .85), which leaves us with 17.25 Kgr/ft³. The engineering downgrade “factor” is a safety factor applied to DI calculations to allow for wear and tear, resin loss and some fouling, as well as variations in the feed stream over the life of the resin. It is usually 10 percent for cation resins and 15 percent for anion resins.

Since we have an anion load of 16.9 gpg, we will have to remove $16.9 \times 20 \times 60 \times 12 = 243,360$ grains. Dividing this by 17.25 Kgr anion capacity, we see we’ll need 14 cubic feet of anion resin. Since the cation will have to produce the water required to regenerate the anion resin, we must now add that quantity of water to our cation load before determining the size of the cation exchanger. The total gallons are $20 \times 60 \times 12 = 14,400$. Assuming 75 gal/ft³ of anion resin required for regeneration, add to that $1,050 = 75 \times 14$. The cation must therefore treat 15,450 gallons ($\times 16.0$ gpg) or 247,200 grains. Dividing this by our cation rating of 24.75 Kgr, we’ll need 10 cubic feet of cation resin.

Resin capacities are dependent on the water analysis (among other things) and therefore not constant for every system. The ratios of various ions to one another will cause the resin capacity to vary as will the quality of effluent one is targeting. Flow rate per cubic foot will also affect capacity as will temperature of service and regenerant. In addition, the quantity of regenerant is usually determined by the leakage values (quality) needed, which is what sets the whole thing in motion. “Leakage,” or what appears to be incomplete removal of unwanted ions, is a result of incomplete regeneration. Keeping in mind “complete” regeneration is all but impossible, we choose a regeneration level producing a leakage we can tolerate as acceptable quality. The engineering of DI systems is a complex science (and, some say, art) and will not be addressed here.

Softener loading

There is more to building a softener than simply measuring hardness of the water and setting the dial. Your customer not only wants his or her water softened today, they want it softened tomorrow, next month and 10 years from now. This means the regeneration procedure must also be a rejuvenation procedure to keep the unit operating satisfactorily for many years. The water analysis can help us determine how to do this.

Softener throughput is influenced not only by hardness, but also by TDS, iron, temperature, flow rate and regeneration level and technique. Since TDS and iron will generally be part of the water analysis, we’ll look at those.

Table 3 Leakage vs. total dissolved solids (TDS) dosage chart

TDS of feedwater*	Pounds of salt
200	2
500	5
800	10
1,200	15
1,500	20
2,000	25

*Expressed as ppm.

Hard water leakage is caused by residual hardness that is left on the resin after regeneration and bleeds off during the service run. Increasing the salt dosage can minimize it. As hard water passes through a resin bed, the hardness is exchanged for sodium (or potassium). The higher the sodium level (or TDS feed level), the higher the tendency for the softened water to leech hardness back off the resin. This reduces the run length (and thus the capacity) between the baseline leakage and the breakthrough leakage. Simply knowing the TDS ahead of time can allow you to avoid costly field calls to remedy low capacity or leakage complaints by adjusting the capacity setting and using a higher salt dose ahead of time. To achieve 5 ppm (or less) leakage during the run, use the following salt settings for various TDS values:

Soluble iron is exchanged onto a cation exchanger as Fe^{+2} . However, with time, it oxidizes to Fe^{+3} and is not readily removed by salt regeneration. If we assign a higher value for iron in determining our loading, we will reduce the throughput volume and, therefore, regenerate more frequently.

A good practice is to treat each ppm of iron as 1-to-3 grains of hardness. As such, in our sample water analysis, we have 10 grains loading from hardness and we add 1 1/2 grains for the iron (total = 11.5). Soluble iron as high as 30 ppm has been successfully treated with a standard softener with 10-to-12 pounds of salt/ft³ regeneration level. Utilizing a resin cleaner is always a good bet. Citric acid (available from most chemical suppliers) works well at a level of one pound per 50 pounds of salt and can be added directly to the brine tank.

Water analysis traps

There are a few things to watch out for in your calculations.

Hardness and alkalinity

Frequently a water analysis will report total hardness (TH) and/or alkalinity (HCO_3^-) in ppm as $CaCO_3$. For the purpose of designing softeners and dealkalizers, these numbers can be plugged in directly as “loading” values. If, however, the mg/L value is also listed, do the conversion to check their math.

Nitrates and nitrites

Nitrate and nitrite are frequently reported in terms of mg/L as N (nitrogen). This is written as NO_3-N and NO_2-N . It's necessary to first convert these values to mg/L as the ion, then to ppm as $CaCO_3$. Since N has a M.W. = 14, and NO_3 has a M.W. = 62, it is necessary to multiply the N value by 62/14 or 4.43 for the NO_3 and 3.29 for the NO_2 . The maximum contaminant level (MCL) for NO_3-N is 10 ppm. This equals 44.3 mg/L for NO_3 ion and 35.9 ppm as $CaCO_3$.

Trace metals

While trace metals, particularly heavy metals, may be present at very low levels, their toxicity usually dictates that they be reported. Their values are usually reported in micrograms (millionths of a gram) and written as ug/L (sometimes the letter “u” is substituted for the Greek letter “μ” or mu). This value is actually in parts per billion (ppb) and, while its value will probably not affect capacity, its presence may influence how you design your system. Do not confuse μg with mg.

It's a common practice to acid-stabilize a water sample before sending it off to a lab. The acidification is to prevent precipitation of metals due to possible pH changes (from loss of CO_2 during warming of sample or agitation). Acidification not only prevents precipitation, it causes precipitated metals (such as aluminum, iron and lead) to solubilize. Be suspect if there is a moderate detailing of ppb quantities of trace metals in the analysis. This sample may have been acidified. The raw water may carry these elements as precipitates, which should be removed by particulate filtration. Take a closer look at the water.

Turbidity

Dirty waters can plug and foul ion exchange units, causing channeling and capacity loss. Use a pre-filter if the turbidity values are >5 NTU (nephelometric turbidity units).

Color

Natural organics (such as tannins) or iron (colloidal, organic or precipitated) may cause color, reported as APHA units. Values for color below 25 APHA are usually not noticeable by eye. Again, try to determine what is causing the color and install proper pre-filtration. Softeners do not remove color. Granular activated carbon (GAC) and/or salt regeneration anion resin can often do the job.

Temperature

Ion exchange systems are usually intended to function with water feed temperatures of 50-to-100°F. Higher temperatures can be detrimental to anion resins in DI systems. A lab-supplied water analysis may list temperature, but it's meaningless. Rather, check with the intended installation site if anion exchange enters into the picture.

Much of the ion exchange process depends upon ions' ability to diffuse into and out of the resin bead matrix. This is temperature dependent and is seriously slowed by cold-water operations. Resin beds should be at least 50 percent larger in diameter and 100 percent larger in volume to effectively handle water streams below 40°F.

Conclusions

Obtaining and using a good water analysis is essential to the proper design of any water filtration system, particularly an ion exchanger. There is much valuable information on a lab analysis that can help you to avoid design errors.

Make sure you understand the water analysis. Check the math to make sure the units add up. Make sure the cations are equal to the anions, and then add in silica to determine total loading.

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