The Basics of Water Chemistry PART 3

by C.F. "Chubb" Michaud

Summary: In Part 1 of this series, we discussed chemistry fundamentals and the formation of ions by various compounds and salts that dissolve in water. We also pointed out that the ion exchange process is simply an example of the applied chemistry we learn from observation. Part 2 examined the water analysis and its conversion to usable information for setting up ion exchange design. Part 3 of this series deals with the selectivity of ion exchange resins and how to best design ion exchange treatment systems for optimizing results. It also provides some useful information on using the Periodic Table of the Elements for predicting selectivity in ion exchange.

Ever wonder why softeners work? How does the ion exchange resin know it's only supposed to remove hardness? Why does it release sodium during the service run and yet we can use a sodium salt to recharge that same resin during regeneration? We can use sea water to regenerate a softener and then use that same resin to soften sea water. How? The answer is ion exchange selectivity. Selectivity is the most important single aspect of ion exchange. Designing your system around selectivity can really make ion exchange work for you.

If we take two soluble salts such as calcium chloride and sodium carbonate, as described in the first part of this series, and mix them together in solution, eventually the calcium will react with the carbonate ion and precipitate out as $CaCO_3$. Since the calcium prefers to be with the carbonate ion, we can say it has a higher "selectivity." Mother Nature likes to have things quietly at rest. If we look around at the myriad of rocks and natural compounds, we might ask, "Why does that compound exist?" We may also ask, "Why is the sea salty?" or "If water is the universal solvent, why doesn't the silica in beach sand dissolve away?" Again, the answer is selectivity. If we solubilize the entire planet in a giant tank of water, then allow the water to slowly evaporate, we would have our rocks and compounds back and in approximately the same purity and quantity.

The tendency of one ion to react preferentially with another is the same principle by which ion exchangers work. Each resin type has its own exchange selectivity preference. Generally speaking, for dilute solutions, trivalent ions are preferred over divalent ones, which, in turn, are preferred over monovalent ones. One would expect calcium with

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Table 1

Cation Selectivity vs. Crosslink Level (DVB)*

Element	4%	8%	16%
Monovalent			
Li (lithium)	0.63	0.51	0.42
H (hydrogen)	0.84	0.64	0.62
Na (sodium)	1.00	1.00	1.00
NH₄ (ammonium)	1.20	1.29	1.41
K (potassium)	1.44	1.46	1.90
Rb (rubidium)	1.56	1.60	1.95
Cs (cesium)	1.69	1.64	1.97
Ag (silver)	2.99	4.30	9.66
Divalent			
Mg (magnesium)	1.87	1.66	1.48
Zn (zinc)	1.98	1.75	1.60
Co (cobalt)	2.04	1.90	1.61
Cu (copper)	2.08	1.94	1.88
Cd (cadmium)	2.13	1.96	2.09
Be (beryllium)	2.17	2.02	2.63
Ni (nickel)	2.18	1.98	1.71
Mn (manganese)	2.16	2.07	2.07
Ca (calcium)	2.63	2.61	3.07
Sr (strontium)	2.97	3.29	4.26
Pb (lead)	4.15	5.00	7.60
Ba (barium)	4.72	5.80	8.78
Trivalent			
Cr (chromium)	4.17	3.84	4.43
Ce (cerium)	4.75	5.35	7.17
La (lanthanum)	4.81	5.40	7.17

NOTE: In this table, sodium (Na) is arbitrarily given a value of 1.00 in each column. The relative strength of sodium attraction goes up with cross linking. If we assign a value of 1.0 to the 4% cross link only, then the selectivity value of sodium becomes 1.25 for the 8% and 1.50 for the 16%.
* DVB, or divinyl benzene, is the crosslinker in most ion exchange resins.

Table 2

Anion Selectivity for Type I Resin

Ion	Selectivity
Dichlorophenate	53
Salicylate	28
Phenate	8.7
I (iodide)	7.30
HSO₄ (bisulfate)	6.10
NO₃ (nitrate)	3.30
Br (bromide)	2.30
NO₂ (nitrite)	1.30
CN (cyanide)	1.30
HSO₃ (bisulfite)	1.30
BrO₄ (bromate)	1.01
Cl (chloride)	1.00
OH (hydroxide)	0.65
HCO₃ (bicarbonate)	0.53
H₂PO₄ (acid phosphate)	0.34
Formate	0.22
Acetate	0.18
F (fluoride)	0.13

NOTE: In this table, chloride is arbitrarily given a value of 1.00.

an atomic number (AN) of 20 to be more selective than family member magnesium (AN=12), but less than strontium (AN=38) or barium (AN=56). Experience –and lab testing – confirms this. We would therefore expect potassium to be more selective than sodium (which it is) and the halogen family (F, Cl, Br, I) to have a pecking order (which they do). In general, the higher the atomic number for a given family the higher the selectivit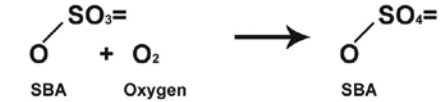y of its ion in an ion exchange system. In concentrated solutions, such as regenerant brines, acids and bases, selectivity can change. In addition, we can alter selectivity by pH for certain resins. Ionic complexes such as gold cyanide and other metallic solutions can have very high selectivity—more so than other divalent or even trivalent ions. This makes the separation of metals possible. Our ability to manipulate the selectivity of ion exchange is what gives it such a high utility.

As the crosslinking level of the standard strong acid cation resin increases, its moisture level decreases. With their polymer strands more compacted (less moisture, less swelling), the higher crosslinked resins have a higher charge density and, thus, attract all cations more strongly.

Table 1 shows the relationship of relative selectivity of certain cations with respect to the crosslinking level of the cation resin. Crosslinking does not change the order of selectivity but it does accentuate the differences. Higher crosslinking spreads the differences and therefore becomes the resin of choice for separating ions of similar characteristics (chromatography). As the crosslinking is reduced, the differences diminish.

Table 2 shows the relative selectivity of selected anions for typical, strong base Type I resins.

Strong acid, weak acid, strong base (I and II) and weak base have different selectivities for the same ion. Selecting the proper resin in the proper form can help you to remove and concentrate most ions from dilute solutions. This may help explain why any one manufacturer may offer dozens of ion exchange resins, which appear to do the same job.
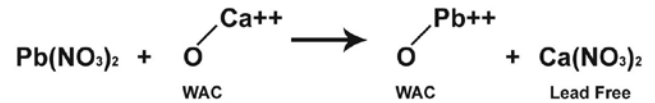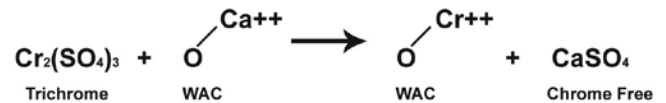
Ion exchange resins can be put into any form and can be regenerated with almost any compound soluble in water. We are not limited to sodium chloride, hydrogen or hydroxide.

EXAMPLE A: Strong base anion can be placed in the sulfite form by regenerating with sodium sodium sulfite which, in turn, will scavenge oxygen from feed streams by converting to sulfate.

❶ **Regeneration**

❷ **Service**

EXAMPLE B: A weak acid resin in the calcium form will still exchange for lead, which makes it very attractive for cartridge and waste treatment application.
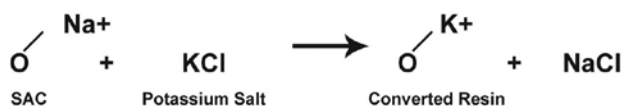
❸

❹

EXAMPLE C: Weak base resins in salt form (acid form) will exchange their acid radicals for ones of higher selectivity. Again, this makes for a very selective scavenger for certain metal contaminated groundwater.

❺ **Service**

❻ **Regeneration**

EXAMPLE D: A strong acid resin can be converted with potassium chloride (KCl) to put resin in the K+ form and be used to scavenge sodium from a reverse osmosis (RO) supply for sodium free water.
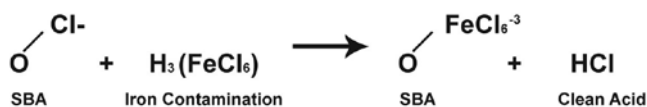
❼ **Regeneration**

❽ **Service**

Other common uses with NaCl or KCl regenerations include the reduction/removal of:

EXAMPLE E: Iron forms a very strong anion complex $(FeCl_6^-)^3$ when dissolved in concentrated hydrochloric acid. Should HCl become contaminated with iron, one can use a strong base anion in the chloride form to remove it. Since the complexed specie only exists in strong HCl, rinsing the spent resin with plain water converts the iron back to a trivalent cation and flushes it from the resin.

❾ **Service**

❿ **Regeneration**

We've discussed selectivity as the backbone of the ion exchange process along with the subtle influence of crosslinking and feed concentration. There's an additional consideration that comes into play that expands the use of ion exchange. That condition has to do with the equilibrium process and we refer to it as mass action. Simply stated, if we have a clean resin in an ionic form, it will undergo exchange with any other ion in solution, regardless of selectivity. We see this in our description of the anion dealkalizer. Bicarbonate is actually further down the list than chloride (selectivity 0.53 vs 1.00). However, the exchange between bicarbonate in the water and the chloride on the resin will take place. The capacity is fairly low (about 5-to-7 kilograins per cubic foot or Kgr/ft^3) but viable, and it only requires a small amount of salt (5 pounds or lbs.) for regeneration. That same resin might exhibit a 20 Kgr/ft^3 capacity in removing sulfates because of selectivity (sulfate selectivity is 6.10).

Table 3

Resin and Their Common Reduction/Removal Applications

Problem	Resin	Regenerant
Alkalinity	SBA II	NaCl or KCl
Arsenic^{+5}	SBA I	NaCl or KCl
Cyanide	SBA I	NaCl or KCl
Copper	SAC	NaCl or KCl
Iron	SAC	NaCl or KCl
Nitrate	SBA II	NaCl or KCl
Selenium	SBA I	NaCl or KCl
Radium	SAC	NaCl or KCl
Sulfates	SBA II	NaCl or KCl
Uranium	SBA II	NaCl or KCl
Fluoride	SBA II	NaCl or KCl

Where:
SAC = strong acid cation exchanger
SBA I = strong base anion Type I
*SBA II = strong base anion Type II*Table

Mass action seeks to form an equilibrium between the ionic concentrations in solution (the feed stream) and the ionic concentration of that same species on the resin. If the resin contains very little of that ion (because of a clean regeneration), then the exchange will occur. This allows the use of anion exchange to remove fluorides fairly effectively if the water chemistry is right. It also allows the use of seawater to regenerate a softener (although there are limitations on the total dissolved solids or TDS of the feed stream).

Conclusion

There are many variables of feed streams and regenerants that will define the performance of an ion exchange application. In addition to the water chemistry of the feed stream, flow rate and regenerant level, the interplay of equilibrium and ion selectivity is key.

In general, the higher the valence of the ion the higher the selectivity. Also, the higher the atomic number within a family (of the same valence) the higher the selectivity.

Ion exchange resins can be made to do more than soften or deionize water by selecting the proper resin and proper regenerant for the job. Any soluble salt, base or acid can be used as the regenerant resulting in the conversion of one or more elements of the feed to a totally different chemistry. It's even possible to achieve selective removal of a single ionic species such as nitrates, sulfates, fruit acids or metals by applied ion exchange choice and proper design.

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Gratitude

Feeling gratitude and not expressing it is like wrapping a present and not giving it.

- William Arthur Ward

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