Episode 23 Getting Down with Anion

Understanding why there is a downward shift in pH after anion resin.

Manufacturing process

- Both cation and anion start with 2 monomers – polystyrene and divinylbenzene (DVB) to form a copolymer.
- **Cation –** most commonly asked for is 8% DVB crosslinked cation resin.
    - During the manufacture 8% of DVB is added.
    - DVB is a cross-linker, the glue that holds the whole bead together.
    - To make a cation functional, you react it with sulfuric acid. This puts a function group on the copolymer called the sulfonic acid group. That's what does the exchange with sodium ion for calcium and magnesium when you're softening.
- **Anion**
    - You take a similar copolymer but there are a few additional steps before you put the functional group on.
    - The most common functional group is an amine called trimethylamine. The manufacturer aminates the copolymer which puts the amine functional group on
    - It has a positive charge, and it has a chloride ion it which is negative.

- **Macroporous vs Gel**
    - The only difference between gel and macroporous are the holes, like swiss cheese, which are true pores going through the resin.
    - When the copolymer is made a porogen, which is an alcohol, is added. The polymer creates the pores around the alcohol when you're making the copolymer
    - The alcohol is washed out and you're left with a macroporous resin (which can be functionalized as macroporous cation or macroporous anion).
    - This macroporous anion resin is functionalized with an amine.

- **The more complicated anion manufacturing process is the reason anion resin is more costly.**

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Residential Dealkalization

There are 2 types of anion resin.

- Type 1 has the trimethylamine functionality on it. Unless properly cycled it may give off a fishy smell.
- Type 2 has a different amine, dimethylethanolamine, DMEA.
    - Type 2 resin has much higher capacity and more efficient regeneration.
    - Type 2 resin (not NSF certified) for industrial purposes may give off a plastic smell. This odor comes from trapped amine left from production.
- **For residential dealkalization a Type 2, NSF 61 certified resin is required (Purolite A-300E). There is no residual odor because the resin is cycled with acid and caustic and rinsed with hot water**.

pH Shift – Water Chemistry

- Softening is done to prevent calcium and magnesium based scales. There are two components in this scale, calcium and magnesium hardness, and alkalinity, which is bicarbonate alkalinity, HCO_3^{-1}.
- When you combine calcium (Ca^{+2}) and the bicarbonate alkalinity (HCO_3^{-1}), calcium carbonate ($CaCO_3$) is formed, and that's the scale that you then form.
- By reducing one of those components, you reduce the potential for forming that calcium carbonate scale.
- Alkalinity can exist as bicarbonate, HCO_3^{-1}; it can exist as carbonate which is CO_3^{-2} and it can also exist as hydroxide.
- In about 95 percent of the cases we face in home residential treatment, your alkalinity is primarily bicarbonate. It's not carbonate, it's not hydroxide.
- In some of the higher pH applications, where your pH is 8 and higher, you're going to have some carbonate in there along with the bicarbonate.
- Applying an A300E type of strong base anion will remove that alkalinity from the water.
- One thing to keep in the back of your mind is that the resin wants to come into equilibrium with the water, which means it wants to have the same concentration of ions on the resin as it does in the water.
- Example
    - High alkalinity – >200ppm in the water and your pH is up around 8 or so.
        - The resin's going to take out enough alkalinity to drop that pH maybe one unit. Leaving it in the neutral or above region. It's not going to create a corrosive environment by dropping below 7.
    - Low alkalinity - 50 to 100,
        - The resin is going to remove all the alkalinity, so your pH is going to be 5, 5.5 or 6. If there is copper in the home you will begin to see blue stains.

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Regardless of which strong base anion resin is being used, knowing the alkalinity in addition to the pH is the only means of determining whether the anion resin will cause a significant drop in pH.

- Where there is low alkalinity pH equilibrium is difficult to attain.
- It takes a very, very long time for any kind of a pH rise to happen, because with every regeneration the process starts over again.

- **An important factor in this is selectivity of the resin for specific ions.**
    - **Cation Selectivity** - In softening the cation resin has a greater selectivity for calcium and magnesium and would rather be on the resin than sodium. Calcium and magnesium bump the sodium off as it goes onto the resin, so your softened water is going to have an equivalent amount of sodium in the water to the hardness that is removed.
    - **Anion Selectivity** – Like cation resin the selectivity for ions is a function of the atomic weight of the resin but also the valence. The selectivity for most anion resins goes as follows:
        - Sulfate, which is divalent, is going to have a greater selectivity for the anion resin, than bicarbonate and chloride and nitrate, which are all monovalent.
        - Once you start treating initially, the anion takes everything out. You're taking sulfate, alkalinity, and nitrate out and exchanging for chloride.
        - As time goes on, the sulfate being taking out is going to be bumping off the alkalinity as well as the nitrate that has been removed during the initial part of the run.
        - Ultimately, as the resin gets closer to exhaustion, it's going to be primarily in the sulfate form, but it's really going to be in the form of in equilibrium with the water.
        - But as a sulfate knocks off the alkalinity, you're going to see pH start rising again. Unfortunately, that's not going to happen until the end of the run, so you're going to have to do something to combat that dealkalization from taking place.

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- What we typically recommend is putting a neutralizer or some type of chemical pH control after the anion resin, to restore the pH.
  - Selectivity of both cation and anion resins are important planning your ion exchange application. Selectivity for standard anions and cations are governed by valence and molecular weight of the ions you want to remove. The higher the valence the higher the selectivity and for equal valence the higher molecular weight ion will have the higher selectivity.
  - In softening with a cation resin in Na form, the resin is more selective for divalent Ca and Mg, therefore the exchange for the monovalent Na on the resin. Since Ca has a higher molecular weight than Mg, the Ca has a greater affinity for the resin than Mg. The cation will have even higher selectivity for trivalent Al.
  - In the case of dealkalization with strong base anion in the chloride form the same principals hold true. The selectivity is greatest for divalent So_4 (sulfate) compared to NO_3 (nitrate), HCO_3 (bicarbonate alkalinity) and Cl (chloride). This is why chloride is exchanged from the anion by the other anions in the water.

There are exceptions of course**. In the case of nitrate select resins, that have a triethyl amine functionality, this amine is more selective for nitrate than it is sulfate. In this case nitrate sloughing will not occur as it will with standard anion resins.**