REMOVAL OF MORE (OR LESS) UNCONVENTIONAL IMPURITIES

By Peter Meyers, Presented at the Ultrapure Water Expo 1998, Pharmaceutical Executive Forum, April 16, 1998

Introduction

In a short presentation, it is somewhat difficult to decide where to place the emphases of the discussion. In this forum, we are to tackle the question of unconventional impurities and means for their removal. This subject is worthy of several days' discussion by itself.

In order to develop a coherent presentation, we will briefly visit a number of areas that are unlikely to affect many water treatment systems and concentrate on several areas we believe are more conventional, but also more topical. Most of this talk will be directed towards the removal conventional impurities such as ammonia, oxidants, and organic leachables, as these are concerns faced by every pharmaceutical water system. However, keeping in the assigned topic of this paper, we will begin with a brief overview of the truly unusual contaminants.

What do we need to Know?

- In order to determine if ion exchange resin is appropriate technology it is necessary to know the basic details of the water to be treated
  - TDS (or conductivity) with min and max if variable
  - pH and Temperature with min and max if variable
  - basic inorganic analysis of ions (Ca, Mg, Na, Cl, SO4)
  - presence or absence of oxidants
  - presence or absence of complexing agents
  - level and type of organic molecules
  - level of suspended solids

Part I - The Truly Unusual

Boron

Boron is present in most surface waters today due to agricultural runoff. Boron is almost always present as borate, a weakly ionized anion. It is not well removed by anion exchange resins due to its poor ionization and low selectivity. For much the same reason, boron is not well rejected by reverse osmosis devices and other membrane processes.

There are three approaches to boron removal.

1. There exist a boron selective resin with methyl glucamine functionality that is capable of removing boron in preference to all other ions. This resin is rather expensive, but can be used as a boron specific trap.
2. Some success has been obtained using manitol to complex with borate, thus forming a larger, better ionized ion that is well rejected by RO membranes and also well removed by ion exchange resins.
3. The third approach is to deionize the water using conventional ion exchange resins, but to regenerate well ahead of exhaustion to other ions, such that, boron is not displaced from the resin.

Chloramine and Perchlorate

These oxidants are relatively stable and do not lend themselves to ready reduction, particularly by granular activated carbon. They are a concern because they can drag through processes and appear in the product water.

Boron Selectivity by Strong Base Anion Resins

- The dissociation constant for boric acid is very very small
- (k1 = 7.3 EXP-10)
- Hydroxide form strong base anion resin selectivity for borate is not much greater than hydroxide and is lower than for other anions commonly encountered
- Separate bed anion units will remove borate better than mixed beds due to higher internal pH (borate is more completely ionized at high pH)
- Highly crosslinked anion resins have higher selectivity for borate than porous anion resins

Boron Removal by Selective Ion Exchange

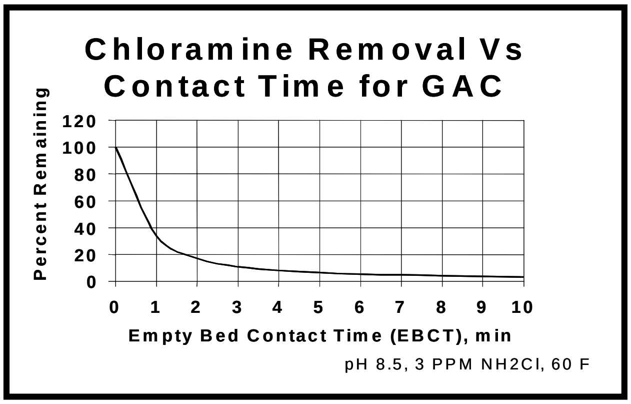
- A true "BORON SELECTIVE" resin does exist
  - It is a weakly basic anion resin
  - with N glucamine functional exchange groups
- It is used in the "free base" form
- It has extremely high selectivity for borate ions under neutral to alkaline operating conditions
- It is regenerated with acid followed by caustic
- It is very expensive

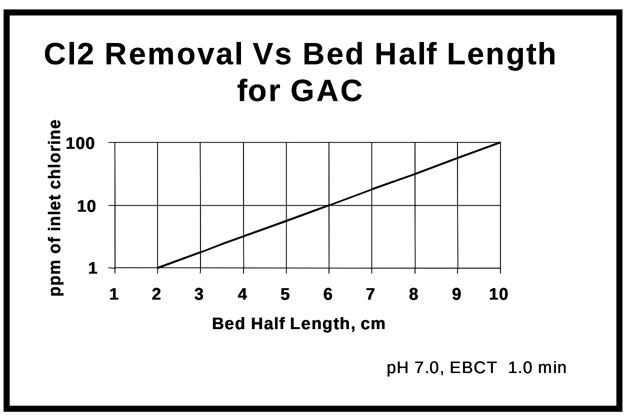
All oxidants can be removed by feeding a sufficient quantity of reducing agent. The most likely being sodium sulfite. They can be also removed by various catalytic means such as KDF, berm or other redox medias.

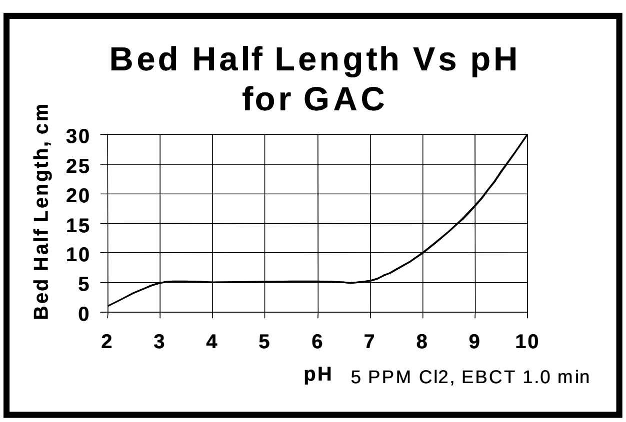
The concern with these mechanisms is that the media itself may create other forms of contamination. For instance, most redox media contains either brass or manganese and can therefore add other unwanted contaminants to the process stream. For this reason, these processes are not commonly used and should obviously be placed upstream of other processes designed to remove the contaminants left over from the reduction of the oxidants.

Catalytic granular carbon can also be used for reduction of oxidants. However, the catalytic properties of carbon are not well understood and the capacity is limited, and the results are somewhat variable.

Nitrate and Nitrite







These ions are relatively common, particularly in surface waters from agricultural areas. They are readily removed in conjunction with deionization processes, but are not as well removed by membrane processes. There are so called nitrate selective resins available. However, these resins are not really more selective for nitrate over chloride than are regular resins. They are nonselective for sulfate, allowing greater loading of nitrate in waters that contain significant fraction of sulfate. All of these resins have selectivity for nitrate, about the same as for chloride. Therefore, the removal of nitrite isn't nearly as complete as that of nitrate.

One technique for removal of nitrite is to oxidize the nitrite to nitrate prior to removal. However, this method involves significant space required due to the retention time needed for the oxidation process to be completed and leaves the opening for excess oxidant to be present in the product water.

Transition and Heavy Metals

It is a little unfair to lump these together, however, there is insufficient space to take each metal separately. Most transition metals are present in small concentrations as cations of various valences and are reasonably well removed by cation exchange resins.

In order of increasing selectivity, there is standard cation resin, weak acid cation resin, and chelating cation resin. These resins are capable of reducing transition metal cations to extremely low levels. However, it is important to note that the resins work within a relatively narrow pH range, that they are also affected by the mix of other ions, and that because they are cation exchange resins, they can only remove cationic forms of the metals. Since transition metals form coordination complexes with various chelants, solvents, and organic substances. It is possible that they are not present in their cationic form. This leads to the more difficult question of determining what form they are in, so that an approach can be developed for their removal.

Radioactive Metals

Radioactive metals such as uranium and radium are present in some well water supplies, particularly in the western states. Radium is always present as a cation. Uranium is present as an anion. They are, in general, well removed by conventional ion exchange resins. However, due to their high selectivity for the resins, they are not easily removed from the resin during regeneration. This leads to long service cycles, but often single use cycling of the resin.

Phosphate

Phosphate is present in many municipal waters, as municipalities attempt to preserve old piping distribution systems. It is generally fed as an orthophosphate complex, but is sometimes fed as phosphoric acid.

Phosphate is not well removed by mixed bed ion exchange resins, because the neutral average pH does not fully ionize the phosphate ion. It is much better removed by single hydroxide form anion beds, such as are present in separate beds. Phosphate loads onto anion resins and is not well removed from the under alkaline conditions. Phosphate can therefore, build up on an anion resin and cause fouling. Phosphate can be removed under acidic conditions.

Aluminum

Aluminum is present in many water supplies due to the use of aluminum sulfate as a coagulant. When coagulation occurs at outside the optimum pH range, traces of dissolved aluminum are added to the product water.

Aluminum is well removed by softening resins and by deionization. However, it is not regenerated from the resin readily due to its trivalent nature. Softening resins that have an appreciable aluminum in the feedwater will gradual become fouled by the aluminum they are removing. Aluminum can be removed by cation resin by acidification.

Part II – More or Less Conventional Impurities

Ammonia

Ammonia is present in almost all waters to some degree. In many cases, it is deliberately added to chlorinated feedwaters to reduce THM precursors. Ammonia is not well removed by membrane processes. It is well removed by deionization processes, but not by softening.

The general approach to ammonia removal would be primary and polishing softeners. Ammonia is removed preferentially to sodium by cation resin, but is displaced by calcium and magnesium. Therefore, a single softener will remove ammonia during the initial part of its cycle, but will then release the ammonia as it becomes exhausted with hardness.

Softening can be used effectively for ammonia removal if the primary softener is allowed to load to a hardness endpoint and a polishing softener is used to remove ammonia. In this case, the primary softener must not be operated to hardness breakthrough, as this would cause an ammonia spike leading to elevated ammonia levels in the final product water.

In deionization systems, ammonia is well removed by hydrogen form cation resin and is generally not a concern.

Organic Acids

All surface waters contain varying amounts of naturally occurring organic acids. The most commonly encountered being tannic and humic. These substances have varying molecular weights and varying amounts of carboxylic functionality. They are to some degree removed by anion exchange resins. However, their low ionization and generally high molecular weight makes them more difficult to remove than average inorganic ions.

There has been much interest in the removal of these substances from drinking water supplies due to their tendency to form THM's when chlorinated. Obviously, membrane processes are quite effective at removal of these substances. However, in cases where a membrane process is not employed, they can be removed effectively by use of anion exchange resins operated in the chloride cycle.

Organic traps are most effective when the anion resin used has a high internal moisture content. The acrylic backbone has proven superior to styrene, as the choice for organic exchange. The key points to keep in mind are the relatively slow diffusion rates. This leads to kinetic sensitivity, both during the service cycle and especially during the regeneration cycle. Organic acids are generally more soluble in high pH solutions; therefore organic traps work better at elevated pH. Because organic traps are removing natural food substance for bacteria and other vial organisms, they are quite susceptible to biogrowths. Acrylic matrix is particularly susceptible to growth of mold and yeast. The most common pitfalls associated with the use of traps are operating them at too high a flow rate and not regenerating them frequently enough. In the first instance, the removal of organic ions is poor, in the second instance, the resin fouls and stops working.

Resin Leachables

With the current cost of validating pharmaceutical water systems and the extremely high cost of failure, it is organic leachables from new ion exchange resins are coming under increasing scrutiny. All new ion exchange resins contain traces of solvents and other organic residue left over from the manufacturing process. These substances gradually mix out of the resin during the first several cycles of use. In cases where new resin replaces old resin, this can present problems with reaching TOC objectives and with validating system for traces of other extractables. The Dow Company did much work on extractables.

The use of ultraviolet light has not been adopted to the degree I thought it was. I suspect this is due to a failure to employ the basic principles required for a successful operation, and the consequent failures of many systems improperly designed.

Closure

The removal of more or less conventional impurities is almost always practical, provided that we take the time to determine what they are, what state they are in, and the degree of removal required. It is also necessary to understand the method by which various removal processes work and to adapt them for the particular system requirements.

There is no substitute for consulting knowledgeable people in the industry and taking their advice. However, there are so many poorly informed consultants it can be bewildering. It is important to choose a consultant that is knowledgeable in the specific process area and contaminant area of interest.