Applications of Weak Acid Cation Resin in Waste Treatment

By Peter Meyers, ResinTech Inc. Presented at the AESF Conference, June 1999

Introduction

Weak acid cation resins have very high selectivity for divalent cations, particularly copper and nickel. This makes them ideal candidates for the removal of various metals from wastewater streams. This type of ion exchange resin has not been widely used by the surface finishing industry. This may be the result of a lack of understanding about how weak acid cation resins work. This paper discusses the chemistry of weak acid cation resins and explores the various potential uses for the removal of metals from wastewater.

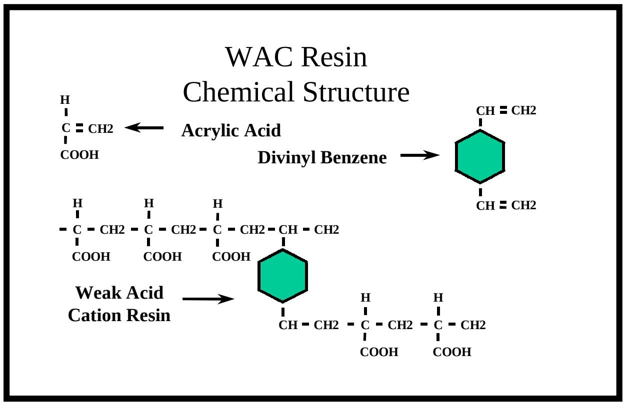
The potential uses of weak acid cation (WAC) resins by the metal finishing industry is often overlooked. This is partly because the term “chelating resin” has become synonymous with metal removal. There is also a wide lack of familiarity with WAC resins and a fundamental lack of understanding of their properties.

Weak acid cation resins offer extremely high capacity; twice that of strong cation resins and 3-4 times that of chelating resins. WAC resins have even higher selectivities for divalent cations than chelating resins, especially at neutral to alkaline pH. WAC resins have relatively low cost and have faster kinetics, compared to chelating resins.

Basic Properties

Weak acid cation resins are all made from acrylic polymers, crosslinked with divinyl benzene (DVB) and functionalized with carboxylic exchange groups.

WAC resins are available as gel type (with microporosity) or macroporous type (with discrete porosity). The largely unsaturated structure of the acrylic matrix permits a very high concentration of carboxylic exchange groups. Weak acid cation resins have the highest capacity of any ion exchange material yet invented. The mobile ion concentration is usually at least 4 normal (equivalent to approximately 16% HCl) and can be in excess of 5 N in some particularly high capacity examples.



The high internal concentration of exchange groups causes WAC resin to swell very significantly when exchanging (very small) hydrogen ions for other cations. During regeneration, the resin can shrink to half its former size, and/or swell to double its size. Since the internal acid concentration of hydrogen form WAC resin is at least equal to 16% HCl, when the resin contacts highly alkaline solutions, a big increase in temperature occurs (as much as 50-100°F temperature rise.

Physical Characteristics of
Weak Acid Cation Resins

- Swell in bases
- Shrink in acids
- Spherical beads
  - 300 to 1200 microns (16-50 mesh)
- Available as:
  - Gel type (translucent)
  - Macroporous type (opaque)

Chemical Characteristics of Weak Acid Cation Resins

- Acrylic DVB polymer with carboxylic functional exchange groups
- 4 N (85 kilograin per cu.ft.) or higher capacity
- Non-ionized when in the hydrogen form
- Very high internal ionic concentration
- Release heat when changing from acid to basic conditions

Weak acid cation resins are available from many manufacturers including (of course) from ResinTech. Some of the most popular are as follows (with apologies to anyone left out).

WAC Resin Suppliers

Manufacturer	Gel	Macro
ResinTech	WACG	WACMP
Dow	MAC-3	None
Rohm & Haas	IRC-86	IRC-76
Bayer	None	CNP-80
Purolite	C-105	C-106
Sybron	CNP	CC

With respect to their resistance to fouling, weak acid cation resins are similar to other ion exchange resins. They are moderately resistant to oxidation, insoluble in solvents, and hydrophilic (water loving). Design limits for flow, pressure loss, temperature, bed depth, etc. are very similar to most other ion exchange polymers.

WAC Resin Operating Limits

Temperature	Approx.. 160 F max*
Bed depth	2 ft min, 6 ft max
Volume flow rate	1-4 GPM per cu.ft.
Linear flow rate	2-15 GPM per sq.ft.
Pressure loss	15-20 PSI max
TDS limit	Approx. 20,000 ppm

*Most manufacturers incorrectly list 212 F (or higher) as the maximum operating temperature for weak acid cation resins.

Fundamentals

Weak acid cation resins have higher selectivity for hydrogen ions than for any other ion. This property is what differentiates weak acid resins from strong acid resins.

The Fundamental Difference Between SAC Resin and WAC Resin

- Weak acid cation resins have **very high selectivity for hydrogen ion** (higher than for any other ion)
- Strong acid cation resins have **very low selectivity for hydrogen ions** (lower than for any other ion)

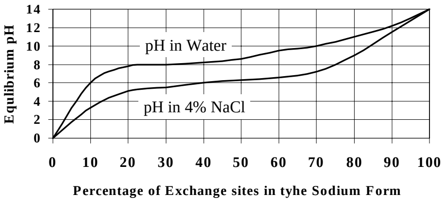
Weak acid cation resins love hydrogen so much that when in the hydrogen form, they are practically non-ionized.* This means they are poor ion exchangers when in the hydrogen form!

*The internal concentration for carboxylic groups is so high, that some groups can share hydrogen ions, thus leading to a small amount of apparent strong acid cation capacity.

No weak acid cation resin can operate for long below a pH of approximately 4.8 (the point below which free mineral acidity can exist).

Weak cation resins are very good buffers (they have from time to time been used as waste neutralizers).

WAC Resin pH Titration Curve



A few weak acid cation systems have actually been operated at slightly more than 100% chemical efficiency (yes, this is possible under ideal conditions). However, most waste treatment systems operate at 50-80% chemical efficiency due to foulants and precipitants that inevitably get into the resin bed.

Operating Limits of WAC Resins

- Even 1 ppm of suspended solids can cause significant fouling over time
- Organic contaminants
  - Cationic polymers and other high mwt cationic organics are particularly bad at any concentration
  - Long chain organics (oils and greases) are bad
  - Low mwt non-ionized organics are generally harmless
- Oxidants degrade all resins over time
- Sudden changes in operating conditions almost always cause increased leakage and low capacity

When in the hydrogen form, WAC resins are limited to neutralizing alkalinity. This means that they only work under neutral to alkaline conditions. As long as there is sufficient alkalinity present, a weak acid cation resin will remove other cations according to its preferences.

When not in the hydrogen form, WAC resins are true ion exchangers and operate at any pH high enough to prevent the formation of free mineral acidity (above a pH of about 4.8).

Exchange for monovalent cations by hydrogen form weak acid cation resin depends on how basic (meaning high pH- the solution is).

Uses of Weak Acid Cation Resins

- In the hydrogen form
  - Neutralize alkalinity by exchanging for any cation (other than hydrogen)
  - Prefer divalent cations to monovalent cations
- When in the sodium form
  - Act as true ion exchangers
  - Greatly prefer divalent to monovalent cations

Bicarbonate alkalinity (with a pH no greater than 8.5) will drive the neutralization with divalent cations, nearly to completion. However, the neutralization of sodium bicarbonate is quite limited, and is approximately equal to the apparent salt splitting capacity of the resin. Sodium carbonate (or sodium hydroxide) are more basic than sodium bicarbonate and drive the neutralization reaction to completion. Thus, it is quite easy to convert hydrogen form WAC resin into the sodium form using soda ash or caustic. Similar neutralization reactions proceed rapidly with other strong bases such as, ammonia, pot ash, etc.

When a hydrogen form WAC resin is converted to the sodium form, it practically doubles in size. This is because it swells to accommodate the larger ions. Since the resin's moisture content remains about the same as in the hydrogen form, the resin must adsorb water from the solution. As previously mentioned, acid/ base neutralization reactions are exothermic and result in the resin becoming quite warm.

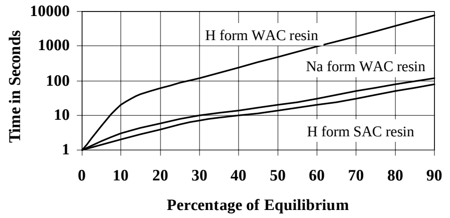
Gel Type Weak Acid Cation Resin Comparison of H Vs Na Properties

Property	Na form	H form
Capacity (meq/ml)	2.0	4.0
Moisture Content (%)	45-55	50-60
Shipping Weight (lbs/cu.ft.)	48	50

The chemical properties of sodium form WAC resin are quite different than that of hydrogen form WAC resin. Kinetics are much faster. There is true exchange of divalent cations for sodium. WAC resin capacity when in the sodium form is about half that of the hydrogen form. This is because the same quantity of exchange sites now occupy twice as much space.

Sodium form WAC resin becomes a good ion exchanger. Its selectivity advantage for divalent cations over sodium is remarkably large. This leads to very low leakage and a large fraction of the resins total capacity being utilized.

WAC Vs SAC Resin
Rate of Exchange



Weak Acid Cation Resin
Following Hydroxide Precipitation

- Usually requires pH adjustment
- Removes most (or all) divalent cations
- Low leakage
- High operating capacity

Sodium Form WAC Selectivities
(at alkaline pH)

NH4	2
Ca	80
Cu	160
Ni	130
Pb	>1000
H	very high

Take these with a dash of skepticisim. Selectivity is very difficult to measure due to the effect of pH.

Hydrogen Form WAC Resin
Following Hydroxide Precipitation

- Advantages
  - Single step regeneration
  - No need to adjust inlet pH in many cases
  - Very high capacity (higher than any other resin)
- Disadvantages
  - Leakage and capacity depend on an excess of alkalinity over divalent cations
  - Resin swells 25-100% during the exhaustion cycle
  - Leakage is usually higher than for Na form operation

Sodium Form WAC Resin
Following Hydroxide Precipitation

- Advantages
  - No swelling during the exhaustion cycle
  - Very low leakage, regardless of alkalinity
  - Consistent effluent pH
- Disadvantages
  - Lower volume capacity than with H form operation
  - Requires two stage regeneration with acid followed by caustic

Applications of WAC Resins in Metal Removal

There are many potential uses of weak acid cation resins in various places around a plating shop. The most obvious is after an existing hydroxide precipitation system. Here, a WAC resin can be used for removal of the final traces of metallic contaminants prior to discharging the waste into a city sewer.

Following Hydroxide Precipitation

Since many metals form hydroxide complexes when the pH is very high, it is usually advisable to reduce pH slightly (to around 6-8) prior to the resin. This pH reduction also helps to prevent post precipitation from fouling the resin.

Although the WAC resin can be used in the hydrogen or in the sodium form, the sodium form is generally preferred because it produces somewhat lower leakage. When in the sodium form, the resin does not depend on maintaining excess alkalinity to drive the neutralization reaction. Hydrogen form resin swells as it exhausts, potentially causing a problem maintaining the desired flow rate.

Hydrogen form resin operating capacities often exceed 2 eq/l with leakage of metals well under 1%. Sodium form capacities are about half (remember that the resin doubles in size) and leakage is usually less than 0.1%.

WAC Resins Following Acid Rinses

This is another very good application for WAC resin. The resin solution pH must be adjusted upward to at least 5.0, but not so high that the metal hydroxide begins to precipitate. This can be accomplished by putting a weak base anion (WBA) exchanger in front of the WAC unit (WBA exchangers only adsorb free mineral acids) or by adding caustic. The weak acid resin is always used in the sodium form because there is not enough (if any) alkalinity present to neutralize a hydrogen form WAC resin.

Removal of Carbonates from Cyanide Baths

This is an interesting potential use for hydrogen form WAC resin. The resin neutralizes carbonates, which then escape as carbon dioxide gas. Weak cation resin does not permit the formation of free hydrogen cyanide and therefore, does not create a problem with potentially lethal vapors.

Unfortunately, the volume of carbon dioxide gas that this process generates is quite remarkable. Each cubic foot of WAC resin has the potential to release approximately 90 cubic feet of gas. The gas formation necessitates specially designed tanks and venting or the WAC resin can be violently expelled from the tank.

Effect of Hardness on WAC Resins

Since weak acid cation resins exchange for all divalent cations, any hardness present must be included in the ionic load on the resin. A moderate hardness concentration (20-50 ppm) is tolerable, but higher levels should be removed before the water is used and becomes contaminated by metals. Water softening is an inexpensive, simple and reliable ion exchange method of doing this using ordinary strong acid cation resin.

Regeneration of WAC Resins

Regeneration of weak acid cation resin is the process where metal cations loaded onto the resin during the service cycle, are removed from the resin. Regeneration permits the WAC resin to be used for many service cycles before it must be replaced.

Regeneration requirements vary depending on the type of removal and on the volume and shape of the tank used. As a minimum, the regeneration schedule consists of the following.

WAC Regeneration Steps

- 1. Backwash
  - Possible air scrub to aid in removal of suspended solids
- 2. Acid injection
  - Possible air mix at end of acid to help dissolve scale
  - Possible acid soak step to improve metal removal
- 3. Slow rinse
  - Helps extend acid contact time
- 4. Fast rinse

In addition to the above, some other (optional) steps may be required.

Added Steps for Sodium Form WAC Regeneration

- A. Caustic injection
  - Must be upflow to accommodate resin swelling
  - Sometimes air mix to aid conversion
  - May have a soak step to aid conversion
- B. Slow rinse
  - May be omitted if soak time is adequate
- C. Fast rinse

Backwash

The weak cation resin bed must be expanded to relieve compaction caused when the resin shrinks (or swells) during the service cycle. Since WAC resins are often used for wastewaters that are none too clean, it is also necessary to expand the resin bed sufficiently to remove suspended solids.

Backwash is accomplished by bringing water into the bottom of the tank, up through the resin bed and out the top. 25-50% expansion is normally recommended. The time of this step should be at least 10 minutes and should be as long as necessary to clean the bed.

In cases of severe suspended solids loading, it may be necessary to air mix after an initial backwash.

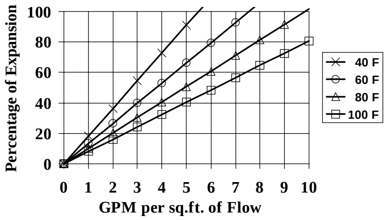
Backwash

- Relieves compaction of the resin that may have occurred during the service cycle. This allows the chemicals used in the next step(s) to flow smoothly through the resin
- Removes suspended solids that have accumulated in the resin bed
- Air mix may be helpful to remove suspended solids
- 25-50% bed expansion recommended
- Minimum 10 minutes duration (or longer)

This will dislodge suspended solids sticking to the resin beads. The backwash step is then repeated.

The importance of backwash is often overlooked. If physical contaminants are not removed from the resin bed, it will eventually plug up and cause problems with water quality and/or throughput.

Weak Acid Cation Resin
Backwash Expansion
(Hydrogen or Sodium Form)



Acid Injection

The acid injection step removes the metals from the resin and returns it to the hydrogen form. During this step, the resin shrinks to about 50-75% of its previous size. Weak acid cation resins adsorb acid slowly. A minimum of 30 minutes of contact time is required, 60 minutes is better. It takes about 4 hours for a weak cation resin to fully adsorb acid. For systems that depend on (close to) perfect regeneration, a soak step at the end of the acid injection can help squeeze the maximum operating capacity and minimum leakage out of the resin.

Any strong mineral acid may be used, but 1-2 N hydrochloric acid is by far the best choice. When sulfuric acid is used, the concentration must be quite low (usually less than 0.2 N) in order to prevent precipitants from forming in the resin. Nitric acid can be used, but is a strong oxidant. This leads to premature deterioration of the resin and can also be an explosive hazard if high concentrations (above 4 N) of HNO_3 are left soaking in the resin bed.

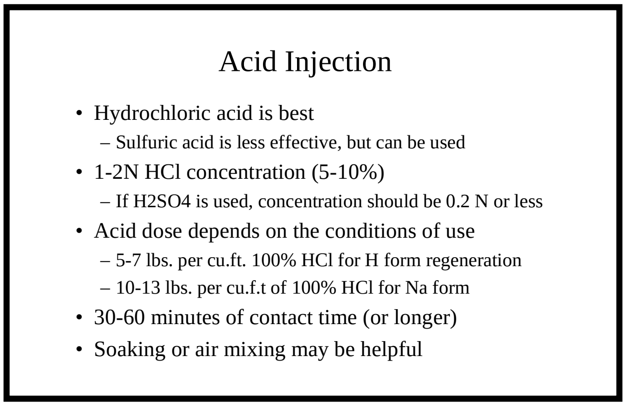
Weak acids, such as citric acid and acetic acid may be used, but since they are more expensive and less effective than strong acids, this is not often done.

The dose rate of acid depends on the conditions of use. For hydrogen form operation, doses of HCl can be as little as 5-7 pounds/cubic foot, (7-10 pounds/ cubic foot for H_2SO_4). For sodium form use, the resin must be completely converted to the hydrogen form in order to completely remove all metallic contaminants. Here the HCl dose should be 10-12 pounds/cubic foot (13-17 pounds/cubic foot for H_2SO_4).

To avoid confusion, when doses are reported for ion exchange resins, they are always as 100% equivalents. For example, 1 gallon of 30% hydrochloric acid contains approximately 2.9 pounds of pure HCl and 1 gallon of 93% sulfuric acid (66° Be) contains approximately 14.7 pounds of H_2S0_4.

If the weak acid resin has been used following hydroxide precipitation, it is very possible that some precipitated metals have become trapped in the resin bed. Here it may be advantageous to have a soak step at the end of the acid injection, to give the precipitants time to dissolve.

Simply mixing the acid with the resin is not recommended because it is far less efficient than a plug flow of acid and does not do a good job removing all the metals from the resin. However, mixing at the end of the acid step may help break down clumps of precipitated metals and dissolve them.



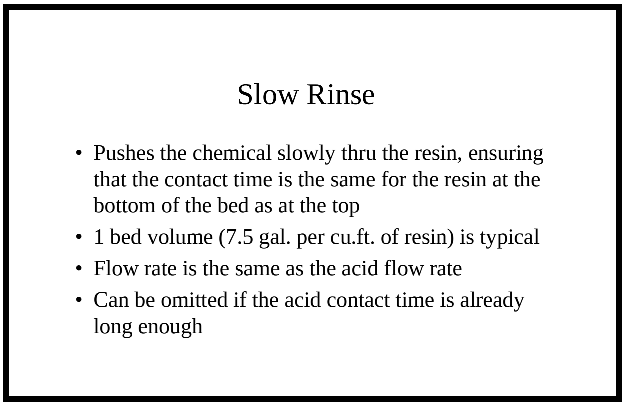
Acid Injection

- Hydrochloric acid is best
  - Sulfuric acid is less effective, but can be used
- 1-2N HCl concentration (5-10%)
  - If H2SO4 is used, concentration should be 0.2 N or less
- Acid dose depends on the conditions of use
  - 5-7 lbs. per cu.ft. 100% HCl for H form regeneration
  - 10-13 lbs. per cu.f.t of 100% HCl for Na form
- 30-60 minutes of contact time (or longer)
- Soaking or air mixing may be helpful

Slow Rinse

The purpose of a slow rinse is to gradually push the chemical through the resin bed, extending the contact time. A flow rate similar to the acid flow is normally used. The time should be sufficient to pass a volume of water through equal to the volume of resin (7.5 gallons/cubic foot).

If the acid injection step is sufficiently long or if an acid soak step is used, the slow rinse step may be omitted. For best results, water used for acid dilution and for the slow rinse, should be free of metal contaminants.



Slow Rinse

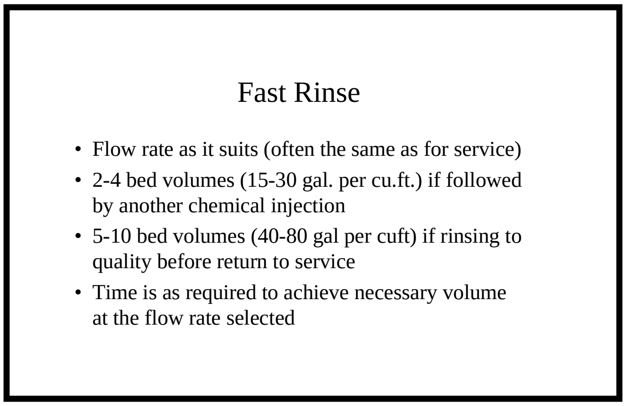
- Pushes the chemical slowly thru the resin, ensuring that the contact time is the same for the resin at the bottom of the bed as at the top
- 1 bed volume (7.5 gal. per cu.ft. of resin) is typical
- Flow rate is the same as the acid flow rate
- Can be omitted if the acid contact time is already long enough

Fast Rinse

The fast rinse removes the last traces of chemicals (in this case, acid) from the resin. The flow rate is often the same as the service flow, but can be any convenient rate that the tank is designed to accommodate. Rinse water can be treated water, but in most cases can also be untreated wastewater.

The volume of rinse water required depends on what the next steps may be. If following this rinse another chemical injection will be performed, then the rinse volume can be minimal, 2-4 bed volumes (a bed volume is 7.5 gallons per cubic foot).

When rinsing to quality prior to a return to service, the rinse requirement can be 5-10 bed volumes (7 is typical), depending on how dirty the resin is and what the end of rinse quality requirement may be. Time is calculated from the chosen flow rate to achieve the necessary volume.



Fast Rinse

- Flow rate as it suits (often the same as for service)
- 2-4 bed volumes (15-30 gal. per cu.ft.) if followed by another chemical injection
- 5-10 bed volumes (40-80 gal per cuft) if rinsing to quality before return to service
- Time is as required to achieve necessary volume at the flow rate selected

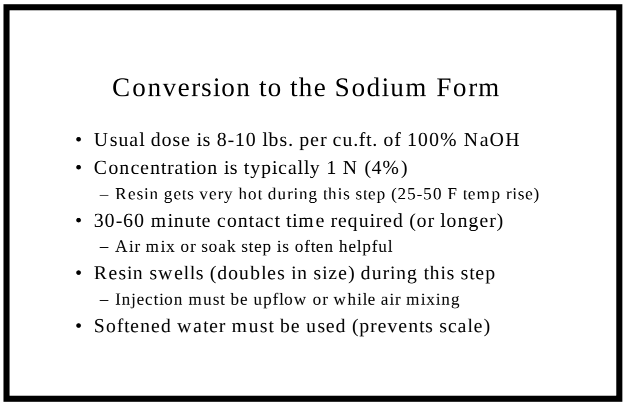
Caustic Conditioning
(Conversion to the Sodium Form)

This conversion is performed to put the resin back into the sodium form in preparation for the next service cycle. It must be done either upflow or by mixing the caustic into the resin. The resin bed must be fluidized during this step because otherwise, the tremendous swelling will break the resin and internals and possibly the tank.

Again, the conversion is slow, requiring about 30-60 minutes for 90% conversion and around 4 hours for 99% conversion. The dose of caustic should be kept around 90-100% of the theoretical resin capacity (typically 8-10 pounds/cubic foot) in order to avoid excessive rinse volume needed to remove excess NaOH. Concentration is unimportant, except that since much heat is liberated during this step, the resin will get very hot if concentrations greater than 1 N (4%) are used. If the caustic will be mixed into the resin bed, there must be enough excess water to allow for the swelling (sodium form resin adsorbs about 2-3 gallons of water per cubic foot).

All water used for caustic injection and displacement should be softened to prevent hardness precipitants from forming in the resin bed.

Following conversion to the sodium form, the excess sodium hydroxide is rinsed out prior to returning to service.



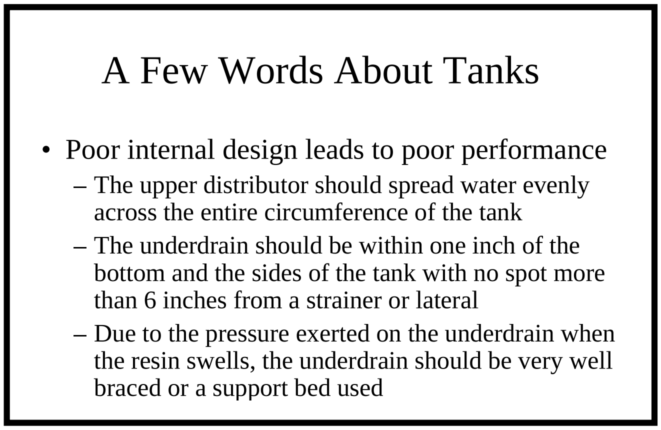
Conversion to the Sodium Form

- Usual dose is 8-10 lbs. per cu.ft. of 100% NaOH
- Concentration is typically 1 N (4%)
  - Resin gets very hot during this step (25-50 F temp rise)
- 30-60 minute contact time required (or longer)
  - Air mix or soak step is often helpful
- Resin swells (doubles in size) during this step
  - Injection must be upflow or while air mixing
- Softened water must be used (prevents scale)

A Few Words about Tank Design

Tall and thin tanks (height/diameter ratio >1) are always better than short fat tanks. Minimum bed depth is 24 inches, based on the most shrunken volume used.

The internals had better be capable of withstanding the pressures exerted as the resin shrinks and swells, or they will break. It is probably worth using a support bed (quartz or garnet) to cover the underdrain laterals (or strainers) and protect them.

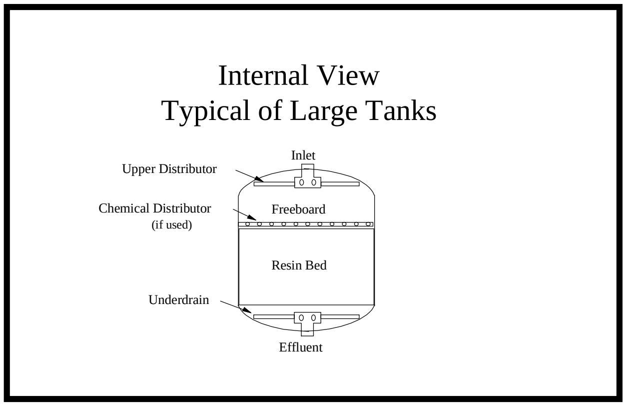


A Few Words About Tanks

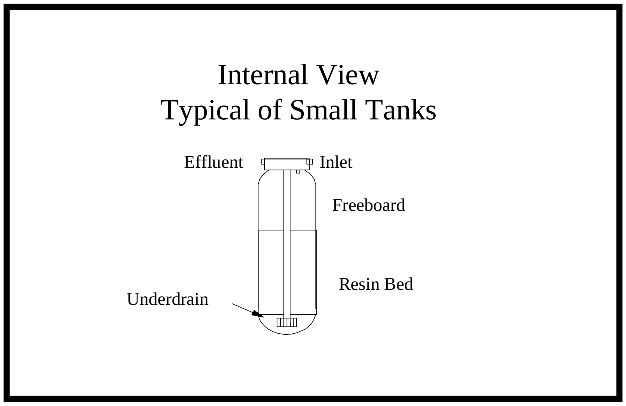
- Poor internal design leads to poor performance
  - The upper distributor should spread water evenly across the entire circumference of the tank
  - The underdrain should be within one inch of the bottom and the sides of the tank with no spot more than 6 inches from a strainer or lateral
  - Due to the pressure exerted on the underdrain when the resin swells, the underdrain should be very well braced or a support bed used

Some tanks (particularly fiberglass) come standard with very poor distribution and collection systems. Make sure the tank has an upper distributor that does not leave any space greater than 9 inches uncovered. The underdrain should cover the entire tank area equally with no more than 2-3 inches difference in elevation between the highest and lowest lateral (or strainer), no more than 6 inches distance between collection points and extending to within about 1 inch of the tank bottom and tank wall. Failure to do this will result in short throughput, high leakage and rapid fouling of the resin.

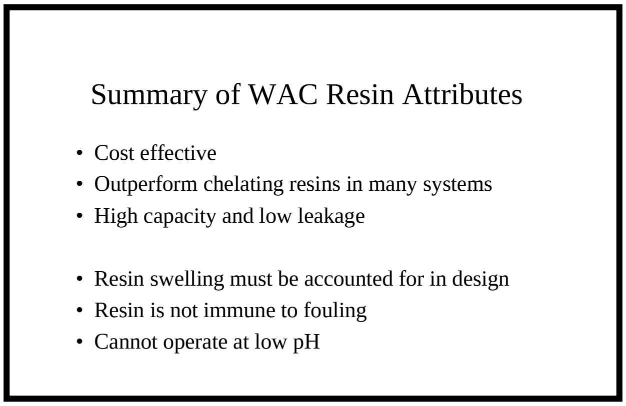
The larger the tank, the more important it is and the more likely it is to have problems if the internal systems are not done properly.



Internal View
Typical of Large Tanks



Internal View
Typical of Small Tanks



Summary of WAC Resin Attributes

- Cost effective
- Outperform chelating resins in many systems
- High capacity and low leakage

- Resin swelling must be accounted for in design
- Resin is not immune to fouling
- Cannot operate at low pH

Closure

Weak acid cation resins are a remarkably effective means of maintaining extremely low concentrations of metallic contaminants in waste effluents from plating shops. They are much less expensive than chelating resins and in many cases will work better. As with all ion exchange systems used in waste treatment, some basic precautions are required to prevent unsuccessful operation.

BIBLIOGRAPHY

1. Kunin, Robert, *Ion Exchange Resins*, Robert E. Krieger Publishing Company, Huntington, NY, 1972

2. Technical Bulletin No. 174, "*amber-hi-lites*," "Acrylic-based Ion Exchange Resins and Adsorbents – Part 2," Kunin, Dr. Robert, Consultant, Rohm and Haas Company, Philadelphia, PA 19105 (Spring, 1984)

3. Technical Bulletin No. 162, "*amber-hi-lites*," "Ion Exchange in Heavy Metals Removal and Recovery," Waitz, William H. Jr., Rohm and Haas Company, Philadelphia, PA 19105 (Fall, 1979)

4. Technical Service Report No. TS-7511, "Engineering Literature on Duolite C-433 and C-464," Diamond Shamrock Chemical Company, Nopco Chemical Division, Redwood City, CA 94063 (1975)

5. Herrera, Thomas, Matejka, Zdenek, and Eliasek, Jaroslav, "*Cation Exchange Kinetics on Carboxylic Acid Resins in a Multicomponent System,*"Elsevier Science Publishers B.V., Amsterdam, Netherlands (1983)

Peter Meyers
ResinTech Inc.
615 Deer Road
Cherry Hill, NJ 08034
Phone: 856/354-1152
Fax: 856/354-6165
pmeyers@resintech.com