

Molybdate Removal by Ion Exchange Resins

Andrew Bishop
ResinTech Inc,
Berlin, New Jersey

ABSTRACT

Use of molybdate in cooling tower treatment can be problematic due to skyrocketing costs and limits on discharge to sanitary sewers. Closed loop cooling systems that once depended on molybdate chemistry are switching to other types of chemical treatment. Prior to making a switch it may be necessary to remove molybdate from the system. Ion exchange is in many cases the best available technology for molybdate removal.

This paper discusses how ion exchange resins can be used for molybdate removal, choices of counter ions and their effect on pH and other ions present in the loop, and potential options for various ion exchange resins, and system configurations.

INTRODUCTION

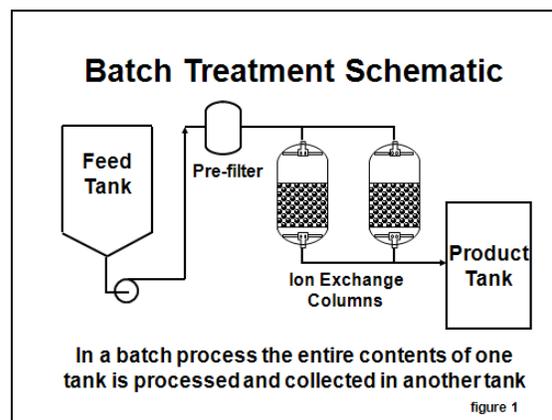
Molybdate is used in water treatment as a corrosion inhibitor. Molybdenum is directly underneath chromium on the periodic table which means the two elements have similar properties and react in similar fashion. When chromate was banned due to its very high toxicity, molybdate was initially thought to be a promising substitute¹. However, soluble molybdate is a good corrosion inhibitor only at fairly high concentrations², still has moderate toxicity³, and is generally too expensive to use in open (evaporative) cooling water systems. Despite drawbacks in open cooling systems, molybdate chemistry has been widely used in smaller closed loop high temperature cooling systems.

Although discharge of molybdate is not federally regulated, its presence in sludges used in Land Applications is limited to 75 mg/Kg (40 CFR 503 – subpart B). This limit has caused some states to prohibit discharge of molybdate containing water from cooling towers. Other States have established voluntary limits. In places where it is no longer permissible to discharge molybdates, it is necessary to remove molybdate from the cooling water, prior to discharge or possible re use.

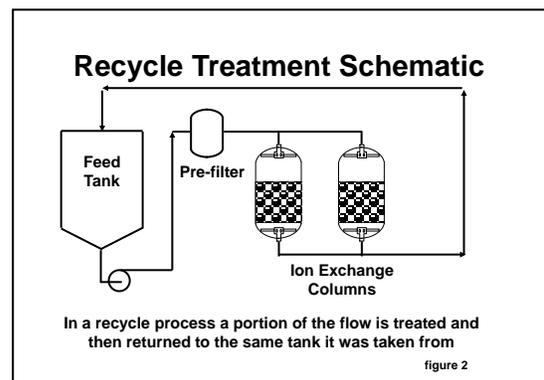
Like chromium, molybdenum forms a divalent “oxy” anion. Because it is a somewhat larger ion than chromate, molybdate is somewhat more preferred by strong base anion resins, although both are preferred over most other anions⁵.

The high preference for molybdate makes ion exchange (IX) resin one of the best available technologies for molybdate removal.

IX works best in a batch process, where an entire batch of water with homogeneous ionic composition is passed through a resin bed and collected in a product tank (figure 1).



The closed loop nature of many molybdate based cooling water systems precludes batch processing. Sidestream treatment (figure 2) recycles the ion exchange product back into the bulk solution and causes the molybdate concentration at the IX inlet to drop over time. This results in somewhat lower capacity than would be obtained by batch processing and significantly higher leakage.



Recycling also introduces the possibility of going too far and causing some of the molybdate that was previously removed,

to be added back into the loop as the resin approaches equilibrium with the bulk fluid.

Another complicating factor is that of the counter ion. Ion exchange resins are tiny plastic beads that take salt out of water and put other salts back in. For every ion removed an equivalent amount of some other ion is added back into the water. Strong base anion resins are generally supplied in the chloride form and will release chloride ions equal to the same equivalent number of molybdate ions removed. Chloride is generally undesirable due to its corrosive properties; therefore some other counter ion may be better suited. Choices of counter ions for molybdate removal include borate, nitrite/nitrate, and bicarbonate/carbonate.

Ion exchange theory

As mentioned in the introduction, ion exchange resins are tiny plastic beads that take salt out of water and put other salts back in. Most modern ion exchange resins are made from cross-linked polystyrene. The copolymer is then functionalized with a variety of acids and bases that are chemically bonded to the copolymer. Although strong base anion resins can be functionalized with a variety of quarternary amines, trimethylamine is the most common functional group in use today. The solid base (the amine) is attached to the resin backbone and is immobilized within the polymer structure. The charge is balanced by a mobile (replaceable) counter ion which is the chloride ion (Cl^-) when the resin is made.

Ion exchange resins have some preference for all ions but generally like

bigger and more highly charged ions better than smaller ions and those that are not fully ionized. We call the mathematical relationship that describes the preference of a resin for various ions the selectivity coefficient. This constant should not be confused with the distribution coefficient which is called apparent selectivity. Apparent selectivity describes a resin's preference for various ions under a given set of conditions and can sometimes be very different than the selectivity coefficient.

A high preference means an ion will load well in the exhaustion cycle but may also mean the ion is difficult to remove during the regeneration cycle. In multi-cycle use, the operating capacity is a function of how well the ions previously loaded are removed during the regeneration process. High selectivity for an ion is not necessarily desirable, nor is low selectivity necessarily undesirable.

Ions in solution must come close enough to a resin bead to penetrate. Ion exchange occurs at the surface of the bead, one ion going inside the resin and a different ion coming back out of the resin. The rate at which ions diffuse through the boundary is the limiting factor for low Total Dissolved Solids (TDS) exchanges (below about 50 ppm TDS).

Ion exchange groups are evenly dispersed throughout the resin beads. This means that most of the resin's capacity is not at the surface but farther inside the beads. For an average sized 0.6 mm diameter resin bead, approximately 25% of the capacity is within 10% of the surface. Once an ion penetrates the resin bead it must vacate

the surface sites and move farther inside the bead before additional ions can exchange at the surface. The rate at which ions diffuse through the resin particles is the limiting factor for higher solution TDS above approximately 250 ppm⁶.

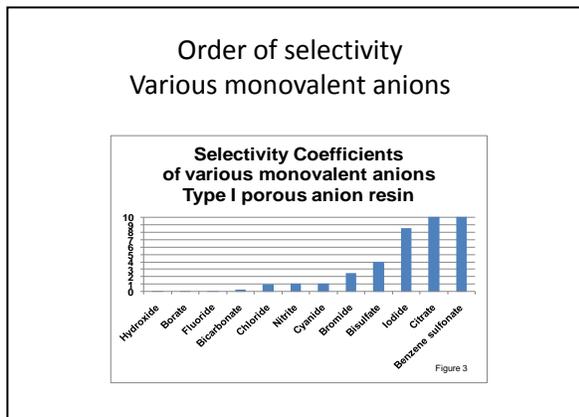
If the resin isn't able to capture all the ions before the water passes by, the ions are not completely removed. This is kinetic leakage. Ions that were not completely removed by the regeneration process and are still in the resin can be displaced by other ions and go back into the water. This is equilibrium leakage.

Some fraction of the ions in the feed always finds their way into the product water. No ion exchange process results in 100% removal.

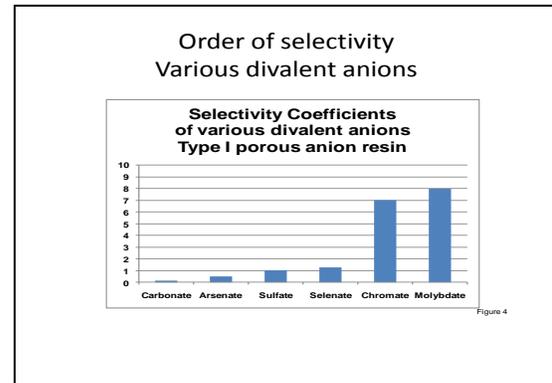
The higher the total ion concentration in the feed, the higher the leakage.

The order of resin selectivity for various ions is shown in figures 3 and 4

Monovalent anions (from lowest to highest):



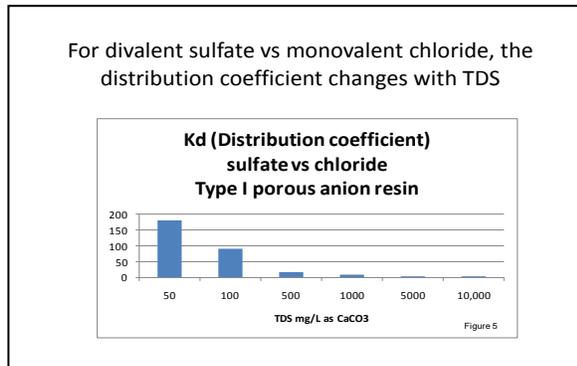
Divalent anions (from lowest to highest)



The divalent to monovalent relationship is concentration dependent

The equilibrium expression used to define selectivity coefficients is dependent on the charge of the ions. When all the ions are either monovalent or divalent, the distribution coefficient and the selectivity coefficient are essentially the same and are fixed by the nature of the resin itself. But when there are mixtures of monovalent and divalent ions present, the distribution coefficient for divalent/monovalent pairs is concentration dependent. Low TDS favors the divalent ions, while higher TDS favors the monovalent ions. In some cases the apparent selectivity (also known as the distribution coefficient) can actually be reversed by using a low TDS for the exhaustion part of the cycle and a high TDS for the regeneration part. This is one of the main reasons why regenerations are typically carried out with relatively concentrated solutions compared to the TDS of the water being treated. An example of how the distribution coefficient changes with concentration is shown in figure 5

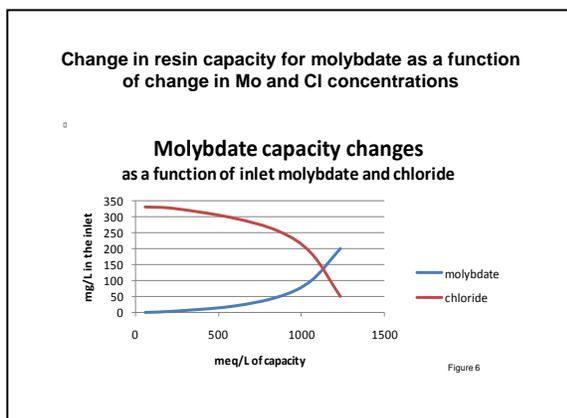
Distribution coefficient for sulfate vs. chloride



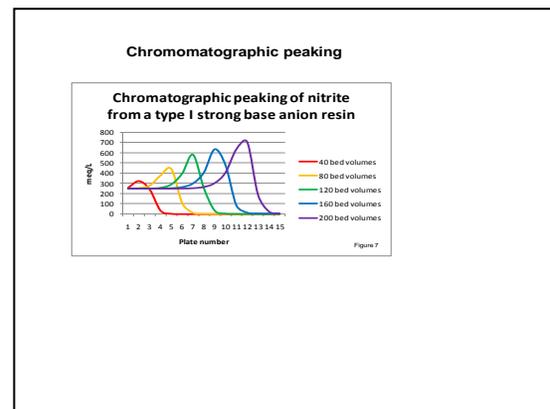
Chromatographic effects

Chromatography is a technique used to separate ions and molecules in a mobile phase according to how fast they move relative to a stationary phase. Ion exchange resins exhibit chromatographic behavior. This means the place where an ion concentrates within a resin bed is neither stationary nor constant. It changes as the resin exchanges for various ions and also when the inlet composition changes.

The following example (figure 6) demonstrates how the composition of a resin bed changes as an ion of interest is first exchanged and then chromatographically displaced downward through the resin bed



In a typical cooling loop, the solution has a high level of molybdate, along with other ions perhaps added as buffers, antioxidants, biocides, and stabilizers. When treatment begins, the resin exchanges most of its ions for molybdate. Essentially molybdate free water is returned to the loop. As treatment continues, the concentration of molybdate in the loop begins to drop. Due to the reduced concentration of molybdate along with the increased concentration of the counter ion, the resins capacity for molybdate decreases (figure 7).



Molybdate that initially exchanged at the top of the resin bed is displaced downward. This chromatographic effect can cause the molybdate level to go back up if the resin is used past the optimum end point and the band of highest molybdate concentration in the resin reaches the bottom of the resin bed.

pH effects

Molybdate is more preferred than almost every other anion; however the resin does have some preference for all anions. Removal of less preferred ions occurs at the beginning of each exhaustion cycle. Later on, the ions that

are not preferred are displaced from the resin in favor of more preferred ions. This phenomenon is known as Chromatographic peaking (dumping). Removing and then dumping a non preferred ion such as bicarbonate or carbonate can result in lowering the pH for a portion of the run each time a fresh resin bed is placed into use followed by a rise in pH as the resin approaches exhaustion. Use of an appropriate counter ion similar to the buffer already in the cooling water can help minimize pH changes caused by the resin.

Choice of counter ion

A useful counter ion is one that is compatible with the other cooling system chemicals. It should not be corrosive. It should cause minimal changes to the concentrations of other ions used and should not cause a large change in pH. It should also be an ion of relatively low preference so that it doesn't reduce the resins' capacity for molybdate.

Buffers such as bicarbonate, borate, and nitrite can be used depending on the chemistry involved and pH requirements for the loop.

Number of change outs needed to reduce molybdate to an acceptable concentration

The simplest approach is to install a bed of strong base anion resin and allow it to recirculate until the resin reaches equilibrium with the water in the loop. This strategy has the advantage of simplicity. It is not necessary to monitor, only to allow enough time for equilibration. The downside to this

approach is that it is not the most efficient way to operate. The most efficient use of resin occurs when the resin is removed and replaced when it reaches maximum loading. When the entire volume of resin is used at the same time the maximum loading often occurs before equilibration and therefore results in less than optimum resin use. Optimizing use (minimizing volume and leakage) requires replacing resin before the leakage increases.

	initial mg/L as the ion	One Big treatment	three smaller treatments
Cl	50	395	405
NO ₂	300	176	151
HCO ₃	60	52	51
BO ₃	100	95	94
SO ₄	30	2	1
MoO ₄	200	2	0.1
CO ₃	90	27	38

Sizing a system

The volume of resin required is a function of several variables, the most important being

1. Loop volume
 - a. The larger the volume, the more resin is required
 - b. Resin use is typically around 1 cu.ft per 2000 gallons of loop volume or less
 - c. Typical volumetric flow used to size a system is 2 to 4 gpm per cu. ft. of resin.
2. Molybdate concentration
 - a. Typical molybdate concentrations do not

exceed several hundred mg/L (also referred to as “parts per million” or “ppm”).

3. Concentration of other ions present at greater than trace levels
4. Target molybdate concentration in the treated water
 - a. Typically less than 5 ppm
5. Preference of counter ion
 - a. Chloride simplest but least preferred for good corrosion control
 - b. Bicarbonate the most likely alternative
 - c. Nitrite and borate also reasonable
6. Time allowable to complete the project
 - a. Systems on side-streams can take a month or longer to reach treatment goals

Regeneration strategies

For the most part, regeneration is beyond what can be done on site. Most treatment systems will use portable exchange tanks and off site regeneration. It is important to select a regeneration facility with a good reputation, preferably someone fairly close and also a company experienced in performing regenerations with chemicals other than salt.

Sodium chloride can be used to effectively remove molybdate from strong base anion resin. Because molybdate is a divalent ion, salt concentration is quite important to help

reduce the resins preference for divalent molybdate. A minimum of 15 lbs per cu. ft. applied at 10% or higher concentration over at least 30 minutes is necessary for good results.

Sodium nitrite is perhaps the best technical choice as it is inexpensive, readily available, readily soluble and can be used in place of sodium chloride with almost no changes in regeneration strategy. Many loops that contain molybdate also contain nitrite so its use is generally compatible with closed loop chemistry. Nitrite will however cause the same pH dip that systems exchanging for chloride can cause. The same general rules for regeneration apply, 15 lbs per cu. ft., >10% concentration, and >30 minutes contact time.

Both sodium borate and sodium bicarbonate can also be used. The advantage is that that both borate and bicarbonate are natural buffers and tend to maintain the loop at slightly alkaline pH. However these chemicals are more difficult to dissolve and the lower concentration obtainable results in a need for higher chemical doses.

Case study 1:

A closed loop cooling system in a large office uses 5,000 gallons of cold water containing 200 parts per million of molybdate which serves as a corrosion inhibitor. There is no storage reservoir. Access to the system is via a bypass line that can treat only about 10% of the full flow rate while the other 90% passes by. The bypass flow rate is 4 gpm.

The operator wants to keep the non molybdate ions intact and to remove the

molybdate to “as close to zero as practical”. The water analysis is:

Bicarbonate	50 ppm (as CaCO ₃)
Carbonate	150 ppm (asCaCO ₃)
pH	9.0 to 10.0
Chlorides	50 ppm (as Cl)
Sulfates	30 ppm (as SO ₄)
Molybdate	200 ppm (as MoO ₄)
Nitrite	300 ppm (as NO ₂)
Sodium Tolytriazole	10 ppm (as the active)
Sodium Tetra Borate	100 ppm (as borate)

The Total Dissolved Solids (TDS) in the loop is approximately 1000 ppm.

The end user wants to explore options as to how best to remove the molybdate and replace it with a borate based inhibitor.

The simplest approach is to deionize the water, removing the molybdate along with everything else. Mixed bed resins remove all the salt from water and are often a viable although expensive method of treatment. The downside of complete demineralization is that the pH of the DI water would be slightly acidic, well below the pH most closed loops wish to maintain. Following treatment, all other chemicals needed would have to be added back in and the system re-stabilized.

1000 ppm of neutral salt is equivalent to approx 35 grains per gallon. Mixed bed capacity varies depending on grade but is typically on the order of 12 kilograins per cu. ft. for new resin and 8 to 10 kilograins per cu. ft. for portable exchange deionization (PEDI) resin.

Using PEDI exchange resin the calculation is as follows:

9,000 grains per cu. ft. / 35 grains per gallon = approx 250 gallons per cu. ft. throughput

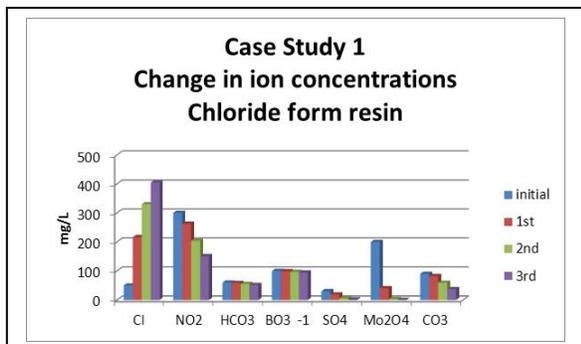
5000 gallons in the loop / 250 gallons per cu. ft. = approx 20 cu. ft. of mixed bed resin needed.

Assuming the sidestream flow rate is 4 gpm it will take 5000 gallons / 4 gpm = 1250 minutes, or roughly one day to reduce the loop concentration by 50%. Complete deionization (99.9% removal of TDS) would therefore require something like 10 days to complete (0.5 to the 10 power equals 0.1 percent) .

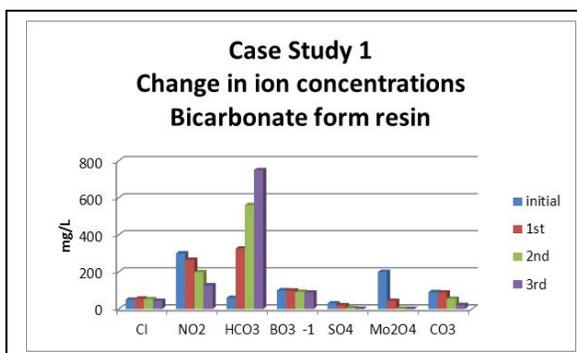
At first glance, a portable exchange mixed bed with about 20 cubic feet of resin could do the job. However, 4 gpm is a bit too low a flow rate for a single 20 cu. ft. mixed bed and it might be better to have several smaller units, perhaps 2 to 3 cu. ft. each, even if this means changing out tanks every day.

Removing all the ions with mixed bed exchange resin is a good option when the TDS of the water in the loop is relatively low but up around 1000 ppm TDS the quantity of mixed bed resin needed becomes problematically expensive. For high TDS a better approach may be a chloride cycle anion exchanger. Molybdate loads preferentially to the other ions allowing good capacity for molybdate and low molybdate leakage. The primary issue with use of a chloride form resin is that chloride exchanges for molybdate and an equal amount of chloride is added on an equivalent basis, perhaps causing chloride to reach an unacceptably high level. In this particular loop example the effluent chlorides will be approximately 450 ppm. A chloride form anion resin will also remove some of the alkalinity,

particularly at the start of the exhaustion cycle, causing the pH to drop. However, in this particular example there is sufficient carbonate present to maintain the pH well above 9



Other choices of counter ion include nitrite, bicarbonate, and borate. In this case, bicarbonate is probably preferred because it causes the least change to the buffered pH of the loop, although nitrite might also be an acceptable counter ion. The point is that there will be roughly 500 ppm of the counter ion in the treated water.



The total quantity of salt form resin is about the same, regardless of the counter ion selected. However, the required molybdate effluent concentration will dictate how best to operate.

If a single large tank of resin is used and allowed to stay on-line until the system reaches equilibrium, the resin beads all have the same average composition,

just the same as if the water and resin were stirred together and then separated. Ion exchange resins work best with batch type operation where the water is pulled from one tank and delivered to another. As the water flows through the resin, the top of the resin bed becomes fully saturated while the resin underneath stays pure, polishes the water from above and reduces the leakage to a minimum.

Chromatographic programs available from several resin manufacturers can be used to evaluate the effects of column vs. batch equilibrium.

A true batch operation with 2.5 cu. ft. of type I strong base anion resin will result in virtually complete molybdate removal to much less than 0.1 mg/L while a single 3.0 cu. ft. tank of resin that is placed in recycle on a loop until it reaches equilibrium will result in approx. 2.4 ppm leakage. The actual leakage will depend on TDS and mix of ions, the leakage stated here is based on the analysis shown above.

A compromise between the two extremes is to use multiple smaller tanks. In this example, if the three cu. ft. of resin is divided up into three one cu. ft. tanks that are allowed to reach equilibrium in sequence, the resultant molybdate leakage is approximately 0.1 ppm. A bit of extra work to set up and change tanks results in significantly lower leakage than if a single larger tanks is used.

Case study 2:

50,000 gallon chilled water loop
Sidestream treatment at 5 gpm

Approx. 1000 micromho
 100 ppm molybdenum as MoO₄
 10 ppm sulfate
 1.5 ppm boron as B
 Balance is nitrite, bicarbonate, and carbonate
 pH is buffered to approx. 8

At 1000 micromho the total cations (or anions) is approx. 600 mg/L as CaCO₃ (12 meq/L)

(600 mg/L as CaCO₃/ 50 mg/L per equivalent of CaCO₃ = 12 meq/L)

PEDI mixed bed capacity is approx. 400 meq/L (roughly 9 kilograins per cu. ft.)

50,000 gallons x 3.78 liters x 12 meq/L / 400 meq/L capacity = 5670 liters resin = 200 cu. ft.

As in the first case, the volume of mixed bed resin needed is so large that it is cost prohibitive to go this direction.

Bicarbonate form strong base anion resin throughput is approx. 4500 gallons per cu. ft.

50,000 gallons / 4500 gallons per cu. ft. = approx. 12 cu. ft.

In order to meet the leakage goal of 0.4 ppm molybdate in the effluent of the loop, it is necessary to split the resin into 3 portions of 4 cu. ft. each

The recycle flow rate selected is 5 gpm. At this flow rate it will take approx. 16 hours for the first 4 cu. ft. tank to become exhausted. The second tank will take approx. 3 days. The third tank approx. 10 days. The total treatment time needed to reach the target goal is approx. 14 days.

Conclusion

Molybdate can usually be removed to acceptable levels by appropriate use of several small portions of strong base anion resin. In order to optimize performance it is useful to use a chromatographic simulator program. Each case can be evaluated and optimized in a relatively short period of time.

References:

1. http://www.gewater.com/handbook/cooling_water_systems/ch_31_open.jsp
2. Molybdenum in Drinking-water, Background document for development of WHO *Guidelines for Drinking-water Quality*, WHO/SDE/WSH/03.04/11/Rev/1
3. Molybdenum Local Limit Development, Ted Graber, Industrial Waste Specialist, EPA Regulatory Compliance Division, Metro Wastewater Reclamation District
4. Best Management Practice and Guidance Manual for Cooling Towers, Prepared by JEA for the control of pollutants discharged to the sanitary collection system, August 2005
5. Duolite Ion Exchange Manual, Diamond Shamrock Chemical Company, 1960
6. F. Helfferich, Ion Exchange, McGraw Hill, New York, 1962