Low TOC MIXED-BED RESINS

by Frank DeSilva

Drugs for human injection consumption, skin lotions and creams all contain n- maceutical water. As such, this water must pass stringent requirements and is referred to as Purified Water (PW), the attributes of which are defined in the United States Pharmacopeia 23 (USP23) and specifies such things as pH, dissolved solids and total solids. There are changes proposed in the new USP23 specifications including conductivity limits and a maximum total organic carbon (TOC) value. The adoption of these new specifications call for an evaluation of existing system design as well as resin selection and treatment.

Demand for Low TOC

The proposed limit for TOC in a purified water system is 500 parts per billion (ppb) or 0.5 milligrams per liter (mg/L). This replaces the prior USP oxidizable substances test used. This new 500 ppb TOC level can easily be obtained by ion exchange resin systems if several considerations are followed. However, meeting the new low TOC numbers can be a problem in water systems that draw from surface waters which have high dissolved organics in them.

Ultrapure water systems that use ion exchange resin as the polishing step to achieve high resistivity (18.3 megohms) use either new mixed bed resin or regenerated mixed bed resin. Regardless, each mixed bed has been highly regenerated to the hydrogen/ hydroxide form. Meeting 18.3 megohms resistivity with a mixed bed resin is not a very difficult task and, in fact, is commonly done. However, achieving and maintaining low levels of TOC from the effluent can be tricky. It is unusual to find less than 1 ppb of organic matter in ion exchange resin treated waters.

What is TOC?

Total organic carbon (TOC) from a resin bed is comprised of materials and solvents leaching from the resin. The organic impurities found in ion exchange resins can be unconverted monomers or low molecular weight polymers. There are also decomposition products and compounds resulting from oxidation or hydrolysis of the organic resins and these may contribute TOC over time. Solvents that may be present and leached from new ion exchange resins are low molecular weight residues, typically un-ionized. The ionized materials that leach from cation and anion resin can sometimes react with each other, yielding high molecular weight salts. These materials are by-products of manufacture.

Cation resins

Cation resin has the potential to leach copolymer pieces that contain sulfonic acid groups and some oxidizable components from the manufacturing process. These substances can be ionized and, if so, are removed by the other type of resin-for example, the sulfonic acid group leaching from the cation resin can be removed by the anion resin. Any TOC that is not removed by subsequent downstream resin will show up in the effluent. However, some of the oxidized components from cation resin can exchange onto and irreversibly foul the anion resin.

Anion resins

Anion resins can shed amine compounds and acetaldehyde from their functional groups. Anion resins will leach copolymer residues from the chloromethylation and amination process. All anion exchange resins degrade over time. This degradation manifests itself as the loss or conversion of strong base capacity. The amines or acetaldehyde that leave the anion resin are ionized and can be removed by a cation exchange bed. In mixed beds, the amine throw from an anion resin near the bottom of the bed may appear in the effluent as TOC. The rate of anion exchange resin decomposition slows rapidly with age and eventually the problem disappears. Fortunately the aging process can be accelerated to eliminate the problems caused by the early decomposition products.

Some ultrapure water systems prefer virgin ion exchange resin for the polishing step because new resin eliminates the possibility of system contamination from regeneration chemicals or contamination from other resin that may have been regenerated together with that batch of resin. There is less of a chance of bacterial contamination with new resin than with regenerated resin. New resins also provide a higher capacity because they have not been exposed to exhaustion cycles. Also, these resins should be very low in metallic extractables because they have never been used for ion exchange. New resin can undergo

special processing to remove the leftover unreacted polymers and monomers and solvents from the manufacturing process.

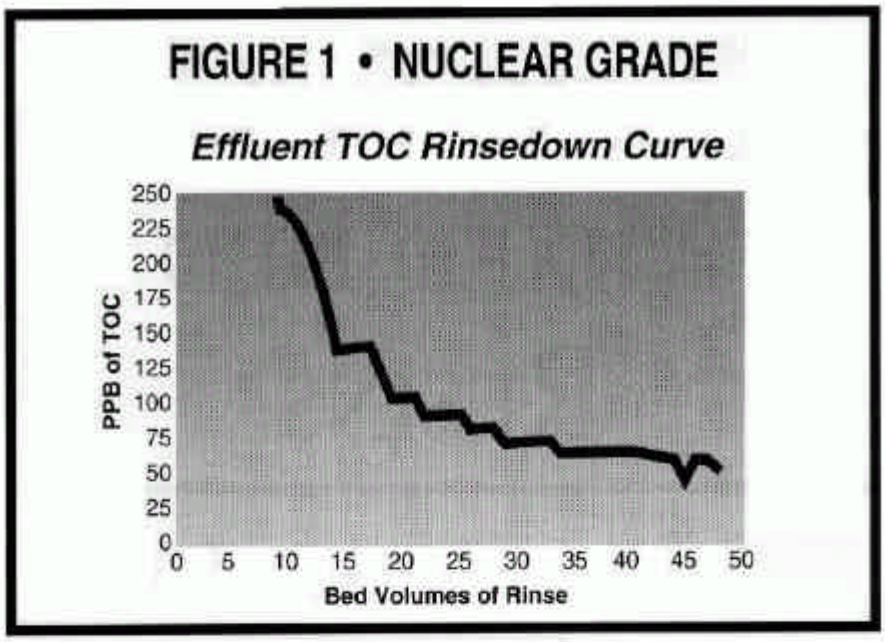
Portable exchange

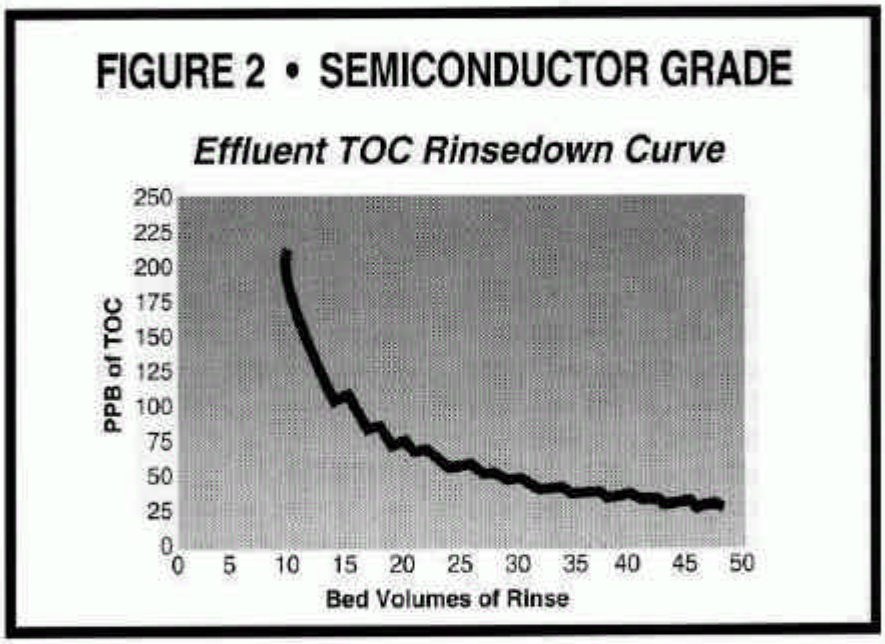
Portable exchange deionization services (PEDI) provide high purity mixed beds for the production of ultrapure water. Any resin that is used for making beds required to produce 18.3 megohms water and low TOC values should first be cycled five or six times to flush out the leachables. The cycling is usually performed as separate bed service on relatively clean inlet water. A convenient way to do this is for the PEDI plant to buy new separate bed cation and anion resin and install that resin in service to provide demineralized water to the PEDI plant. After the resin has been exhausted and regenerated in service five or six times, it can be put into the high 6purity mixed bed service.

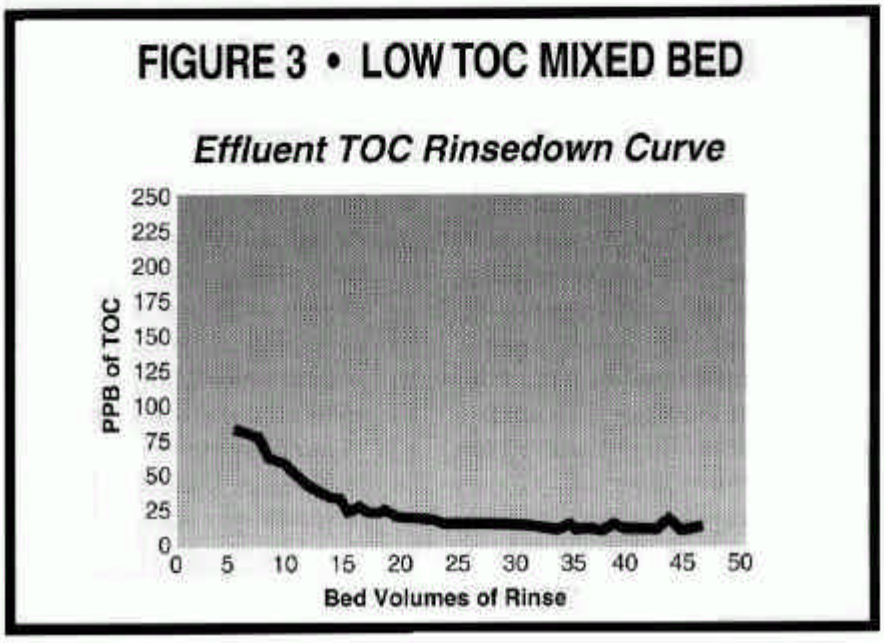
This cycling process performs two functions. First, the simple process of treating water with the new resin ex poses each cubic foot of resin to thousands of gallons of water. This throughput can be looked at as an extensive rinsing process. Second, the shrinking and swelling that the resin beads undergo as they exhaust and regenerate helps to flush out the teachable materials.

Some users of such a PEDI service have their own segregated batch of ion exchange resin that is not mixed with other resins when it is brought in for regeneration. PEDI service is usually cheaper than new resin, but there is a possibility of system contamination from the regeneration process. The PEDI plant should be inspected and audited to make sure that it is suitable for pharmaceutical applications, and that the resin batches are actually segregated and not mixed with other resin that may have been used for industrial applications.

It can be expensive for a semiconductor or pharmaceutical company to obtain its own resin tanks and resin in addition to making sure that the resin is segregated. The PEDI company should provide written records-these records are necessary for on-site inspections and perusal by the FDA.







New resin

PEDI plants or end users that do not have the flexibility or time to cycle a resin for low TOC mixed bed service may purchase new mixed bed resin that has been preconditioned. Resin manufacturers have developed mixed bed processing techniques that remove the traces of manufacturing by-products and minimize the amine throw from the anion component. These techniques are usually proprietary, but involve chemical conversions and extensive rinsings. The resultant mixed bed is one that, when placed in service, will rinse up quickly to 18.3 megohms resistivity and, at the same time, the effluent TOC levels will drop to the specified levels. The faster the mixed bed rinses to quality the better, since the rinsing process uses up time, water and some exchange capacity.

Three graphs are presented that show the actual TOC rinsedowns of virgin mixed beds that are available in the marketplace. The first, a standard nuclear grade, takes a long time (measured in bed volumes of rinsewater) to reach low TOC levels. Given enough water, almost any mixed bed will rinse down to lower TOC numbers. The second graph shows a semiconductor grade mixed bed that is certified to produce 18.3 megohms resistivity water. The TOC rinsedown shows effluent levels of less than 50 ppb TOC in 50bed volumes. Finally, the last curve is a low TOC preconditioned mixed bed. The specifications call for less than 25 ppb TOC in less than 25 bed volumes. This particular batch easily meets that specification, eventually rinsing down to less than 10 ppb TOC!

Summary

End-users that require ultrapure water produced by ion exchange with low TOC have a choice of portable exchange services or purchasing preconditioned ultrapure mixed beds.New, preconditioned low TOC mixed bed resin can save the user time and rinse water by providing low TOC effluent water after a minimum of rinsing. It is always a good idea to get the TOC rinsedown certification curve with each batch that is purchased.

About the Author

Francis J. DeSilva has been in the water treatment industry for more than 15 years. He has a Master of Science in environmental engineering from New Jersey Institute of Technology and a Bachelor of Science in environmental science technology from Florida Institute of Technology. DeSilva is currently National Sales Manager for ResinTech, Inc. of Cherry Hill, NJ and can be reached at
Phone:(856) 354-1152
fax (856) 354-6165)
Email:fdesilva@resiontech.com
Website: www.resintech.com

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