THE PRODUCTION OF ULTRA LOW TOC RESINS

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Abstract

The latest requirements in Ultrapure Water for wafer production call for low parts per trillion (ppt) leakage of inorganic ions and sub-Parts per billion (ppb) of TOC. Due to the difficulty in reliably obtaining ppt levels of inorganic ions from regenerable mixed beds, (even with enhanced separation), a trend has developed to use virgin mixed beds as final polishers.

Introduction

Carefully regenerated virgin mixed beds can meet the desired levels of inorganic ions. However, virgin resins contain leachable organic residues that make it difficult or impossible to achieve sub-ppb TOC levels without lengthy pre-start up rinse procedures.

We have developed processes for substantially reducing the leachable TOC levels in virgin resins and have used this technology to produce VIRGIN MIXED BEDS that routinely produce sub-ppb TOC water with less than 50 bed volumes of rinse.

Operating results from full scale production batches of the cation, anion and mixed resins showing the effect on TOC effluent levels will be presented.

In recent years, the semiconductor industry has placed great emphasis on the reduction of inorganic ions, such that it is no longer considered state of the art to merely produce 18.2 megohm water. Individual inorganic ions are now measurable into the low parts per trillion. However, the removal of leachable organics has lagged behind. The current best technology to measure organic contamination in ultra pure water is still several orders of magnitude higher than that of inorganic contamination

Contaminant levels of 10 parts per billion of total organic carbon (TOC) are yesterday's news. Levels of 1 to 5 parts per billion TOC are today's news. To make the headline in tomorrow's news, it will be necessary to provide virgin resins that can rinse quickly to less than 1 part per billion of TOC.

Properly operated demineralization systems with adequate pretreatment are already able to produce TOC levels below 5 ppb from tap water sources. The configuration of these systems most likely includes most of the following components; activated carbon, vacuum degasser, chloride cycle organic trap, 254 nm UV, reverse osmosis, first stage mixed beds, second stage 185 nm UV, polishing mixed beds, and membrane filters. It is not unusual to see TOC levels below 10 ppb in the treated water as it enters the polishing mixed bed. In such cases, the polishing mixed bed can be the limiting factor in the final TOC levels, and can also be a major source of TOC in the final effluent.

There are four basic causes or sources of TOC leakage from mixed beds:

1. Equilibrium & kinetic leakage of TOC from the supply water either breaking through from the inlet source or accumulating on the resin from previous cycles.
2. Chemical degradation of the ion exchange resins, i.e. thermal or oxidative
3. Non-ionized organics not removed (or added) by upstream processes.
4. Substances leaching from the resin itself (leachable TOC); i.e. impurities left in the resin from the manufacturing process.

In a well designed and properly operating system, the first three sources are prevented or reduced to very low levels. The largest source of TOC leaving the polishing mixed beds is leachable TOC from the resin itself. Leachable TOC levels are highest in new resins and gradually rinse out with use. It is not surprising to see brand new resins that do not produce or maintain as low a TOC value as a well operated used resin on the same water.

This paper discusses the sources and causes of leachable TOC in virgin mixed bed resins, and the results of efforts at ResinTech to exclude and remove these contaminants from finished mixed bed products.

What are the Leachables?

All resins used in high purity mixed beds are manufactured from styrene and divinylbenzene. Styrene monomer is very pure. Divinylbenzene, which is typically supplied as a 55% solution, contains a significant amount of organic impurity. Suspension stabilizers, organic catalysts and other organic additives are also used during the polymerization process. The use of solvents as pore forming substances in the polymerization stage in the manufacture of macroporous resins also contributes to the level of potential leachables.

The conditions of polymerization and the impurities in the divinylbenzene lead to various undesirable side reactions during the polymerization stage. Polymer strands are created that are not connected to the main three dimensional crosslinked polymer structure. The molecular weight of the unattached polymer chains decreases with decreasing crosslinkage. The concentration of unattached polymer chains increases with decreasing crosslinkage. Low crosslinkage also leads to polymer instability and susceptibility to oxidative decomposition. The problem is compounded when the degree of crosslinkage is not homogeneous within the resin beads. Increasing crosslinkage increases the chance of uneven crosslinkage. This results in higher molecular weight leachables that are more difficult to remove from the finished resin.

Cation exchange resins

Sulfonation and the final processing of cation resin affects the type and level of leachable TOC left in the finished product. The sulfonation step, in most cases, involves solvents as swelling agents. The degree of sulfonation determines the proportion of terminated polymer chains that are sulfonated. This determines whether or not the polymer strands are ionized.

The main source of cation leachables is the unattached polymer chains left in the resin after manufacturing. Increasing crosslinkage increases the molecular weight of these chains and makes them more difficult to remove from the resin. Uneven crosslinkage causes the concentration of this material to increase.

The manufacturing process for cation resins leaves them in the hydrogen form. In ultrapure applications it is not desirable to convert the resin to the sodium form. Hydrogen form cation resins are potentially corrosive. This often limits the degree and selection of post manufacturing cleansing procedures. Since there is no chemical conversion step used to make hydrogen form resin, the purging of leachable TOC by regeneration does not occur.

When virgin cation resins are placed in service for the first time, the low molecular weight portion of the leachable TOC is rapidly purged. The higher molecular weight fractions are purged slowly. A portion of the TOC that is anionic due to its sulfonation is exchanged by and may cause fouling of the anion resin, but a substantial amount appears in the effluent as TOC.

Cation resins can be degraded by oxygen or high temperatures and create leachables at extremely low levels, too low to be a factor (for now). However, undercrosslinked cation resins have proven to produce high levels of leachables due to oxidation and/or thermal instability, in condensate polishing applications.

Anion resins

Leachable TOC from new anion resins is significantly different than leachables from cation resins. First, the polymer generally has significantly lower levels of divinylbenzene crosslinkage (3 to 4 % vs. 8 to 10 %). This causes anion resins to be less susceptible to uneven crosslinkage, and causes the unattached polymer chains to have relatively low molecular weights.

The chloromethylation and amination steps cause the resin to undergo wide changes in pH and temperature. The additional processing steps facilitate TOC extraction. In between and following these steps, there are additional rinses and cleansing operations. These provide added opportunities for removing the polymeric residue formed during the initial polymerization step.

The anion resin manufacturing process leaves the resin in the chloride form. Anion resins used in mixed beds need to be supplied in the hydroxide form. Therefore, it is necessary to convert (regenerate) anion resins to the hydroxide form prior to use. The regeneration process also helps to remove manufacturing residue.

It is extremely unusual to see high molecular weight leachables coming out of anion resin. The leachables are predominantly related to the instability of the amine functional groups. Leachable TOC from anion resins typically consists of trimethylamine, methanol, and low levels of a host of other low molecular weight alcohols and aldehydes.

"As is" Mixed Beds

If a routine production lot of hydrogen form cation resin is mixed with a well-regenerated, but otherwise non-treated, anion resin, there is a well established pattern of TOC leachables that comes out of the resin when it is first placed into service.

There is an initial blush of organic material that comes out of the resin at levels of several parts per million. This consists of traces of the solvent used in the manufacturing process, methanol (from the anion resin), and un-ionized low molecular weight polymers (primarily from the cation resin). These compounds wash out of the resin rather quickly, and a typical clean mixed bed resin will rinse to something in the neighborhood of 50 parts per billion of TOC in a reasonably short period of time. Trimethylamine and low molecular weight ionized cation leachables are generally exchanged by the resin and although released, do not appear in the mixed bed effluent.

The level of TOC leaching from the resin levels off, and the leachables coming from the resin continue at approximately 50 parts per billion for an extremely long period of time. While rinsing down to 50 ppb lasts for hours or possibly days, the second effect lasts for weeks or possibly months. Resins produced without special manufacturing or post manufacturing processing will continue to leach significant levels of TOC over their entire lives. Resins that are poorly made can continue to leach TOC in excess of 100 parts per billion for many months.

Removal of Leachable TOC From New Resins

Clearly, there are some steps in the manufacturing process where the formation of leachables can be reduced. For example, a resin with uneven crosslinkage may never be able to produce very low levels of leachable TOC. A resin with low crosslinkage will decompose at a relatively rapid rate and will fail to produce extremely low TOC. Most resin manufacturers are able to control the process well enough to avoid these types of problems.

In order to reach leachable TOC levels of less than 50 parts per billion, post manufacturing processing or modification of the manufacturing process is required. In the past, one could perform this post treatment by repeated cycling of the virgin resins. Many of the service exchange DI companies would take their new ultra pure resins and place them in separate bed service until they had 5 to 10 exhaustion and regeneration cycles, then move them to their ultra pure mixed bed resin float. This process typically yielded mixed beds that produced effluent TOC levels less than 10 parts per billion. However, the practice is not now widely used because of concerns of contamination during the cycling and the time lag involved to cycle and exhaust the resin 5 to 10 times. Also, even after this procedure, the organic levels are still higher than current requirements in the most demanding applications and the cation resin is no longer 100% in the hydrogen form.

Beyond Cycling

To get to even lower leachable TOC levels than can be reached by cycling resins, it is necessary to modify the manufacturing process or perform post manufacturing treatment to cleanse the cation and anion components.

ResinTech has developed a post manufacturing process for making mixed bed resins that can produce demineralized water with extremely low leachable TOC levels. The basic process involves extraction of both high and low molecular weight organics from the resin components prior to mixing. The process development took 2 years, first working in the laboratory and then scaling up to plant size batches. This data is proprietary and cannot be shared.

Extraction Data

The first series of graphs show extraction curves for various separate component resins. In all cases, there is a rapid initial build-up of TOC, followed by a gradual increase. The general shape of the curves is the same for every resin that we have tested. Curves for Type II anion resin are shown first as these resins throw relatively high levels of TOC and it is easier to see the relative trend of multiple extractions that occur.

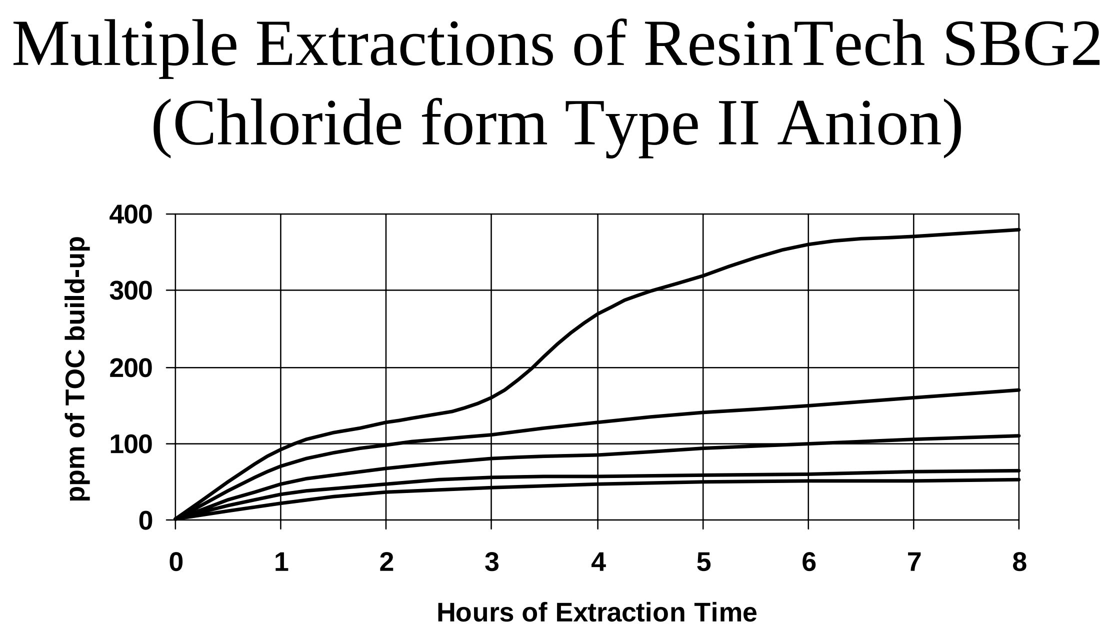

Figure 1

Figure 1 shows a series of TOC extraction(s) from a type II anion resin (ResinTech SBG2).

The resin was soaked for an extended period of time and the TOC measured periodically. The rate at which the TOC level in the liquid phase rises is initially quite rapid. However, the curve soon turns over and reaches a maximum where no further extraction occurs. At this point, the leachable TOC equilibrium between the resin and the liquid.

The liquid was then purged from the system, the resin rinsed clean, a new batch of liquid added to the system, and the soaking process repeated. The second curve shows the same general shape as the first one, but with a more gradual discharge and lower final concentration in the liquid.

It is believed that the double change in the slope of the curve during the first extraction is caused by the high and low molecular weight fractions within the resin. The higher molecular weight organics take longer to exit the resin and cause the second hump in the curve. The family of curves shows that after many successive extractions, the lowest practical limit is reached. This level is the polymer itself gradually decomposing. It depends on the degree of crosslinkage, the evenness of crosslinkage of the polymer structure, and the specific conditions of the extraction process. It represents the lowest possible background contamination under the chosen conditions.

The higher molecular weight extractables take longer to come out of the resin. Increasing the temperature increases the rate at which the high molecular weight material exits the resin beads. However, increasing the temperature increases the rate of resin decomposition, therefore, a balance must be struck between extractant temperature and extraction time.

Multiple Extractions of ResinTech SBG2 (Chloride form Type II Anion)

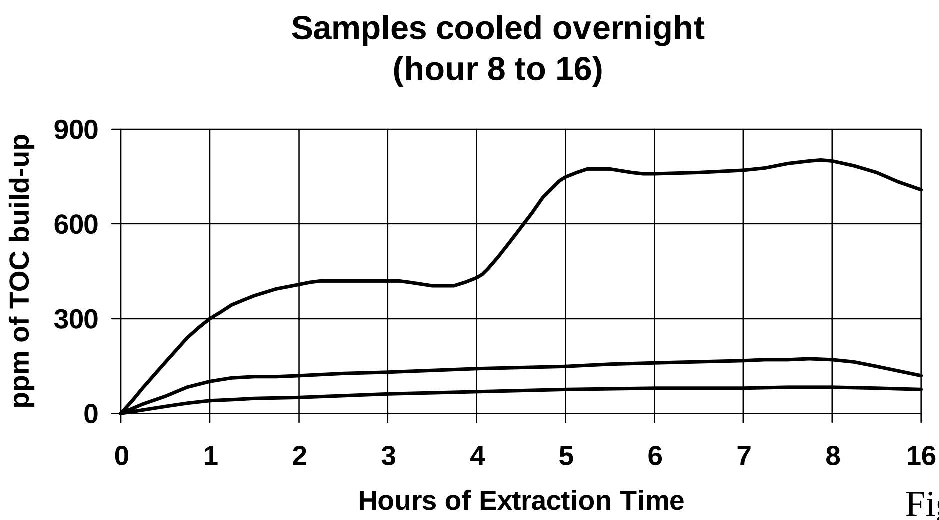

Figure 2

Figure 2 is a similar curve for a different lot of ResinTech SBG2. In this test, the resin was cooled before the solution was drained. Since the organics are soluble in both the resin and liquid phases, there is an equilibrium between phases that is temperature dependent.

The relatively high concentration of extractables in type II resins makes them undesirable for ultrapure water applications requiring very low TOC.

Multiple Extractions of ResinTech SBG1
(Chloride form Type I Standard Anion)

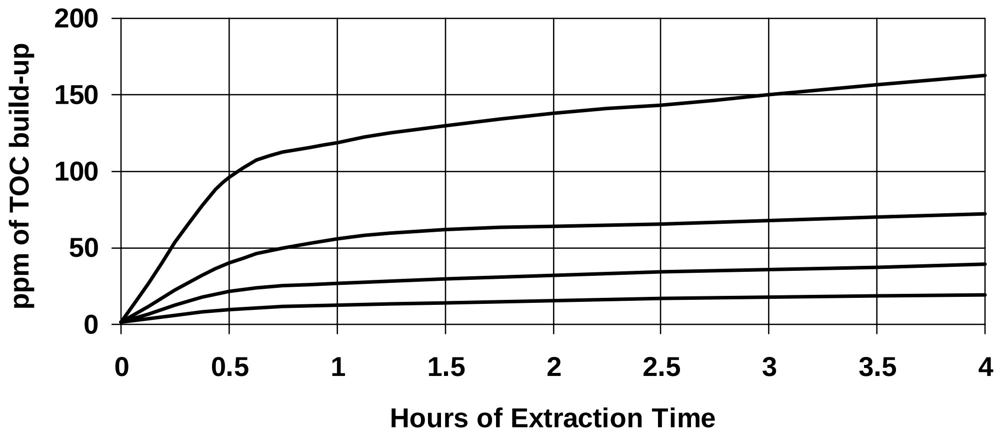

Figure 3

Figure 3 shows a similar family of curves for a Type I anion resin. Type I resin reaches equilibrium faster than does a Type II resin, has less organic material to extract, and reaches a lower final level. The final rate of TOC buildup is less than 1 ppm/hr. In a dynamic system the flow of water provides a dilution factor of about 75 indicating that the resin in Figure 3 after 4 stages would initially leach less than 15 ppb of TOC.

Multiple Extractions of ResinTech CG8
(Sodium form 8% gel Cation)

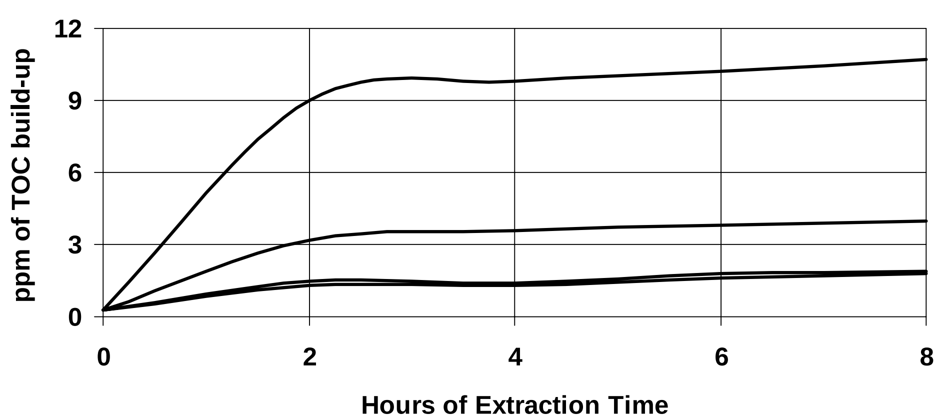

Figure 4

Figure 4 shows a typical multiple extraction of a cation resin. The leachable levels are an order of magnitude lower than that of anion resins. Note that the double hump is still present in the third and fourth extractions. This high molecular weight fraction, if not removed, would prevent this resin from ever producing extremely low TOC.

Extractions can be performed under flowing rather than static conditions. Figures 5 & 6 show continuous extractions of Type I porous and standard anion resins.

Continuous Extraction of ResinTech SBG1P
(Hydroxide form Type I Porous Anion)

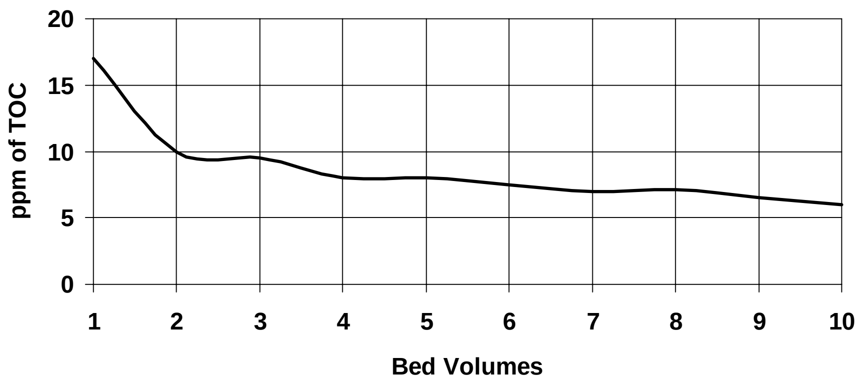

Figure 5

Continuous Extraction of ResinTech SBG1
(Hydroxide form Type I Standard Anion)

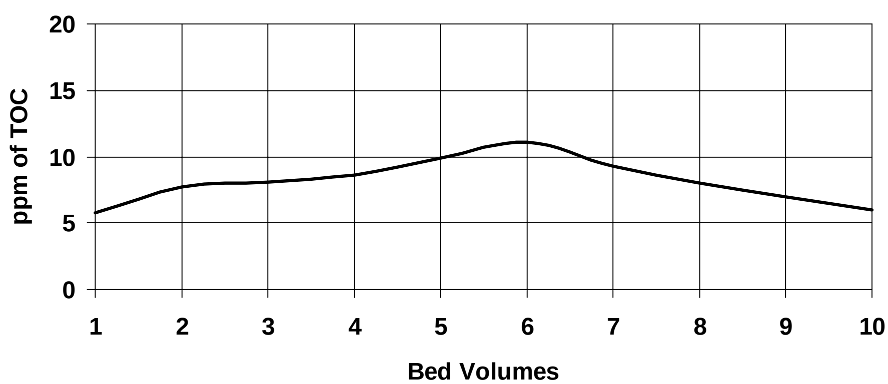

Figure 6

Note the hump in the curve for ResinTech SBG1. This resin has relatively high crosslinkage, approximately 8% DVB compared to a Type I porous anion, which is approximately 4% DVB. This increased crosslinkage results in a fraction of higher molecular weight organics that is retained in the resin, causing the hump in the curve. The absolute value of the TOC in the extract is about the same as for the more porous resin.

Mixed Bed Data

As they say, the proof is in the pudding. The following graphs are actual TOC rinsedown curves from testing of various mixed beds.

Figure 7 is a rinsedown curve from a competitive mixed bed sample from Company S, showing a mixed bed that obviously has not been post treated in any way. The high TOC, even after extensive rinsing, is probably caused by the cation component being supplied in the hydrogen form without adequate post treatment to remove leachables. There appears to be a relatively large amount of high molecular weight extractable in this sample.

TOC Rinsedown
Mixed Bed "S1"

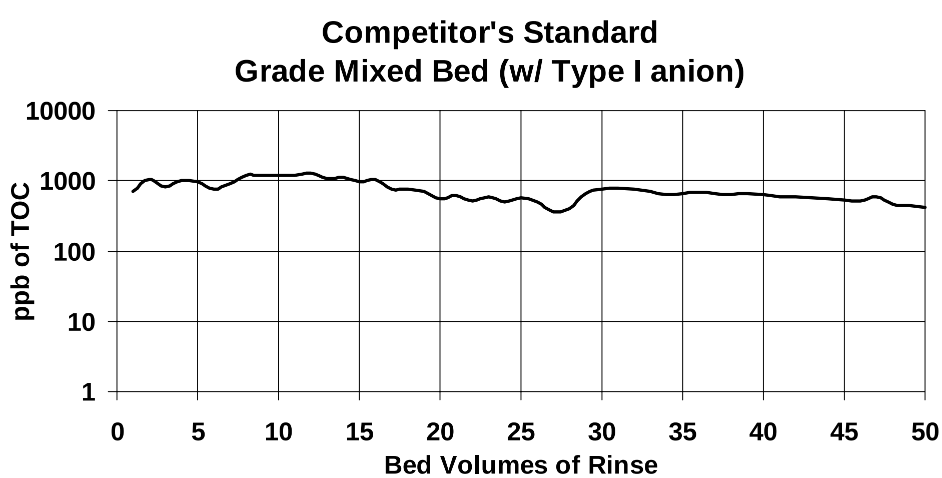

Figure 7

TOC Rinsedown
Mixed Bed “R1 & R2”

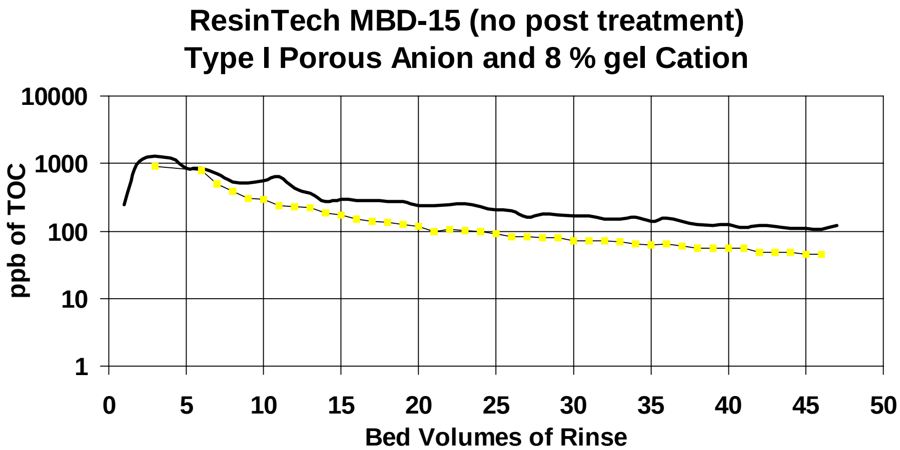

Figure 8

Figure 8 shows the TOC rinsedown curves for two typical production lots of mixed bed from ResinTech that did not receive any special post treatment. The cation components were regenerated from the sodium form, resulting in lower TOC levels than observed from company S.

Figures 9, 10, & 11 are rinse down curves from mixed beds made from component samples from Company D, mixed with ResinTech post treated reference components. These samples show well-manufactured, clean products (probably with some post treatment).

TOC Rinsedown
Mixed Bed “D1”

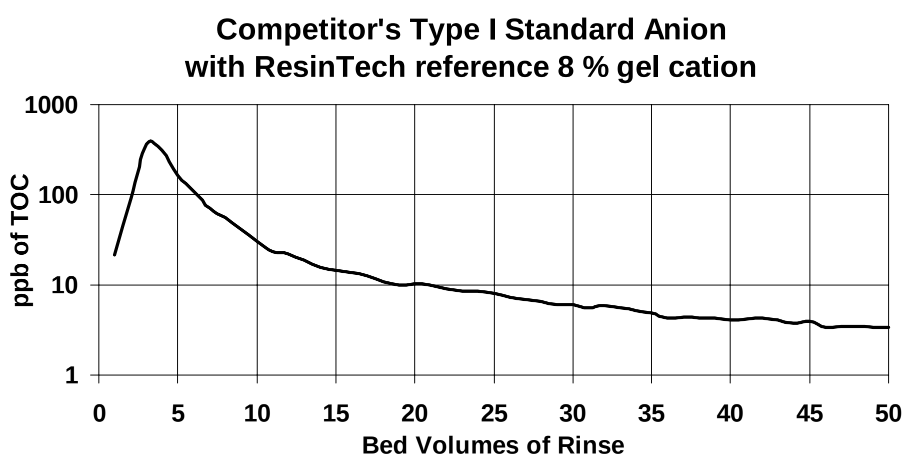

Figure 9

TOC Rinsedown
Mixed Bed “D2”

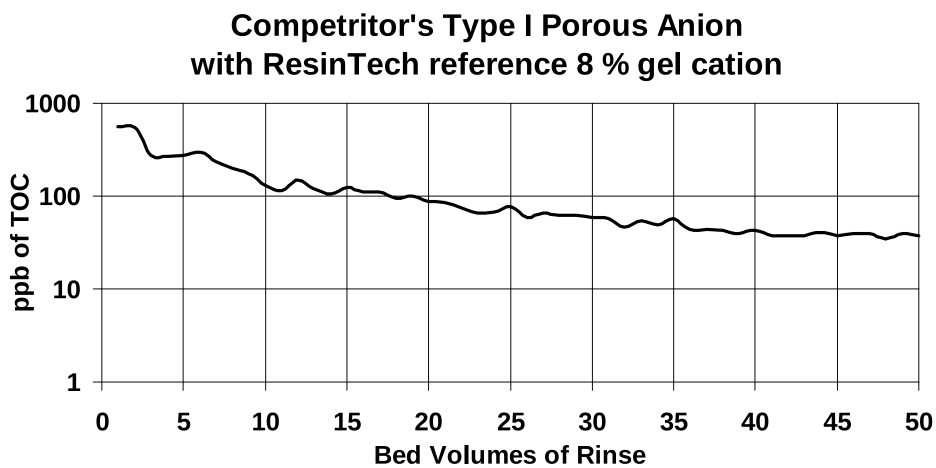

Figure 10

TOC Rinsedown
Mixed Bed “D3”

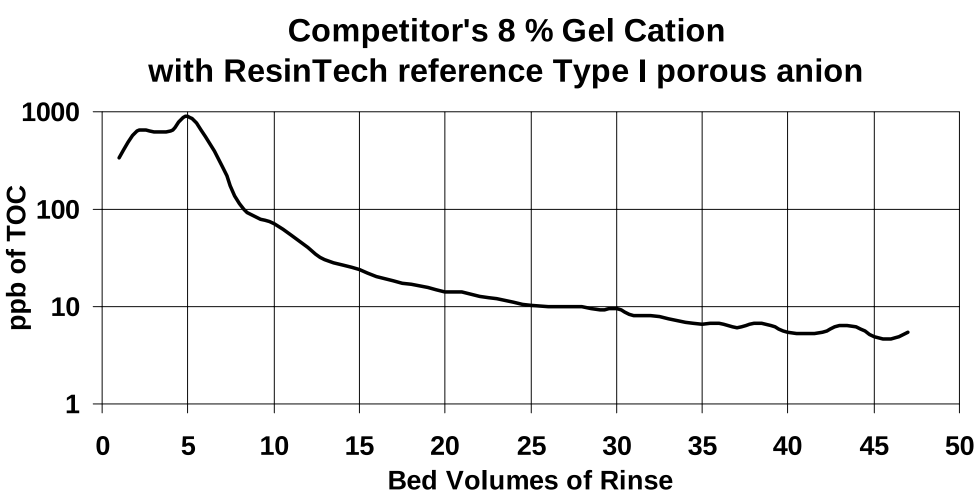

Figure 11

Figure 12 is from a mixed bed made with a Type II anion resin. This type of mixed bed always produces much higher TOC than mixed beds made with Type I resins.

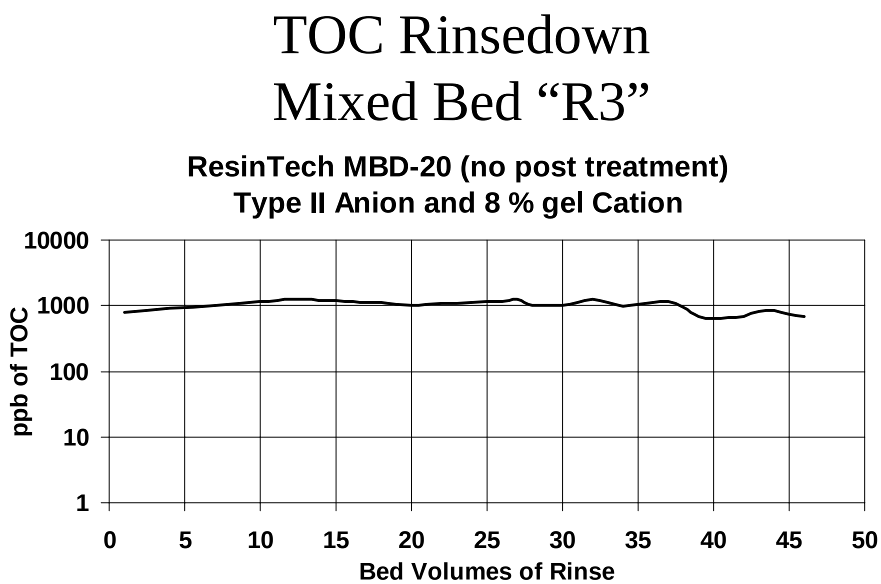

Figure 12

Figure 13 is a rinse down curve from a sample of ResinTech’s 10 % crosslinked cation resin mixed with an untreated anion. The leachables are reasonably good, but the baseline remains constant over a long period of time, as the high molecular weight material from the cation resin continues to leach out.

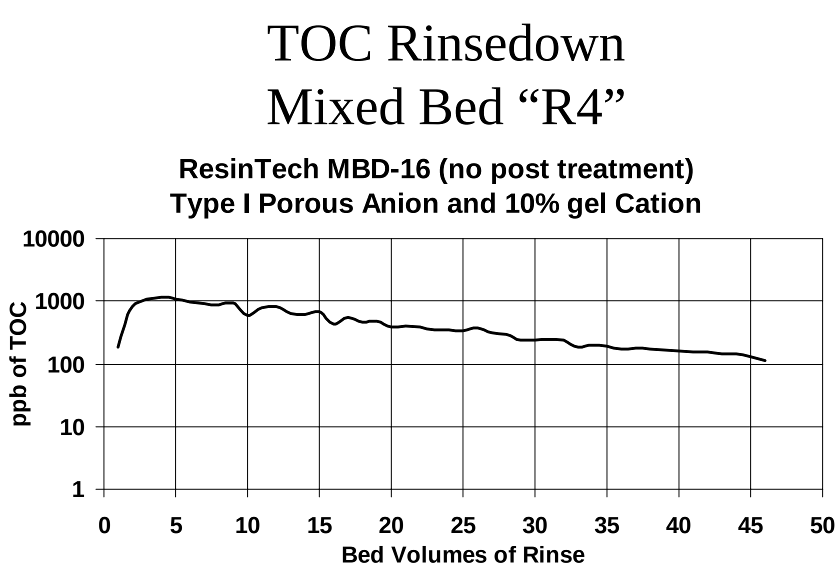

Figure 13

Figure 14 shows the rinse down curves from two older production lots of ResinTech's low TOC mixed bed resin (vintage 1995-96). This shows a rather low baseline of TOC, and a relatively rapid rinse down to 10 ppb. At that time, this performance represented a state-of-the-art low TOC mixed bed resin.

TOC Rinsedown
Mixed Beds "R5 & R6"

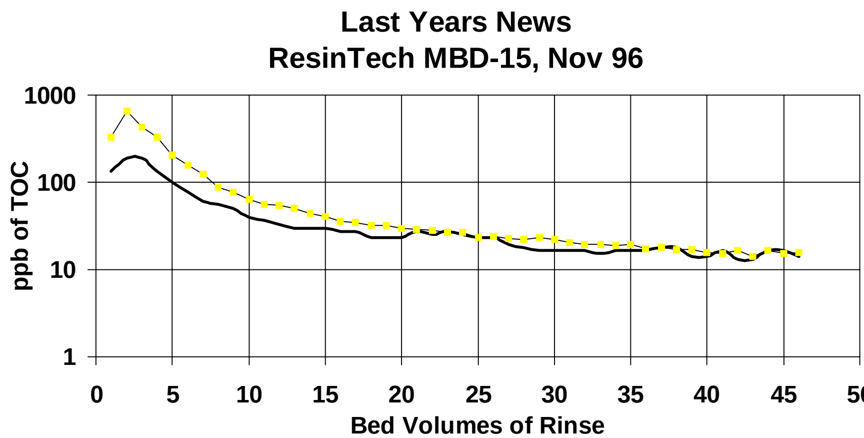

Figure 14

Figure 15 shows the rinse down curves from two recent production lots of ResinTech low TOC mixed bed resin, which was made according to the latest process developed. The initial rinse out is very rapid and the resin flatlines down in the noise of our TOC analyzer. This type of result is now consistently produced from LTOC process.

TOC Rinsedown
Mixed Beds "R7 & R8"

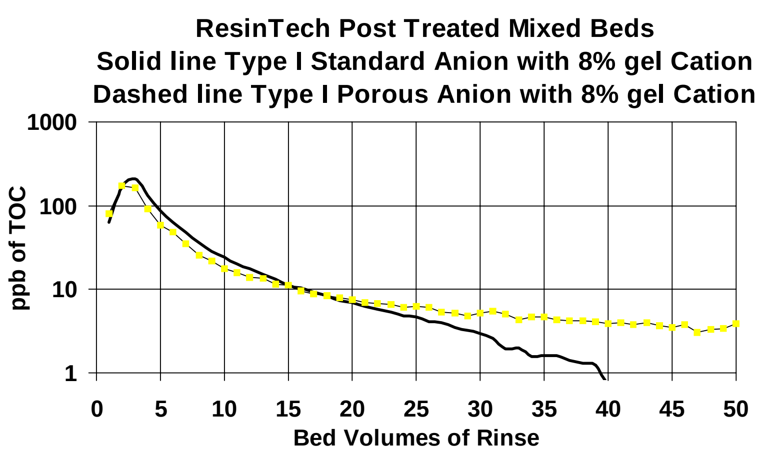

Figure 15

During storage, the hydroxide form anion resin sites decompose slowly and give off low molecular weight amines, which are a form of leachable TOC. This causes leachable TOC levels to increase over time. However, the amine based leachables rinse out relatively rapidly and the resin continues to flatline in the 1 to 2 ppb area. Figure 16 illustrates this effect.

TOC Rinsedown
Mixed Bed "R9"

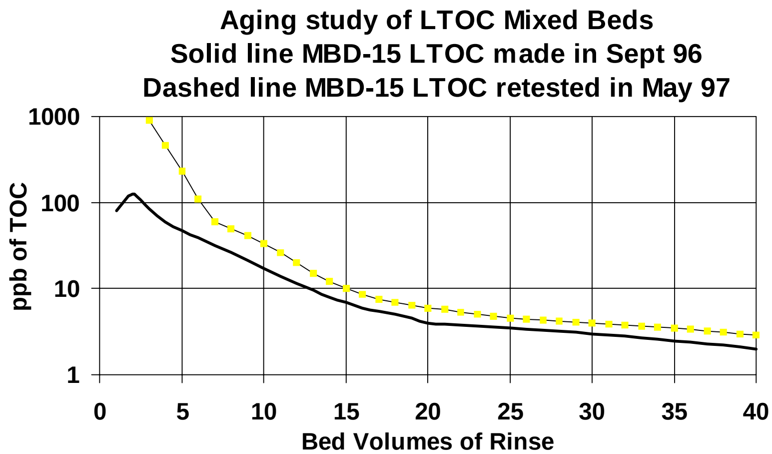

Figure 16

Summary

As can be seen from these graphs, it is possible to post-treat resins to make virgin mixed beds that can produce low TOC effluents, around 1 ppb soon after startup. At ResinTech, this is done on a routine production basis. A few batches have been produced that rinse down to less than zero on our TOC analyzer (when the blank is subtracted). Barring the controversy about measuring TOC's accurately under 1 ppb, virgin mixed resins are now available that can produce TOC levels less than 1 ppb.

Bios

Michael C. Gottlieb holds a Bachelor of Science degree in Chemical Engineering from the New Jersey Institute of Technology. He is the founder and President of ResinTech Inc, an ion exchange resin supplier and manufacturer headquartered in the United States.

Mr. Gottlieb has served in a variety of positions in the development and marketing of ion exchange resins during the past 30 years.

Throughout his career, Mr. Gottlieb has actively participated in a multitude of chemical and engineering organizations relating to water treatment and ion exchange including:

The Advisory Board of the International Water Conference
The American Institute of Chemical Engineers
The American Society of Testing and Materials (ASTM)
The American Water Works Association (AWWA)
The Engineers' Society of Western Pennsylvania
The Ion Exchange Task Force of The Water Quality Association
The Science Advisory Committee of The Water Quality Association

He has served as Chairman of the ASTM Committee on Bead Ion Exchange Resin, and also as chairman of the Ion Exchange Committee of the American Water Quality Association.

He is well known for his writing and presentation of numerous technical papers and published articles throughout the world. Mr. Gottlieb has been a pioneer in the development of computer software relating to ion exchange applications and technology. He recently co-authored the ion exchange chapter of the third edition of the AWWA: Water Treatment Plant Design Manual.

Peter Meyers is Technical Manager for ResinTech Inc. His responsibilities include: providing technical assistance to customers, managing laboratory operations, and overseeing process and production applications.

Prior to joining ResinTech, Peter was the Technical Manager for L*A Water Treatment. During his 20 years with L*A Water Treatment, his duties included the design of ion exchange systems, analysis of resin and water samples, and technical support. His experience ranges from many types of make-up demineralizers, polishers and softeners, to process design and hardware operation.

Peter is a graduate of MT San Antonio College, in California. He has authored numerous papers about ion exchange and holds several patents related to water treatment.