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"Boron Removal From Ultrapure Water By Boron Selective Ion Exchange"

By

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Abstract

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Boron selective ion exchange resin has been available for many years. To date, the only commercial use of this resin has been removal of boron from saturated brine. AMD Austin has made several enhancements to their UPW system to reduce the boron loading on the mixed beds, but nothing has made a significant impact. If the boron selective resin could be used to remove boron ahead of the mixed beds, there might be a potential operating cost savings sufficient to justify adding boron removal ion exchange to the system.

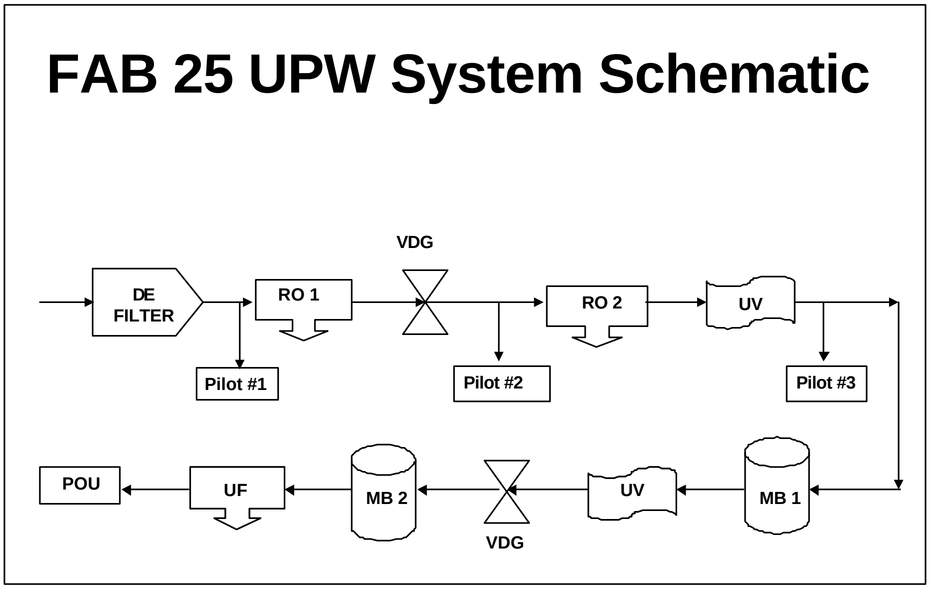
Two pilot plants, each of 1.5 gpm capacity were installed in late 1998, to determine the feasibility of using boron selective ion exchange. One pilot is after the first pass RO, the other after the second pass RO. Both pilot plants have been running continuously for more than 6 months without regeneration and with non detect effluent boron concentrations. AMD is currently evaluating the economics of adding a full sized boron ix to their UPW system.

In the paper, we will discuss progression of events in the microelectronics industry that led AMD to reduce boron to below detectable levels in its UPW supply to FAB 25. We will also discuss the theory of boron removal by ion exchange, the design of the pilot plants, the lab data concerning leakage of various ions (including B, Si, Cl, Na, & TOC), and the economics driving the project.

The Problem

The typical levels of boron in the raw water supplying AMD's facility in Austin, Texas are in the neighborhood of 0.25 ppm. Since boron is used in the production of microprocessors as a doping agent, AMD decided that any boron that remained in the Ultrapure Water (UPW) used in FAB 25 might be detrimental to the performance and yield of product. This led to a specification that the UPW should have no detectable boron. The strict boron specification presented a serious challenge for the design and operation of the UPW system servicing FAB 25.

When operating the UPW system, in order to maintain a non-detectable level of boron, the mixed bed ion exchange units needed to be regenerated about four times more often than they would if they were regenerated based on silica breakthrough. The practice of "short cycling" the mixed beds resulted in approximately 120 regenerations each year. Frequent regenerations were physically detrimental to the ion exchange resins and also resulted in added costs for equipment maintenance. Although FAB 25 was able to meet the FAB requirement of no detectable boron, any alternative that eliminated the need to short cycle the ion exchange units, reduced labor cost and/or operating cost, needed to be investigated.



RO Improvements

Boron is present in water as a weakly dissociated anion and can exist in various forms depending on pH and concentration. At neutral pH, boron is mostly present as un-dissociated boric acid, which is poorly rejected by reverse osmosis (RO) membranes. As pH increases, boron takes on the form of borate, which is well rejected by RO. The initial membranes installed in the first pass RO system at FAB 25, were cellulose acetate (CA). This type of RO membrane can only withstand a maximum pH of approx. 5.0. The first improvement made at FAB 25 was to replace the CA membranes with thin film composite membranes (TFC). This allowed the pH to be increased as high as 10.0.

With this change, the boron rejection increased from less than 30% to more than 90%. However, the decreased boron in the mixed bed feedwater obtained by operating at pH of 10, was offset by increased sodium (caused by the addition of sodium hydroxide used to increase pH). AMD found that by operating the RO systems at a feedwater pH of approx 9.5, that boron rejection was improved to around 85-90% without any significant increase in sodium concentration leaving the mixed beds. The overall effect of the RO improvements was to reduce mixed bed regenerations from approximately 120 per year to around 100 per year, leaving considerable room for further improvement.

Ion Exchange Pilot Study

AMD facilities teamed up with ResinTech and with Ultrapure & Industrial services (UIS) to investigate the use of a specialized ion exchange resin that had been used for years in chemical processing, to remove boron from concentrated salt solutions. This resin had the right characteristics as far as removal of boron, but since it was used in an industry where acceptable quality levels are measured in parts per million (PPM) rather than parts per billion (PPB), there was no data available to demonstrate its performance in a UPW system.

Additionally, the potential for leaching of total organic carbon (TOC) needed to be determined. The existing boron selective resins were not available in the special high purity grade required to meet TOC levels specified for UPW systems. ResinTech went to work to develop a special process for treatment of the boron selective resin, to remove organic impurities. AMD facilities designed a pilot study, which incorporated a column of the ResinTech boron specific ion exchange resin (BSIX) upstream of a column of the mixed bed resin currently used in FAB 25. A single column of the typical FAB 25 mixed bed resin was also run in parallel to the pilot as a control. Results of the pilot will be discussed further on in the paper.

Boron Chemistry In Mixed Bed Exchange Systems

The problem with boron removal by ion exchange resin (particularly by mixed beds) is that boron is essentially non-ionized at any reasonable pH. K_1 for boric acid is approximately10^{-10}. At any pH below approximately 10, boron is mostly present as un-ionized molecular boric acid. Since ion exchange resins only exchange substances that are ionized, this means that boron is not well removed by ion exchange at neutral pH.

In a mixed bed polisher at neutral pH, the anion resins capacity for boron compared to other ions is essentially zero. Boron passes through the resin bed slowly; therefore mixed bed exchange is somewhat effective at removing boron. However, long before a mixed bed is exhausted with ions such as alkalinity or silica, any boron that has entered the top of the resin bed will slowly move down thru the resin bed and will be displaced. In some cases, the boron concentration leaving the resin can be higher than the inlet concentration. This is characteristic of the exchange for ions that have very unfavorable selectivity. This means that mixed bed ion exchange resins will never be a risk free method to remove boron.

One way to overcome the difficulty is to provide naked strong base anion exchangers in front of the mixed beds. The advantage of a naked anion exchanger over a mixed bed is that the internal pH of the pure anion resin is much higher; therefore boron is better ionized and better removed. However, such a system suffers from the potential problem of hardness scale, if any hardness is present in the feed water, and will still dump boron, if operated past boron break thru.

Selective Boron Removal Theory

Back in the early 1950's, it was discovered that borate ion reacts with manitol and other polyhydric alcohols to form a larger and more fully ionized anion. In 1955, a leading manufacturer of ion exchange resins patented a synthetic ion exchange polymer with N-methyl glucamine functionality. In addition to being a weakly basic ion exchanger, this resin showed exceptional selectivity for boron. In those days, the limit of detection from boron was around 1 part per million, but the new resin could remove boron to below the limit of detection from almost any solution, including saturated brine.

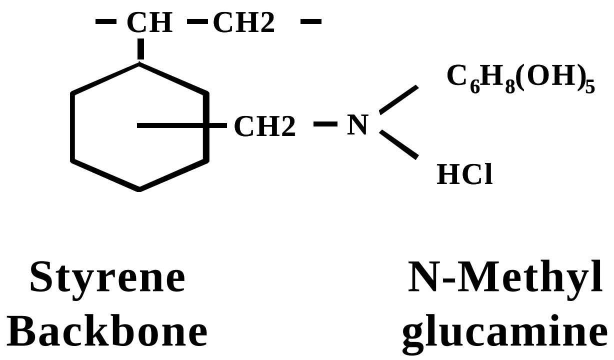
It was hoped that this new resin could be used in several applications, including agriculture and the nuclear power generation industry. However, over the years only one commercial application was developed for the boron selective resin, that of purifying magnesium chloride brine. Since the market for this specialized resin was limited, the price remained high and other potential uses never became cost effective. Although the patents have long since expired, the small market and low demand have help to keep the cost of the resin high. Today, the price of boron selective resin is about half of what it was 30 years ago. There is every reason to think if a significant market for this resin can be developed, the price will drop further. The economics of boron removal by selective exchange is made significantly more favorable if the cost of resin decreases.

Anion resins are produced with a variety of functional exchange groups, all based on various amines. Resins produced with tertiary amines, such as trimethylamine, form strongly basic exchange groups. This class of resin can split salts and can remove weakly ionized compounds, such as carbonic acid, silicic acid, and even boric acid. However, a strong-based anion resin's preference for various ions depends in part on their degree of ionization. Carbonic acid is weakly ionized; K_1 is approximately 10^{-5}. Silicic acid is even weaker; K_1 is approximately 10^{-7}. Boric acid is weaker still; K_1 is approximately 10^{-10}. Boric acid is so poorly ionized that the anion resin in a mixed bed exchanger shows almost no preference for borates or boric acid. Although some borate is removed, the unfavorable selectivity causes the wave front to be non-self sharpening and borate moves through the resin bed well ahead of the other ions.

Anion resins that are produced with secondary amines, such as dimethylamine or methyl glucamine form weakly basic anionic exchange groups. This class of anion resins cannot split salts. Weak Base anion resins can only absorb acids. They cannot remove significant amounts of weak acids, such as carbonic, silicic, or boric by ion exchange, except when the pH of the solution is very low.

Methyl glucamine has a chemical structure that is very similar to manitol. It forms a very strong coordinate bond with boron. A weak base anion resin made with methyl glucamine has, in addition to its normal weakly basic anionic exchange capacity, a chelating capacity that is specific for boron. Except for the unusual amine, the boron selective anion resin is very similar to other weakly basic anion exchange resins. It cannot be used in a mixed bed because of its relative inability to remove other weakly ionized anions, such as carbon dioxide and silica. It can be used as a boron selective trap to remove boron ahead of the mixed bed ion exchange systems.

Chemical Structure of
Boron Selective Resin



Concerns About Boron Selective Resins

Up until this study was conducted, almost nothing was known about the boron selective resin, with respect its performance in ultrapure water systems. In the only known commercial use, that of purification of saturated magnesium brine, the BSIX resin was reported to be very slow reactive. This could have been due to inherent problems with the kinetics of the resin or it could be due to the high ionic strength of the solution that it was traditionally used in. The original research work was done 30 years ago when the limit of detection for boron was much higher than it is today; little was known about the ability of this resin to operate at boron concentrations in the low or sub ppb area. There are still some questions about the cleanliness of the boron selective resin, particularly whether it can be produced with ultra low leachable TOC levels. These questions needed to be answered before the boron selective could be considered for ultrapure water use. These studies are still ongoing, particularly with respect to the use of the BSIX resin following the second pass RO system.

Pilot Plant

The potential cost savings of using the boron selective resin and the desire to find a more efficient way of removing boron from the UPW supply was the primary reason for AMD to initiate a pilot study to investigate the boron specific ion exchange resin.

The first location considered was the filtered water, supplying the UPW make-up system. The reasons supporting a pilot run in this location were minimal impact on the existing system, relatively easy installation, and relatively low material and construction cost. A pilot plant was installed in this location in mid 1998 and operated for several weeks. However, it was virtually impossible to determine boron concentrations against the relatively high salt background, which required high dilution to protect the analytical equipment. The results were inconclusive and the raw water location was abandoned.

AMD decided to restart the pilot plant at two new locations. The first location was after the first pass RO, but before the second pass RO. The second location was after the second pass RO, but before the primary mixed beds. Pilot plant #3, (after the second pass RO) was also set up with a mixed bed polisher following the boron selective resin, to test the results of the boron specific resin as pretreatment to the mixed bed resins used at FAB 25. A second mixed bed was installed in parallel to pilot plant #3, which processed the second pass RO effluent directly. This would enable a comparison to the existing mixed bed configuration, as a control to the experiment. A third bed of ResinTech mixed bed was also operated as part of a separate trial, and was not part of the boron pilot testing (it did perform quite well).

Objectives

The objectives of the pilot plant were to study boron leakage, to determine the capacity of the boron selective resin under conditions that would actually be encountered in an operating facility, and to compare the mixed bed characteristics of boron breakthrough against silica and/or sodium breakthrough in the absence of boron. At the same time, AMD felt it important to analyze for both organic and inorganic contaminants that might leach out of the boron specific resin (TOC, silica and sodium, among others). In addition it was desired to determine the operating cost and the kinetic ability of the resin to operate at significant space velocities.

For the project to be economically viable, it had to provide boron free feed water to the mixed beds, and the mixed beds had to obtain significantly longer throughput prior to leakage of any other ion. It was expected that the next ion to leak after boron would be silica.

Analytical Methods

Sample collection procedure; Samples were collected in 250ml PTFA sample bottles that were rinsed at least five times with UPW. The sample bottles were filled with UPW and allowed to condition for several weeks prior to the actual sample collection. Teflon tubing was plumbed into the selected sample locations and allowed to continuously rinse to drain. At the designated sample collection time, the sample was directed into the sample bottles. Each bottle was rinsed with sample water an average of three times before the sample was collected. After the sample collection was completed, the bottles were capped and labeled with sample collection date/time/and location. Separate sample bottles were used to collect the samples for Silica, Boron, Trace Metals, and Ion analysis. This was done to prevent/minimize cross contamination during the sample preparation and analysis.

Methodology

Silica was analyzed using the Hach Colorimetric method in grab sample mode on the Series 5000 Silica analyzer.

Boron and Trace Metals were analyzed on the ICPMS.

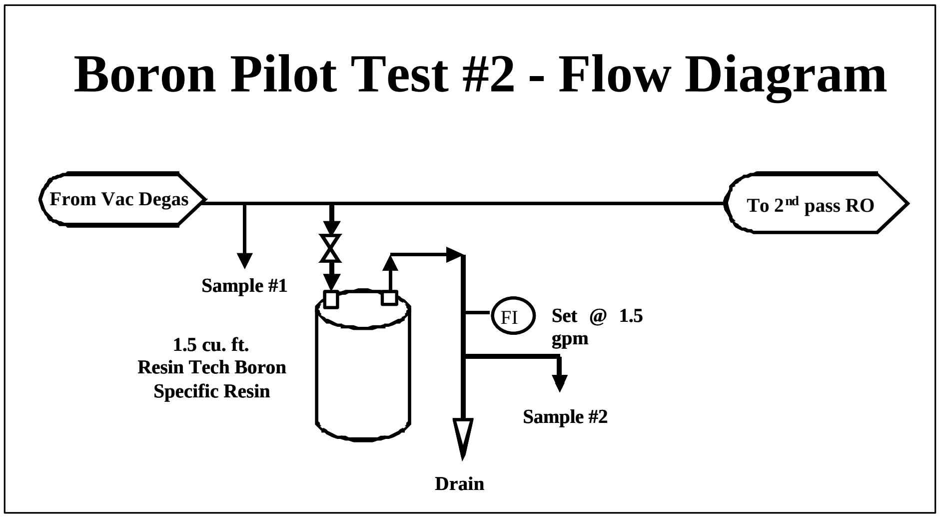
Ion analysis was performed using the Dionex DX-500 Bench-top IC analyzer from grab samples. TOC data was measured and recorded using the Anatel A-1000 TOC portable analyzers.

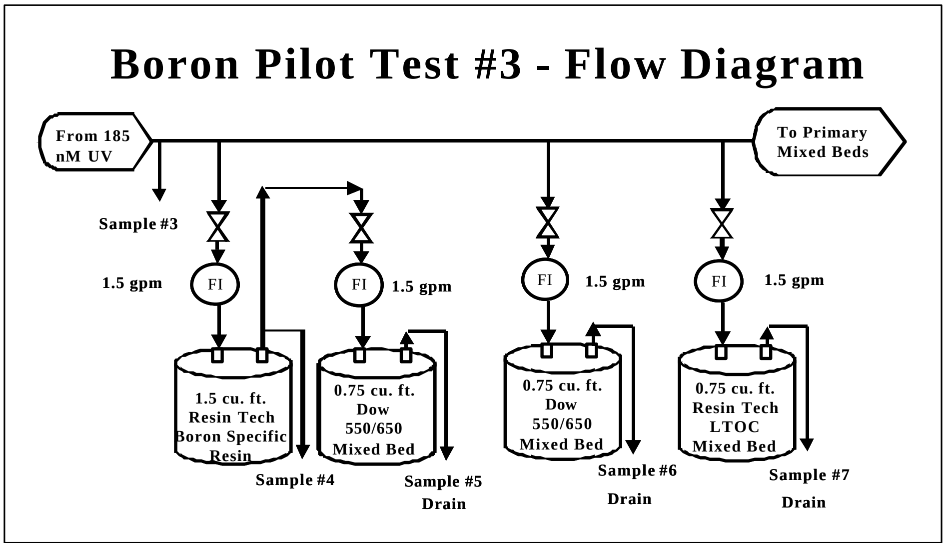
Pilot Plant Description

The Boron Pilot testing was completed in the three locations. Pilot 1, which was located in the raw water feed, was determined to be ineffective because the analytical measurements could not be accurately determined due to the high background interference. Pilots 2 and 3 were operated on a long-term basis. Pilot 2 was set on post vacuum degasification. It was a single column of boron specific resin as noted below. Pilot 3 was installed on Post 185 UV prior to the primary mixed beds. It was set-up utilizing boron selective resin in series with the existing mixed bed resin and with a control mixed bed resin column. Samples were taken at multiple locations as indicated in the flow diagram. All samples were tested and reported.

Lab analysis consisted of the following:
UPW Lab: Testing/Analysis:

a) T.O.C.	on line	continuous	graphed weekly
b) Sodium	grab	weekly	graphed weekly
c) Trace Metals	grab	weekly	graphed monthly
d) Boron,	grab	weekly	graphed monthly
e) Cations	grab	weekly	graphed monthly
f) Anions	grab	weekly	graphed monthly
g) Silica	grab	daily	graphed weekly
h) Resistivity	on line	continuous	graphed weekly


Boron Pilot Test #2 - Flow Diagram


Boron Pilot Test #3 - Flow Diagram

Pilot Plant Data

The pilot plant operation was quite successful, as might be expected; otherwise we probably would not be presenting this paper. Boron was removed from both first and second pass RO effluents to below the limit of detection. Boron did not dump from the resin upon exhaustion. The mixed beds following the BSIX system and the RO system, operated to silica break without any detectable leakage of boron. The boron selective resin was successfully regenerated. Leakage of TOC leachables was manageable and leakage of inorganic ions negligible once the resin reached equilibrium.

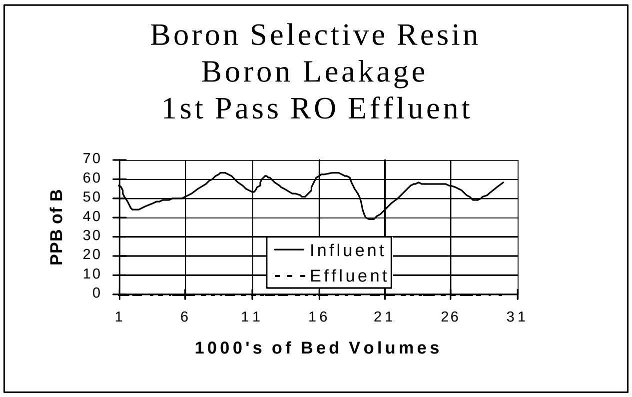
The pilot plant data clearly demonstrates the technical suitability of the BSIX resin to remove boron as part of an UPW system.

Raw Water Pilot

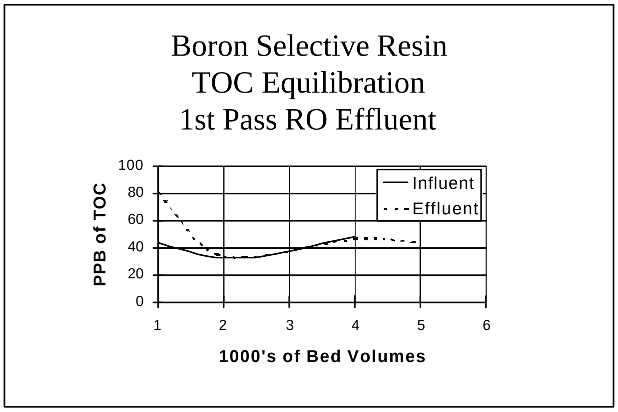
The early raw water pilot plant removed somewhere between 70% and 100% inlet boron, depending on which set of numbers we looked at. However, AMD's lab has no confidence what–so-ever in this data, due to problems of matrix elimination. We are not reporting any other data.

First Pass RO Pilot

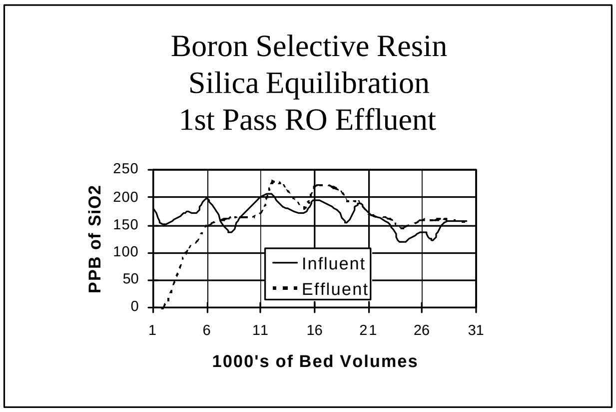
Boron leakage from boron selective resin, located after the first pass RO, was non-detectable until boron broke at approximately 30,000 bed volumes of throughput.



Inlet boron, after the first pass RO, varies between 40 ppb and 65 ppb (as "B"). The resin leached a significant concentration of TOC for the first 2,000 bed volumes. Thereafter, the inlet and outlet TOC's were essentially the same. TOC concentrations were in the 40-50 ppb range.

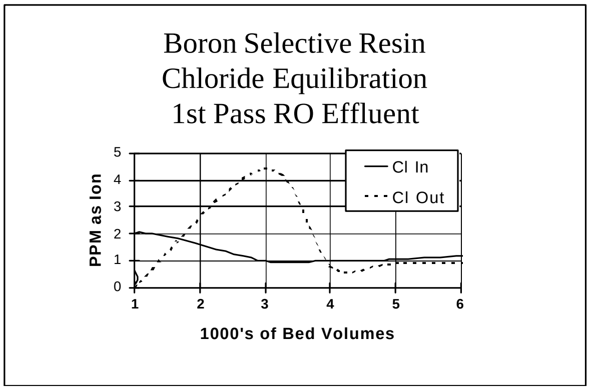


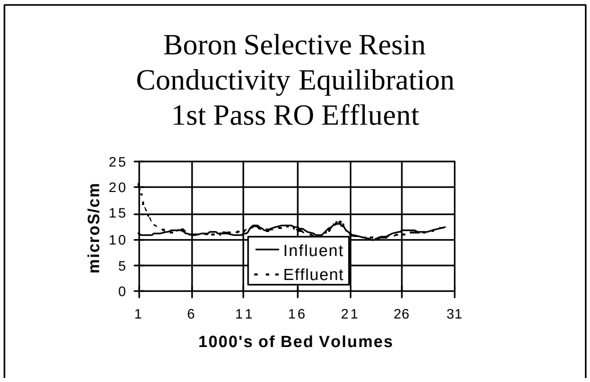
With respect to silica, a surprising result was that for the first 5,000-6,000 bed volumes, silica was removed.

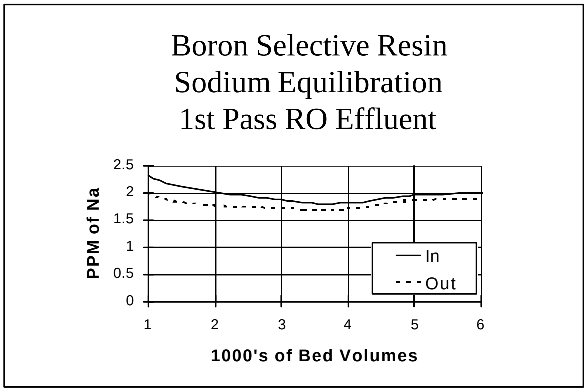


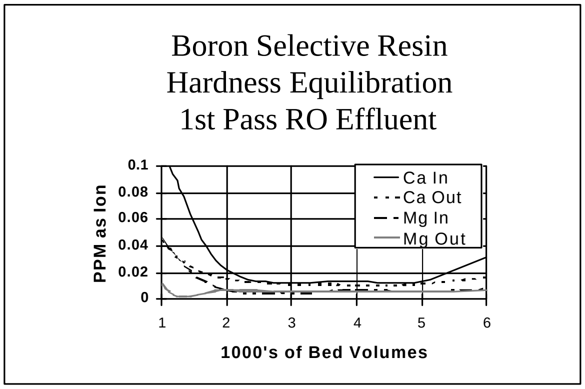
We had some concerns that silica would be dumped from the resin. However, the dumping phenomenon did not occur and the inlet and outlet silica concentrations stabilized after the first 6,000 -7,000 bed volumes. Silica removal is probably a function of the portion of the total anionic capacity that is strongly basic.

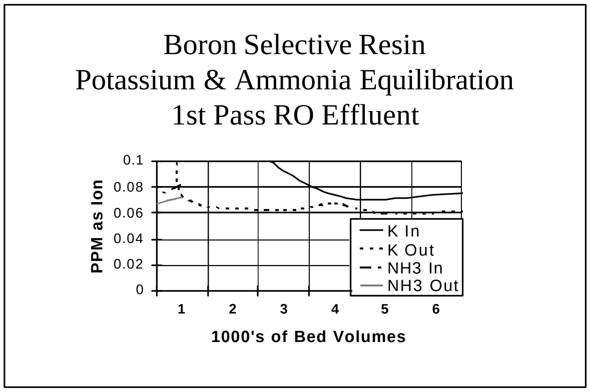
We tracked the leakage of various inorganic ions until they equilibrated. Due to restrictions on the length of this paper, it is not possible to show all the data. However, with the exception of chloride, other ions were removed initially, and then rapidly reached equilibrium with the inlet concentrations.

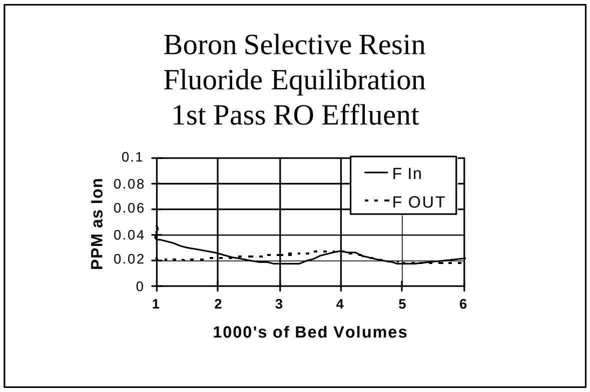




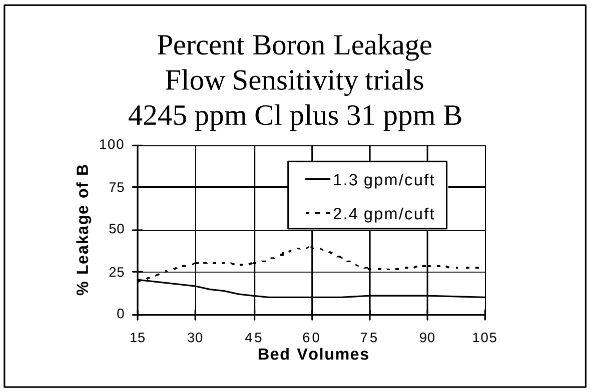

Boron Selective Resin
Sodium Equilibration
1st Pass RO Effluent

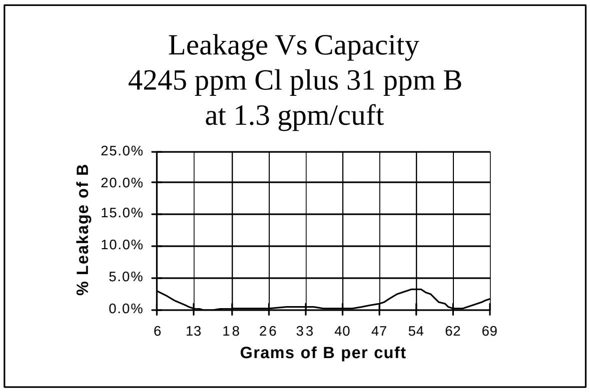

Boron Selective Resin
Hardness Equilibration
1st Pass RO Effluent


Boron Selective Resin
Potassium & Ammonia Equilibration
1st Pass RO Effluent


Boron Selective Resin
Fluoride Equilibration
1st Pass RO Effluent

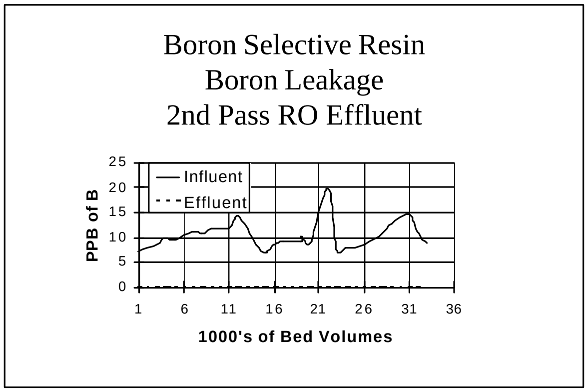
The capacity of the boron exchange resin for boron was approximately 100 grams of boron per cu. ft., very similar to laboratory results with higher boron concentrations. The initial pilot plant was operated 1gpm/cu. ft.; a subsequent exhaustion performed 2 gpm/cu. ft. produced very similar results.


Percent Boron Leakage
Flow Sensitivity trials
4245 ppm Cl plus 31 ppm B

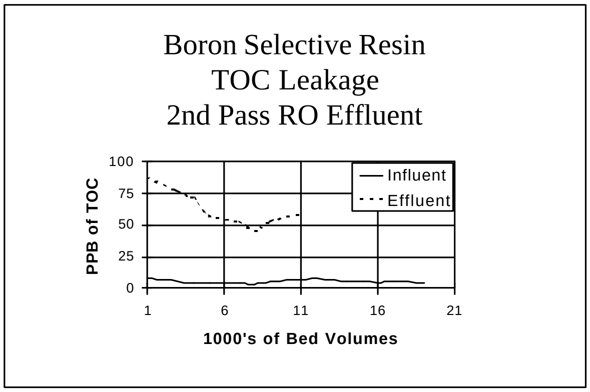

Leakage Vs Capacity
4245 ppm Cl plus 31 ppm B
at 1.3 gpm/cuft

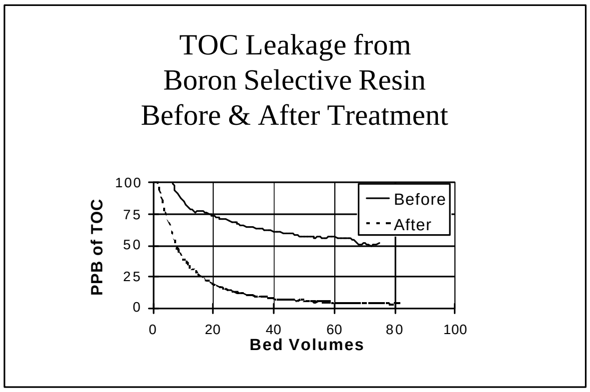
Second Pass RO Pilot

The boron selective resin located after the second pass RO system also showed non-detectable boron leakage, throughout the length of the pilot test program (approximately 8 months).



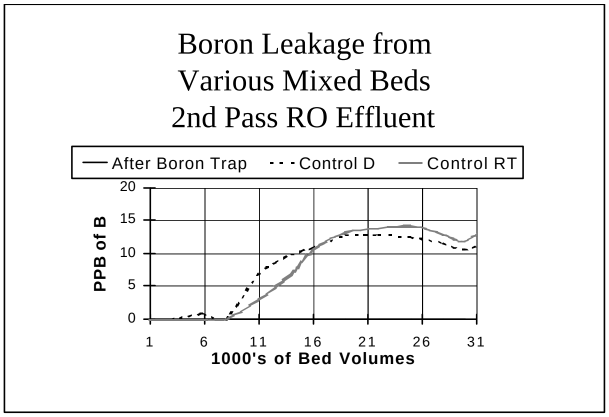
TOC leakage from the boron selective resin in this location was less than good. Even after thousands of bed volumes of the thru-put, TOC leakage was in the neighborhood of 40 - 50 ppb. A subsequent test with specially prepared boron selective resin demonstrated that the majority of this TOC could be removed, however the lowest baseline leakage of TOC that we obtained in these tests was in the neighborhood of 4 – 5 ppb, much higher than is typically acceptable in ultrapure water systems.

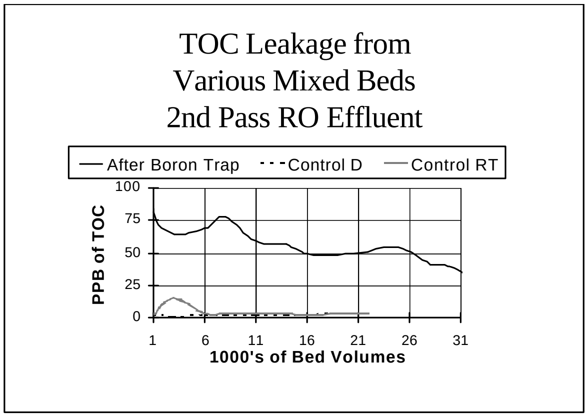




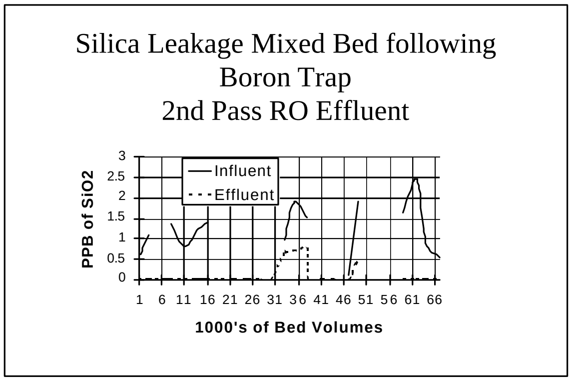
Other than a tendency of the freshly regenerated bed to leach a little bit of chloride ion, the inorganic leachables were practically non-existent, certainly well within the limits of feed water to the primary mixed beds.

Boron leakage from the control mixed beds showed that boron broke at approximately 8,000 bed volumes.





This is very similar to the performance of the full scale mixed beds. The mixed bed following the boron trap did not break on boron, but did break on silica at approximately 31,000 bed volumes, demonstrating that the boron selective resins increased the mixed bed throughput by a factor of approximately 4.



Silica breakthrough of the mixed bed following the boron trap occurred at approximately the point where the calculation shows that the resin would be exhausted to alkalinity break.

Due to concerns about TOC leachables, the BSIX resin may not be suitable for use following the second pass RO, at least for the most stringent of applications. Fortunately, the capital cost of placing the BSIX system after the first pass RO system is similar to that of the second pass RO, since the increase in equipment size is offset by the less expensive material of construction.

More work is needed to produce a BSIX resin with low enough TOC leachables to take advantage of the lower operating cost associated with the second pass RO location.

Regeneration

Boron selective resin is regenerated in a two-step process. In the first part of the process the pH is reduced. Reducing the pH, protonates the coordinate exchange sites, thus eliminating the chelating bond between the resin and the boron.

Boron Selective Resin Regeneration

- Backwash
    - Flow 2-3 gpms/sqft
    - Time 10-20 minutes
- Acid Injection
    - Dose 4 lb per cuft of HCl (or 6 of H_2SO_4)
    - Con 3-5%
    - Time 30-40 minutes
- Acid Displacement
    - Flow Same as for acid
    - Vol 7.5 gal per cuft
- Acid Rinse
    - Vol 40 gal per cuft
    - Flow as it suits
    - Time as required to achieve volume required

After the boron is stripped with acid, the resin is returned to the free base form by regeneration with sodium hydroxide. This step is necessary to remove the protons attached to the coordinate sites and also to strip chloride and/or sulfate ions from the resin. This prevents inorganic leaching during the initial portion of the next service cycle.

- Caustic Injection
    - Dose at least 6 lb per cuft (probably more)
    - Con 4-6%
    - Time 30-40 minutes

- Caustic displacement
  - Flow Same as for caustic
  - Vol 7.5 gal per cuft
- Final Rinse
  - Vol 40-60 gal per cuft to 100 mmho endpoint
  - Flow As it suits
  - Time As required to achieve endpoint desired
- Typical Rinse volume required *

To 100	mmho	40-60 gal per cuft
To 10	mmho	80-120 gal per cuft
To 1	mmho	120-180 gal per cuft

* Note: Rinse volumes for new resin are about half the above

We confirmed that the capacity for boron is independent of the capacity for other ions, by regenerating the resin with caustic. Under alkaline conditions, the boron that is loaded onto the resin does not come off, but other ions do come off.

The boron selective resin can undoubtedly be regenerated hundreds of times. In the pilot plant the resin was regenerated a total of 3 times in the roughly one year period that the various pilot plants operated. Since this is a macroporous anion resin, it is anticipated that the useful life will be in excess of 5 years. Certainly there was little change in the resins properties during the year that the pilot plant operated.

Boron Selective Resin Attributes

Attribute	New	One Year Old
Total Capacity meq/ml	0.95	0.89
Moisture	48.8%	52.2%
Whole Beads	100%	99+%

Economics

Short cycling mixed beds for prevention of boron leakage is an expensive and labor-intensive process. The major cost associated with this process is the large volume of ultrapure water used in the regeneration of the resin and the cost associated with the waste treatment of that water. In addition, the chemical costs and manpower required to support the additional regenerations are also are significant. Boron selective resin is currently about 3 times the cost of ordinary anion resin and represents about half the cost of a completed installation.

The results of the pilot test show that the operating cost of a boron selective trap is quite favorable, as compared to the cost of short cycling a mixed bed. A return on investment will occur somewhere around two-years after system start-up, based on the design configuration implemented in the pilot plant #2. Once the original capital investment is recovered, the cost of ownership of the boron selective resin system is approximately 75% less expensive to operate, as compared to short cycling a mixed bed ion exchange system. In addition, boron selective exchange saves approximately 1% of the water used by the typical ultrapure water site, which in some cases can be tens of millions of gallons per year.

Summary

Boron selective exchange is a practical and economical method of removing boron, as part of an UPW system. The resin is capable of reducing boron to non detectable levels from either first pass or second pass RO effluents and allows the mixed bed polishers to operate to the breakthrough of the next ion, which in most case is silica. This in turn can extend the throughput of the mixed beds by 3 to 4 times. Boron selective resin does not add any objectionable contaminants to the product water, although the question of TOC leachables, at this time, probably prevents its use after the second pass RO. Compared to other methods of operation, this is one of the best available technologies for boron removal.

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Company Profiles

AMD

AMD is a global supplier of integrated circuits for the personal and networked computer and communications markets. AMD produces processors, flash memories, and products for communications and networking applications. AMD processors, including the AMD-K6-2, AMD-K6-III and AMD Athlon product families, power computers manufactured by nine of the top ten computer OEMs in North America.

AMD's mobile processors are used in more than 50 percent of notebook computers sold in the retail market to consumers and small businesses. Founded in 1969 and based in Sunnyvale, California, AMD had revenues of $2.5 billion in 1998. (NYSE:AMD – news). Additional information about AMD and its products is available at http://www.amd.com/news/news.html.

Ultrapure & Industrial

Ultrapure & Industrial is a service exchange DI and equipment supply company. They hold the local Culligan franchise for the Austin area. Ultrapure & Industrial services the semiconductor market with exchange tank DI systems. They are known for their entrepreneurial spirit and ability to respond very rapidly to a customers needs. They also provide very pure and carefully regenerated resins for the exchange tank market.

RESINTECH, Inc.

ResinTech is a manufacturer and supplier ion exchange resins. They are known for their leading edge technical support and high quality products. ResinTech is actively involved in research to provide the purest resins to the semi-conductor market and are the only resin manufacturer currently actively pursuing applications research.

Bios

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.

Dan Wilcox is a Facilities Engineering Section Manager for AMD in Austin, Texas. His responsibilities include supporting ultrapure water, chemical, CMI slurry, wastewater, process cooling/heating water, and exhaust scrubber systems for AMD's Austin wafer fabs. Prior to working at AMD, Dan was an Engineering Manager for US Filter in Colorado Springs. Dan is a graduate of Northeastern University in Boston, MA with a B.S. in Mechanical Engineering.

Scott Walsh is a Semi Conductor Sales Manger for Ultrapure and Industrial Services. His responsibities include: providing technical solutions to customer requests in all water related aspects of ultrapure water and reclamation, coordinating engineering through equipment installation and maintenance, including project management.

Prior to joining Ultrapure and Industrial Services, Scott was a Project Manager for Radian, Inc. His duties included sales of Radian's engineering services and related project development and project management in the Electronic and Mechanical Engineering Group. His experiences range from mechanical product development, to marketing of finished product to related fields of circuit board design and development and production.

Marcel Montalvo is Senior Fluids Engineer for AMD Austin Texas. His responsibilities are design and sustaining engineering of ultrapure water, chemical, CMP slurry, and wastewater at the AMD Austin facilities. Marcel has over 20 years of ultrapure water, wastewater and chemical experience.

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