

# Start-up and Operation of a Zero Liquid Discharge Process for Boron Recovery from FGD Wastewater

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**KEYWORDS:** Trace Contaminant Removal, Selective Removal, Boron, Boric acid, Borate, FGD Wastewater Treatment

**Abstract:** Boron can be present in the wastewater of FGD scrubbers and must be removed. Dow Water & Process Solutions and Infilco Degremont, Inc. have developed an end-of-pipe system to remove boron contamination down to required discharge limits. This report will present the results of a successful plant start-up and operations.

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Waste water from Flue Gas Desulfurization (FGD) processes is experiencing ongoing scrutiny. By its very nature, this stream largely contains non-hazardous salts with traces of contaminants. Thus one strategy for dealing with this stream is to remove the trace contaminants and allow discharge of the non-hazardous salts.

This paper will focus on work on selective removal of boron from FGD waste water and the start-up and operation of a full scale treatment system. This paper follows extensive lab and pilot testing of the treatment process.

## Background

Boron is a paradoxical contaminant to deal with in waste water. From a health standpoint, at low levels it is a micronutrient for many plants and

animals while at higher levels it is a poison. Different plants can withstand different boron levels. For example, the optimal boron concentration range is 0.3–0.5 mg/L for citrus and grapes but is 0.5–0.75 mg/L for corn. Boron levels even slightly higher are detrimental to these crops. (1)

Boron has been linked to potential human health problems. Boron is readily absorbed from the gastrointestinal tract and shows some accumulation in bone. There is no evidence that boric acid is degraded in the body. Boron is a suspected essential trace element for humans, but this is yet to be proved. The Health Reference Level for boron has been set at 0.7 mg/L. (2)

The US EPA has prepared a document in 2008 titled **Health Effects Support Document for Boron** (3) where they

conclude that “boron does not occur in the public water systems at a frequency and at levels of public health concern at the present time.”

The WHO limit for boron is set at 0.3 ppm for drinking water and there is some speculation that this limit will be increased to 2.4 ppm. Thus it has been left to state and regional regulatory agencies to set limits on boron discharge in waste water. Currently levels in the tens to hundreds of ppm are under discussion.

Since boron is naturally occurring in some coal deposits, (4) it is logical that it will accumulate in the scrubber water from a flue gas desulfurization (FGD) process.

### Removal Options

The most prevalent treatment options for boron have been discussed previously (5).

- Reverse Osmosis (RO)
- Coagulation-precipitation
- Non-selective ion exchange
- Selective boron removal media

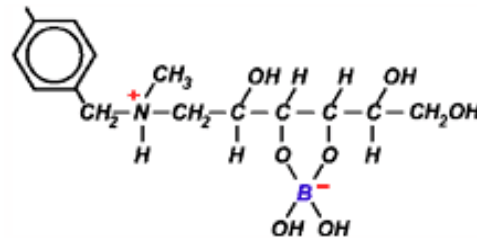
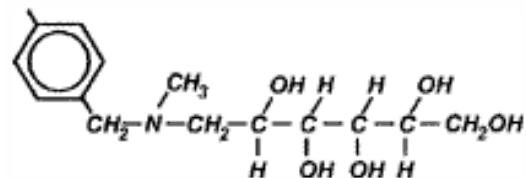
Due to the presence of high background levels of non-hazardous salts, reverse osmosis was not a viable option. RO merely splits the stream into salt rich and salt lean streams that will require further treatment. Coagulation precipitation was not feasible due to the relatively low concentrations of boron present in the waste water that are already below the solubility limit for common boron salts. Boron has a relatively low selectivity for anion exchange resins so the high

concentrations of sulfate and chloride make this option unacceptable.

### Boron Selective Resin

Boron selective resins (BSR) are available from a number of ion exchange producers. Most are based on macroporous styrene divinylbenzene copolymers.

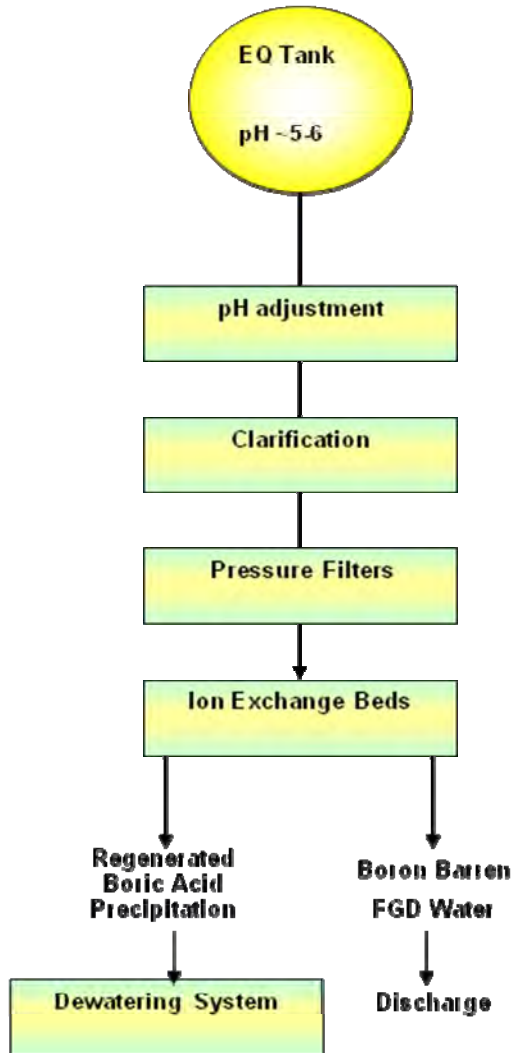
#### *Structure of Boron Selective Resin in the Free Base form and B loaded form*



The glucose molecule is believed to exist in the chair form where a pair of axial alcohol groups project away from the glucose ring. These groups are in a desirable confirmation to form a cis-diol with the borate molecule, eliminating a water molecule and forming a very stable complex. Once the complex is formed, it can be disrupted with acid conditions that hydrolyze the complex and release the borate. Under these same conditions, the tertiary amine group acts as an acid absorber to load with an acid molecule. When the resin is in the conjugate acid form, it will not absorb a borate molecule. Thus the

resin must be converted from the acid conjugate form to the free base form by neutralizing with base to complete the regeneration process.

**Figure 1. Conceptual Process Design**



Simply removing boron from an FGD wastewater stream is not sufficient if it means having to dispose of the concentrated boron waste into the same receiving discharge source through a different pipe. A zero liquid discharge component of the process is needed to complete the work. Once the boron is removed from the wastewater it needs to be recycled, reused or converted to a

solid form that can be transported and sold or disposed of.

### Methods Section

Boron analysis was performed by a colorimetric method using Azomethine H. See Appendix 1. The method is linear from 0.25 to 5 ppm with a detection limit of 0.2 ppm. Samples were diluted as needed to put them into the linear response range. The standard was Boric acid, purchased from a commercial supplier. All concentrations were expressed as ppm of B calculated from boric acid.

### Laboratory Testing on FGD Waste Water

FGD wastewater was supplied by an eastern US coal fired power plant (Source 1) for the purposes of these initial tests. Due to shipping and storage, some precipitate formed and was left in the bottom of the shipping container, not included in this testing. The clear, room temperature effluent was pumped through a bed of Boron Selective Resin and fractions of the treated water analyzed for boron.

Figure 2 shows that boron was removed from the FGD wastewater down to the detection limit (0.5 ppm B) for about 17 bed volumes until the boron started to break through. Complete breakthrough occurred between 20 and 25 bed volumes. FGD wastewater was also obtained from another source (Source 2) and tested with similar results. Figure 3.

Acid regeneration of the boron selective resin was also performed. See Figure 4. The acid eluted the boron as a

concentrate with the peak concentration of about 5,000 ppm B and an average concentration for the entire peak of about 3,000 ppm B. The acid regenerated resin was rinsed with water then neutralized with a NaOH rinse. The resin was used again in a column loading study shown in Figure 2 as column study 2. As can be seen from the figure, the second loading run is essentially the same as the first loading run.

### **Boron Precipitation Studies**

The concentrated boron recovered from the ion exchange operations was used to investigate precipitation of the boron into a solid. Jar tests were performed with a series of divalent cations and pH adjustment. They showed that almost 80% of the boron could be precipitated from solution. This result meant that the basic outline of a process was possible; use of a boron selective resin to remove the B from the FGD waste water, regeneration of the resin with acid and precipitation of the boron from solution with divalent cations and pH adjustment.

### **Acid Regeneration Studies**

Strong mineral acids such as HCl or H<sub>2</sub>SO<sub>4</sub> are required to disrupt the association of glucose-borate complex thus releasing the boron to elute from the media. See Figure 4.

The chemistry of the attachment of the N-methyl glucamine to the benzyl ring of the styrenic plastic backbone results in a secondary amine functional group. These amine groups will protonate under strong acid conditions to act as an acid absorbing group, in effect consuming an acid molecule during the

elution. Further testing of the resin while it is still in the acid conjugate form showed that boron would not load onto the resin from the FGD solution. The resin needs to be post neutralized with base to completely restore it for the next loading cycle.

### **Proof of Concept Evaluations**

A series of proof of concept tests were conducted to compare the feasibility of continuous ion exchange and fixed bed processes (5). An eastern US coal fired power plant generously supplied 1,000 liters of fluid for this lab testing. The conclusions follow:

1. Boron could be effectively removed from FGD waste water to levels of less than 1 ppm B.
2. Boron loading on the media was optimized at 5.71 g B per liter of resin.
3. Boron can be regenerated off the resin with acid and the B mass balanced between loading and elution.
4. Optimization of the regeneration resulted in increasing the concentration of the boron to 4,000 to 5,000 ppm levels.
5. Cycle testing allowed for the optimization of the amount of acid and rinse water due to their obvious impact on the overall economics of the process.
6. Testing showed that fixed and continuous ion exchange process removed boron from the FGD wastewater, used similar amounts of acid for regeneration, and used similar amounts of base for neutralization. The CIX offered the advantage of reducing the volume of water used. Economic analysis of the data

showed that a fixed bed equipment configuration was less capital intensive, providing greater redundancy and was thus the best option.

A typical acid elution curve (Figure 5) shows that a portion of the boron eluting before the elution of the bulk of the excess regenerant acid.

The base use is already economized by the use of a patented continuous recirculating fast rinse process. This work is described in "Alkaline regeneration of N-Methyl-D-Glucamine Functional Resins" WO 2006/110574 A1 by Charles Marston. (6)

### **Field Testing of the Process**

A three month field pilot test was performed on site at an eastern coal fired power plant to validate the results of the proof of concept testing that was done earlier. The pilot unit was supplied with FGD wastewater at the discharge point. The fluid was filtered and collected in storage tanks for use in the columns studies.

The boron concentration in the feed waste water varied considerably. It fluctuated between 250 and 350 ppm over the course of the testing. While the feed boron concentration changed, it did not impact the removal efficiency for the boron selective resin. In all cases boron removal was measured to <5 ppm.

The results of the field pilot plant confirmed the results of the proof of concept testing. Fresh and warm FGD wastewater from the process did not cause any problems with the

performance of the resin or the boron precipitation steps.

A typical elution profile is shown in Figure 6. The shape of the elution curve is very similar to the data generated in the proof of concept testing. The same basic steps of boron removal, acid elution, acid rinse and resin neutralization were performed. By running multiple column studies, these basic process steps could be optimized to make the most efficient use of chemicals and rinse water.

### **Field Pilot Conclusions**

Field pilot optimization and testing lead to the following conclusions:

- The concentration of the boron in the recovered concentrate was increased by approximately 66% from the results in the proof of concept pilot testing.
- The volume of boron concentrate recovered was reduced by approximately 66%.
- The acid usage was reduced by approximately 37%.
- Caustic for the final neutralization step was reduced by 40%.

### **Simulated Aging Study of the Boron Selective Resin**

As part of the pilot study, a simulated resin aging study was performed to determine if there were any detrimental effects of long term exposure of the resin to the FGD wastewater. By using a fast flow rate through a small amount (1 cubic foot) of resin, the exposure was the equivalent of 4.5 years of service for the media. The results of that testing confirmed that there was no significant

deterioration of the boron selective resin.

### **Commercial Installation**

Based on the laboratory evaluations, proof of concept testing, field pilot plant evaluations, an economic model of the process was developed, submitted to the customer and approved for full scale implementation. The installed system comprises two resin trains of two vessels each to be operated in a lead-lag configuration. Service water, 98% Sulfuric Acid, 30% Hydrochloric Acid, and 50% Sodium Hydroxide are plumbed to all vessels. Vessels are controlled primarily on volume throughput, as the boron analysis process takes several minutes to complete. Acid regeneration is primarily performed with sulfuric acid, because of economic reasons and that the concentrated boron waste produced is lower in acid than when using HCl. HCl is used periodically to clean the beds of any accumulated calcium to avoid sealing off the active sites on the beads.

The process design of two lead-lag trains offers redundancy of operation and flexibility in operations. Typical daily operation involves one resin train operating in lead-lag configuration. Once the lead bed is exhausted, it is taken out of service for regeneration and run on the lag bed alone.

### **Block diagram of the process**

A computer rendered 3D layout of the boron waste water treatment system is shown in figure 7. The design is for a 250 gpm operation.

The process consists of two lead-lag beds of the boron selective ion exchange resin. The plant layout shows chemical storage, filtration equipment, boron precipitation and dewatering system.

### **Analytical Method for Boron Analysis**

On line boron analysis was provided by a new inline system developed by NextChem. The method consists of acid-base pH adjust followed by back titration after mannitol addition (7).

### **Performance Data for the system**

System began operation in early January 212, with regulatory compliance of <82 ppm achieved on-time in early February. Figure 8 illustrates the influent and effluent concentrations achieved based on monitoring data over a two month period. All effluent readings from the system to date have been below the compliance level. Figure 9 illustrates the boron levels in the reclaimed acid and regeneration waste through March. These have both reached stable levels slightly lower than what was predicted in the pilot testing, which can be attributed to the acid that is diluted in situ versus a pre-diluted acid and less control over collection windows. Figure 10 shows a typical elution/regeneration, which compares favorably to the results obtained in the pilot testing. The higher conductivity levels can be attributed to rinses being less effective in a larger vessel versus the smaller pilot vessels, but have not adversely affected rinse volumes.

### **Ongoing Boron Selective Ion Exchange Resin Analysis**

Tracking the condition of the boron selective ion exchange resin in this operation is of critical importance to the ongoing success and economics of this operation. Boron selective ion exchange resin samples are removed from the process after various periods of time of operation for lab analysis. The resin was tested for total exchange capacity, water retention capacity and magnified photographs were taken to examine the physical integrity of the media. This data was compared to virgin media and summarized in Table 1. The results show that after 7 months of service, the media has not lost any ion exchange capacity and water retention capacity of the media has increased only slightly.

Magnified photographs of the used Boron Selective media show negligible levels of broken beads. The resin is in very good condition.



The “as received” resin was also tested for accumulation of metals and precipitants. A standard test for calcium and iron fouling was performed that consisted of acid stripping the resin and AA analysis of the strip acid for Ca and Fe. Analysis showed <10 ppm Ca and Fe which indicates that no inorganic fouling has occurred. Samples were also analyzed by XRF to look for the presence of other metals. This analysis indicated that no significant levels of any

other metals have accumulated on the media.

Resin analysis will be performed on a regular basis throughout the life of the media so that the data can be used in the life cycle analysis.

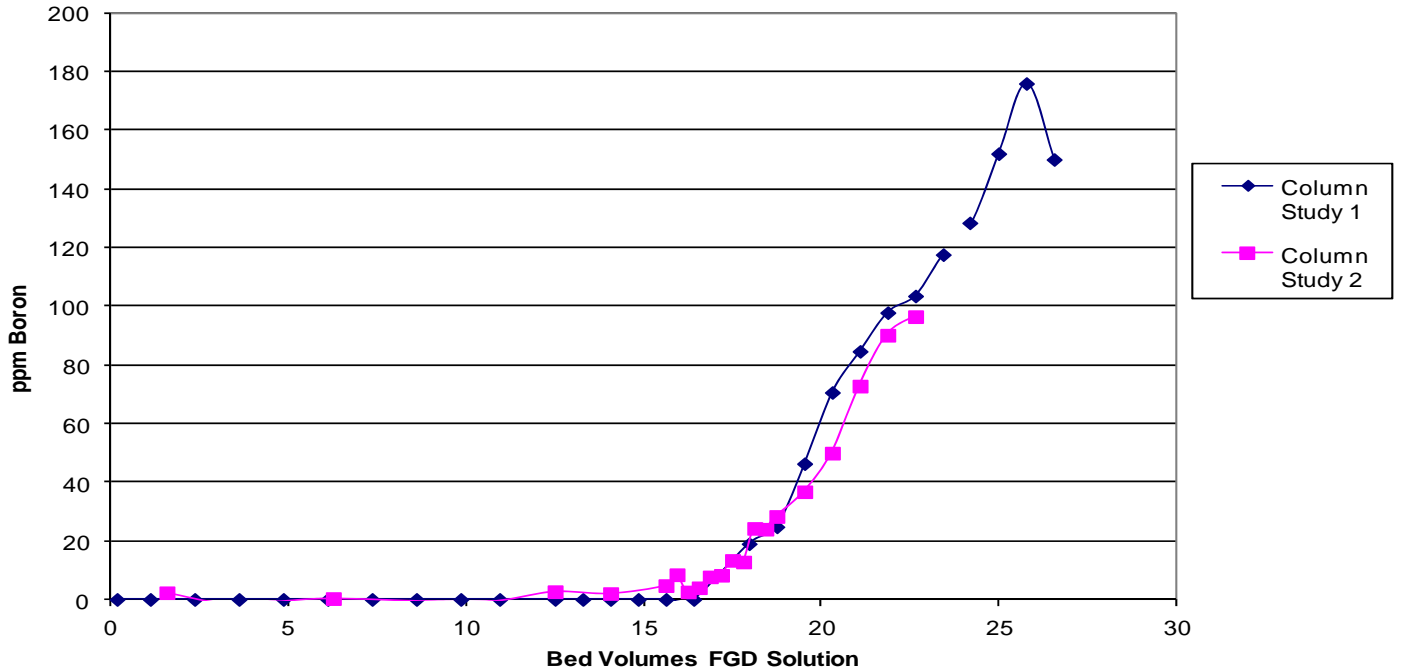
### **Economic Analysis**

The chemical operating cost for the process was calculated to be <\$5 per lbs of boron removed during the pilot and design phase of the project. Initial operating costs are well within this estimate and further refinements are underway.

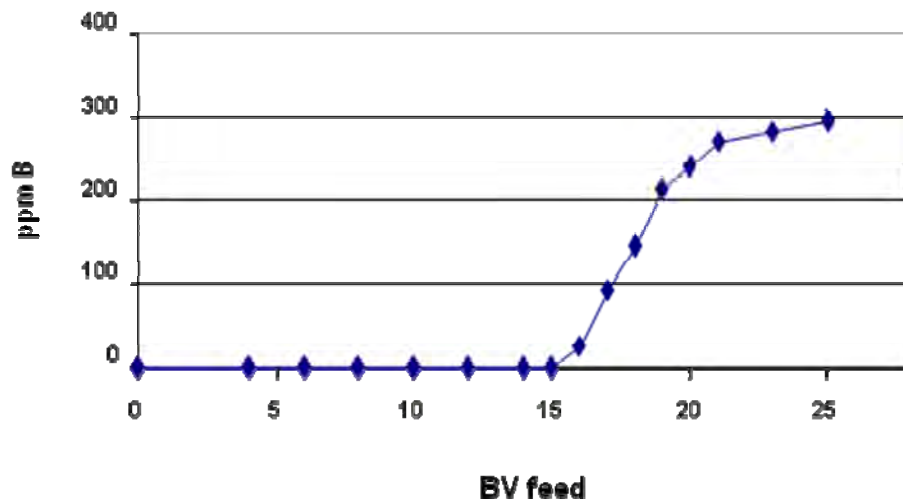
### **Conclusion**

In conclusion, boron can be selectively and effectively removed from FGD waste water at full scale.

**Figure 2. Boron removal column testing of FGD Wastewater from a coal fired power plant in the eastern US (Source 1).**

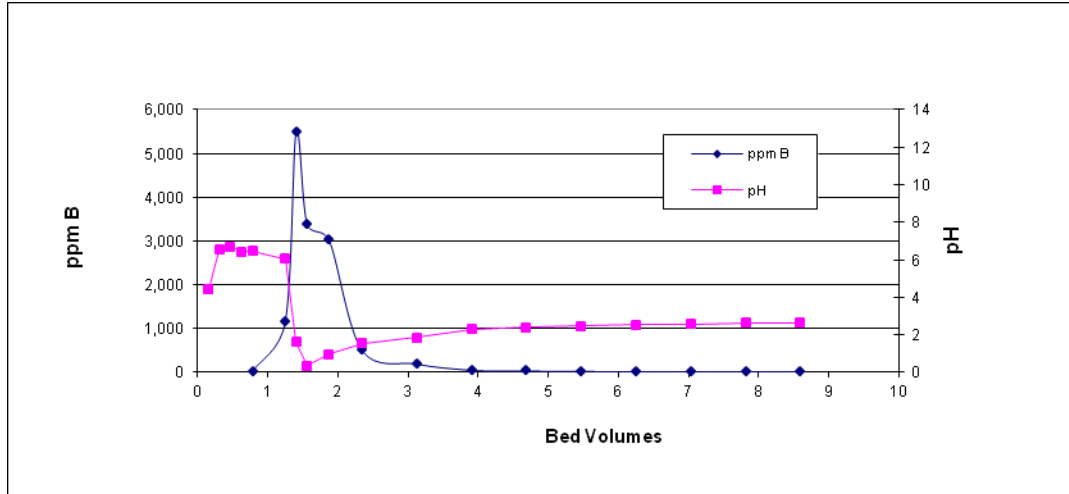


**Figure 3. Boron removal column study from FGD wastewater from a coal fired power plant in the eastern US (Source 2).**

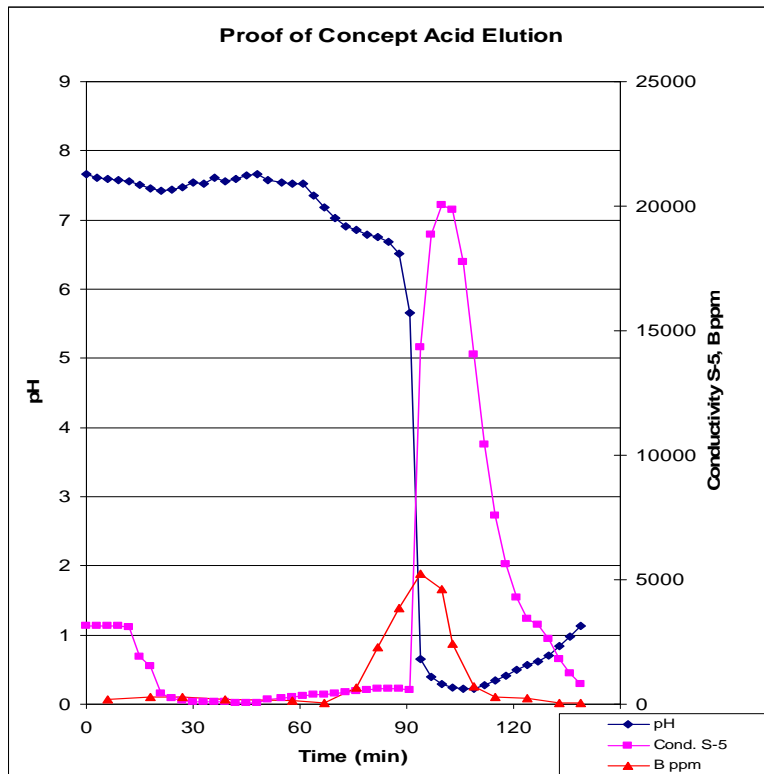




**Figure 4. Acid elution of Boron Selective Resin loaded with FGD waste water from Source 1.**



**Figure 5. Typical Regeneration Profile from Proof of Concept Testing**



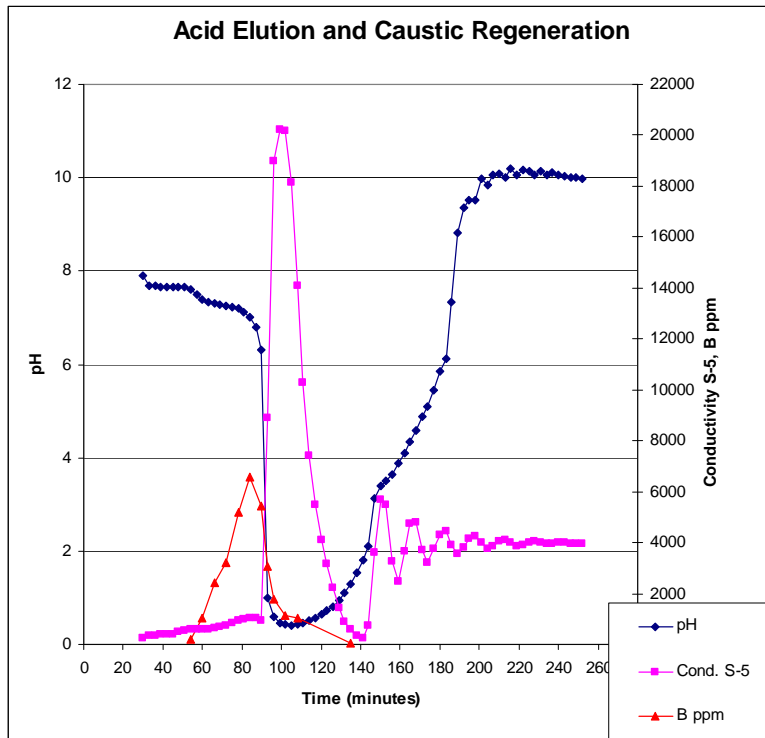
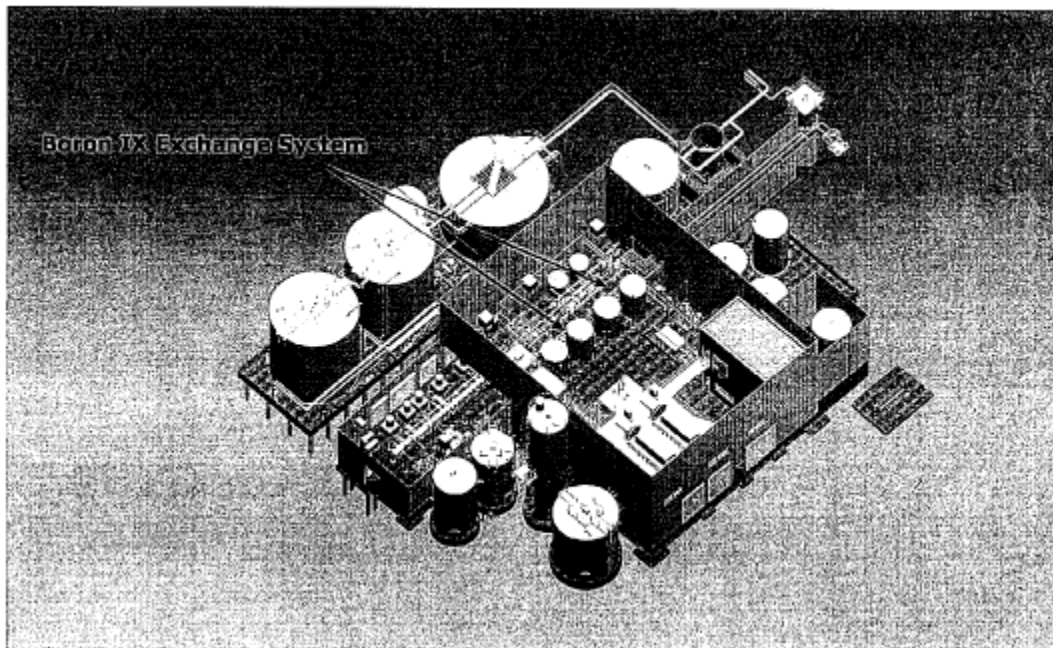
**Figure 6. Acid Elution profile from Field Pilot testing****Figure 7. Computer rendered 3D layout of the Boron waste water treatment system.**

Figure 8. System Boron concentrations, influent vs. effluent

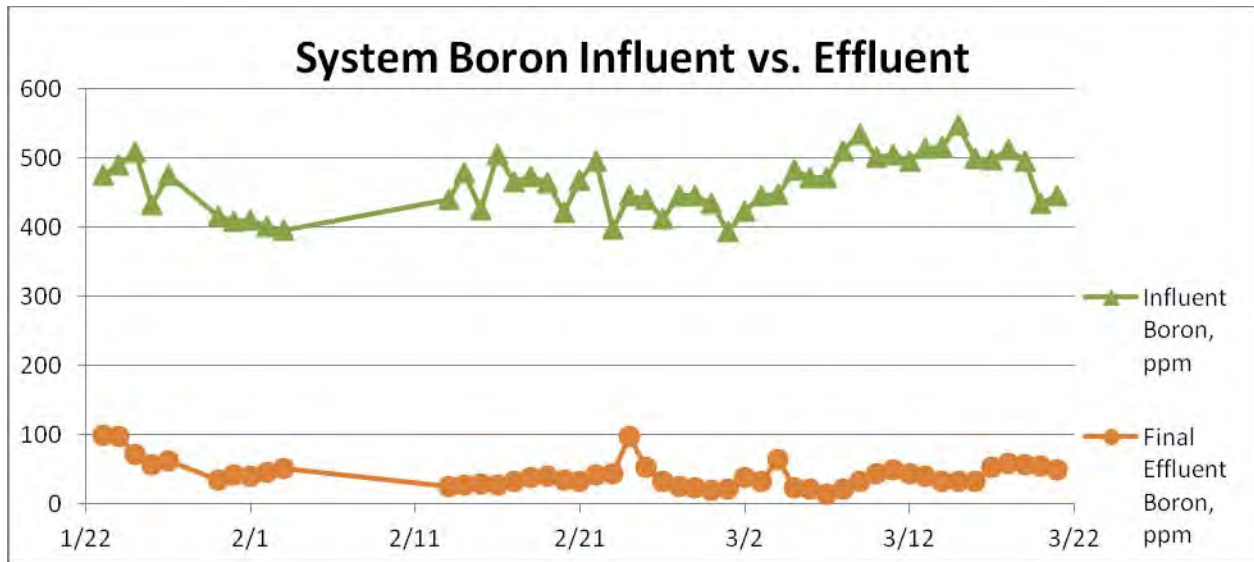
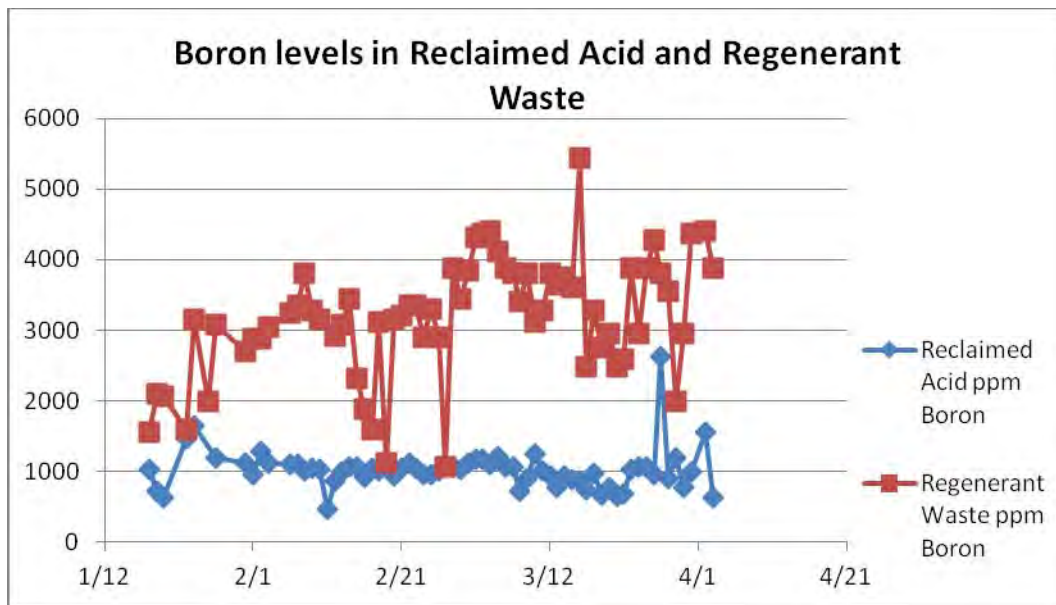


Figure 9. Boron levels in Reclaimed Acid and Regenerant Waste



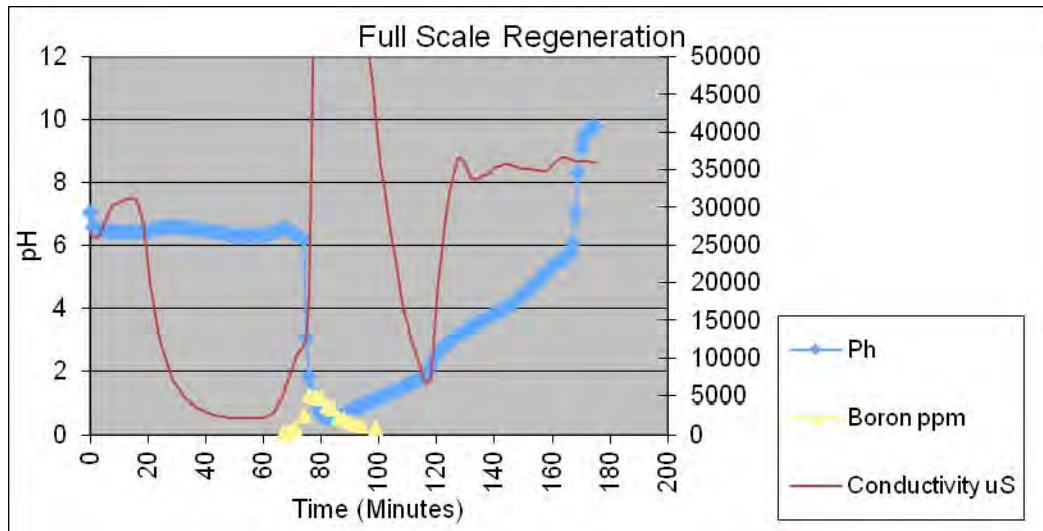
**Figure 10. Full Scale Plant Regeneration**

Table 1. Lab analysis of field used boron selective ion exchange resin and comparison to virgin media

Sample	TEC*/WRC**	4 Months Age	7 Months Age
Virgin	0.9/54.1		
Vessel 1A			0.9/54.6
Vessel 1B		0.9/55.5	0.9/56.2
Vessel 2A		0.8/56.2	0.8/55.7
Vessel 1B			0.8/56.7
*Total Exchange Capacity			
**Water Retention Capacity			

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6. C. Marston (2006) WO Patent 2006/110574 A1.
7. Vendor technical information provided by Tim Pearson of NextChem.  
tpearson@nextchem-analyzers.com

## Appendix 1. Analysis of Boron

### Preparation of chemicals

**Azomethin H solution.** Dissolve 2 g of Azomethin H into about 160 mls of DI water. Once it is fully in solution add 6 g of ascorbic acid and bring into solution. Dilute to a final volume of 200 mls. Keep refrigerated. Typically lasts about 1 week.

**Reaction solution.** Combine 250 g ammonium acetate, 250 mls DI H<sub>2</sub>O, 80 mls of 20% H<sub>2</sub>SO<sub>4</sub>, 5 mls con. H<sub>3</sub>PO<sub>4</sub>, 2 g citric acid and 1 g EDTA. Keep refrigerated.

**Boron Standard solution.** Prepare a boron standard solution that is conveniently diluted to prepare a standard curve from 0.5 to 5 ppm as B in 5 mls aliquots.

Boron samples and unknowns should be diluted so that they are in the expected range of 0.5 to 5 ppm as B.

### Analysis

Dilute B standard solution for standard curve as 5 ml aliquots of solution. Dilute unknowns so that they are in the expected concentration range of 0.5 to 5 ppm as B in 5 ml aliquots.

Combine the Azomethin H solution and the Reaction solution on a 1:1 ratio immediately before needed. Prepare enough solution so that 2 mls of solution are available for each B test and the blank. This solution rapidly degrades so do not use for more than one set of tests and standards.

Add 2 mls of the combined Azomethin H/Reaction solution to 5 mls of the B standards and unknowns. Immediately mix and store in a dark place for 30 minutes to allow color to develop. Measure the absorbance at 412 nm against a blank of 5 mls DI water and 2 mls of the combined Azomethin H/Reaction solution. Plot the absorbance versus the B concentration. Determine the linear correlation and convert the absorbance for the unknowns to a B concentration and multiply by the dilution factor to get a final B concentration.