A Zero Liquid Discharge Process for Boron Recovery from FGD Wastewater

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ABSTRACT: Boron can be present in the wastewater of FGD scrubbers and must be removed. An end-of-pipe, zero liquid boron discharge process has been developed to remove boron contamination down to required discharge limits. This report will present the results of a successful three month pilot test.

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 common application for boron removal is from sea water. Boron is present in sea water at concentrations ranging from 4 to 7 ppm. Because of detrimental effects to citrus, the limit is often set at 0.5 ppm. Three techniques are utilized to mitigate boron: (1) increasing the dissociation of boric acid by increasing pH prior to reverse osmosis, (2) utilizing a second pass reverse osmosis system, potentially coupled with pH adjustment; and (3) development of improved boron rejection membranes. This last option is holding great promise as a cost effective way to deal with the issue.

Boron removal from aqueous solutions with conventional sedimentation and biological treatment processes have not been reported as successful.

Coagulation-precipitation processes are also not effective at reducing boron levels when the levels of boron are low. Boron salts are somewhat soluble. They are problematic as they form poly borate complexes under certain conditions. They are subject to hydrolysis so their solubility can not be determined directly. Calcium borate salts are slightly soluble at 1 g/liter or approximately 1,000 ppm. Since the molecule is 22.1% B, the resulting solubility is approximately 250 ppm as B. The presence of other cations and anions also impact this solubility making this issue a very complicated one.

Boron is present as boric acid so it is an anion and could be removed as such with an anion exchange resin. Unfortunately, boron is a “weak affinity” anion so it has a low selectivity coefficient for conventional anion exchange resins. In the presence of any of the common anions in water systems such as carbonate, chloride, or sulphate, any borate that is initially removed by the resin is quickly displaced by the other anions and released to the treated water.

Boron can be effectively removed from sea water and wastewater with boron selective chelating ion exchange resins. This is the only media identified as effective at removing boron.

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

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.

But 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. Once the boron is removed from the wastewater it needs to be recycled or reused or converted to a solid form that can be transported and sold for recycle or disposed. A zero liquid discharge component of the process is needed to complete the work.

Methods Section

Boron analysis was performed by a colorimetric method using Azomethin 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.

Scope of Investigation

The information discussed in this paper is the result of collaborative laboratory and field studies conducted by The Dow Chemical Company and Infilco Degremont in an effort to achieve unusually low boron concentrations in the wastewater discharge from a power plant FGD system.

For the purposes of organizing this paper, these development efforts can be presented in three stages; Laboratory Testing, “Proof of Concept” Column testing and Field Testing.

Laboratory Testing on FGD wastewater

Since Boron Selective Resins are well known to selectively remove boron from different wastewaters, it was necessary to see if the boron in FGD wastewater could be removed with this media.

At first glance, FGD wastewater is fairly briny water. Characterization of FGD blowdown from various coal power plants shows that TDS levels are in the tens of grams per liter range. Since this is in the same range as sea water, it seemed like a reasonable test to perform.

FGD wastewater was supplied by an eastern US coal fired power plant (Source 1) for the purposes of these initial tests. Since the fluid was shipped and stored before the testing, 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 1 shows that boron was removed from the FGD wastewater down to the detection limit 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 eastern coal fired power plant (Source 2) and tested in lab columns. See Figure 2. Similar removal results were obtained.
Acid regeneration of the boron selective resin was also performed. See figure 3. 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 1 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 loading from FGD wastewater was also investigated for sensitivity to pH. Samples of wastewater were pH adjusted to the desired pH, placed in contact with boron selective resin and allowed to come to equilibrium. The amount of boron left in solution was measured and loading determined by subtraction.

**Boron Loading vs. pH**

![Boron Loading vs. pH](image)

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 H₂SO₄ are required to disrupt the association of glucose-borate complex thus releasing the boron to elute from the media.

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.

Boron can be separated from the HCl by an ion exclusion method. Here the mixture of boric acid and HCl are added to a column of anion exchange resin in the Cl form and eluted with water. The chloride is excluded from the interior volume of the beads so it travels through the resin column faster than the boron. This separation is demonstrated in Figure 4.

While these column studies demonstrated the feasibility of the removal of boron from FGD wastewater, an insufficient quantity of fluid was available to evaluate a process. To this
end, 1,000 gallons of FGD wastewater was obtained from an eastern coal fired power plant (Source 2) for “proof of concept” testing under laboratory conditions.

Proof of Concept Testing Summary

During this phase of the testing, two equipment configurations were evaluated; a continuous ion exchange process (CIX) and a fixed bed process.

A series of loading and elution tests were performed to collect mass balance data that could be used to develop a set of operational parameters for the separation process. A typical elution profile is shown in Figure 5. The basic steps of an ion exchange regeneration are as follows.

1. Rinse off the FGD wastewater from the last loading step.
2. Elute the boron with concentrated acid to recover the boron concentrate
3. Rinse off the excess acid
4. Neutralize the resin with base in a closed loop recirculation fashion

The purpose of this phase of the testing was to optimize the various steps of the resin regeneration to minimize the chemical use, minimize the water use, maximize the boron concentration in the recovered boron and minimize the volume of recovered boron concentrate.

Conclusions from Proof of Concept Testing

1. Boron Removal from FGD waste water. Pilot testing showed that the Boron Selective Resin consistently removed boron from the FGD wastewater to levels of less than 1 ppm. Data from mass balances (MB) 2 to 4 show these low levels. See Table 1.

2. Optimization of B loading
During the testing (MB4) the B loading was increased to 5.71 g B loaded per liter of resin by increasing the feed flow rate. See Table 1.

Table 1. Mass Balance Results

<table>
<thead>
<tr>
<th>Mass Balance</th>
<th>B conc. in Barren FGD (ppm)</th>
<th>Flow rates (mls/min)</th>
<th>Boron Loading (g B/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB2</td>
<td>0.54</td>
<td>1,387</td>
<td>4.5</td>
</tr>
<tr>
<td>MB3</td>
<td>0.23</td>
<td>1,308</td>
<td>4.0</td>
</tr>
<tr>
<td>MB4</td>
<td>0.30</td>
<td>1,627</td>
<td>5.71</td>
</tr>
</tbody>
</table>

Table 2. Mass Balance Results

<table>
<thead>
<tr>
<th>Mass Balance</th>
<th>Boron Effluent Conc. (ppm)</th>
<th>Rinse water use (%)</th>
<th>Acid use (moles H+/liter of resin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB2</td>
<td>-</td>
<td>18.5</td>
<td>5.56</td>
</tr>
<tr>
<td>MB3</td>
<td>1963</td>
<td>15.6</td>
<td>4.17</td>
</tr>
<tr>
<td>MB4</td>
<td>1508</td>
<td>12.8</td>
<td>4.51</td>
</tr>
<tr>
<td>MB5</td>
<td>8180</td>
<td>7.5</td>
<td>1.39</td>
</tr>
</tbody>
</table>

It is very clear that the boron is regenerated off of the resin with acid. This point was not really in question based on the simple column studies that were done in the earlier lab work.

4. Boron effluent concentration optimization.
Optimization of the boron concentration during regeneration was desirable as it impacts the precipitation efficiency. The data shows that the boron concentration has been increased to the 4 to 5,000 ppm levels from earlier studies.
by tuning the acid wash water flow, the concentrated acid flow and the unit step times.

5. Optimize acid and base use for economic calculations

Optimizing the amount of acid used and the rinse water volume are of obvious impact to the overall cost of the treatment. Table 2 shows significant reduction in both the acid use and rinse water use in this testing.

The base use is already economized by the use of a 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. (5)

Unfortunately, due to the limited availability of FGD feed solution, completion of the optimization work would require access to larger volumes of fluid that could only be done on site at a coal fired power plant.

Technical analysis of the data showed that both a fixed bed 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, requiring less redundancy and was thus the best option. The field pilot was configured accordingly.

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 ranged by about 100 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 FGD wastewater from the process did not cause any problems with the performance of the resin or the following 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.

Summary of Field Pilot Testing

- 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%.

A simulated 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 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.

**Plant Flow Diagram**

A copy of the proposed plant flow diagram can be found in Figure 7. The FGD wastewater is pretreated by pH adjustment then sent to a clarifier and pressure filtration unit. This effluent is then sent to the Boron Selective Resin where the boron is removed and the treated effluent is directed to discharge. The system consists of the vessels holding the resin and tanks to hold service acid, service caustic, service water and reclaimed acid. The boron concentrate produced by the BSR system is sent to a dewatering system that recovers the boron as a solid.

**Economics of Boron Removal**

The unit operations of boron removal with a selective resin followed by precipitation, coagulation and filtration are by their nature sized differently. The ion exchange part of the process is sized based on the hydraulic flow rate and the concentration of the boron to be treated. Since the boron selective resin produces a boron concentrate, the precipitation, coagulation and filtration part of the process is sized by the output of boron from the ion exchange treatment.

This pilot data was used to generate a capital and operating cost for a system for consideration by the client. The chemical operating cost was determined to be <$5 per lbs of boron recovered.

A number of interesting observations have been made during the course of these investigations. A patent disclosure has been filed on these observations.

**Conclusions**

In conclusion, a zero liquid discharge for recovering boron from FGD waste water has been investigated, laboratory evaluated and pilot plant tested. The process uses a Boron Selective Resin that is very selective in removing boron from the wastewater as a concentrated stream. This boron concentrate can now be dewatered to generate a solid waste for disposal or sale.

**References**

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

![BSR-1 Boron Removal Column Study 1](image)

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

![BSR-1 Loading with FGD wastewater](image)
Figure 3. Acid elution of Boron Selective Resin loaded with FGD waste water from Source 1.

BSR-1 Regeneration with 7% Hydrochloric Acid

Figure 4. Separation of Boron from HCl with an ion exclusion process.
Figure 5. Typical Regeneration Profile from Proof of Concept Testing
Figure 6. Acid Elution profile from Field Pilot testing

Acid Elution and Caustic Regeneration

[Graph showing pH and conductivity over time]

- pH
- Conductivity S-5
- B ppm
Waste Water Treatment System
Boron Recovery

EQ Tank
pH ~5-6

FGD Chloride Purge
Alkaline Solution

pH adjustment

Clarification

Pressure Filters

Ion Exchange Beds

Regenerated Boric Acid
Boron Barren FGD Water

Dewatering System
Discharge

1st Rinse (Potable Water)
Acid Regenerating
2nd Rinse (Potable Water)
Caustic Neutralization

Figure 7. A block diagram of the Wastewater Treatment System for Boron Recovery
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 H2O, 80 mls of 20% H2SO4, 5 mls con. H3PO4, 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.