To the Graduate Council:

I am submitting herewith a thesis written by William O'Neil Rains entitled "State of the Art Technology for Aqueous Boron Recovery." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment for the degree of Master of Science, with a major in Chemical Engineering.

R.M. Counce, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor and
Dean of The Graduate School

STATE OF THE ART TECHNOLOGY FOR AQUEOUS BORON RECOVERY

A Thesis

Presented for the

Master of Science

Degree

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William O'Neil Rains

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Dedication

This thesis is dedicated to my parents

Lucinda Rains

and

Eugene O'Neil Rains

for fostering a perspective which encourages achievement.

And to

Rhonda McCann

for her consistent support.

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Abstract

This study identified several methods for recovering phenylated boron compounds and their decomposition by-products from industrial waste streams. The selected processes were ranked in accordance with pollution-prevention principles in order to identify the best option. The selected options were solvent extraction and sorption following a hydrolysis or oxidation pre-treatment. Laboratory data was collected for the potential sorption process using a pyridine-based polymer resin and regeneration using isopropyl alcohol.

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1. Introduction

1.1 Boron Occurrence in Industry

Boron is used in many industrial applications from glass-making to detergents to medicine. Some boron compounds of the most importance to industry are electron-deficient compounds such as boric acid and other tri-substituted boron compounds which behave as Lewis acids by virtue of the fact that they lack a complete octet of electrons. Their Lewis acid character makes these organic and inorganic boron compounds important as catalysts for a number of reactions. There are a number of organic boron compounds that are used in quantity in industry, but a group of the more common organoboron compounds are phenylated boron compounds.

Phenylated boron compounds are quite common in the waste waters of many industrial plants. Triphenylborane is a common catalyst in the plastics industry because of its ability to improve the linearity of polymer products (Cotton and Wilkinson, 1988). Another common phenylated boron compound, sodium tetraphenylborate, is used as a specific precipitant for cesium-137. When either of these compounds are present in wastewaters, their hydrolysis and degradation products are also present. As a result, many industrial waste waters may contain dilute amounts of tetraphenylborate anion, triphenylborane,

diphenyl boric acid, monophenyl boric acid, phenol, boric acid, and biphenyl or benzene. These waste waters may also typically contain dissolved salts.

1.2 Research Objective

The focus of this study is to determine an ideal state-of-the-art boron recovery process. The media to which the process is applied is an aqueous stream containing boric acid and organic boron species. The stream's boron concentration may be up to 400 ppm and it may contain up to 10% dissolved salts. The treatment options considered for the recovery processes are: evaporation, precipitation, reverse osmosis, solvent extraction, and sorption. To select the appropriate technology the selection criteria established for the processes are:

1) The process must reduce boron to less than 50 ppm though reduction to less than 5 ppm is preferable.
2) The process should operate effectively in the presence of dissolved salts.
3) The process should not be overly energy intensive.
4) The process should remove both inorganic and organic forms of boron.
5) Any new reagents used should be transparent to the environment.
6) The recovered boron should be in a form to be easily recycled.

In section 2, boron chemistry is reviewed so that the special nature of any boron compounds of interest to this study is not overlooked. This review also examines the toxicity of boron compounds so that the recovery process meets the environmental, health, and safety requirements of both the regulatory and in-plant environments. In Section 3, several treatment options are considered based on their ability to remove soluble boron compounds from aqueous streams. The options are screened determining those with the capability of achieving this objective within the indicated constraints. Treatment options selected by this screening step are examined in section 3.6 to determine what additional data must to be collected to ensure that the chosen option will meet the objective. Section 4 describes the experimental program while Section 5 discusses the results. Section 6 offers some conclusions from this study and Section 7 provides a brief summary and offers some opportunities for future research.

2. Background

2.1 Boron Chemistry

The primary inorganic forms of boron of interest are the boraxes and boric acid. Boric acid, H_3BO_3, is a weak acid which behaves as a Lewis acid by accepting an OH^-,

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+. \qquad (1)$$

The pK_A for boric acid in dilute solutions is 9.24; however, at above 0.1 molar, lower pH values are measured than predicted by this constant. This is believed to be caused by stronger polymeric boric acid species (Herman, 1964). Table 1 and Table 2 give some properties of boric acid (Herman, 1964).

At higher temperatures boric acid tends to dehydrate (Stocchi, 1990). At 100°C, boric acid is largely dehydrated to HBO_2,

$$H_3BO_3 \leftrightarrow HBO_2 + H_2O. \qquad (2)$$

At 140°C, boric acid is largely dehydrated to $H_2B_4O_7$,

$$4H_3BO_3 \leftrightarrow H_2B_4O_7 + 5H_2O \qquad (3)$$

Table 1. Solubility of Boric Acid in Water

Solubility of Boric Acid in Water

Temperature °C	% Boric Acid in Solution
0	2.48
20	4.8
40	8.02
60	12.9
80	19.1
100	28.2
107.8	31.5
117.1	36.7
126.7	42.3

Table 2. Boric Acid Vapor Pressure

Vapor Pressure (mm Hg) at 1 atm of Steam

Temperature °C	Boric Acid Vapor Pressure
109	0.62
129	2.7
142	6.3
158.8	8.67
180	15

and at complete dehydration,

$$2H_3BO_3 \leftrightarrow B_2O_3 + 3H_2O. \quad (4)$$

Boraxes are the naturally occurring sodium salts of tetraboric acid. They usually exist in hydrated forms such as $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2B_4O_7 \cdot 5H_2O$ and if heated above 200°C become anhydrous. Boraxes may be prepared from boric acid by reacting boric acid with caustic or Solvay soda (Stocchi, 1990):

$$4H_3BO_3 + Na_2CO_3 \leftrightarrow Na_2B_4O_7 + 6H_2O + CO_2. \quad (5)$$

Sodium perborate, $NaBO_2 \cdot H_2O_2 \cdot 3H_2O$, and sodium perborax, $Na_2B_4O_7 \cdot H_2O_2 \cdot 9HO$, are also commonly used in industry for their ability to release oxygen. The boron halides such as BF_3 and BCl_3 are also important because they behave as strong Lewis acids and are commonly used as catalysts in industry (Stocchi, 1990). BF_3 may be prepared by:

$$3HFSO_3 + H_3BO_3 \leftrightarrow BF_3 + 3H_2SO_4. \quad (6)$$

BCl_3 may be prepared by:

$$B_2O_3 + 3C + 3Cl_2 \leftrightarrow 3CO + 2BCl_3. \quad (7)$$

There are many organic boron compounds. Among the most common organic boron compounds are those formed by substituting alkyl or aryl groups onto boric acid. These include boronic acid, borinic acid, tri-alkyl borane, tri-aryl boranes, tri-alkoxy borates, and tetra-aryl boranes etc. (Herman, 1964).

One of the most frequent reactions that boric acid undergoes in industry is its esterification with an alcohol or phenol (Herman, 1964):

$$H_3BO_3 + 3ROH \leftrightarrow (RO)_3B + 3H_2O. \qquad (8)$$

Other reactions important to industrial applications include the redox reactions organic boron compounds may undergo. In some cases, it may be possible to oxidize an organic boron compound back to an organic compound and boric acid. For example, consider the oxidation of triphenyl borane with hydrogen peroxide:

$$(C_6H_5)_3B + 3H_2O_2 \leftrightarrow H_3BO_3 + 3C_6H_5OH. \qquad (9)$$

Since the peroxide is consumed and the excess decomposes to water and oxygen, this type of reaction is an environmentally sound method for converting some organic boron compounds back into boric acid. Triphenylborane may also hydrolyze:

$$(C_6H_5)_3B + 3H_2O \leftrightarrow 3\,C_6H_6 + H_3BO_3. \qquad (10)$$

2.2 Inorganic Boron Toxicity

In an industrial process where boron is present in a waste stream, for environmental and possibly for economic reasons, it is likely there will be a step to recover the boron. The processed stream will then either be discharged directly into surface waters or combined with other waste to be treated at the plants' waste water treatment facility. The effluent from the treatment facility will eventually be discharged to surface waters. Boron remaining in the effluent after the recovery process may be toxic to microorganisms in the treatment facility as well as in the natural environment. Therefore, it is necessary to establish maximum boron concentrations in the influent to and effluent from the treatment facility.

In order to assess what these concentration limits should be, the toxicity of inorganic boron to microorganisms in waste water treatment processes is examined in this section. Then, boron's toxicity to life forms in the natural environment is examined to determine a target maximum concentration of boron in the effluent from the treatment facility.

In determining the level of inorganic boron which is toxic to biological treatment processes, it is important to define toxicity. In some cases, inorganic boron concentrations have been reported to be toxic when the biomass's oxygen utilization is repressed by 50%. Other studies have defined the toxic level of inorganic boron as that resulting in a 10% decrease in gas production, where gas

production is understood to be representative of biological activity. Another consideration of toxicity studies is acclimatization. Since many microorganisms may acclimatize to certain substances, a facility operating at a steady state of boron levels will certainly tolerate higher concentrations of boron than a facility that is periodically subjected to boron.

Gerike (1976) concluded that boric acid in concentrations of up to 10 mg/L could inhibit a sludge process and that there is no adaptation of organisms to the element boron, while another concluded that adaptation to sodium borate allowed for concentrations up to 10 mg/L of boron. Gerike attributed this apparent contradiction to differing experimental techniques and performed his own studies, from which he concluded that present levels of inorganic boron in aerobic sewage treatment plants do not inhibit the process.

Another study concluded that 200 mg/L of inorganic boron in the form of boric acid will reduce gas production by 10% (Pomeroy, 1974). When boron is added as borax instead of boric acid, 750 mg/L are required to reduce the gas production by 10% (Pomeroy, 1976). The borax buffered the solution to near neutral, and the experimenters believe that this pH adjustment may have reduced the boron toxicity. They also observed that iron salts reduce the toxicity of boron, while sulfates and boron together are more toxic than either alone. Another study concerned with the effect of boron on aerobic processes found that boron levels of 30 mg/L will not impair the activated sludge process (Pomeroy,

1976). This study also found that adding sulfate seems to increase the toxicity of boron, and points out that boron as low as 10 mg/L may affect the process if the system is not acclimatized. These studies make the important point that other species may affect boron toxicity and that the addition of inorganic boron to a waste treatment facility should be continuous for the sludge to remain acclimatized.

The author of one study concluded that the influent level of boron to a treatment plant should not exceed 2 mg/L, which includes some margin of safety as well as sludge recycle considerations (Wong, 1984). The York, Pennsylvania City Sewer Authority has established a boron limit of 5.0 ppm on waste from industrial users (Buzzard, 1987). This indicates that a concentration as high as 5.0 ppm is probably tolerable for biological treatment processes.

Considering theses sources and investigations together; it is probable that a biotreatment system, once acclimatized, could likely handle 10 ppm of boron without significant impairment of the process. This, however, may not be the concentration level that is acceptable for discharge. The boron remaining in the effluent from the biotreatment process will leave the boundary of the plant and be discharged into the environment. The natural environment may be more sensitive to inorganic boron than biological treatment facilities, since the environment contains a broader spectrum of life forms. This consideration, the potential

for future regulations, public concern justify an examination of inorganic boron's toxicity in the natural environment.

Prevailing boron concentrations in surface waters vary widely because of geography, climate, and human activities. Boron occurs naturally in the form of borosilicates found in sedimentary rock, especially in marine clay sediments. When the clay and rock break down, the boron is released as $B(OH)_3$, $B(OH)_4$ and complex polyanions. One estimate gives the annual, worldwide, natural release of boron as 360,000 tonnes (Butterwick, 1989). Commercial deposits typically are found in regions known for volcanic activity.

The concentration of boron in sea water is about 5 mg/L while tap water has a boron concentration between 0.4 and 4.9 ppm (EPA, 1991). Boron concentrations in geothermal waters vary widely from region to region (Chen and Choi, 1979). The principle mechanism for boron removal from natural water sources would appear to be sorption on clays. In the United States, freshwater boron concentrations average about 0.1 mg/L with the highest concentration found in the West, where 5 to 15 mg/L boron have been reported (Butterwick, 1989). Average boron levels in surface waters in the U.S. are available based on regions of the country (Butterwick, 1989). For example, the average boron level for surface waters in the Western Gulf section of the country is given as about 2.9 mg/L, while that for the Southwest-Lower Mississippi region is about 1.3 mg/L. The effluent limit for boron from a particular plant site will probably

be based on the concentration of boron naturally occurring in the receiving stream.

Three sources give extensive tables representing the results of boron toxicity tests performed on microorganisms, aquatic invertebrates, fish, commercial crops, birds, and larger mammals (Butterwick, 1989; Eisler, 1990; EPA, 1991). The U.S. Fish and Wildlife Service recommends maintaining boron levels in the aquatic environment at 1 mg/L or less (Eisler, 1990). The Environmental Protection Agency (EPA) concluded that there is not sufficient data to establish a water quality control criteria for boron to protect aquatic organisms (EPA, 1991). Butterwick (1989) points out that while laboratory tests conducted using natural waters produce a variety of different results, as compared to tests using reconstituted water. An example from this study is that the rainbow trout embryo is the most sensitive to boron with a 'lowest observable effect concentration' of 0.1 mg/L. However, healthy rainbow trout have been found which live in waters containing 13 mg/L of boron. The study then points out that two other works confirm that studies using reconstituted laboratory water do not effectively predict the responses of organisms in natural waters (Butterwick, 1989).

In summary, it seems likely that inorganic boron can be tolerated up to around 1 ppm in a biological treatment facility. The boron limit for industrial effluent will probably be dependent on the existing levels of boron in nearby surface waters.

2.3 Phenylated Boron Toxicity

The toxicity of phenylated boron is of interest here because it is likely typical of several organic boron compounds. The concern over the toxicity of phenylated boron compounds arises from concern over sending a waste stream containing these compounds to a bioreactor. Boric acid and phenol are both toxic by themselves so an investigation of the toxicity of the phenylated boron compounds is warranted in this research.

It was found that phenylboric acid has a greater bacteriostatic effect than boric acid, but that it is not as strong as phenol alone (Seaman and Johnson, 1931). A study of 127 organic compounds found that phenylboric acid was one of the best potential insecticides because it required relatively small concentrations to produce the desired effect (Brown et. al., 1948). Plants also may be affected by phenyl boronic acid. It has been noted that some arylboric acids may be beneficial at low concentrations but become toxic at concentrations around 122 ppm phenyl boric acid (Torssell, 1956). Sodium tetraphenyl borate also produces a similar effect, which may be attributed to the breakdown of the compound into diphenyl borinic acid and biphenyl. It has been demonstrated that sodium tetraphenyl borate is more toxic and less beneficial than boric acid; its greater toxicity may be due to the phenolic groups and benzene released during breakdown of the compound (Kaplan et. al., 1988).

One study concluded that increasing the salt concentration or lowering the pH of a solution will increase the toxicity of phenylated boron compounds (Arnold et. al., 1988). This study also provides a model for determining the increasing toxicity of solutions with increasing salt concentrations. Mills and Scwind (1990) concluded that the breakdown of phenylated boron compounds is not a biological process. The results also conclude that the degradation of these compounds is about twenty-five times faster when dissolved organic matter is present, indicating that indirect photochemical degradation is the primary mechanism of breakdown. The study also indicates that dissolved oxygen may slow the process of degradation by 50%, which may be important in a biotreatment process.

It is known that tetraphenyl borate breaks down into diphenyl borinic acid and that this breaks down ultimately to boric acid. However, the mechanism for the last step is still unknown (Sandu, 1992). To summarize, the toxicity of phenylated boron is similar to the toxicity of phenol and boric acid combined. It is not possible to determine from the available literature what concentration of phenylated boron compounds could be tolerated in a bioreactor or what the phenylated boron concentration of the effluent discharged to surface waters should be.

3. Treatment Options

The treatment options for removing and recovering boron from aqueous solutions considered in this study are: evaporation, precipitation, reverse osmosis, solvent extraction, and sorption. In the following section the ability to achieve the desired objectives subject to the indicated constraints is discussed. The results of the evaluation of the treatment options are shown in Table 3.

3.1 Evaporation

In an evaporation process, the solvent is taken off as a vapor such that the solubility limit of the solute is exceeded, which results in crystallization of the solute. Using differences in solubility, it is possible to separate the different boron compounds by fractional crystallization. Evaporation allows the recovery of both phenylated and inorganic boron compounds without the addition of new reagents, making it the only process considered in this study that is not likely to require additional reagents as is shown in Table 3.

A study by Wong and Kaiser it has been showed that about 5-9 mg/L of boron was detected in the overhead; this was attributed to boric acid's volatility (Wong and Kaiser, 1984). The high solubility of boric acid requires the evaporators to operate at

Table 3. Evaluation of Treatment Options

Treatment Options	Process Recovers Both Organics and Inorganics	Process Has Potential To Reduce Boron To <1 ppm	New Reagents Are Transparent to Environment	Boron Form Is Easily Recyclable	Process Is Minorly Affected By Presence Of Dissolved Salts	Process Is Not Energy Intensive (Relative)
Evaporation	yes	no	yes	no	no	no
Precipitation	no	no	no	no	no	yes
Reverse Osmosis	yes	yes	no	no	no	yes
Solvent Extraction	yes	yes	no	yes	yes	no
Sorption	yes	yes	no	yes	yes	no

high concentrations, allowing for substantial amounts of boric acid to crystallize. These results indicate that evaporation is not likely to achieve the aqueous discharge goal of the ideal boron removal treatment. Any dissolved salts in the waste stream will be present in the crystal product, preventing recycling of boron without additional steps. Thus, evaporation-based treatment processes are strongly affected by salts. Another difficulty associated with evaporation for boron recovery is that the boron is obtained in solid form. A dissolution step and a step to remove the salts from the crystal product is likely in order to recycle the boron recovered by this method. The boron is not in a form that can be easily recycled. Another disadvantage of the evaporation process is that it would be energy-intensive, because nearly the entire waste stream would have to be vaporized. Table 3 shows that, compared to other options, the only advantages to evaporation as a removal process are that both organic and inorganic boron can be recovered and no new reagents are added to the stream.

3.2 Precipitation

In treating a boron-containing aqueous waste stream with precipitation, a reagent such as lime is added to the stream and a boron precipitate is formed. Precipitation can remove the inorganic forms of boron and may possibly remove some of the organic forms. Farmer and Kydd (1980) demonstrated that by

using multiple stages with various precipitants, residual boron levels may be reduced to below 10 ppm. Another study indicated that a precipitation scheme reduced boron from 1.7 mg/L to 0.2 mg/L (Wong and Kaiser, 1984). No evidence has been found for a precipitation process which effectively reduces boron levels from several thousand ppm to less than 5 ppm. This is likely due to the large amounts of reagent necessary to push the equilibrium toward precipitation. Another drawback is that if reagents are used new secondary wastes are created. If the dissolved salts are also precipitated, then even greater quantities of reagent would be necessary. In addition, it has been demonstrated that certain salts may inhibit precipitation of boron compounds while others may promote it (Farmer and Kydd, 1980). As a result, the precipitation option is considered unsuitable because of its failure to remove both forms of boron, meet the concentration goal of less than 50 ppm, creates new waste streams, and is adversely affected by the presence of salts. These results are shown in Table 3. Also, the precipitate from this process would typically be burnt, which is entirely undesirable since incineration releases boron into the environment with no chance of recovery. Secondly, the strong chemical bonds formed by the precipitation process are inherently less reversible than bonds formed by other processes. In order to recover the precipitated boron, it would be necessary to use additional reagents and process steps to put the boron in a recyclable form. This would create new wastes which would have to be dealt with. However, if the precipitate could be treated with

strong acid to liberate boric acid, then a phase change would not be required and the energy requirements will not be great.

3.3 Reverse Osmosis

In a boron recovery process based on reverse osmosis, applied pressure drives the water across a semipermeable membrane while the solute is concentrated on the feed side. In general, the species to be concentrated must exist in a form which has a molecular weight greater than 120 or exists as an ion (MacNeil, 1988). Reverse osmosis has been used in several studies to purify water with boron rejection near 60% achieved; however, the initial concentrations of boron in the studies were already close to 1 ppm (Jarrett, 1978; Folster et. al., 1980). Many organic boron compounds will be rejected by reverse osmosis membranes because their molecular weight exceeds 120. However, a substance may be added to complex the boric acid to obtain a higher molecular weight. This is likely to be necessary, since even at moderately high pH some boric acid exists in an unionized form which will not be rejected by a reverse osmosis membrane. The possible addition of new reagents and the creation of new boron compounds or complexes is a drawback because they create new secondary wastes. For this reason, Table 3 shows that reverse osmosis removes both forms of boron but at the cost of adding new reagents to the stream.

The effect of dissolved salts on the reverse osmosis process is to raise the osmotic pressure, raising the necessary applied pressure and creating an additional constraint on operating conditions. Any salt present in the original solution will be recovered along with boron in the reject stream; therefore the boron will not be in an easily recycled form. If the reverse osmosis process could be applied without a complexing agent, the only energy requirement would be to develop the pressure driving force which, for a liquid, would not be great. But, the process without a complexing agent could not recover the boric acid.

3.4 Solvent Extraction

In solvent extraction processes used for boron removal, the aqueous stream is contacted with an immiscible solvent. A solvent is chosen that has a higher affinity for the solute than for the feed phase. It has been demonstrated that there are a number of solvents into which boron compounds will dissolve (U.S. Patent, 1961; U.S. Patent, 1963; Counce, 1994). It is likely that a extraction process will remove both inorganic and phenylated boron compounds from the aqueous stream to less than 5 ppm. A drawback is that it is unlikely that the tetraphenylborate anion would dissolve into a nonpolar solvent. An advantage of solvent extraction as a boron-removal process is

that after the solvent is stripped of the boron, the boron can be recycled and the solvent can be used again.

Another potential advantage to the process is that a suitable solvent might be found which is used as a feed in the process that generates the boron waste. This solvent and the boron could be recycled together as a feed to the main process without a second step. Since it is probable that a suitable solvent could be found, Table 3 indicates that the boron would be recovered in a recyclable form without a reaction or separation step. The effect of salt on this process is negligible; in fact, it may even help phase formation. The drawback is that it would likely be necessary to evaporate the solvent to recover the boron, making the solvent extraction process energy intensive.

3.5 Sorption

Using sorption as a boron-removal treatment, the species to be removed is contacted with a solid phase which has an affinity for the species. Typically, this affinity is due to either chemical or physical mechanisms. The two main mechanisms for sorption are referred to as adsorption and ion exchange. The substance to be removed may either be adsorbed to the solid or it may exchange with an ion already on the surface. Sometimes a third mechanism referred to as chemisorption may occur, in which electrons are shared between the solid and species to be removed are formed.

Using the ion exchange process, the boron ions exchange with active groups on the resin, which is the term for the solid substrate. This process is reversed in the regeneration step, in which the active groups exchange boron ions with the regenerate. There are boron-specific resins, such as Amberlite IRA-743, which could serve this purpose; however, these resins require a two-step regeneration process (Buzzard, 1987; Rohm and Haas, 1989). It is likely that ion exchange can remove ionic boron compounds to less than 5 ppm. A drawback for using ion exchange for boron removal is that in order for this process to work, the boron must exist in anion form, which is not likely for many organic boron compounds.

The effect of dissolved salt in the ion exchange is that if the resin was not highly boron-selective the salt ions would load onto the resin, reducing efficiency. The regenerate stream would probably have to be evaporated, leading to an energy-intensive process.

In adsorption, weak chemical interactions hold the boron compounds to the surface of the solid phase. It has been shown that boron, as boric acid, will adsorb onto aluminum, magnesium, and iron oxide materials. Desorption is typically accomplished by altering the pH. Activated carbon has also been shown to remove boron as boric acid to near 1 ppm and can be expected to remove the organic boron (Chen and Choi, 1979). Regeneration is typically accomplished with a pH swing. Dissolved salts may compete for sites on the adsorbent but do not reduce the efficiency greatly.

Besides the traditionally used activated carbon, there are new adsorbents which may remove both inorganic and organic forms of boron. One category of these are the weak base resins, which may be regenerated, in some situations, with alcohol, which in many cases, may be preferable to a pH swing regeneration. If these new resins may be regenerated easily they may provide an attractive option for boron removal by sorption.

The main advantages of adsorption as a sorptive boron treatment are the same as for ion exchange, with the additional advantage that unionized organics may be adsorbed. As with ion exchange, the regenerate fluid might have to be distilled, leading to an energy-intensive process. As in solvent extraction, there is a potential that a regenerate might be found for a resin that is also a feed to the process producing the boron waste. This would eliminate a process step for recovering boron from the strip solution because the regenerate containing the boron might be directly recycled. Table 3 shows the optimistic assumption that such a regenerate fluid could be found.

3.6 Treatment Option Conclusions

From the analysis of the treatment options summarized in Table 3, it can be seen that solvent extraction and sorption offer the most appropriate removal options based on the criteria established for this study. Both processes are feasible and leave the boron in recoverable form. In addition, if an appropriate resin

or solvent was found, then the regenerate or solvent could be recycled to the waste-producing process without an additional step or large loss of reagent.

The difficulty with both processes is that it is uncertain whether these options can recover all the boron species. To solve this problem for both, it is recommended that a pre-treatment of the waste stream be implemented which will convert the phenylated boron compounds to boric acid. The phenylated boron compounds could be converted to boric acid and benzene by hydrolysis or to boric acid and phenol by oxidation.

There are several advantages to thus breaking the recovery process into two steps. Since the phenylated compounds break down abiotically over a long period of time and due to their toxicity, it is likely that it would be necessary to convert them to organics and boric acid before sending a waste stream containing them to a biotreatment system or discharging it to surface waters. The two-step process also simplifies the boron recovery step because the recovery will only involve one boron species, allowing the recovery step to be much more specific. The two-step process also allows for the recovery of phenol or benzene. Also, if the boron in the waste stream is the result of a process which produces a trisubstituted boron compound for use as a catalyst, then the tetraphenyl borate must be oxidized to be useful again.

The selection of a pre-treatment option for this conversion is beyond the scope of this study. Thus, in the selection of an appropriate boron removal technology, it is assumed that the

boron compounds have been converted to boric acid prior to a recovery step by one or the other of the pre-treatment technologies described here.

3.6.1 Selection Of Technology

Both sorption and solvent extraction coupled with a pre-treatment step appear to offer feasible recovery processes. Since the data required for a full economic analysis of either boron-removal process is not currently available, it is not possible to determine whether either sorption or solvent extraction would make the most attractive boric acid recovery system.

The solvent extraction process is likely to have three steps: contacting the two phases, stripping the solvent of the boron and water, and stripping the water of solvent prior to discharge. Sorption has only two steps, loading and regeneration. Sorption is less sensitive to process upsets and usually offers a more concentrated solute stream than solvent extraction.

Since the stream under consideration is a waste stream, the boron concentration is dilute. It is likely that a solvent extraction system consisting of three steps will be much more costly than an sorption step. Because of this, it is difficult to recommend a solvent extraction system for a dilute stream. In cases where the boron concentration is much higher, there is a possibility that solvent extraction might be more economic.

As a result of these considerations, the focus of this study is investigation of the sorption alternative as the boron-recovery process that best meets the selection criteria. Solvent extraction for recovery of boric acid will not be investigated; however, the solvent extraction alternative should not be eliminated from consideration when higher concentrations of boron are present in the waste stream.

3.6.2 Boron Sorbents

In using sorption as a boron-recovery process, the best-known sorbent that can sorb boron compounds is activated carbon; however, there are also polymer-based resins which may work for boric acid. These include tertiary amine (weak base) and phosphate-based resins. There are also sugar-based resins (cis-diols) which are very boron-specific.

The sugar based resins make use of boron's strong affinity for adjacent hydroxyl groups. The regeneration of these resins is difficult and often requires two steps.

Boric acid is sorbed to the amine and phosphate resins by virtue of its Lewis-acid character. The weak base resins include a nitrogen to donate an electron pair to boric acid, thus filling its octet. The phosphate-based resins have an oxygen with two lone pairs to donate. Any resins capable of donating electrons in the Lewis-base sense are candidates for boron removal.

In applying pollution-prevention considerations to the design of an adsorption system, the selection of the resin requires not only that it remove boron but that the regenerate fluid is harmless to the environment. To meet this objective, it is necessary to identify the best candidates for sorbents and regenerate fluids.

The difficulty with regenerating a weak base or phosphate-based resin with acid is that the acid must then be removed with a weak basic solution. This will produce an acidic salt solution such as aqueous magnesium chloride, another waste species. If the resin is regenerated with base, then the recovered boron will be a salt such as sodium borate; such a form of boron may not be easily recycled. Likewise, stripping boric acid off of carbon by adjusting the pH also creates a salt.

An alternative to this problem is to regenerate these resins using organic substances. If toluene can be used to wash the boric acid off of carbon or if alcohol can be used to remove boric acid from the polymer resins, the problems of pH swing regeneration could be avoided. To accomplish this, the resin used to recover the boron from the waste stream must not bind the boric acid so tightly that it requires tremendous amounts of alcohol to regenerate the resin. But the resin also must bind the boric acid strongly enough to effectively remove it from the waste stream.

4. Experimental Results

4.1 Sorbents and Regenerates

Two sorbents were studied as suitable for effective boron recovery in a sorptive process. Reillex-425 from Reilly industries is known to remove some weak acids and to be regenerated with methanol. IRA-743 from Rohm and Haas is known to be boron-specific but is regenerated with acid and base. These two resins were tested to determine ability to remove boric acid. The regenerate fluids tested were methanol and isopropyl alcohol (IPA).

4.2 Analytical Boron Determination

For this study, boron concentrations were determined by the mannitol method. Boric acid is weak enough such that direct titration will not provide acceptable results. However, boric acid complexes with mannitol to form a much stronger acid which may be titrated. The following method was used to determine boron concentration:

1) The sample to be determined was weighed and then mixed with 50 mL of distilled water.

2) Then 5 drops of methyl red indicator were added to the sample.

3) If the sample was red, then 0.1 N NaOH was added until just one drop turned the solution yellow. If the sample was yellow, 0.1 N HCL was added until just one drop turned the solution red.

4) 5.0 grams of mannitol was added, which will turn the solution distinctly red if boric acid was present.

5) After the mannitol was dissolved by swirling, 5 drops of phenolphthalein indicator were added.

6) The solution was then titrated with 0.1 N NaOH until the phenolphthalein endpoint was reached.

7) The weight percent boric acid is then calculated by:

$$\% \text{ Boric acid} = \frac{(0.06183)(\text{Normality titrant})(\text{mL titrant})(100)}{(\text{mg Weight of sample})} \quad (11)$$

where 0.06183 is the milliequivalent weight of boric acid.

This method was tested against standards and found to be accurate to around 0.005% boric acid (50 ppm boric acid or 9 ppm boron). Since boric acid may esterify with isopropyl alcohol, this method cannot be used for IPA/boric acid samples. In order to

determine these concentrations, boron-containing samples were sent to Kenwill Laboratories in Maryville, TN, where boron was determined by ICP. These results were confirmed by mass balance, and thereafter boron concentrations in IPA were determined solely by mass balance, as explained in Section 4.5.

4.3 Batch Sorption Studies

Batch sorption studies were performed so that an equilibrium isotherm could be generated for each resin. These isotherms describe how the boric acid concentration in the fluid phase affects the concentration in the solid phase.

Boric acid was purchased from Mallinckrodt chemical company in a purity of 99.9999%. The dissolution of boric acid is slow; therefore, the solution was analyzed before its use in these studies to ensure complete dissolution. The Rohm & Haas resin IRA-743A is from lot number 7-1153 and the Reilly resin Reillex-425 came from lot number 10506AC. Mannitol and the indicators were purchased from Mallinckrodt. NaOH was purchased in the form of 0.1 N standardized solutions to avoid the problems that arise from soluble CO_2.

Varying amounts of resin were placed in 120 mL bottles to which 50 mL of boric acid solution was added. The bottles were then placed on a shaker for 24 hours. The solution was then decanted and the final concentration of boric acid was measured by the mannitol method. The loading on the resin was then

determined by mass balance. Inherent in this analysis was the assumption that the boric acid which disappeared did indeed load on the resin rather than converted into an undetectable form. This experimental method was employed on each resin.

4.4 Batch Desorption Studies

Desorption experiments were necessary to determine the regenerability of each resin which in turn determined the operational capacity of the resin. Anhydrous IPA and Methanol purchased from Baxter were the regenerate fluids tested.

Varying amounts of resin were added to 120 mL bottles and loaded with boric acid as in the sorption tests. The solution was then decanted and analyzed to ensure the results fell upon the isotherm previously constructed. 100 mL of the alcohol was then put into the bottles and they were placed on a shaker for 24 hours. Then the alcohol was filtered from the resin. The resin was then exposed to another 50 mL of a boric acid solution for 24 hours. The final solution was analyzed. By knowing the initial and final boric acid concentrations and the isotherm, mass balance calculations were used to determine the desorption isotherm. In one set of tests which involves both resins, the IPA supernant was saved and sent to an outside lab and analyzed by ICP. These results were confirmed by mass balance and established that the missing boron was present in the IPA.

The resin was then 'cycled' to ensure that desorption by IPA was also regenerating the resin. Cycling the resin was performed by loading and desorbing a resin about six times in a row.

4.5 Heat of Sorption

Since it was not possible to control the temperature of a sample on a shaker for 24 hours, the experiments to determine the heat of sorption were not performed at equilibrium. A sample of resin was exposed to a solution of boric acid for 1 hour at room temperature while another was exposed at an elevated temperature. The results from the room temperature isotherm were then compared to the equilibrium isotherm to ensure that the sample was close to about 80% of the equilibrium value. From the near-equilibrium data at two different temperatures obtained by this method, the heat of sorption can be calculated.

4.6 Salinity Studies

To determine if NaCl interferes with the sorption of boric acid, boric acid solutions were made which contained up to ten percent salt. Sorption tests were repeated using these boric acid solutions and the results were compared to the salt-free isotherm.

5. Results and Modeling

The data collected in the laboratory is shown in Table 4. This data are displayed in graphical form in Figures 1-7.

5.1 Sorption Isotherms

Reillex-425 and IRA-743A sorbents were studied in accordance with the method outlined in section 4.3. The data are shown in Table 4 and displayed graphically in Figures 1 and 2. A examination of Figure 1 indicates that the Reillex-425 isotherm is slightly unfavorable or linear at best. An unfavorable isotherm is one which is concave-up when loading is plotted as a function of the fluid phase concentration. Concave-up isotherms will tend to broaden the mass transfer zone during bed operation and hence are undesirable. The shape also suggests a type II or possibly a type III isotherm according to Brunauer's classifications (Hines and Maddox, 1985). These types of isotherms suggest the formation of multilayers because they do not saturate. This is not unreasonable, since it is known that boric acid will polymerize as it nears its solubility limit (see section 2.1).

Figure 2 demonstrates that the sorption of boric acid by IRA-743A is a favorable one which will tend to narrow the mass transfer zone during bed operation. This is a type I isotherm according to Brunauer's classifications. It is frequently referred to

Table 4. Equilibrium Data for Sorption of Boric Acid.

Boric Acid in Water				Boric Acid in Isopropyl Alcohol	
Reillex-425		IRA-743A		Reillex-425	
Weight % Boric Acid	Loading* mg/g	Weight % Boric Acid	Loading* mg/g	mg/g** Boric Acid	Loading* mg/g
0.06	0.34	0.01	6.20	0.16	0.03
0.08	0.65	0.01	11.50	0.26	0.17
0.21	1.34	0.02	12.98	0.26	0.48
0.37	3.02	0.05	14.57	0.39	0.28
0.38	2.98	0.09	15.80	0.43	0.70
0.69	7.20	0.13	17.12	0.53	0.75
0.85	9.70	0.20	18.16	1.45	0.78
1.48	12.58	0.24	19.62	2.46	0.83
2.15	20.19	0.34	20.20	2.98	0.97
2.54	21.78	0.48	23.30	4.08	1.09
2.79	27.92	2.59	52.75		
3.30	35.54	3.88	74.50		

*All Loadings are based on fully hydrated wet resin weights.

**Concentration in mg boric acid/g IPA, S.G.=0.8.

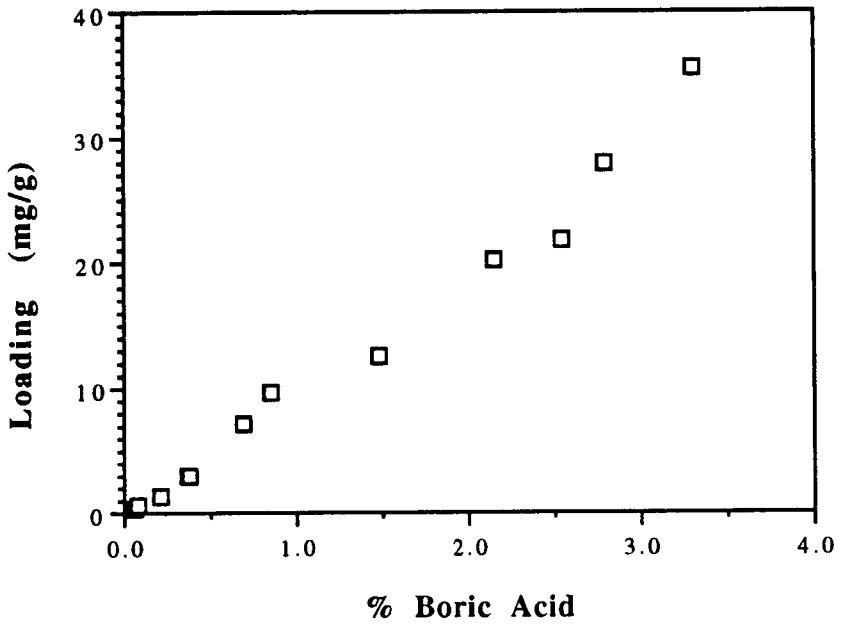

Figure 1. Reillex-425/Boric Acid Isotherm

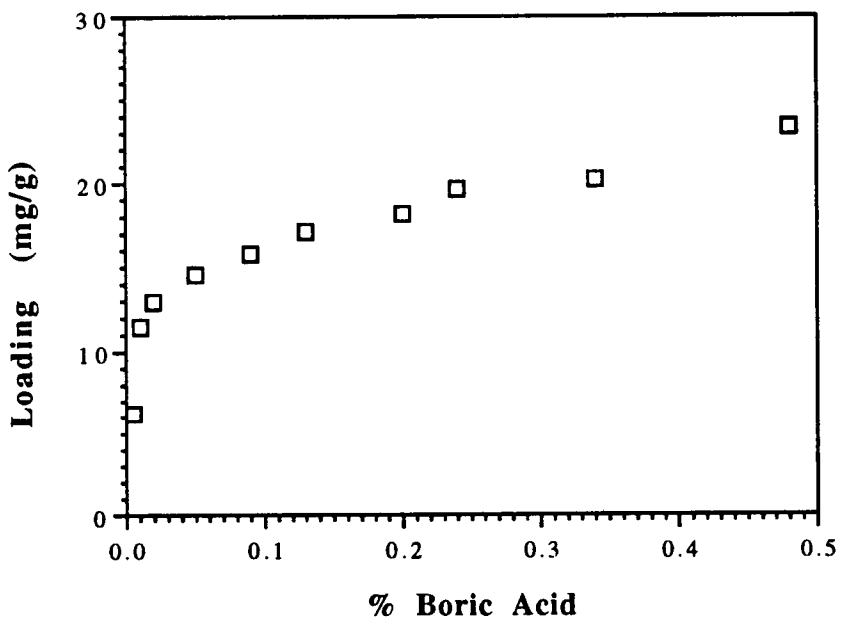

Figure 2. IRA-743A/Boric Acid Isotherm

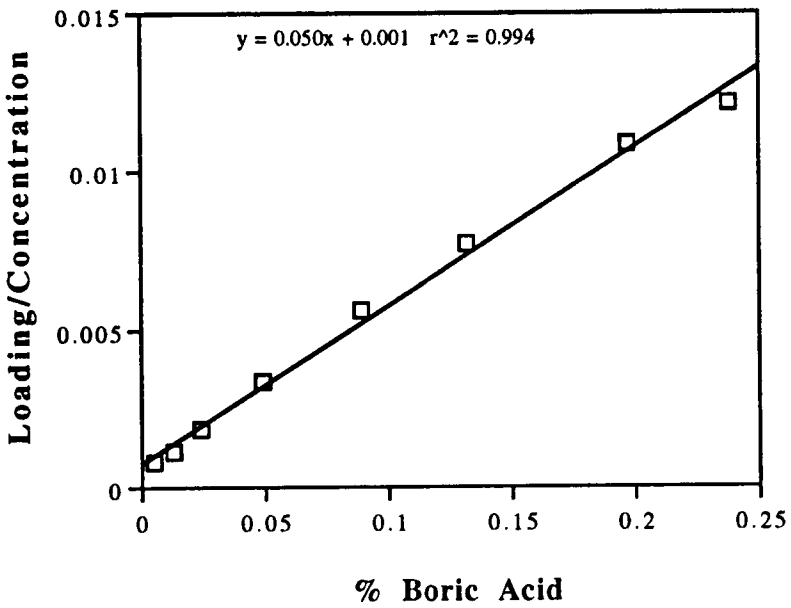

Figure 3. Langmuir Fit for IRA-743A/Boric Acid

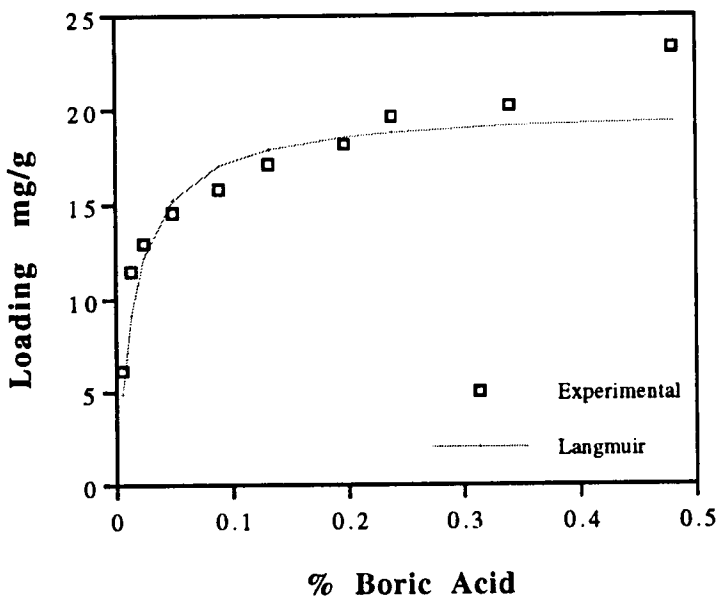

Figure 4. Langmuir Isotherm for IRA-743A/Boric Acid

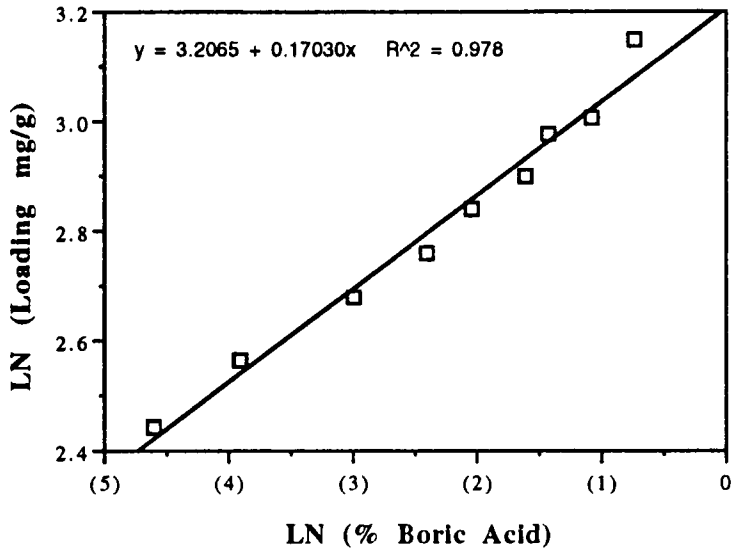

Figure 5. Freundlich Fit for IRA-743A/Boric Acid

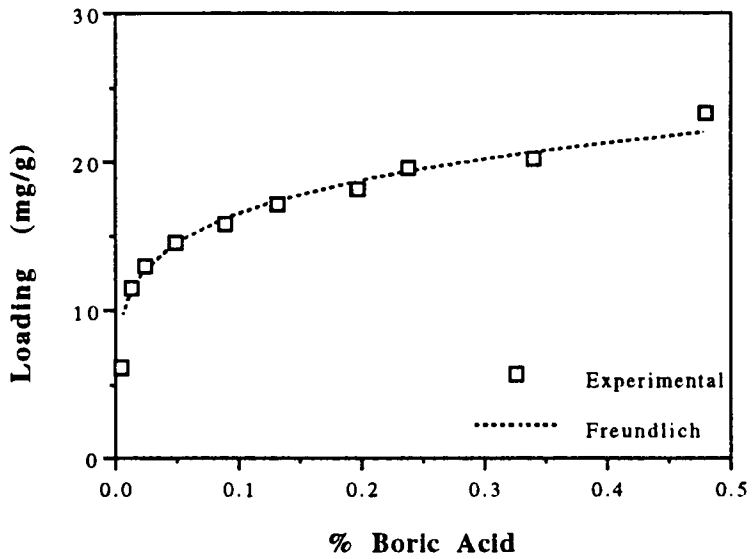

Figure 6. Freundlich Isotherm for IRA-743A/Boric Acid

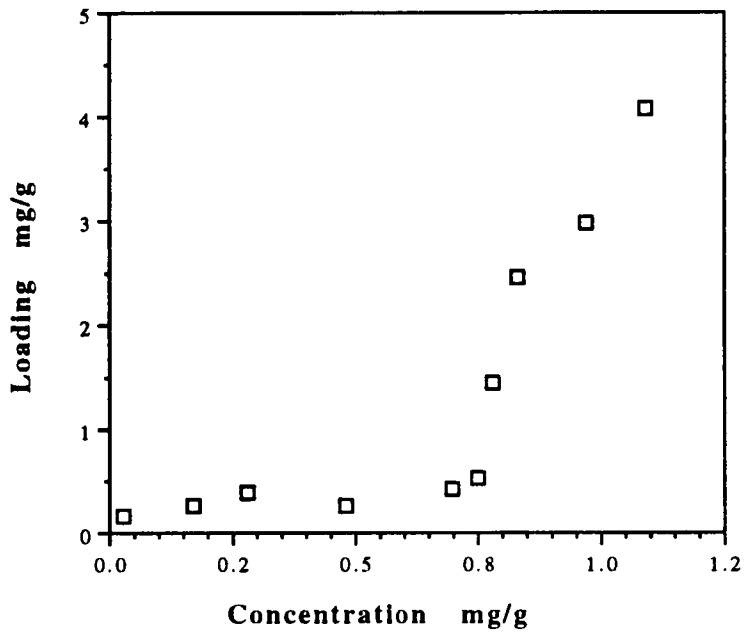

Figure 7. Isotherm for Reillex-425/Boric Acid in IPA*

*Concentrations in mg Boric Acid/g IPA, S.G.=0.8
Loading in mg Boric/g wet resin

as the Langmuir type, because it approaches a limiting behavior corresponding to complete monolayer coverage which is characteristic of chemisorption.

Comparison of the data on both sorbents given in Table 4 shows that in the concentration range of interest, the IRA-743A resin has a far greater capacity than the Reillex resin. The only situation in which the Reillex resin can be competitive is in a concentration range of 2.5% boric acid or higher, which is an order of magnitude higher than the concentration range of interest. The isotherm data for the IRA-743A data is modeled using two different models, the Langmuir isotherm and the Freundlich isotherm. The Langmuir isotherm is of the form:

$$\frac{q}{q^{sat}} = \frac{KC}{1+KC} \qquad (12)$$

where q is the loading on the resin, q^{sat} is the maximum loading on the resin, C is the fluid phase concentration, and K is an equilibrium constant. The Freundlich isotherm, which is mainly used for correlating data, is given as:

$$q = KC^{1/n} \qquad (13)$$

where q is the loading on the resin, C is the fluid phase concentration, K is a constant, and n is a constant. Figure 3 shows a plot which is used to determine the constants in equation 12. This analysis gives the a value of 19.99 for q^{sat} and 65.55 for K.

Figure 4 shows the Langmuir fit to the data along with the data itself. Upon examination, it is evident that this model does not accurately reproduce the data at higher concentrations. Figure 5 shows a plot which is used to determine the constants in equation 13. The results give a K-value of 24.69 and an n-value of 5.87. Figure 6 shows that the Freundlich form predicts the data well over the concentration range of interest. All loadings are reported as milligrams of boric acid per gram of wet resin. The theoretical loading capability of IRA-743A is 30.6 mg boric acid per gram of resin (Rohm and Haas,1989). The theoretical hydrogen ion capacity of Reillex-425 is 5.5 mmoles/gram resin (Reilly Industries, 1989).

5.2 Desorption

Regeneration of each of the two resins was attempted with methanol and IPA. The resin IRA-743A was not found to be regenerable with either alcohol. After a washing with either alcohol, the resin exhibited only around a 10% recovery in capacity. After repeated washings with either alcohol, there was only slight improvement in capacity. The apparent initial regeneration is probably due to the portion of the boric acid within the pores that is unsorbed. During regeneration, this amount leaves the resin by mass action, and during subsequent reloading, the alcohol in the pores of the resin particles dilutes the

sample. This hypothesis is supported by the finding that the recovery of capacity is nearly independent of the amount of regenerate used. The functional groups of this resin are cis-diols with which the boric acid esterifies (Rohm and Haas,1989). Both methanol and IPA are apparently unable to break this ester to any appreciable degree.

Regeneration of the Reillex-425 resin was successful. Table 4 gives the data collected for regeneration using IPA, and it is shown in graphical form in Figure 7. An interesting observation from examining the data for Reillex-425 is that boric acid loads less onto the resin from IPA than from water. This observation promotes the use of IPA as a regenerate.

5.3 Heat of Sorption

"Near-equilibrium" constants at two different temperatures for each resin were determined. These constants were used in conjunction with the integrated Van't Hoff equation, which assumes the enthalpy of sorption does not vary greatly over the temperature range considered. This approach yields a heat of sorption of around -30 kcal/mole for IRA-743A and around -240 kcal/mole for Reillex-425. It should be stressed that these numbers were determined for conditions that were close to chemical equilibrium, therefore these values are provided for approximating sorption at different temperatures. These numbers are not unreasonable. Osipow states that in sorption processes in

which chemical bonds are formed, the heat evolved is on the order of 10 to 100 kcal/mole (Osipow, 1962).

5.4 Salinity Effects

Both resins were exposed to boric acid solutions which were made from 10% NaCl solutions. The data points obtained from both resins fell within 5% of the salt-free isotherm. This indicates that salt either does not compete for sites on the resin or sorbs to a different site. It should be noted, however, that the kinetics of sorption are likely to be affected by salt content, since the hydration and hence the pore size of a polymeric resin would be affected by total ionic strength. In addition, NaCl is a salt which does not alter the pH of a solution. In the case of an acidic or basic salt, the sorption of boric acid onto Reillex-425 might be affected based on examination of the functional groups discussed in section 5.2.

5.5 Economic Analysis

In order to assess whether the use of Reillex-425 can be economically feasible, a "best case" analysis was performed. The best possible situation is when a sorption bed is free of kinetic and mass transfer resistance. This allows a bed of resin to load to equilibrium so that there is no unused portion of bed.

The bed is arbitrarily considered to be 6 feet in diameter containing 20 feet of resin. The dominating operating cost is the resin cost at $900 per cubic foot of resin. The main economic benefit is the value of the recovered boric acid, $700 per ton. By neglecting other operating costs such as labor and depreciation, the profit or cost of an industrial operation using Reillex-425 is a function of resin life. Figure 8 shows three arbitrary streams with inlet concentrations of 2.5%, 1.0%, and 0.5% boric acid. The flow rate of all streams is 100 gallons per minute and a 99% recovery is assumed. The resin must last around 2000 load-strip cycles in order to be profitable for a 2.5% boric acid stream and nearly 6000 cycles for a 1.0% stream. A 0.5% stream may not be profitable at this flow rate.

The curves in Figure 8 may be lowered closer to the profitable zone when an estimate of savings from lowered disposal costs of the boric acid stream is available. Because these savings can vary widely, an arbitrary value was not included.

Reilly industries has indicated that a resin very similar to Reillex-425 has been cycled 18,000 times without a loss of capacity using traditional acidic regeneration (Marlo, 1995). An industrial ion-exchange expert maintains that exotic polymer resins have a life on the order of 1000 cycles (Pease, 1995). These statements demonstrate that for a feasible preliminary economic analysis, resin life may be the most sensitive parameter.

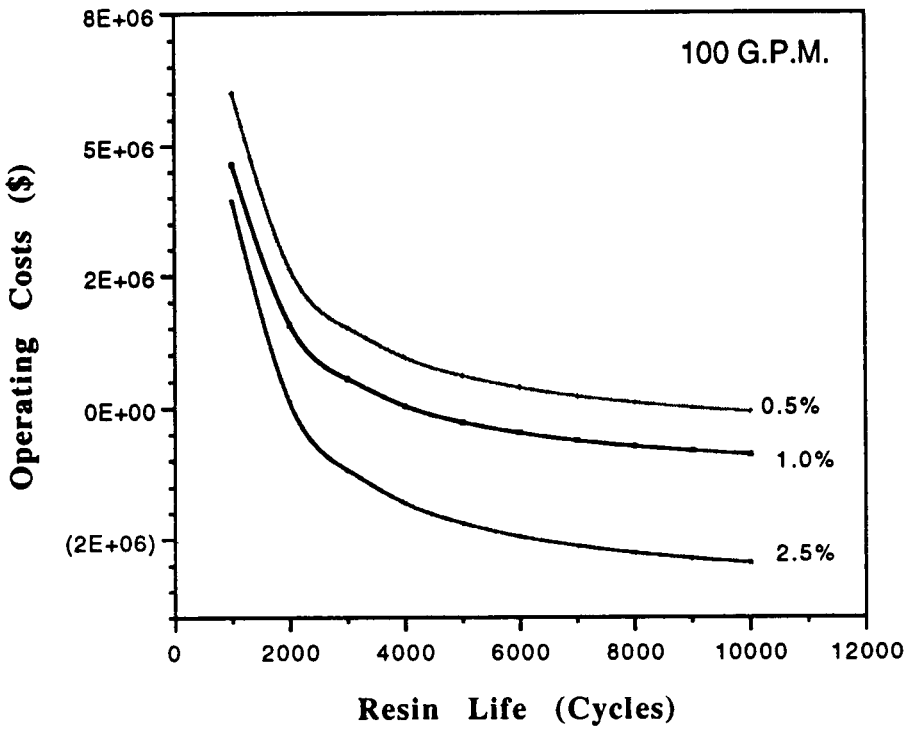

Figure 8. Operating Cost vs. Resin Life

6.0 Conclusions

Several conclusions were obtained as a result of this study. It was determined that boric acid may not be tolerated in a bio-treatment facility at concentrations higher than 10 ppm. The toxicity of organic boron compounds is likely to be greater than that of boric acid alone. As a result of this and other considerations, it is recommended that a pretreatment step involving hydrolysis or oxidation of the organic species precede the recovery step.

Sorption and solvent extraction appear to be the most attractive boron-recovery alternatives, with several benefits over precipitation, evaporation, and reverse osmosis. It has been demonstrated that sorption of boric acid and subsequent regeneration employing isopropyl alcohol may be accomplished using the sorbent Reillex-425 resin. This process has the additional advantage that the regenerate fluid may be directly recycled. Because the salt did not affect the sorption of boric acid and the unusually high heat of sorption, the mechanism is probably chemisorption. In order for the Reillex-425 process to be industrially feasible, not only the kinetics of sorption but the resin life must also be experimentally determined.

7.0 Summary

The focus of this study was to identify research and development needs for a state-of-the-art boron-recovery process. The media considered was an aqueous stream containing boric acid and phenylated boron species. The boron concentration may be up to 400 ppm and the stream may contain up to 10% dissolved salts. The treatment options considered were: evaporation, precipitation, reverse osmosis, solvent extraction, and sorption.

Boron chemistry was reviewed so that the special nature of boron compounds is not overlooked. It was also necessary to examine the toxicity of boron compounds so that the recovery system can meet the external constraints of the legal and plantwide environment. This search revealed that inorganic boron may be tolerated up to around 10 ppm in a bio-treatment facility, while it was inconclusive as to what concentration of phenylated compounds could be allowed. It was noted that the legal limit for discharging boron to the environment is likely to be determined by the prevailing concentration of the regional surface waters.

To select the appropriate technology from the treatment options the selection criteria established for the processes were:

1) The process must reduce boron to less than 50 ppm though reduction to less than 5 ppm is preferable.

2) The process should operate effectively in the presence of dissolved salts.

3) The process should not be overly energy intensive.

4) The process should remove both inorganic and organic forms of boron.

5) Any new reagents used should be transparent to the environment.

6) The recovered boron should be in a form to be easily recycled.

The treatment options considered were ranked using the above criteria, and it is found that sorption offers the most attractive option. However, solvent extraction was not eliminated for application to more concentrated waste streams. Based on several considerations, it is recommended that a pretreatment step be implemented which would either oxidize or hydrolyze the organic compounds into boric acid and phenol or benzene.

Two boron sorbents were identified for study. Reillex-425 from Reilly industries is known to remove some weak acids and be regenerated with methanol. IRA-743 from Rohm and Haas is known for being boron-specific, but is regenerated with acid and base. The regenerate fluids selected for this study were methanol and isopropyl alcohol. Sorption isotherms are generated for each sorbent, and regeneration using alcohol on each sorbent was attempted. The findings are that IRA-743 has a much higher capacity than Reillex-425 in addition to a favorable isotherm.

Laboratory findings also revealed that Reillex-425 is the only sorbent tested which can be appreciably regenerated with alcohol. A brief economic analysis reveals that the resin must be durable in order for a process using Reillex-425 to be profitable.

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Vita

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