

# Boron Treatment Technology for CCR Wastewater, Ash Leachate, and Groundwater

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## INTRODUCTION

This paper summarizes a laboratory investigation completed to identify possible boron capture technologies. Multiple possible inorganic sorbents were screened to assess their ability to remove boron from leachate and other boron-laden waste streams. The investigation identified two proprietary sorbents which are capable of removing up to 99% of dissolved boron from solution.

## BACKGROUND

Boron is a naturally occurring minor element which can be enriched in some aqueous environments, such as industrial discharge, geothermal water, or seawater. Boron's predominant aqueous species at circumneutral pH is an uncharged complex,  $[B(OH)_3]^0$ , with a  $pK_a$  of 9.1. Above pH 9.1, the predominant species is the tetrahedral borate anion,  $[B(OH)_4]^-$ , which can form complexes with cationic species and facilitate the precipitation or adsorption of the complex onto positively charged substrates. This complex-forming process does not occur naturally in soils or coal combustion residue (CCR) waste streams due to a paucity of positively charged minerals at neutral pH. Thus, boric acid and borate are notoriously mobile.

The United States Environmental Protection Agency (USEPA) does not regulate boron in drinking water, as it has limited toxicity to humans. The USEPA has set a Lifetime Health Advisory value of 5.0 milligrams per liter (mg/L) for adults<sup>1</sup>. Several states have set stricter drinking water criteria for boron, with values ranging from 0.60 to 1.0 mg/L<sup>1</sup>. Recently, boron was listed as an Appendix III constituent in the USEPA's 2016 Coal Combustion Residuals Rule [40 CFR.257]<sup>2</sup>.

The new regulatory guidance for boron has resulted in increased interest in boron capture or treatment technologies. Few naturally occurring sorbents possess the documented ability to capture and sequester boron from waste streams due to the limited formation of boron complexes. Ion exchange resins and other commercially

available engineered sorbents generally have limited specific capacity for boron, which is further decreased by the presence of competing salts.

Geosyntec completed a laboratory investigation in which the reaction of boron with certain inorganic materials fostered the formation of cationic boron complexes which were susceptible to adsorption and removal from solution. The feasibility of using this approach to remove boron from leachate was evaluated in combination with several organic and inorganic sorbents. Our efforts led to the discovery of two proprietary boron sorbents that are readily available and have favorable cost performance ratios.

## METHODS

### *Batch Sorption Studies*

Initial screening was completed to evaluate the potential of several sorbents to remove boron from either a solution prepared with deionized (DI) water or a salt solution (synthetic leachate). The synthetic leachate, whose composition is summarized in Table 1, was used to better evaluate performance in landfill leachate or similar waste streams.

Table 1. Synthetic Leachate Composition

Ingredient	In 1 L DI:
NaB <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.088 g
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.60 g
CaSO <sub>4</sub>	2.00 g
Na <sub>2</sub> SO <sub>4</sub>	0.20 g
K <sub>2</sub> SO <sub>4</sub>	0.10 g

Several sorbents were combined with an ionizing agent (IA) to assess the impact of the agent on boron sorption. The sorbent combinations included:

- control (no sorbent)
- granular activated carbon (GAC)
- 1:1 GAC: IA
- 1:1 Sorbent 1: IA
- 1:1 Sorbent 2: IA
- 1:1 Sorbent 3: IA
- 1:1 Sorbent 4: IA

Each sorbent combination mixture was prepared on a by weight basis. The samples were prepared using either granular or powdered IA to assess the effect of IA surface area on boron removal. Ten (10) g of total solids was added to a 250-milliliter (mL) polypropylene cone-bottom sample tube containing 200 mL of a boron solution. Four different combinations of sorbents and solutions were used:

- 10 mg-B/L DI with granular IA samples;
- 10 mg-B/L in synthetic leachate solution with granular IA samples;
- 40 mg-B/L DI with powdered IA samples; and

- 40 mg-B/L in synthetic leachate with powdered IA samples.

Each set of experiments was prepared in duplicate. Results of the chemical analyses for boron were used to calculate average values.

### *Column Studies*

Based on the results of the batch sorption experiment, column studies were conducted to further test the hypothesis regarding sorption via the formation of a positively charged complex. Powdered IA and sand (added to improve the porosity of the columns) were combined with organic and inorganic sorbents to assess boron removal from a synthetic leachate. The sorbent materials were chosen to represent cost-effective and widely available media. The sorbents mixtures were prepared on a by weight basis and included:

- 4:3:3 sand:IA:Sorbent 1
- 4:1:1 sand:IA:Sorbent 2
- 4:3:3 sand:IA:Sorbent 3

Sorbent 2 was prepared at a lower active sorbent ratio due to its highly impermeable nature when wet at higher concentrations. The materials were wet-packed in 3-inch diameter polyvinyl chloride (PVC) columns. A 10 mg-B/L DI solution was passed through each column in a bottom-up fashion at an approximate flow rate of 3 milliliters per minute (mL/min). The effluent was captured approximately every 3 hours and measured for pH using an AccumetXL probe calibrated daily to pH=4.00, 7.00, and 10.01. The effluent was filtered using 0.45  $\mu\text{m}$  syringe tip filters and the filtrate was sent to a commercial analytical laboratory for analysis of boron, magnesium, and potassium concentrations using USEPA Method 6010C.

### *Effluent pH Column Studies*

Additional tests were conducted to investigate the ability of different materials to buffer the effluent pH without reducing boron sorption capacity. Three 3-inch diameter columns were packed with a blend of 4:3:3 sand:IA:Sorbent 3 (w:w:w). Sand was mixed with either pH Buffer Material 1 or 2 (pHBM1 and pHBM2) (both 1:1 w/w mixtures) and packed downgradient of the primary sorbent material to determine if the organic acids in these materials could buffer the effluent pH to between pH 6 and 9. Sand by itself was used as a control for pH buffering. A 10 mg-B/L synthetic leachate solution was passed through each column in a bottom-up fashion. The flow rate was increased over the duration of the experiment as shown in Figure 1.

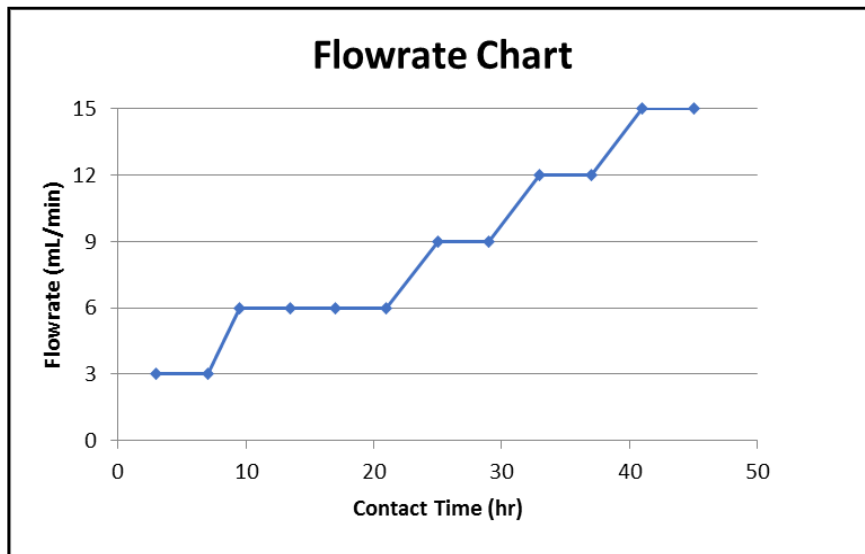


Figure 1: Flow Rates for Effluent pH Column Studies.

As in the experiments described above, the effluent was captured approximately every 3 hours and measured for pH using an AccumetXL probe calibrated daily. The effluent was filtered using 0.45 micron syringe tip filters and the filtrate was sent to a commercial analytical laboratory for analysis of boron, magnesium, and potassium concentration via USEPA Method 6010C.

## RESULTS

### *Batch Sorption Studies*

Initial batch sorption experiments were completed to assess different sorbent material combinations for their ability to remove boron from either a DI or synthetic leachate solution. Control solutions with no sorbent did not show any loss of boron to the container walls during the experiment. The results for the active sorbent combinations are shown in Table 1.

Table 1. Batch Sorption Study Results.

Sample	% Boron Remaining			
	DI		Synthetic Leachate	
	Granular	Powdered	Granular	Powdered
Sorbent 1:IA	112	4	109	13
Sorbent 2:IA	113	5	109	7
GAC	76	41	69	38
GAC/IA	101	8	98	13
Sorbent 3:IA	88	4	80	11
Sorbent 4:IA	115	32	99	10

Values greater than 100% recovery represent error within the analytical method. The results indicate that boron removal was greater when a sorbent material was combined

with powdered IA than granular IA. These results suggest the surface area of IA is an important factor in the formation of sorbing complexes. Additionally, greater removal was seen for GAC combined with powdered IA as compared to GAC alone, suggesting IA is important for the sorption process. The amount of boron removed from the DI solution was approximately the same ( $\pm 10\%$ ) or greater in DI solution versus from the synthetic leachate, suggesting that competition for sorption sites could inhibit the efficacy of the sorbent. The addition of both powdered and granular IA resulted in higher pH values samples (Table 2).

Table 2. pH Values for Batch Sorption Samples.

Sorbent	DI		Synthetic Leachate	
	Initial pH	Final pH	Initial pH	Final pH
Control	8.82	8.94	8.21	8.73
	8.22	9.03	7.91	8.79
Sorbent 1:IA	8.9	10.44	8.23	10.19
	10.19	10.64	10.23	10.34
Sorbent 2:IA	8.95	10.87	8.53	10.6
	10.20	10.21	8.53	10.35
GAC	9.32	10.06	8.53	8.74
	9.23	10.18	8.25	8.87
GAC/IA	9.3	10.72	8.6	10.16
	9.30	11.07	10.33	10.44
Sorbent 3:IA	8.25	9.37	7.22	8.91
	10.08	10.36	9.90	10.23
Sorbent 4:IA	9.43	10.84	8.44	10.03
	10.48	11.50	10.24	10.90

### Column Studies

Column studies were completed to further characterize the boron sorption mechanism identified during the previous batch studies. A 10 mg-B/L solution was passed through columns containing Sorbents 1-3 mixed with IA. The removal efficiency of each column is shown in Figure 2.

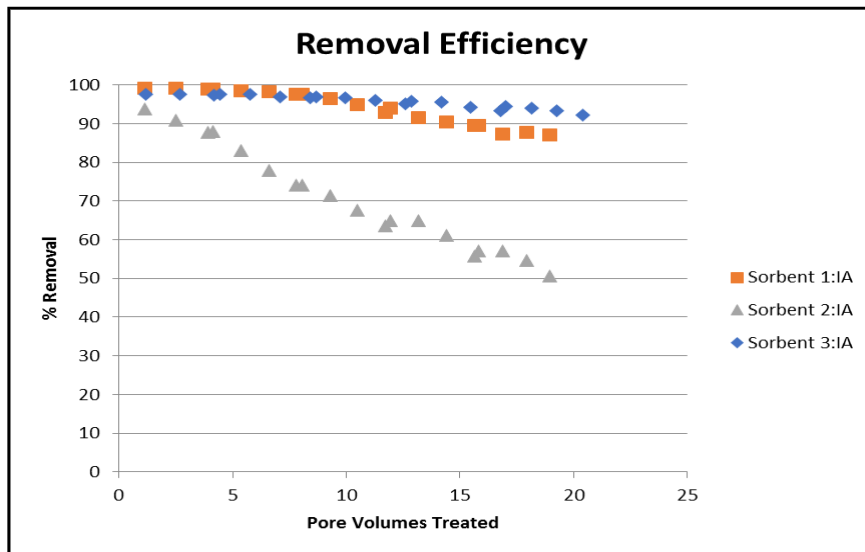


Figure 2: Column Study Removal Efficiency Results

Both Sorbent 1 and 3 combined with powdered IA effectively removed greater than 90% of the aqueous boron after 18 pore volumes. The Sorbent 2:IA mixture proved the least effective at removing boron from solution, with a removal efficiency of approximately 50% after 18 pore volumes. While some of the reduced efficiency can be attributed to a lower concentration of active sorbent, mixtures at higher concentrations proved hydraulically impermeable and were deemed impractical for real-world use.

The pH of the column effluent was also measured, with consistent pH readings higher than pH=10 (Figure 3) for all three sorbent combinations. Discharging treated water with these elevated pH values could be problematic if the receiving soil or water body cannot restore pH to circumneutral levels. Therefore, we also tested a method for reducing pH after boron treatment.

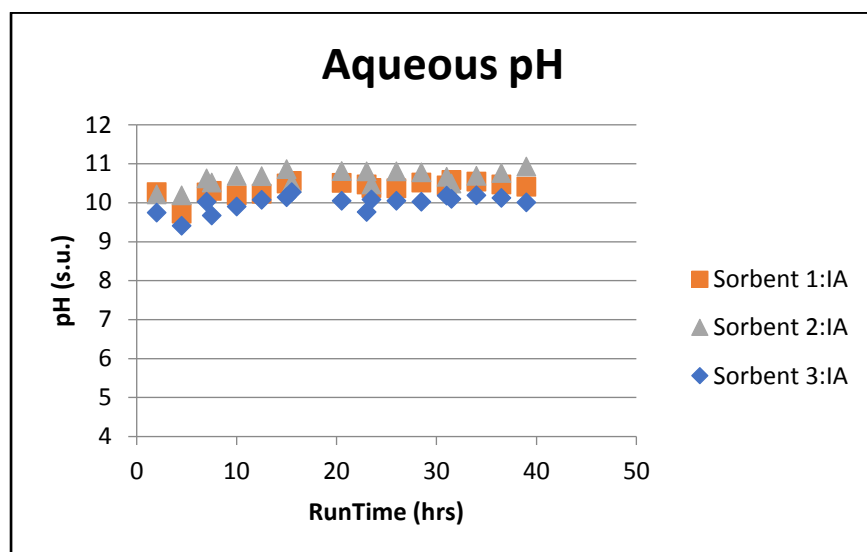


Figure 3: Column Study Effluent pH Measurements.

### Effluent pH Column Studies

An additional column study was completed to test the design of a two-phase system to remove boron while discharging an effluent waste stream with a circumneutral pH. After treating approximately 60 pore volumes of synthetic leachate, both the addition of pHBM1 and pHBM2 as a downgradient buffer appeared to maintain boron removal efficiencies above 80% while neutralizing discharge pH due to the release of organic acids (Figures 4 and 5, respectively).

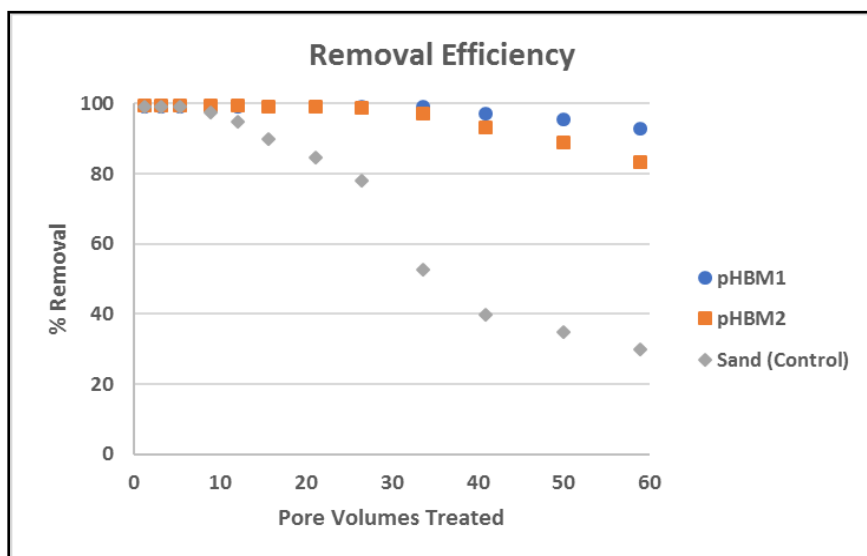


Figure 4: Effluent pH Column Study Boron Removal Efficiencies.

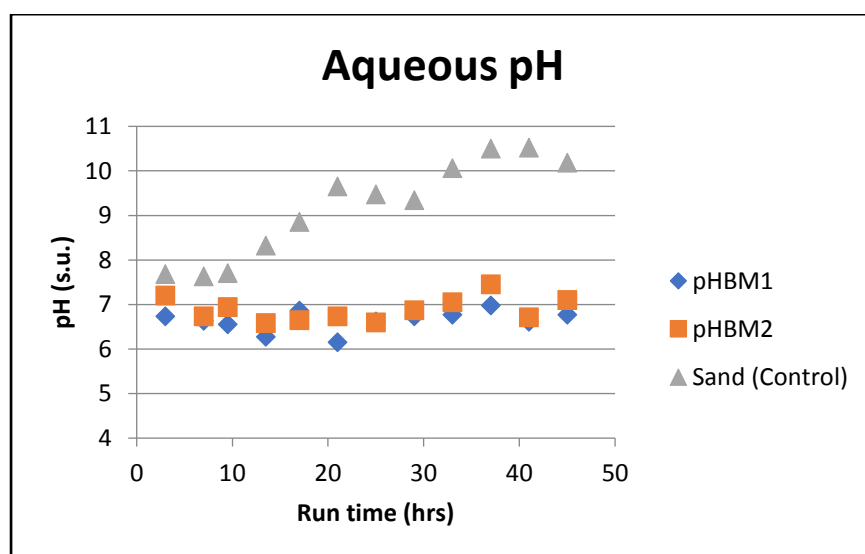
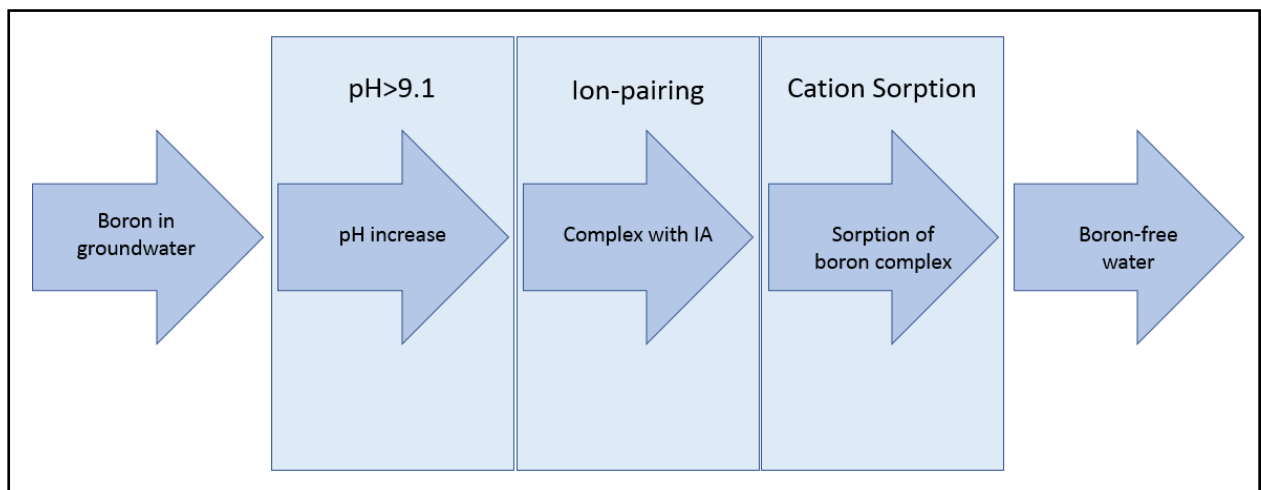


Figure 5: Effluent pH Column Study Effluent pH Measurements.

### DISCUSSION

Together, the results of these experiments indicate that boron can be effectively removed from an ionic solution using a cost-effective and simple technique. The use of powdered IA to serve as a complexation agent is a necessary step in the formation of boron-containing complexes which can be sorbed from solution<sup>3</sup>. A schematic of the multi-step complexation and sorption process is shown in Figure 6. While a pH above 9.1 is essential for the formation of IA complexes, a reduction in effluent pH did not result in the release of boron back into the waste stream.



**Figure 3: Process Diagram Illustrating the Formation of Boron Complexes with IA and Subsequent Removal from Aqueous Solution.**

Additional investigation is still necessary to further develop this technology. The effects of pHBM1 and pHBM2 on effluent biological oxygen demand (BOD) was not measured. Additionally, the concentration of competing anions or other possible constituents of concern (heavy metals) were not measured to evaluate the effect of this treatment system on their behavior.

## CONCLUSION

The results of this investigation have identified a multi-step process to remove boron from a complex waste stream while generating a waste stream with circumneutral pH. The sorbent materials used were chosen to represent cost-effective and widely available products. These results suggest a cost-effective remedy for boron impacts to groundwater or similar waste streams could be developed.

[1] USEPA. Drinking Water Health Advisory for Boron. Document Number 822-R-08-013. May 2008.

[2] 40 CFR § 257 Subpart D. October 19, 2015.

[3] K. Sasaki, H. Takamori, S. Moriyama, H. Yoshizaka, T. Hirajima. 2011. "Effect of saw dust on borate removal from groundwater in bench-scale simulation of permeable



reactive barriers including magnesium oxide," *Journal of Hazardous Materials* 185: 1440–1447