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Boron Removal from Lithium Pentaborate ($Li_2B_{10}O_{16} \cdot 10H_2O$) Solution Using Ion Exchange Resin

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Abstract: Recovery of deuterium oxide (D_2O) e.g., heavy water from lithium pentaborate, $Li_2B_{10}O_{16} \cdot 10H_2O$ (represented as LiPB), solution in heavy water is achieved by using a mixed bed (MB) ion exchanger. Boron removal capacity for the strong base anion exchange resin was found to increase with an increasing concentration of boron in the inlet solution of ion exchange column. With 0.2 M LiPB (i.e., 2 M Boron) the anion resin in the mixed bed showed four to five times the boron removal capacity observed with 0.001 M LiPB. This increased capacity is attributed to the existence of polymeric borate species at higher boron concentration. A similar high capacity for the strong base anion exchanger could be obtained in batch equilibration of the resin with 0.2 M LiPB. However, column experiments with simple anion exchanger yielded boron slip from the beginning of the run but, nevertheless, nearly realized the LiPB concentration–dependent higher boron removal capacities mentioned previously. The mixed ion exchange method of D_2O recovery appears to be a better alternative to the distillation method.

Keywords: Lithium pentaborate, ion exchange, heavy water, polymeric boron species

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INTRODUCTION

A solution of lithium pentaborate (LiPB: 0.17 M) in heavy water, deuterium oxide (D_2O), held in Zircaloy-2 tubes in the reactor core—is employed as liquid poison in the secondary shutdown system (SSS) of the 220 MWe pressurized heavy water reactors (PHWRs) of current Indian design (Narora 1 and 2, Kakarapar 1 and 2, Kaiga 1–4, Rajasthan 3–6 Atomic Power Stations). The secondary shutdown system employing LiPB has the capacity for fast shutdown of the reactor in the event of the failure of the primary shutdown system, which employes cadmium bearing control rods. After charging the LiPB solution in the SSS, it becomes necessary to recover the heavy water from the balance solution freeing it from the LiPB. Currently the recovery of D_2O from this solution is done by distillation employing evaporators and condensers. At the end of distillation the concentrated LiPB slurry is disposed of after a large amount of dilution to keep the D_2O concentration level in the receiving body of water at the permissible level ($\sim$150 ppm). Simultaneously Li and B also are diluted and discharged.

Ion exchange can be an alternate method, but if boron is sorbed as monomeric species, then a large quantity of anion exchange resin may be required, which becomes a major disadvantage. The pH-dependent existence of polymeric boron species is indicated in literature (1–4). At higher boron concentrations and at relatively lower pH, the formation of pentaborate ($B_5O_8^-$) and tetraborate ($B_4O_7^{2-}$) and their sorption on strong base anion exchanger resin in the concentration rage of 0.2–0.6 M boric acid and in the pH range of 5–11 are also cited in the literature (5). In a study of the boron thermal regeneration system (BTRS) using temperature-dependent absorption of boron on anion exchange resin for reactivity control of pressurized water reactor, domination of polyborate ions (tetramer, trimmer, and dimmer) in solution with decreasing temperature and increasing concentration of boron was confirmed (6). Formation of polymeric species beyond 0.025 M boric acid concentration was also shown during the separation of ^{10}B and ^{11}B isotopes using ion exchange chromatography (7). Use of a boron selective ion exchange resin, Amberlite XE 243, for boron removal from waste waters of boric acid and borax plants (0–1600 ppm boron) was reported, and a mathematical relationship was developed to predict the effluent boron concentration of the resin column with a given influent boron influent concentration and flow rate (8). Rejection of boron concentrations of 4.5 ppm in sea water to acceptance of 0.1 ppm for drinking and agricultural use, using FILMTEC^{TM} sea water reverse osmosis (SWRO) membrane, was demonstrated (9). A pseudo–second order kinetics using heterogeneous fluid-solid reaction models for boron removal on the boron-specific ion exchange resin Amberlite IRA 743 was suggested (10). Heavy water (D_2O) recovery from the LiPB solution in the SSS system is a very specific problem and in this connection no literature information is available, especially literature regarding the anion exchange breakthrough capacities achievable, the type of ion-exchange bed to be employed, etc. In order to look into the possibility of boron removal as polymeric and/or monovalent species from LiPB solution at ≈0.2 M concentrations, ion exchange experiments with aqueous LiPB solutions of varying concentrations (0.001–0.2 M) were performed as batch equilibration runs and also in columns with anion as well as mixed bed (1:1 capacitywise) resins. Results of this study are presented in this paper. A run with 0.2 M LiPB solution prepared in D_2O was also performed to confirm the applicability of results obtained with aqueous solutions in light water to systems employing solutions prepared in D_2O.

EXPERIMENTAL

Lithium pentaborate, $Li_2B_{10}O_{16} \cdot 10H_2O$, prepared by M/s Thermax, India (11), was characterized by thermogavimetric (TG) analysis (loss of 10 moles of H_2O) (Fig.1a) and X-ray diffraction (JCPDS–27-1224) (Fig. 1b). Beginning of the loss of water crystallization at 150°C is evident from the TG curve. At the same point heat loss due to evaporation of water of crystallization is also observed in the differential thermal analysis (DTA) curve.

All chemicals used were Analytical Reagent (AR) grade. All solutions were prepared in distilled water. In order to prepare a mixed bed resin column employing strong acid cation and strong base anion exchange resins in an ion-exchange capacity ratio of 1:1, calculated amounts of Amberlite 120 LR strong acid cation resin and Amberlite IRA-400 strong base anion resin were packed in the 1.0 cm diameter glass column to a height that will present adequate contact time as well as sample volume collections necessary for breakthrough studies. The LiPB solution of required concentration was passed through the column at a 5–6 mL/min flow rate. The effluent of the column was monitored for specific conductivity, pH, boron, and lithium concentration. Boron (B) and lithium (Li) analysis were done by using an Inductively Coupled Plasma–Atomic Emission Spectrophotometer (ICP–AES) (Jobin Yvon, Horiba Group) and an Hitachi–180 ICP Atomic Absorption Spectrophotometer in emission mode, respectively. The boron concentration was also counterchecked at lower concentrations with the Alizarin red method and at higher concentration by titrimetry using sorbitol. Conductivity was measured using a WTW-LF 56 conductivity meter, and pH was measured using a DOTSON digital pH meter with a combination glass electrode. For a column run with LiPB solution in D_2O, 99.9% D_20 was used for preparing the solution.

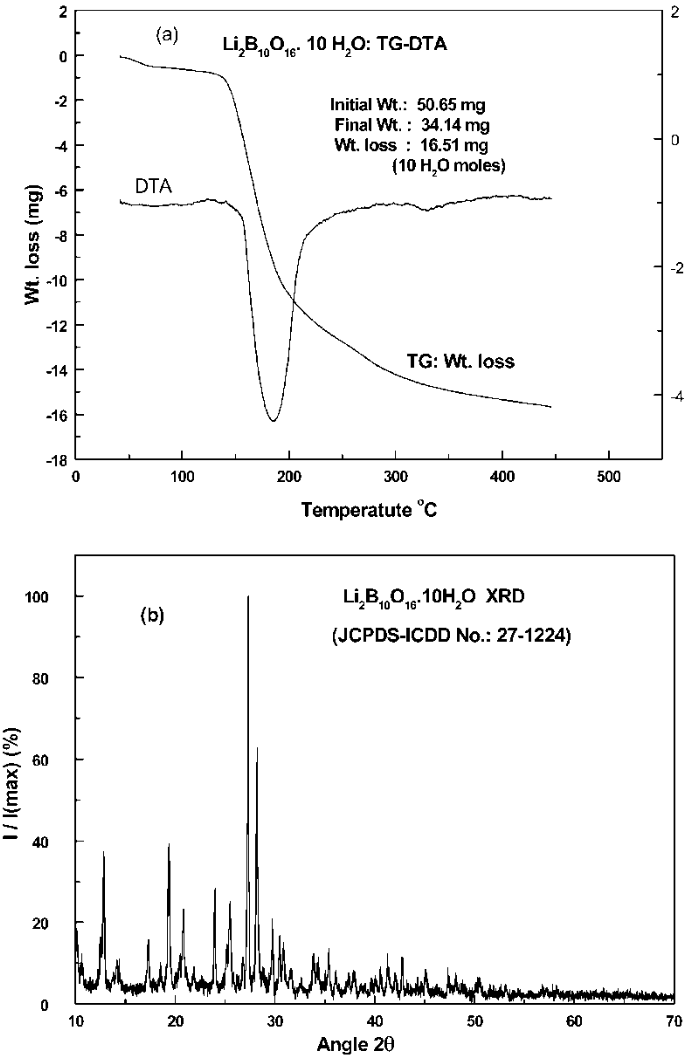


Figure 1. (a) TG-DTA of $Li_2B_{10}O_{16} \cdot 10H_2O$ (LiPB) and (b) XRD spectra of $Li_2B_{10}O_{16} \cdot 10H_2O$ (LiPB).

RESULTS AND DISCUSSIONS

Batch Experiments with Anion Resin

A 5 mL amount of strong base anion exchange resin in OH^- form (having an experimentally determined capacity of 0.8 meq/mL) was equilibrated with

100 mL of 1, 10, 50, 100, and 200 mM LiPB solution for 8 h on a mechanical stirrer and allowed to stand overnight. The supernatant was analyzed for boron and the boron absorbed by resin was found by taking the difference between initial and final boron concentrations. Figure 2a shows the observed capacity of the resin for boron absorption with increasing concentration of boron in solution, which indicates existence of polymeric boron species at higher boron concentration (4). Table 1 shows the data from batch experiments. The pH values observed at the end of equilibration indicate the conditions

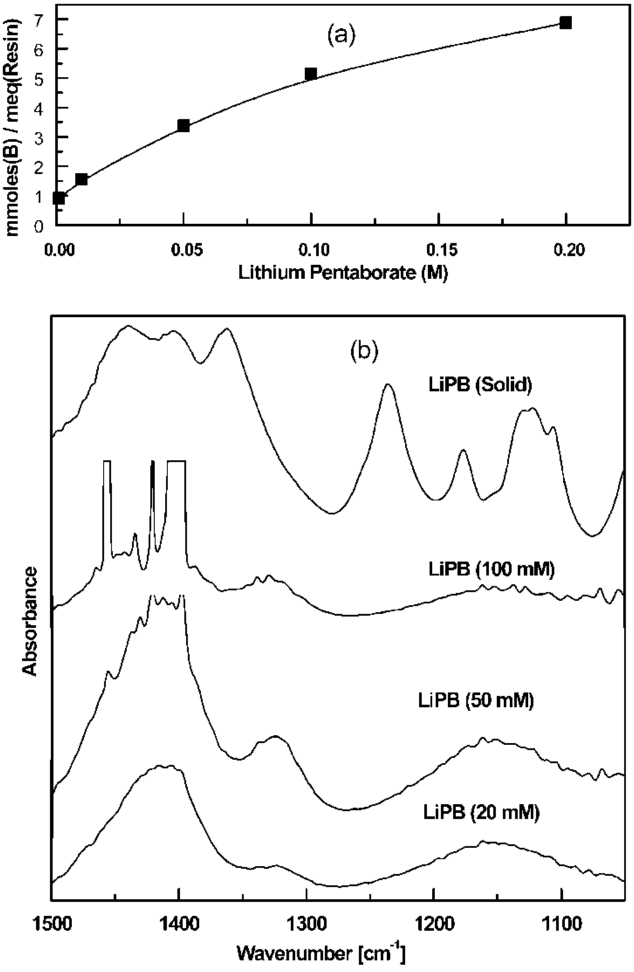
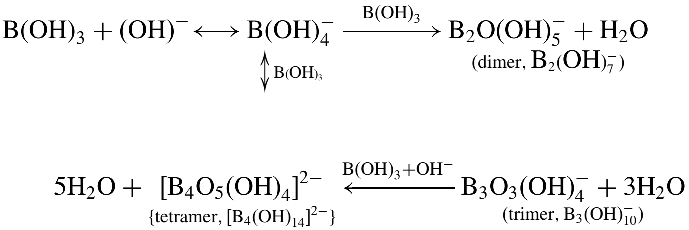


Figure 2. (a) Equilibrium boron removal on anion exchange resin (batch experiment) and (b) IR spectra of LiPB solutions and solid.

Table 1. Boron removal by anion exchanger: results of batch experiments

				Observed boron removal capacity	
Initial concentration (mM) LiPB/B	Initial pH	Final concentration after equilibration (mM) LiPB/B	pH after equilibration	mmols/ mL of resin	mmols/ meq of resin
1/10	8.7	0.095/0.95	11.4	0.2	0.25
10/100	8.6	3.78/37.8	9.4	1.2	1.5
50/500	8.1	36.5/365	8.5	2.7	3.4
100/1000	7.7	79.4/794.3	8.1	4.1	5.1
200/2000	7.2	172.6/1726.2	7.5	5.5	6.9

favorable for the formation of polymeric boron species: at a temperature of 323 K, in the pH range 8–9, and in concentrated boron solution (0.6 M boron), about 20%–50% of boron speciates as trimer while 80%–50% exists as an undissociated boric acid molecules.



$$B(OH)_3 + (OH)^- \longleftrightarrow \underset{\updownarrow\, B(OH)_3}{B(OH)_4^-} \xrightarrow{B(OH)_3} \underset{(\text{dimer},\ B_2(OH)_7^-)}{B_2O(OH)_5^-} + H_2O$$

$$5H_2O + \underset{\{\text{tetramer},\ [B_4(OH)_{14}]^{2-}\}}{[B_4O_5(OH)_4]^{2-}} \xleftarrow{B(OH)_3+OH^-} \underset{(\text{trimer},\ B_3(OH)_{10}^-)}{B_3O_3(OH)_4^-} + 3H_2O$$

In the pH range of 7–8 and at >50 mM total B concentration, about 20% of boric acid exists as trimer while the remaining ~80% exists as undissociated boric acid. However, in the pH region 9–10, boric acid exists as a tetramer (5–20%), trimer (20–50%), monomer (5–20%) and as $B(OH)_3$ (20–40%). In the pH range 10–11, it exists as tetramer (~20%), trimer (~20%), monomer orthoborate ion (30–70%), and $B(OH)_3$ (5–15%). Beyond pH 11 boron essentially speciates as $B(OH)_4^-$. In dilute boron solution (≤50 mM boron) it is only undissociated boric acid and orthoborate ion species that are significant. Since at higher LiPB concentrations (≥50 mM) end of run pHs observed were mostly in the range 7–8, boron existing as a trimeric species could be the cause for the high boron removal capacity observed.

Figure 2b shows infrared spectra of 20 mM, 50 mM, and 100 mM LiPB solution as well as solid LiPB. With the increasing concentration of LiPB, IR spectral features, especially in the 1300–1500 cm^{-1} region, were found to resemble crystalline LiPB, which indicates the presence of polymeric species with increasing boron concentration.

Column Experiments with Anion Resin

Experiments using only an anion resin column (height: 20 cm, diameter: 1 cm,) and those with a column containing layers of anion resin (height: 10 cm, diameter: 1 cm) at the top and a layer of cation resin (of similar dimensions) at the bottom showed significant boron removal. But the boron breakthrough curves were not sharp and from the beginning of the run boron leakage in the column outlet was observed (Figs. 3a and 3b). While with 2 mM the LiPB anion column can yield about 1.1 mmol B/meq capacity, with 200 mM LiPB a capacity of about 3.8 mmol

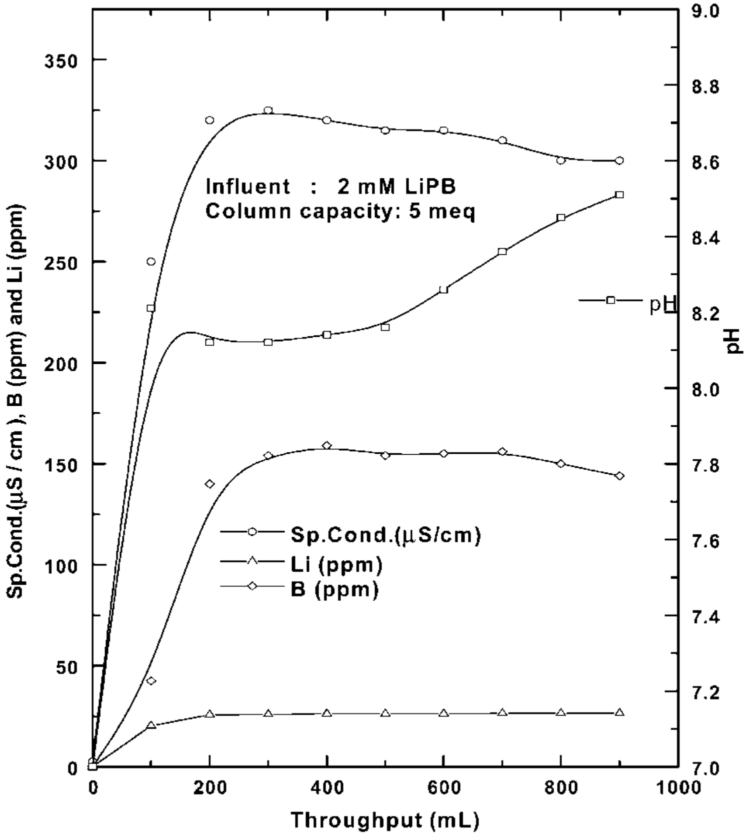


Figure 3a. Boron removal on anion exchanger: column experiment with 2 mM LiPB.

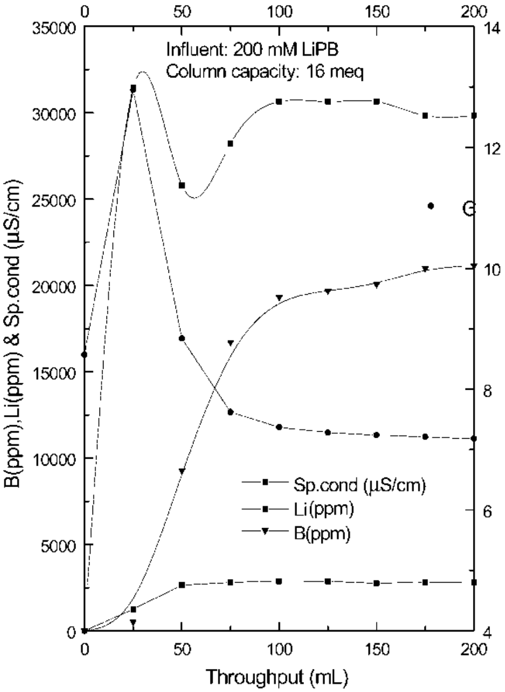


Figure 3b. Boron removal on anion exchanger: column experiment with 200 mM LiPB.

B/meq could be realized. This observation can be explained by the pH-dependent formation of orthoborate as mentioned earlier. The OH^- ions released due to the exchange of anionic polymeric (especially trimer) boron species and the orthoborate ion can cause local increase in pH of solution as it passes through the anion bed. At higher pHs more boron speciates as orthoborate limiting the anion bed capacity for boron removal. This increase in pH can also displace some of the absorbed boron species, thereby causing boron slip through the bed. The buffering action possible in a batch run seems to be limited in a column run. Hence, to avoid the change of solution pH while passing through the resin bed, in all further experiments mixed bed ion exchange resin column containing cation and anion resin was used in a 1:1 capacitywise ratio.

Column Experiments with Mixed Bed Resin

Five runs with varying inlet LiPB concentrations were performed. The inlet LiPB concentrations and observed boron removal capacities are shown in

Table 2. Boron removal parameters for LiPB solution in column experiments with mixed bed resin

Run no.	Breakthrough boron absorption capacity found (mmols B/meq resin)	Major boron species expected	Column capacity (meq)	Column influent LiPB M	B M	pH	Sp.cond. µS/cm
1	1.25	$B(OH)_4^-$	10	0.001	0.010	8.7	145
2	2.25	$B_3(OH)_{10}^-$	10	0.010	0.100	8.6	1,200
3	3.00	$B_3(OH)_{10}^-$	20	0.050	0.500	8.1	4,850
4	3.75	$B_3(OH)_{10}^-$	20	0.100	1.000	7.7	9,000
5	5.00	$B_3(OH)_{10}^-$	30	0.200	2.000	7.2	24,750
6 (D_2O)	5.00	$B_3(OH)_{10}^-$	30	0.200	2.000	7.7	25,000

Table 2. At 0.2 M LiPB concentration it is seen that capacity for boron removal observed (5 mmols/meq resin) is four times the capacity obtained in an 0.001 M concentration.

In the first run, as boron concentration was low (10 mM), the boron speciates as monomer (orthoborate $B(OH)_4^-$ ion 10%) and undissociated boric acid molecules (90%). It is reported that at <20 mM boron levels polymeric boron species are nonexistent (4, 12). As the $B(OH)_4^-$ is removed on passing through the resin, more $B(OH)_3$ can convert to $B(OH)_4^-$ and, hence, essentially all the boron can be sorbed as singly negatively charged monomeric species only. The observed capacity of 1.2 meq/mL for anion exchange resin is close to the capacity expected for boron monomer removal (0.8 meq/mL). Breakthrough characteristic curves for boron, lithium, pH, and specific conductivity for the five runs are shown in Fig. 4. With increasing influent LiPB concentration from 1 mM to 200 mM [(B): 10 mM to 2.0 M] boron removal capacity increases. At 200 mM LiPB (2.0 M boron), the boron removal capacity is 5 mmols/meq anion resin as against 1.2 mmols/meq observed at 1 mM LiPB. The pH of the inlet LiPB solution decreases with increasing boron concentration and an equilibrium pH in the rage of 7.2–8.7, which is observed in the previously mentioned boron concentration range, is favorable for the existence of polymeric species. The increased capacity shown by the anion resin at higher boron concentration in mixed bed configuration indicates that the pH of the inlet solution continues to be in the pH range favorable for the existence of polymeric species as it passes through the mixed bed. At these pHs, conversion of undissociated boric acid to polymeric species (especially as trimer) could be the reason for the observed high capacity

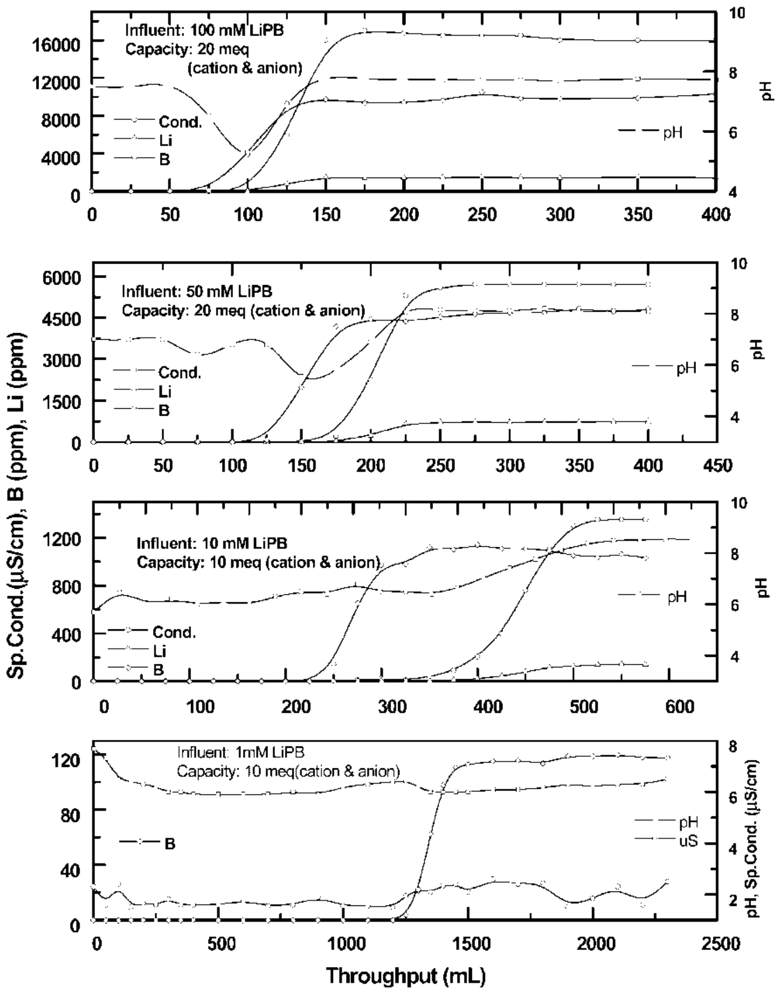


Figure 4. Sp.conductivity, pH and Boron breakthrough curves for various LiPB influent concentrations in column experiments with mixed bed resins.

realized by the anion resin. The possible reactions occurring in the solution/resin could be represented as:

In solution:

$$\begin{array}{l} Li_2B_{10}O_{16}\cdot 10H_2O + 2H_2O \longrightarrow 2LiBO_2 + 8H_3BO_3 \\ 2LiBO_2 + 4H_2O \longrightarrow 2LiOH\ (\text{alkaline}) + 2H_3BO_3 \\ \hline Li_2B_{10}O_{16}\cdot 10H_2O + 6H_2O \longrightarrow 2LiOH + 10H_3BO_3 \end{array}$$

At high boron concentration:

$$3B(OH)_3 + OH^- \longrightarrow B_3(OH)_{10}^-$$

$$(H_3BO_3) \quad \text{speciation at high B concentration}$$

On anion resin:

$$R_4N^+OH^- + B_3(OH)_{10})^- \longrightarrow R_4N^+B_3(OH)_{10})^- + OH^-$$

On cation resin:

$$RH^+ + LiOH \longrightarrow RLi^+ + H_2O$$

At low boron concentration:
In solution:

$$B(OH)_3 + OH^- \longrightarrow B(OH)_4^-$$

On resin:

$$R_4N^+OH^- + B(OH)_4)^- \longrightarrow R_4N^+B(OH)_4)^- + OH^-$$
$$RH^+ + LiOH \longrightarrow RLi^+ + H_2O$$

Table 3 shows the variation of pH around the breakthrough point in the studies on boron removal from LiPB solutions in light water using mixed bed resin. Before boron breakthrough, at LiPB concentration ≤ 50 mM, the column outlet solution has a near neutral pH (~7.0), while at LiPB ≤ 10 mM the outlet pHs were acidic (pH ~6.3). The excess cation capacity available in the column is lower at higher LiPB concentrations. At higher Li^+ in solution, due to the poor selectivity of Li^+ over H^+, there can be a cationic slip of LiOH, which could be the cause for the higher pHs observed. At lower LiPB concentrations, wherein the mixed bed column had higher residual cation capacity and complete removal of Li^+ occurs, the result could be more acidic pHs. At breakthrough, in the case of higher inlet LiPB concentrations (≤ 50 mM), there is a pH drop of 0.5–2.0 units. The high free boric acid concentrations observed at breakthrough in the case of concentrated LiPB solutions appears to be the cause of this pH drop. At lower LiPB concentrations (≤ 10 mM) no such pH drop is observed since the pH before breakthrough is already lower for the reasons mentioned earlier. The steady-state pHs observed after breakthrough in the higher LiPB cases (≤ 10 mM) are as expected, e.g., close to the pHs of inlet solution. In the case of 1 mM LiPB solution, the steady state pH after breakthrough is still acidic since Li^+ breakthrough has not been reached due to the excess cation capacity.

Figure 5 compares the breakthrough curves for 0.2 M LiPB solution in light and heavy water. In both media boron breakthrough characteristics observed are similar. The existence of polymeric boron species in concentrated LiPB solution is shown in D_2O medium also. A capacity 5 mmol/meq of resin

Table 3. Variation of pH around breakthrough point in the studies of boron removal from LiPB solution in light water using mixed bed resin

		pH			
Solution concentration of LiPB (mM)	Mixed bed resin meqs of cation:anion capacity	Before boron breakthrough	At boron breakthrough	Steady state after breakthrough	Residual capacity at breakthrough %
200	30:30	6.7	6.2	7.2	0
100	20:20	7.5	5.5	7.7	25
50	20:20	7.0	5.9	8.0	40
10	10:10	6.4	6.5	8.2	55
1	10:10	6.2	6.0	6.2	75

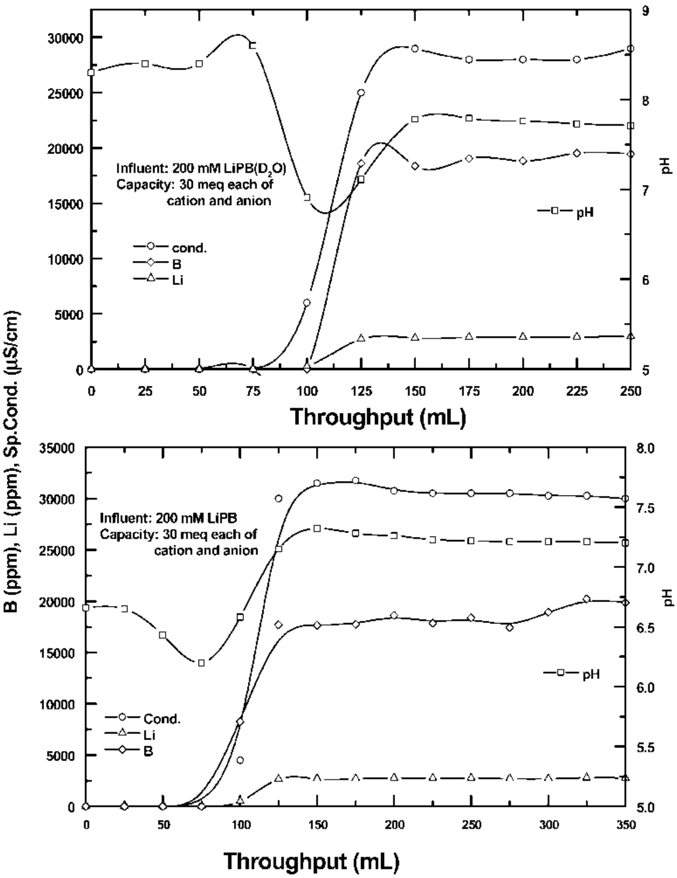


Figure 5. Breakthrough curves for 200 mM LiPB solution in light and heavy water media in column experiments with mixed bed resins.

for boron removal is obtained in both the media. The apparent pH in D_2O solution measured with a combination electrode calibrated for light water applications is expected to be higher by 0.4 units than are the pHs observed in light water solutions. The pH before boron breakthrough in D_2O solution is 8.4 as compared to 6.7 seen in light water. Since this difference is more than 0.4 units, it appears that Li slip to the extent of ~6 ppb (much below the detection limits of flame photometric technique) could be the reason for the excess alkalinity. The slower rate of Li^+ exchange in D_2O solution could be the cause for such a slip. At boron break through, the pH observed is 6.9 in D_2O solution as compared to 6.2 in H_2O solution, which indicates the suppressed dissociation of boric acid in D_2O. The steady state pH of 7.7 observed after boron breakthrough in D_2O solution as against 7.2

in H_2O solution under similar conditions shows the buffering effect in $LiOD + D_3BO_3$ solution is able to bring the pH difference close to the expected values between D_2O and H_2O solutions.

Case Study

In the secondary shut down systems of pressurized heavy water reactors of the generation currently operating in India, 0.17 M LiPB is used as a liquid poison. In these reactors there is a need to recover D_2O from the LiPB solution prepared in excess of the actual amount required. A question arose as to whether large quantities of ion exchanger would be required to remove lithium and boron from the solution used for freeing D_2O and whether the evaporation/condensation method would be more advantageous than the ion-exchange method. The ion-exchange method was evaluated as a sequel to the studies reported in this work, and the evaporative method was qualitatively compared with the ion-exchange method.

Figure 6a shows the breakthrough curves obtained in the column experiments for boron removal from LiPB solution in the concentration range 1 mM–200 mM while Fig. 6b depicts the boron removal capacities of the ion exchange resin (expressed as mmols of B/meq of resin) in the mixed bed column as a function of LiPB concentration. At 170 mM LiPB an interpolated boron removal capacity of 4.5 mmols/meq of resin is obtained. Use of an anion resin of theoretical capacity 1.1 meq/mL is assumed in the calculation. In order to remove boron from 1 L of 170 mM LiPB solution using the boron removal capacity value mentioned earlier, about 344 mL of anion resin would be required. In order to remove lithium from this solution a cation resin with a theoretical capacity of 1.8 meq/mL is assumed, a cation resin of 189 mL would be needed. A mixed bed column employing a volume ratio of cation to anion as 1:1.8 with a total resin volume of 533 mL would be adequate, assuming 100% column efficiency. At 90% column efficiency assumed for an operation involving mixed bed resin a total resin volume of 600 mL (cation 210 mL, anion 390 mL) is needed for recovering all the D_2O from 1 L of 170 mM LiPB solution in heavy water. In deboronating 1500 L of 0.170 M LiPB solution, the requirement for cation resin is 315 L and that for anion is 585 L. Two 500 L volume capacity resin columns each having 158 L of cation and 293 L of anion would be able to accomplish this task. At the end of separation, the column could be drained off all liquid. After deboronation, the cation and anion resins can be separated from the mixed bed configuration and regenerated with acid and alkalies, respectively. The regenerated resins are ready for reuse. The regenerated effluents can be neutralized and then can be evaporated in a solar pond to recover solids. There need not be any discharge to the environment. In the ion exchange method, the deboronation occurs at room temperature

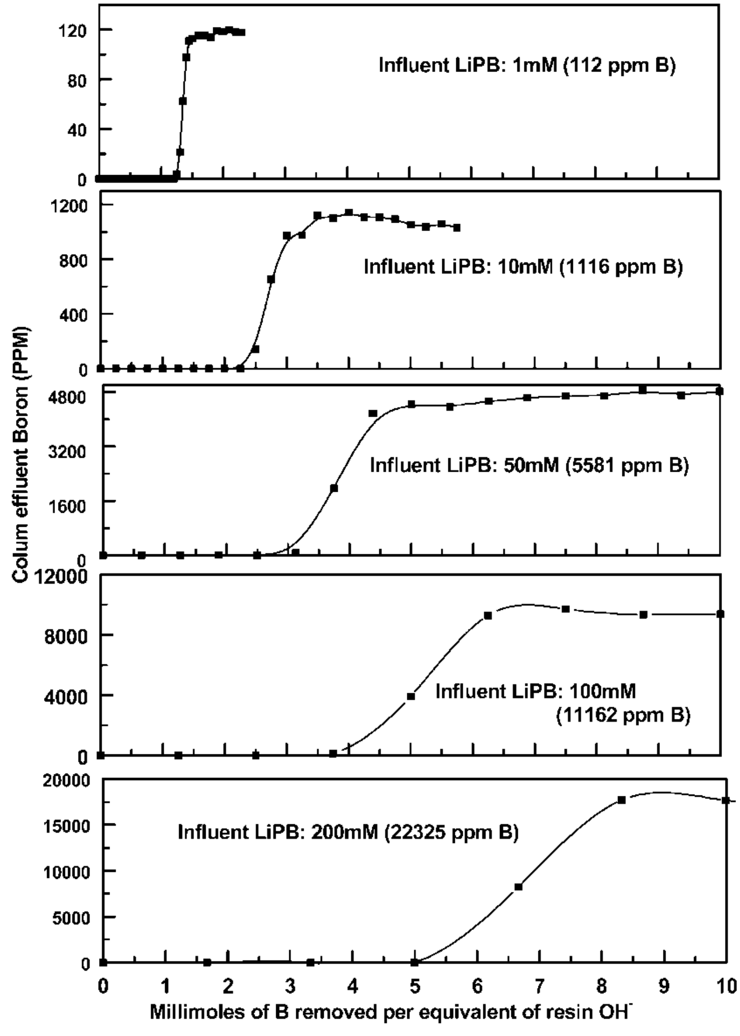


Figure 6a. Breakthrough boron removal in column experiments with mixed bed resin as a function of influent boron concentration.

and resins can be reused after regeneration. The evaporative-condensation method is energy intensive and requires a variety of equipment: namely, evaporator, condenser, and receiver, etc. The residue left at the end in this method has either to be diluted and disposed of to keep D_2O concentration in the water body at the natural level or the residue has to be totally dried by heating, taken out in light water as slurry, and then evaporated in a solar pond.

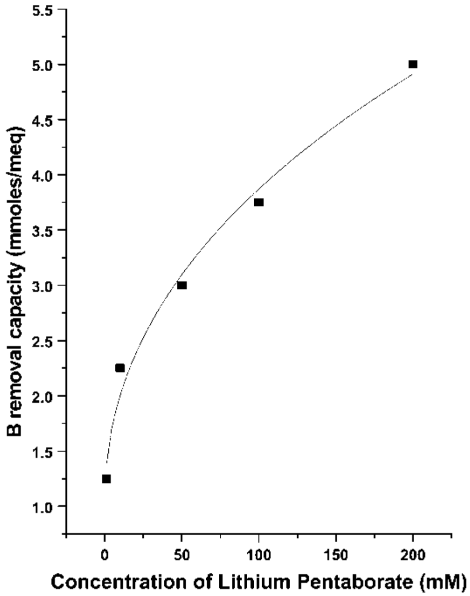


Figure 6b. Boron breakthrough capacity as a function of LiPB concentration observed in column experiments with mixed bed resin.

CONCLUSIONS

1. The boron removal capacity shown by anion exchange resin increases with increasing LiPB concentration. A capacity of 4.5 mmols B/meq of anion resin (of theoretical capacity 0.8 meq/mL) has been realized in the column experiment at 170 mM LiPB concentration. Even a batch equilibration run has yielded this increased capacity.
2. The anion resin taken in mixed bed form has given a sharp breakthrough and shown the high capacity for boron removal. The pH variation in the range of 6.5–7.0 occurring in the column appears to be favorable for the formation of polymeric boron species. A simple anion column yields boron slip right from the beginning of the treatment.
3. The ion exchange method of separating D_2O from LiPB solution seems to be advantageous compared to the evaporative method.

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