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Boron removal by Donnan dialysis

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ABSTRACT

The mechanism of the diffusive boron transfer through anion exchange AMX (Neosepta) membrane was evaluated by multiple regression methods. It was found that Donnan dialysis (OH^-–$B(OH)_4^-$ exchange) phenomena dominates over simple boric acid diffusion dialysis. Thus to enhance boron fluxes as well as its removal efficiency the process should be carried at as high as possible receiving solution pH while the feed solution pH should be maintained low.

Keywords: Boron removal; Ion-exchange membrane; Donnan dialysis

1. Introduction

Boron compounds belong to the second class of the toxicological danger [1] and the recommended by the WHO permissible concentration of boron in drinking water is 0.5 mg/L [2], and in the European Union 1 mg/L [3].

Many methods for removing of boron from waters have been investigated: chemical precipitation with inorganic (lime, salts of aluminum and magnesium) and organic compounds (polyvinyl alcohol, hydroxycarboxylic acid), adsorption, extraction, ion exchange (particularly utilizing Amberlite IRA-743 resin), reverse osmosis, electrodialysis and electrocoagulation [4].

Electrodialysis of boron containing waters, using AMX and CMX commercial membranes, was examined in our previous work. The boron containing water was preliminarily desalinated industrial landfill leachate from Tarnowskie Góry (Poland) chemicals storage facility and contained mainly boric acid, at around 75 mg/L concentration. Boron is transferred through the anion-exchange membranes in its anionic form ($B(OH)_4^-$) from the diluate (feed) to the concentrate (receiving solution). Under alkaline conditions significant amount of boron occurs in ionized form of boric acid, but to ensure the relatively high value of boron flux through the membranes, it is essential to keep the receiving solution pH high at moderate to low pH of the feed solution. It was found that high initial diluate (feed) pH value does not enable reliable boron flux through the membrane which may be explained by high mobility of hydroxide ions as related to borate anions. Thus, OH^- ions are primarily transported from the depleted diffusion layer through the membrane, that leads to hydroxide content decrease and subsequent decrease in borate content, that is the mobile form of boron. Higher than 100% boron electric current efficiency observed at concentrate pH of 12.0 suggested that electrodialysis is enhanced by other than electromigration process, more particularly by Donnan dialysis, so we decided to further investigate this phenomena in separate [5,6].

Shimada et al. examined the removal of boron from aqueous solution with polyvinyl alcohol membranes under the conditions where one side of membrane was kept acidic and the other alkaline (pH 10). The borate ions formed a complex with the membrane, and the chemical potential gradient compelled borate transport [7].

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In the studies conducted by Bryjak et al. Donnan dialysis was investigated as a new method for regeneration of boron selective resins. Authors describe the transport of boron from boric acid aqueous solution containing 1000 ppm of boron and from boron selective resin DOWEX XUS 43594.00 slurry containing 1000 ppm of boron, to the high saline brine coming from the first stage RO. They used solution of pH between 8.5–10.5. The same pH was kept in both compartments during the measurements. One of the membranes used in their study was AESD-2 interpenetrating polymer membrane (IPN). The membrane is fabricated from polyethylene modified with a copolymer of styrene and divinylbenzene, functionalized with dimethylethanoloamine, and has a thickness of 180 mm. They investigated two kind of salts NaCl and Na_2SO_4 as the borate drivers [8]. The values of borate fluxes are listed in Tables 1 and 2.

In [9] boron removal from aqueous solution by Donnan dialysis, using Neosepta AHA, AFN and AMH membranes, as a function of concentration, effect of accompanying ions and pH was studied. The highest pH used in investigations was 11.5, and the driving force assumed was chloride ions concentration gradient.

In this paper the results of removing boron by utilizing Donnan dialysis are presented. The possibility of removing boron from aqueous solution containing 75 mg B/L to NaOH solutions of varying pH by Donnan dialysis was examined in laboratory. The fluxes of boron and hydroxide were evaluated in terms of feed and receiving solution chemical composition.

Table 1
Fluxes of borate, 10^9 mol/cm^{2}s [8]

pH	IPN membrane	
	The boron driver:	
	Cl^-	SO_4^{2-}
8.5	1.53	0.82
9	1.53	0.67
9.5	1.77	0.75
10	1.92	0.60
10.5	1.98	0.73

Table 2
Normalized fluxes of borate, 10^9 mol/cm^{2}s [8]

pH	IPN membrane	
	The boron driver:	
	Cl^-	SO_4^{2-}
8.5	2.75	1.48
9	2.75	1.21
9.5	3.19	1.35
10	3.45	1.08
10.5	3.56	1.31

The driving force in Donnan dialysis is the chemical potential gradient, there is a stoichiometric exchange of co-ions through an ion-exchange membrane, and the process ends only when the Donnan equilibrium is reached. In this process the electroneutrality of the solutions is uphold, so stoichiometrically equal amounts of co-ions should flow from the feed to the receiving solution [10–15].

In our particular case, the concentration difference of hydroxide ions (OH^-) between the two solutions compels the hydroxide ions to diffuse into the feed solution. This creates an oppositely directed equivalent borate transport from the feed solution to the receiving solution.

2. Experimental

A module equipped with four anion-exchange AMX Neosepta (Tokuyama Co.) membranes was used in the investigation (Fig. 1). AMX membrane is made from styrenedivinylbenzene copolymer and is strongly basic, which means that ion exchange groups are quaternary ammonium salts. The thickness of AMX membrane is 140 mm. The experiments were performed in a batch mode. A thin spacer allowed single stack 0.40 mm membrane to membrane distance. The working membrane area was 842 cm^2 and linear flow velocity varied in the range of 7–8 cm/s.

Deionized water of natural pH and pH corrected to the value of 11 or 12, by the addition of small volume of 0.1 or 1 M NaOH, were applied as the receiving solution. Thus OH^- ion was applied as boron driver. The boric acid solution containing 75 mg/L of boron was applied as a feed solution. About 2 L of feed and receiving solutions were used for each test. Boron concentration was controlled in both feed and receiving solutions. Boron content was measured fluorometrically, as a fluorescent complex with

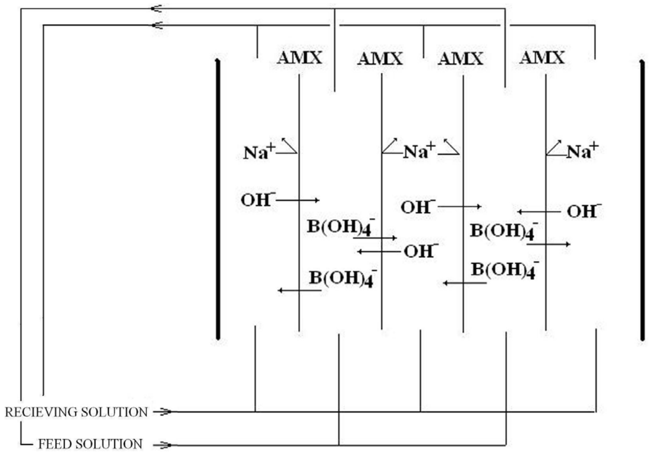

Fig. 1. The principle of boron removal by Donnan dialysis in a stack with anion-exchange membranes.

chromotropic acid in alkaline environment at 313 nm excitation and 354 emission radiation wavelengths. In this range, the relationship between emission intensity and concentration was linear in the range of 0.01–2.5 mg B/L. The samples of higher concentration were diluted in order to match the above linearity range. Before each test, the membrane module was rinsed for 4 h with the boric acid solution containing 75 mg B/L to avoid later boron adsorption and accumulation into the membrane that would affect the measurement results.

To determine hydroxide concentration, pH of feed and receiving solutions were measured and calculated from the ionic equilibrium based on equations shown below, valid at around 25°C:

$$[H_3O^+] = 10^{-pH} \tag{1}$$

$$[OH^-] = \frac{10^{-14}}{[H_3O^+]} \tag{2}$$

If the solutions' pH is known, borate concentration could be calculated from boric acid dissociation product constant and total (analytical) boron concentration. Usually in aqueous solutions boric acid is in its non-ionized form; since its dissociation constant is low $pK_a = 9.27$ at around 25°C [16]:

$$H_3BO_3 + 2H_2O \rightleftarrows B(OH)_4^- + H_3O^+$$
$$K_a = \frac{[H_3O^+]\cdot[B(OH)_4{}^-]}{[H_3BO_3]} \tag{3}$$

Mass and ion-charge balance equations for the feed solution are then as follows:

$$C_a = [H_3BO_3] + [B(OH)_4^-] \tag{4}$$

$$[H_3O^+] = [OH^-] + [B(OH)_4^-] \tag{5}$$

The above balance equations for the receiving solution, containing mainly borate and sodium hydroxide (except the experiment, where deionized water was the receiving solution), are as follows:

$$C_b = [Na^+], C_a = [H_3BO_3] + [B(OH)_4^-] \tag{6}$$

$$[Na^+] + [H_3O^+] = [OH^-] + [B(OH)_4^-] \tag{7}$$

Borate concentration could be then calculated from the following equation:

$$[B(OH)_4^-] = \frac{K_a C_a}{K_a + [H_3O^+]} \tag{8}$$

While the concentration of the boric acid from the boron mass balance as follows:

$$[H_3BO_3] = C_a - [B(OH)_4^-] \tag{9}$$

Finally, the sodium ion concentration in the receiving solution can be determined by rearranging ion-charge balance equation as follows:

$$[Na^+] = [OH^-] + [B(OH)_4^-] - [H_3O^+] \tag{10}$$

where C_a and C_b — analytical concentrations of boric acid and sodium hydroxide.

If concentration changes during the process are known, minute fluxes of particular ions could be calculated from the relation:

$$J_i = \frac{dc_i}{dt}\cdot\frac{V_{soln.}}{A} \tag{11}$$

where J_i — molar flux of component i, mol/m^2·s; c_i — concentration of component i, mol/L; t — time, s; $V_{soln.}$ — solution volume, L; A — active area of the membrane, m^2.

At first concentration time data were fit with various linear, polynomial and exponential empirical relationships by applying Curve Expert 1.3 software. Such empirical $C - t$ curves, however, the one that fits the data with the lowest variance (highest R^2) were taken for further consideration, and constituted the base for minute boron flux determination based on Eq. (11).

3. Results

When deionized water was used as receiving solution (Fig. 2), boron concentration decreased only slightly with time and was limited to a large extent when compared to receiving solution of elevated pH. Such a limited decrease in feed solution boron concentration was observed because boron existed in the boric acid (non-ionized) form only in both feed and receiving solutions. As a consequence, the feed boric acid concentration – receiving solution boric acid concentration equilibrium was produced readily and macroscopically, no further boron transport was observed. Moreover, this equilibrium does not favor high boron removal degree that can be clearly seen in Fig. 2, especially when $t > 350$ min.

In the case of alkaline receiving solution processing (Fig. 3 and 4), much stronger decrease in the boric acid feed concentration than in the case of previously discussed neutral deionized water was observed. This can be also seen in the flux vs. time curve (Fig. 5) where the highest boron fluxes are observed in the case of the highest pH receiving solution while the lowest for neutral distilled water. Also the extent to which boron was removed from the feed solution increase with the pH of the receiving solution; the receiving solution pH of 12 produced as low as 2 mg/L boron concentration after 210 min while the neutral receiving solution produced the least — 55 mg/L only.

The above observations suggest that both the kinetics (flux) and equilibrium (boron removal degree at infinite time) of the dialysis process is strongly affected by the pH of the receiving solution. Two distinctly different phe-

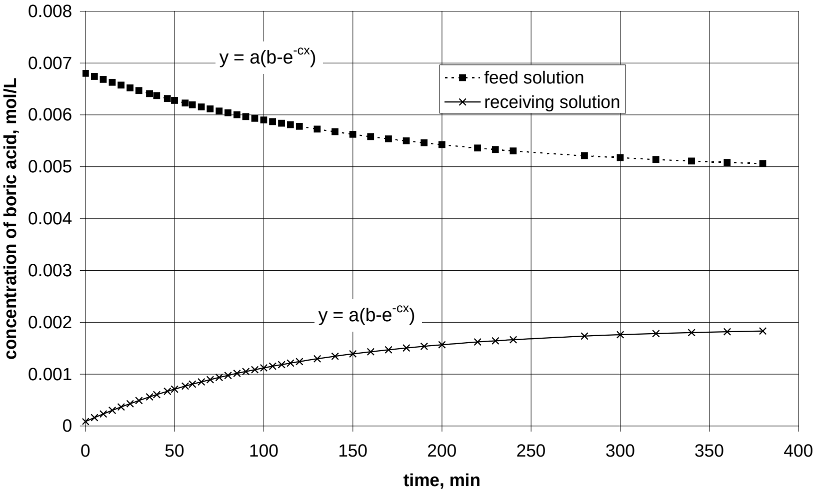

Fig. 2. Boric acid concentration vs. time, receiving solution — deionized water.

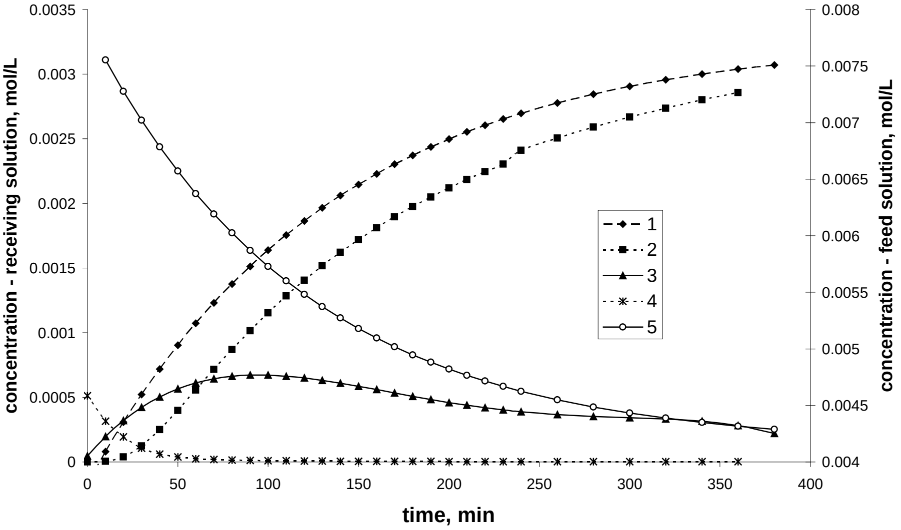

Fig. 3. Concentration vs. time, receiving solution — NaOH aqueous solution of pH 11. 1 – Total boron concentration in receiving solution, 2 – fraction of non-ionized form (H_3BO_3) in receiving solution, 3 – fraction of ionized form ($B(OH)_4^-$) in receiving solution, 4 – hydroxide concentration in receiving solution, 5 – boron concentration in feed solution (all in non-ionized form).

nomena may contribute to the above observation: boric acid diffusion or Donnan dialysis where the hydroxyl–borate ion exchange facilitates boron transport. In the case of boric acid diffusion H_3BO_3 concentration gradient constitutes the driving force for boron transport while in the case of Donnan dialysis, the OH^- concentration difference between the receiving and feed solution does. In each case, the linear relationship between the given driving force and boron flux is suspected, including concentration polarization phenomena at fixed mass transport coefficient (fixed solution linear velocity), therefore we concluded that the dominant boron transport mechanism may be determined by multiple regression exploration of the data collected. Those calculations were conducted applying Statistica (Statsoft) software. The correlation matrix shown in Table 3 suggests the strong linear correlation between boron flux and receiving solution hydroxyl concentration and some negative correlation with receiving solution boric acid content as well as feed solution hydroxyl concentration. This suggests Donnan dialysis, governed by the receiving solution hydroxyl concentration, is the dominant boron transport mechanism since there is only slight, statistically not significant correlation between boron flux and boric acid feed solution minute concentration.

The results of the further analysis of the data collected by applying multiply regression methods are summarized in Table 4. The constant in the linear multiple model applied was presumed to be equal to zero. Despite the fact that the inward method for statistically significant

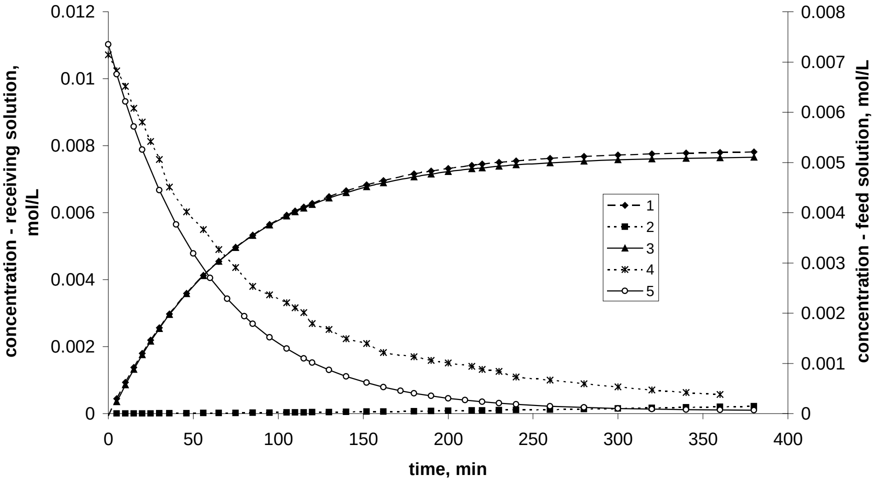

Fig. 4. Concentration vs. time, receiving solution — NaOH aqueous solution of pH 12. 1 – total boron concentration in receiving solution, 2 – fraction of non-ionized form (H_3BO_3) in receiving solution, 3 – fraction of ionized form ($B(OH)_4^-$) in receiving solution, 4 – hydroxide concentration in receiving solution, 5 – boron concentration in feed solution (all in non-ionized form).

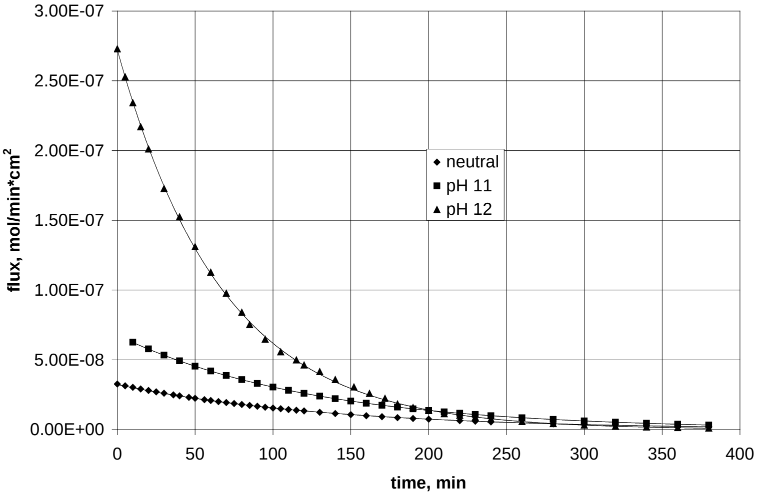

Fig. 5. Flux vs. time.

Table 3
Correlation matrix

Variable	Boron flux, J_i
Boron flux, J_i	1.00
Feed solution H_3BO_3 concentration	0.10
Receiving solution H_3BO_3 concentration	–0.46
Feed solution borate concentration	–0.07
Receiving solution borate concentration	0.03
Feed solution OH^- concentration	–0.20
Receiving solution OH^- concentration	0.927

($p < 0.05$) factors elimination method was chosen, all the examined variable linear regression estimates were found to be statistically significant at the presumed significance level.

The highest value of the normalized linear regression estimate observed for receiving solution hydroxyl content at approximately two times lower value of that coefficient with respect to the boric acid feed concentration. This also suggests the dominant character of the receiving solution hydroxyl concentration governing the boron transport mechanism, namely Donnan dialysis. Such a conclusion is also supported by the positive value of the feed solution specific borate concentration. However, the significant simple boric acid diffusion dialysis should be also taken into account since feed boric acid content specific estimate value in Table 2 is significantly high. In addition, the high value of the receiving solution boric acid concentration specific multiply regression estimate suggest boric acid back diffusion beimg the dominant process to cause boron flux shortage and as such may be identified as the one that limits the effectiveness of boron removal to a greater extent.

Table 4
Multiple regression results, $R^2 = 0.988$

Variable	Normalized estimate	Estimate, m/min	Estimate standard error, m/min
Feed H_3BO_3 molar conc., mol/L	0.427	5.06×10^{-5}	2×10^{-6}
Feed $B(OH)_4^-$ molar conc., mol/L	0.574	8.01×10^{-2}	8×10^{-3}
Receiving solution H_3BO_3 molar conc., mol/L	–0.231	-1.11×10^{-4}	7×10^{-6}
Receiving solution $B(OH)_4^-$ molar conc., mol/L	–0.423	-7.22×10^{-5}	5×10^{-6}
Feed OH^- molar conc., mol/L	–0.287	–0.42	5×10^{-2}
Receiving solution OH^- molar conc., mol/L	0.851	1.85×10^{-4}	3×10^{-6}

Based on the above, it may be concluded that the boron removal process should be carried out at as high as possible receiving solution hydroxyl ion content (alkalinity) in order to assure both high Donnan dialysis and boric acid dialysis rate as well as to prevent boric acid back diffusion to the feed solution.

The values of borate fluxes are listed in Tables 5 and 6.

Then an attempt was undertaken to compare the results presented by Bryjak et al. [8], concerning the AESD-2 IPN membrane (see Tables 1 and 2) and our results (see Tables 5 and 6) obtained using the AMX membrane. As concerns the applied membrane properties, both mentioned membranes are similar, which makes the comparison possible to perform. Bryjak et al. [8] did not, however, precisely explained whether they presented the initial or average flux values.

From the data presented in Tables 1–2 and 5–6 it is seen that hydroxide applied as boron driver in the Donnan dialysis process offers better results than sodium chloride or sodium sulfate. Thus the normalized flux value observed at pH = 12 (that corresponds to 0.01 M, Table 6) is higher than that observed in the case of both Cl^- and SO_4^{2-} (Table 2) despite the fact that concentration of OH^- ions as driver is two orders of magnitude lower than concentration of Cl^- or SO_4^{2-} (1 M) drivers in spite of a much lower boron concentration in the feed solutions (respectively 75 and 1000 mg/L).

When sodium or potassium hydroxide is considered as dialysis boron driver, obtained final receiving solution, consisting mainly of borate acid sodium or potassium salt, may be possibly used as a component of boron containing multi-component fertilizer that may be recognized as another advantage of the proposed Donnan dialysis mode.

Table 5
Fluxes of borate, 10^9 mol/cm^{2}s

pH	AMX membrane	
	The boron driver: OH^-	
	Initial flux	Average flux (during 200 min)
11	0.83	0.54
12	4.50	1.68

Table 6
Normalized fluxes of borate, 10^9 mol/cm^{2}s

pH	AMX membrane	
	The boron driver: OH^-	
	Initial flux	Average flux (during 200 min)
11	1.16	0.76
12	7.20	2.35

4. Conclusions

The mechanism of the diffusive boron transfer through the anion exchange AMX (Neosepta) membrane was evaluated by multiple regression methods. It was found that Donnan dialysis (OH^-–$B(OH)_4^-$ exchange) phenomena dominate over simple boric acid diffusion dialysis. Thus to enhance boron fluxes as well as its removal efficiency, the process should be carried out at as high as possible receiving solution pH while the feed solution pH should be maintained low.

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