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A environmentally friendly process for boric acid and sodium hydroxide production from borax; bipolar membrane electrodialysis

Jülide Erkmen[a,*], Sinan Yapici[b]

[a]*Faculty of Engineering and Architecture, Chemical Engineering Department, Kafkas University, Kars 36300, Turkey, Tel. +90 474 2257717; Fax: +90 474 2251279; email: jerkmen@hotmail.com*
[b]*Engineering Faculty, Chemical Engineering Department, Atatürk University, Erzurum 25240, Turkey, email: syapici@atauni.edu.tr*

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ABSTRACT

In this study, the production of boric acid from borax was carried out by electrodialysis with bipolar membranes. The current efficiencies for boric acid and sodium hydroxide production by bipolar membrane electrodialysis were determined to be between 93.13 and 99.53%. In addition, the products with purity up to 99.52% (in weight) H_3BO_3 and 99.12% (in weight) NaOH were obtained. This method gives a facility of producing of sodium hydroxide and boric acid without any harmful waste material and offers an alternative process to commercial production methods for boric acid and sodium hydroxide.

Keywords: Borax; Boric acid; Sodium hydroxide; Electrodialysis; Bipolar membrane

1. Introduction

Boron, which is one of less available elements in the earth, is an important substance used widely in the chemical industry for the production of numerous chemicals such as fiber glass, ceramic, detergent, fire-resistive substances, insulators, etc., and in a number of industries such as agriculture, metallurgy, and nuclear [1]. Turkey has the largest boron reserves in the world; it is estimated that Turkey has approximately 61% of the known world reserves [2]. Turkey's commercially recoverable boron reserves are colemanite ($Ca_2B_4O_8{\cdot}5H_2O$), pandermite ($CaB_6O_9{\cdot}7H_2O$), ulexite ($NaCaB_5O_9{\cdot}8H_2O$), and tincal ($Na_2B_4O_7{\cdot}10H_2O$) [3].

Many studies on the upgradation of boron minerals were made by some researchers [4–8]. Boric acid (H_3BO_3) is produced industrially from borate minerals; generally by the reaction of earth alkali metal borates with strong acids to form boric acid. In Turkey, boric acid is obtained by the reaction of colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$) concentrates with sulfuric acid.

Many methods have been proposed for the production of boric acid from borax, such as boric acid production from a solution of borax [9]. Boric acid is produced from boron minerals, using mainly strong acids such as sulfuric acid, hydrochloric acid, and nitric acid. However, in these processes, the equipment life is short due to strong acidity, and high acid cost [10]. The most commonly used commercial method is the process which uses sulfuric acid to produce boric acid from tincal [11]. All these processes employing strong acids produce hazardous wastes such as $Ca(NO_3)_2$, Na_2SO4, $CaSO_4$, and cause serious environmental pollution. Researchers have been more concerned with the environmental risks of the wastes from boric acid production processes and

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*Corresponding author.

boron-containing wastes [12,13] and its toxicity to exposed workers [14,15]. Besides, all these processes require multi-stage operations, usually performed at high temperatures and are often dangerous.

Bipolar membrane electrodialysis (BPMED) is a technique, which is well adapted to convert a salt into its conjugated acid and base [16]. The technique is based upon the use of a bipolar membrane to dissociate water to H^+ and OH^- [17]. Some researchers studied the regeneration of concentrated organic and inorganic acids by BPMED [17–21].

There are increasing demands for alternative process solutions, which are more energy efficient and less harmful to the environment, over the classical production processes. Since, in the production of acid and base, conventional methods generate large amounts of chemical wastes, BPMED can be considered as an alternative technique for acid and base production from salts, avoiding the use of strong acids [21]. The purpose of this study is to investigate an alternative, environmentally friendly process, BPMED, for the production of boric acid and sodium hydroxide.

2. Experimental

2.1. Materials

Chemicals ($Na_2B_4O_7 \cdot 10H_2O$ (Borax), H_2SO_4, H_3BO_3, NaOH, and Carmine indicator) used in the experiments and analysis were purchased from MERCK. Ion-exchange membranes and bipolar membranes were provided from PCA GmbH. Table 1 illustrates main characteristics of the commercial membranes used in this work. The cathode is stainless steel and the anode is Pt/Ir-MMO coated Ti-stretched metal. The applied voltage was supplied and controlled by a direct-current source.

Table 1
Main characteristics of the homopolar membranes used in this work

	PC acid 60	PC SK
Transference number		
KCl (0.1/0.5 N) [a]	>0.95	>0.95
Acid (0.7/3 N) [b]	55	
Resistance (Ω cm$^{2)}$	~2	~2.5
Water content (wt%)	~17	~9
Ion exch. capacity		
Strong basic (meq/g)	ca 1.14	n/a
Weak basic (meq/g)	ca 0.45	

[a] Calculated from potentiometric measurements.
[b] Observed current efficiencies.

The analysis of boron was performed by Carmine method and was monitored by UV spectrophotometer (Mapada V-1100) at a wavelength of 585 nm. The analysis of sodium was carried out by flame photometer (Sherwood 410).

2.2. Methods

The arrangement of the membranes in the laboratory cell is shown in Fig. 1 which illustrates the scheme of laboratory cell of process. The laboratory cell was composed of three cells with three compartments. The three-compartment cell was obtained by combining the bipolar membrane cation exchange with conventional electrodialysis cell and anion-exchange membranes. The solutions circulated through the compartments were H_3BO_3 solution between the bipolar and the anion-exchange membranes, NaOH solution between the bipolar and the cation-exchange membranes, and borax solution between the cation- and anion-exchange membranes [22]. Thus, $B_4O_7^{=}$ ions pass across the anion-exchange membrane and Na^+ ions pass across the cation-exchange membrane. These ions were combined with H^+ and OH^- ions coming from bipolar membrane, producing H_3BO_3 and NaOH.

When expressing in a simple way, the reactions occurring in the cell can be written as follows:

Anode reaction: $2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$

Cathode reaction: $2H_2O^+ + 2e^- \rightarrow H_2 + 2OH^-$

Acid compartment: $2H^+ + B_4O_7^{=} \rightarrow 5H_2O \rightarrow 4H_3BO_3$

Base compartment: $Na^+ + OH^- \rightarrow NaOH$

The overall reaction for the process can be expressed as:

$$Na_2B_4O_7 + 8H_2O \rightarrow 2NaOH + 4H_3BO_3 + 1/2\,O_{2(g)} + H_{2(g)}$$

Fig. 2 illustrates the concentration profile and material balance of this process. The mass balance of the acid compartment can be written as:

$$V\frac{dC_{Na^+}}{dt} = A\sum J_{Na^+} \tag{1}$$

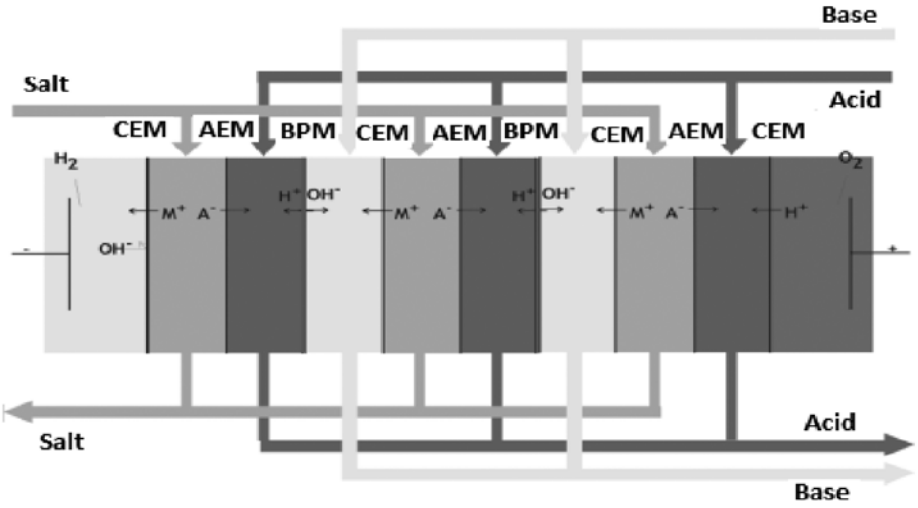

Fig. 1. Schematic diagram of laboratory cell for boric acid production by (BPM: bipolar membrane, CEM: cation-exchange membrane, AEM: anion-exchange membrane [23]. Adapted from PCCELL GMBH).

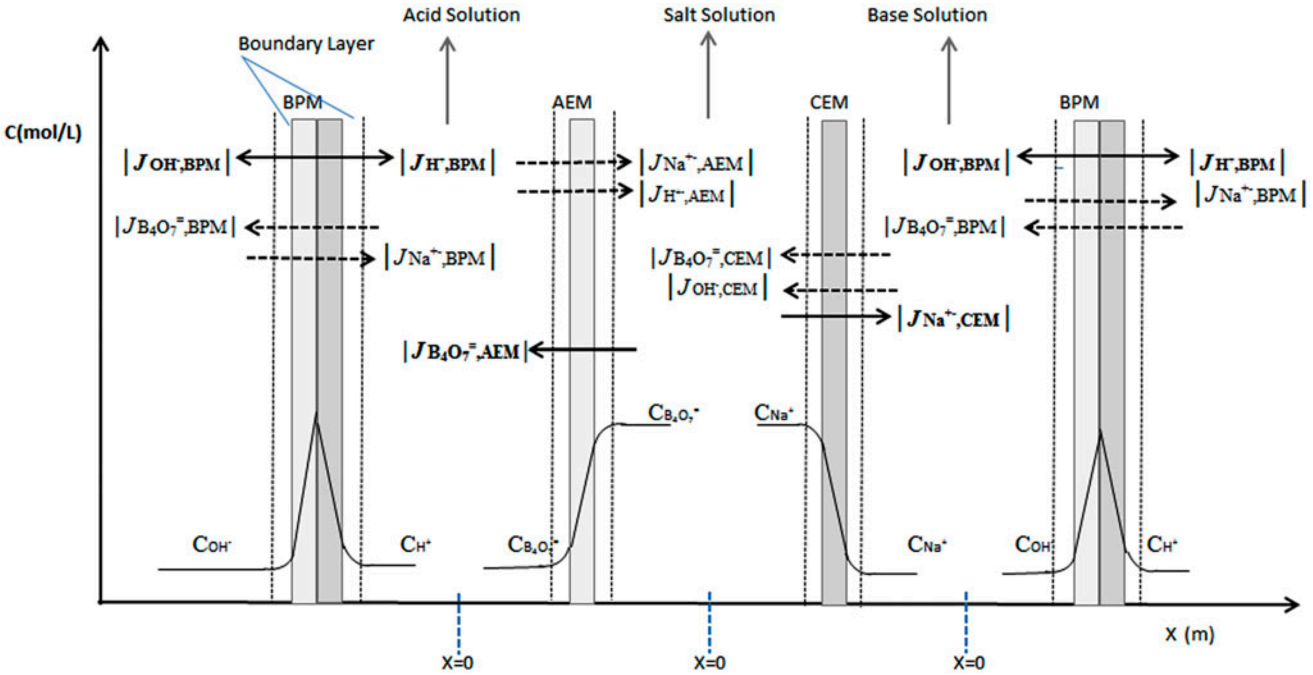

Fig. 2. The concentration profiles and material balance of this process for all membrane separated by an electrolyte solution.

$$V\frac{\mathrm{d}C_{B_4O_7^{2-}}}{\mathrm{d}t} = A\sum J_{B_4O_7^{2-}} \tag{2}$$

$$\Delta C_{B_4O_7^{2-}}Q = (C^{\mathrm{Out}}_{B_4O_7^{2-}} - C^{\mathrm{in}}_{B_4O_7^{2-}})Q = (J_{B_4O_7^{2-}\,\mathrm{BPM}} - J_{B_4O_7^{2-}\,\mathrm{AEM}})A^{\mathrm{M}} \tag{3}$$

The mass balance of the base compartment:

$$\Delta C_{\mathrm{Na^+}}Q = (C^{\mathrm{out}}_{\mathrm{Na^+}} - C^{\mathrm{in}}_{\mathrm{Na^+}})Q = (J_{\mathrm{Na^+BPM}} - J_{\mathrm{Na^+CEM}})A^{\mathrm{M}} \tag{4}$$

$$C_{\mathrm{Na^+}} = J_{\mathrm{Na^+}}; \quad C_{\mathrm{H^+}} = J_{\mathrm{H^+}} \tag{5}$$

The flux of the hydronium ion can be written as:

$$J_{H^+} = \frac{I_{app} - I_{lim}}{Z_{H^+}F} \tag{6}$$

The flux of the sodium ion can also be written as:

$$J_{Na^+} = T^{app}\frac{I_{app}}{Z_{Na^+}F} \tag{7}$$

Assuming that the flow through the compartments is well mixed, add the contribution of bulk flow to the mass transfer is negligible in boundary layers, the driving force becomes the electric field for migration, and concentration gradient for diffusion. The sum of the transport of an ion occurs by the contribution of diffusion and migration. For two sides of bipolar membrane, the salt ion transport in a solution can be expressed by the equation, based on the Nernst–Planck equations:

$$J_i = J^{mig} + J^{dif} = -D_i\frac{dC_i}{dx} - D_i\frac{Z_iC_i}{RT}\frac{dV_i}{dx} \tag{8}$$

In this study, four values of the initial borax concentrations (0.025, 0.05, 0.075, and 0.1 M), three values of the flow rate (0.38, 0.5, and 0.75 L/min), three values of the cell temperature (25, 40, and 50°C) and five values of the applied potential (5, 7.5, 10, 12.5, and 15 V) were tested. For each experiment, the original solutions before starting the electrodialysis had the concentration of about 1×10^{-6} M for H_3BO_3 in the acid compartment and about 1×10^{-6} M for NaOH in the base compartment to assure electrical conductance.

3. Results and discussion

Because of the large number of experiments, in this paper, some sample data were considered for each parameter. To test the reliability of the readings and measurement, the cell was operated under the same conditions at different times. The reproducibility of the experimental results is given in Fig. 3. These experimental results show that the cell operated steadily.

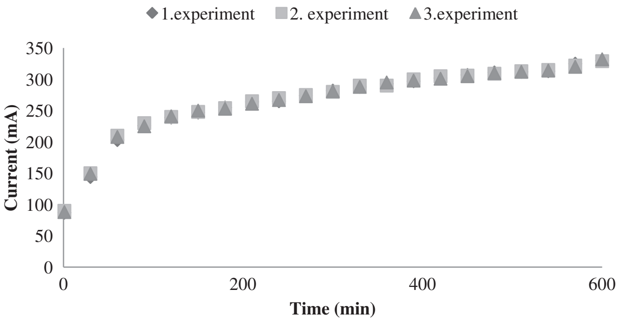

Fig. 3. Repeatability of experiments (0.5 L/min, 0.1 M, 50°C and 15 V).

3.1. Effects of potential on production of boric acid and sodium hydroxide

One of the important parameters for BPMED process is the applied potential value [23]. Fig. 4 shows the behavior of current with time at different applied potentials. As seen from this figure, the current increased with applied potential and time. This increase can be a result of the increase in migration of the ions with the increase in the potential difference, which is the driving force of ionic migration, and the increase in the dissociation rate on the electrolyte surface with increasing potential. The maximum current achieved for 5, 7.5, 10, 12.5, and 15 V were 10, 16, 44, 65, and 105 mA, respectively, in 480 min. The measured results for the conversion of (at 25°C, 0.38 L/min and 0.025 M) borax into sodium hydroxide and boric acid are presented in Figs. 5 and 6. It can be seen from these figures that the sodium hydroxide and boric acid concentration increased with a parallel behavior of that of current with time at a specified potential.

3.2. Effect of concentration on production of boric acid and sodium hydroxide

Fig. 7 illustrates the effect of the initial salt concentration on current values; increasing initial salt concentration increased the current with time for a specified concentration at a constant applied potential. The maximum current achieved for the initial

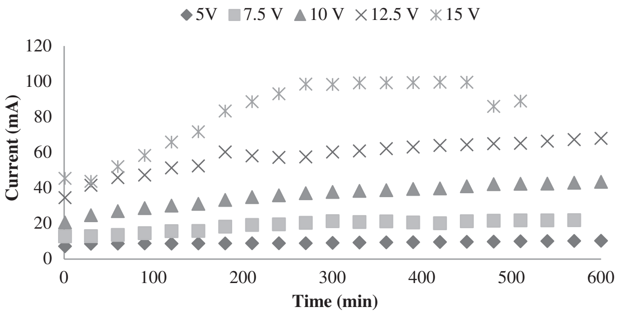

Fig. 4. Current–time curves at various applied potentials (25°C, 0.38 L/min and 0.025 M).

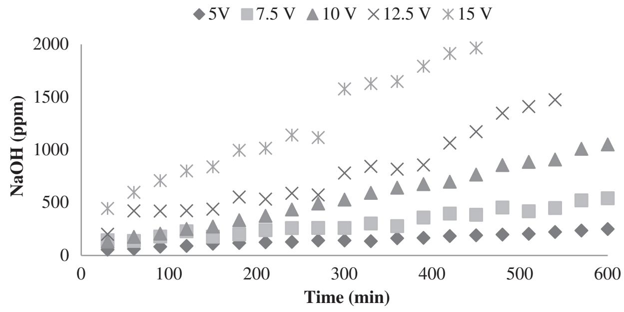

Fig. 5. NaOH concentration–time curves for base compartment at various potentials (25℃, 0.38 L/min and 0.025 M).

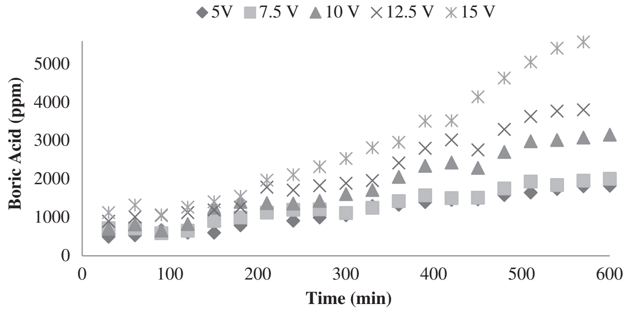

Fig. 6. Boric acid–time curves for acid compartment at various potentials (25℃, 0.38 L/min and 0.025 M).

concentrations of 0.025, 0.05, 0.075, and 0.1 M was 60, 64, 82, and 116 mA, respectively, in 600 min. This effect can be attributed to the increase in the concentration gradient, thus in the driving force for diffusion, between the bulk of the solution and at the interfaces of electrodes and membranes.

Figs. 8 and 9 present the conversion of borax into boric acid and sodium hydroxide at different initial salt concentrations. It can be seen from these figures that the sodium hydroxide and boric acid concentrations increased almost linearly with time at a specified initial salt concentration.

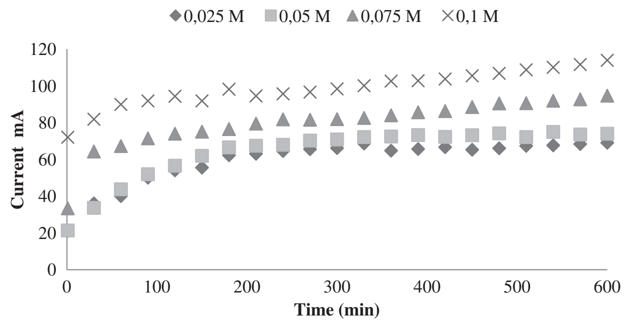

Fig. 7. Current–time curves at various borax concentrations (10 V, 0.5 L/min and 25℃).

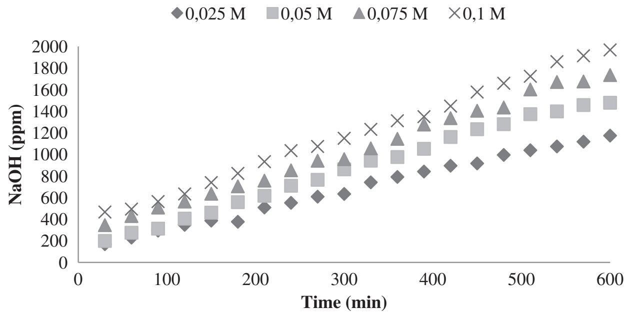

Fig. 8. NaOH concentration-time curves for base compartment at various borax initial concentrations (10 V, 0.5 L/min and 25℃).

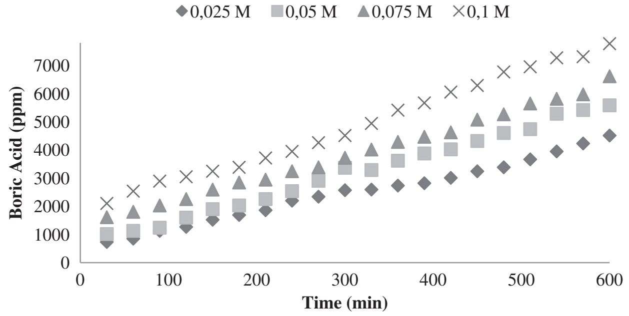

Fig. 9. Boric acid concentration–time curves for acid compartment at various initial borax concentrations (10 V, 0.5 L/min and 25℃).

3.3. *Effect of flow rate on production of boric acid and sodium hydroxide*

The effect of the flow rate of the electrolytic solution is given in Fig. 10. As seen from this figure, at a constant applied potential, the current increases when the flow rate increases. The maximum current achieved was 99, 159, and 174 mA for 0.38, 0.5, and 0.75 L/min, respectively, in 390 min. This increase results in the thinning of the boundary layer over the surfaces of the electrodes and the membranes, and in the increase in turbulence; therefore both of these results in an increase in the rate of the transport of ions from bulk to the interfaces.

The experimental results for the formation of (15 V, 0.025, and 25℃) boric acid and sodium hydroxide from borax are presented in Figs. 11 and 12, which exhibit similar behavior with time as the previous ones. It can be seen from these figures that sodium hydroxide and boric acid concentration increased linearly with time at a specified flow rate.

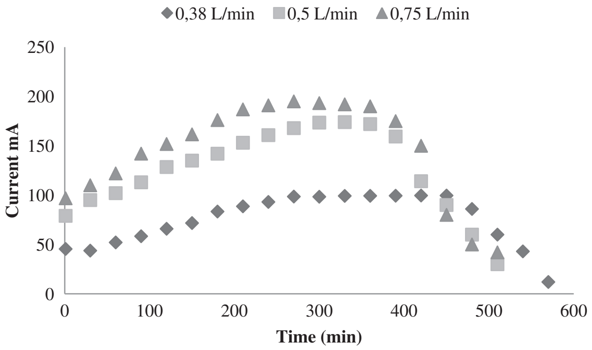

Fig. 10. Current–time curves at various flow rates of borax solution (15 V, 0.025 M and 25˚C).

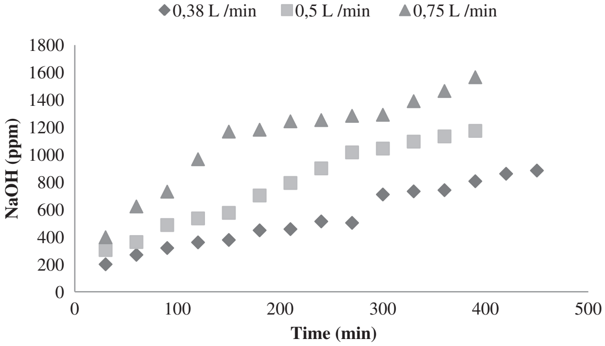

Fig. 11. NaOH concentration–time curves for base compartment at various flow rates (15 V, 0.025 M and 25˚C).

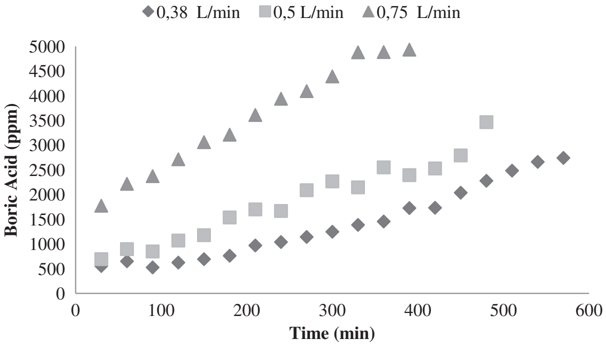

Fig. 12. Boric acid concentration–time curves for acid compartment at various flow rates (15 V, 0.025 M and 25˚C).

3.4. Effect of temperature on production of sodium hydroxide and boric acid

It can be seen from Fig. 13 that the current increased with increasing temperature at constant applied potential. The maximum current achieved for 25, 40, and 50˚C were 115, 230, and 313 mA, respectively, in 550 min. This shows that the temperature of the cell contents is also an important parameter for the process. Temperature increase is expected to increase the diffusion coefficient for the diffusion across the boundary layer over the surfaces and across the membranes, and also the reaction rates on the electrodes.

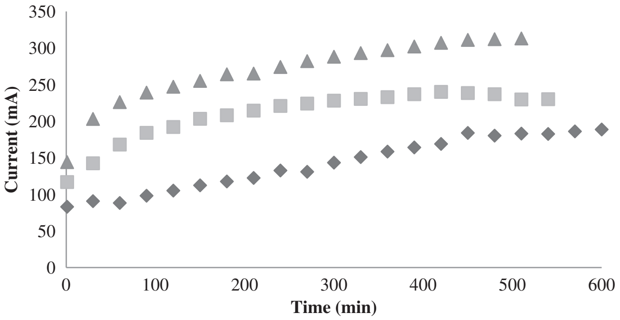

Fig. 13. Current–time curves at various temperatures of borax solution (15 V, 0.5 L/min and 0.1 M).

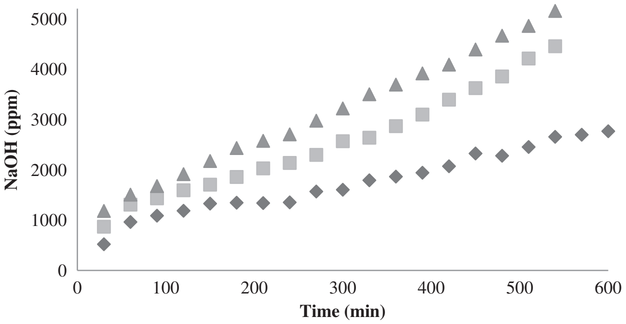

Fig. 14. NaOH concentration–time curves for base compartment at various temperatures (15 V, 0.1 M and 0.5 L/min).

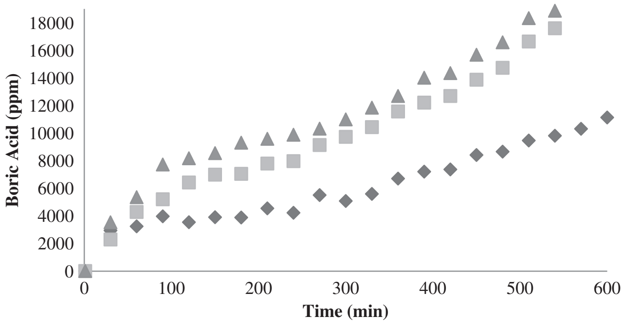

Fig. 15. Boric acid concentration–time curves for acid compartment acid compartment at various temperatures (15 V, 0.1 M and 0.5 L/min).

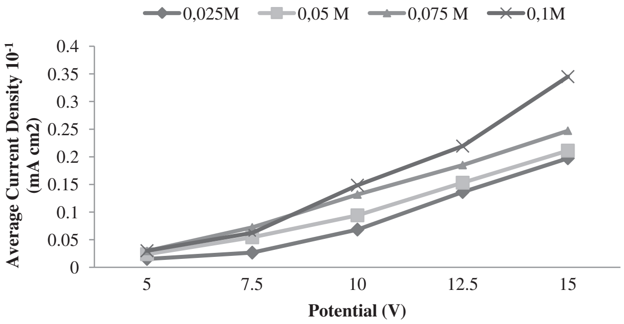

Fig. 16. Average current density–potential curves for different concentrations at 0.5 L/min.

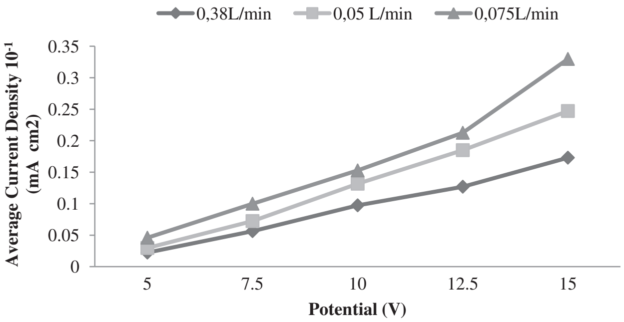

Fig. 17. Average current density–potential curves for different flow rates at 0.075 M initial salt concentration.

The change for the conversion of (15 V, 0.5 L/min, and 0.1 M) borax into boric acid and sodium hydroxide in the process is given in Figs. 14 and 15. In this case, the similar behavior with time is also observed again.

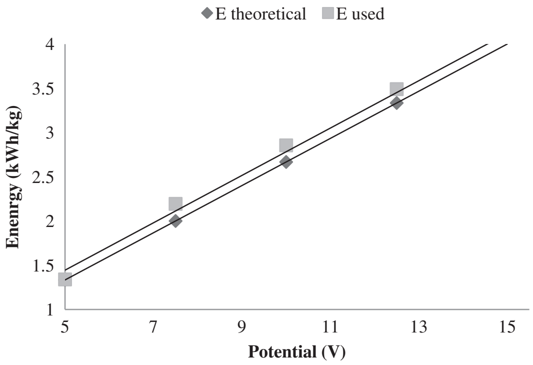

Fig. 18. Amount of energy required for the process (25℃, 0.1 M, 0.5 L/min and 15 V).

3.5. *Current efficiency and energy consumption*

As seen in Figs. 16 and 17, the average current density increased with the initial salt concentration and the flow rates of the electrolytes at a specified applied potentials, respectively. They also increased with increasing electrodialysis period. For the conditions of the system temperature of 25℃, the initial salt concentration of 0.1 M, the flow rate of 0.5 L/min, and the applied potential of 5 V, the current efficiency was calculated to be 99.53%. This value is in the range recorded in the literature. For example, current efficiencies up to 99.9 percent are recorded in the literature in this kind of works [17]. Table 2 shows some current efficiency values, ranging 0.9310–0.9953. Fig. 18 shows a comparison of energy consumption of the system; it is seen that theoretically consumed energy value and the real energy consumption value of the system are very close to each other for the process. This behavior shows that this process is

Table 2
Current efficiency and energy consumptions of experiments

Temperature	İnitial concentration (M)	Flow rate (L/min)	Potential volt	Current efficiency	*E*—H_3BO_3 (kW h/kg)	*E*—NaOH (kW h/kg)
25	0.025	0.38	5	0.96041	1.128932	3.560477
25	0.025	0.38	7.5	0.95208	1.708211	5.387436
25	0.025	0.38	10	0.97783	2.195183	6.923269
25	0.025	0.38	12.5	0.87108	3.111743	9.813959
25	0.025	0.38	15	0.93714	3.470899	10.94668
25	0.075	0.38	7.5	0.96271	1.689343	5.327928
25	0.025	0.50	10	0.95686	2.266246	7.14739
25	0.05	0.50	10	0.96735	1.690601	5.331895
25	0.075	0.50	7.5	0.96200	2.328209	7.342813
25	0.075	0.50	10	0.93139	2.321147	7.320541
25	0.010	0.50	5	0.9953	1.089289	3.435449
25	0.010	0.50	10	0.93422	1.7835097	5.6249153

energetically efficient, promising a potential for practical applications [24].

For the conditions at which the high current efficiency of 0.9953 was obtained, the energy consumption was 3.4354 kW h/kg NaOH or 1.0893 kW h/kg H_3BO_3 with an average current density of 3.05 mA/cm^2. In addition, the product purities up to 99.52% H_3BO_3 for boric acid and 99.12% NaOH for sodium hydroxide were obtained at these conditions.

4. Conclusions

From all the results presented above for the production of boric acid and sodium hydroxide using BPMED, the main characteristics of the present work can be summarized as follows:

(1) This configuration allows the production of acid and base with very good energy efficiencies and with no harmful waste to environment.
(2) Increasing the applied potential, concentration, flow rate, and temperature has an increasing effect on the production rate.
(3) The study indicates that boric acid in high purity up to 99.52% can be produced in a single operation with BPMED.
(4) This work shows that BPMED has a potential to be an alternative for the production of H_3BO_3 and NaOH from borax to that of the conventional one.

In spite of the above mentioned positive results, the work needs further study in pilot scale to determine the operational problems before practical application for the production. This new process is attractive and has a promising potential due to high energy efficiency and low impact on the environment.

Acknowledgment

The support of Atatürk University for the project BAP-2011/136 is highly appreciated. The authors are grateful to Mehmet Emin Arzutuğ for assistance in the experiments and valuable ideas.

Nomenclature

A^M — total active membrane area (m^2)
AEM — anion exchange membrane
BPM — bipolar membrane
C — concentration (mol/L)
CEM — cation exchange membrane
C_{H^+} — salt proton concentrations in the acid chamber (mol/L)
C_{Na^+} — salt cation concentrations in the acid chamber (mol/L)
D_i — ion diffusion coefficients (m^2/s)
F — Faraday constant (F = 96,485 A s/mol)
I_{app} — applied current density (A/m^2)
I_{lim} — limiting current density (A/m^2)
J — ion flux across the membrane (mol/m^2 s)
J_{H^+} — proton concentrations fluxes (mol/m^2 s)
J_{Na^+} — cation concentrations fluxes (mol/m^2 s)
Q — volume stream of product (m^3/s)
R — universal gas constant (8.314 J/ mol K)
T — cell temperature (K)
T^{app} — actual transport number (A/A)
t — time (s)
V — electric potential (V)
x — dimension perpendicular to membrane (m)
Z_{H^+} — electrochemical valence of the proton
Z_{Na^+} — valence of the ion

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