


Article

# Boron Recovery from Organic Solutions Used in Brine Treatment through a Water Stream

Alejandra Cerda <sup>1</sup>, Mackarena Jara <sup>2</sup>, Osvaldo Yañez <sup>2</sup>, Yahaira Barrueto <sup>3</sup>  and Yecid P. Jimenez <sup>1,4,\*</sup>

<sup>1</sup> Departamento de Ingeniería Química y Procesos de Minerales, Facultad de Ingeniería, Universidad de Antofagasta, Av. Angamos 601, Antofagasta 1240000, Chile; alejandra.cerda.diaz@ua.cl

<sup>2</sup> SQM, El Trovador 4285, Santiago 7550000, Chile; mackarena.jara@sqm.com (M.J.); osvaldo.yanez@sqm.com (O.Y.)

<sup>3</sup> Departamento de Ingeniería Metalúrgica y Materiales, Universidad Técnica Federico Santa María, Valparaíso 2340000, Chile; yahaira.barrueto@usm.cl

<sup>4</sup> Centro de Economía Circular en Procesos Industriales (CECPI), Facultad de Ingeniería, Universidad de Antofagasta, Av. Angamos 601, Antofagasta 1240000, Chile

\* Correspondence: yecid.jimenez@uantof.cl

**Abstract:** This research evaluates the modification of the lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) production process and particularly the boron removal step, which currently employs a recirculated stream. This recirculated stream is a liquor with low boron content but rich in lithium, currently being wasted. In this process, the recirculating stream is substituted with a freshwater stream. Boron is re-extracted from the loaded organic stream to form an input stream for a boric acid process. Under certain operational conditions, the formation of emulsions was observed; due to this, the analysis of emulsion formation involved controlling the pH of each sample, which lead to the development of a procedure to prevent such formations. From this analysis, it was determined that emulsions form in water with pH values below 1.3 and above 6.9. In addition, a speciation analysis showed that the concentrations of the  $\text{H}_2\text{BO}_3^-$  and  $\text{H}^+$  species influence the formation of emulsions. The mass balance of the process showed that by replacing the recirculated stream, boron recovery of 89% was achieved, without the need to add new stages or equipment.

**Keywords:** boron; re-extraction; McCabe–Thiele analysis; speciation; emulsion



**Citation:** Cerda, A.; Jara, M.; Yañez, O.; Barrueto, Y.; Jimenez, Y.P. Boron Recovery from Organic Solutions Used in Brine Treatment through a Water Stream. *Minerals* **2024**, *14*, 265. <https://doi.org/10.3390/min14030265>

Academic Editor: Yijun Cao

Received: 10 January 2024

Revised: 22 February 2024

Accepted: 29 February 2024

Published: 1 March 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Boron has been used in various industries, including agriculture, glass and ceramic, due to its versatility. As industry and technology have advanced, the demand for this element has increased over time [1].

Boric acid ( $\text{H}_3\text{BO}_3$ ) finds applications in numerous industries such as dermatology, livestock and mining, serving as both an antiseptic and fungicide. Boric acid can be obtained from more than 230 boron-containing minerals. [2]. There are many methods for extracting boron from various solutions, such as chemical precipitation [3], adsorption on metal hydroxides [4,5], ion exchange [6,7], membrane methods (electrodialysis, reverse osmosis) [8] and extraction with organic solvents [9].

In the lithium carbonate process, boron found in the brines of the Salar de Atacama is extracted during the solvent extraction stage to prevent it from becoming an impurity. At the SQM company, a stream is recirculated from the separation stage to extract boron [10,11].

The extraction of boron is crucial in lithium carbonate production as it hampers the process. Currently, a recirculated stream from the separation stage, known as the low-boron mother liquor (LBML), is used for this purpose. However, this recirculated stream generates liquid industrial waste (LIW) that requires treatment for disposal. Since this stream is rich in lithium, diverting it from the main treatment process, an alternative approach is to utilize

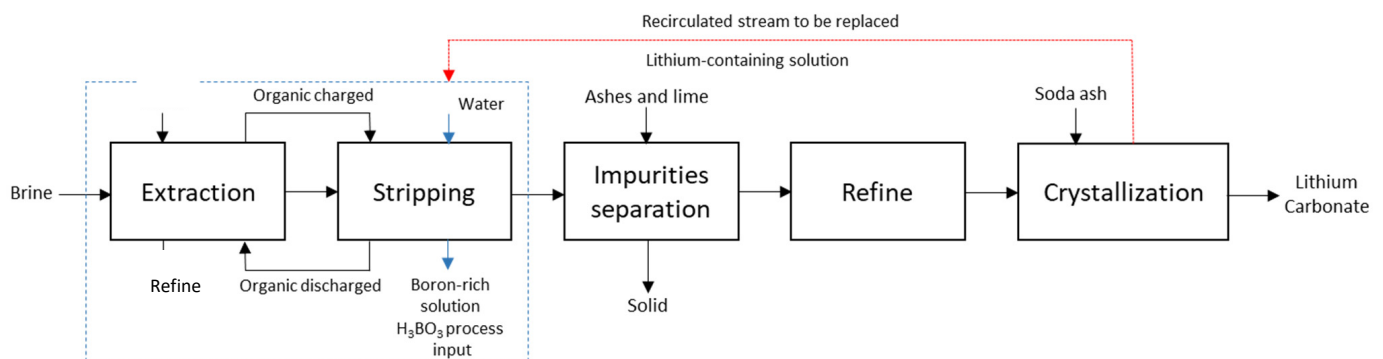
it in the lithium process to enhance its yield and replace it in the solvent extraction stage with a new stream.

Boron can be extracted using various solvents. Researchers utilized 2,2,4-trimethyl-1,3-pentanediol as an extractant to recover boron from lithium-rich brines, yielding 99.95%. Re-extraction performed with NaOH resulted in a yield of 99.99% [12]. Boric acid forms a complex with the extractant, forming two C-O-B ester bonds. In other studies, 2-ethylhexanol was used as the boron extractant in brine, with water as the stripping agent. The process involved three countercurrent stages, yielding 99.5% for extraction and 97.8% for stripping. A product with 95.5% purity was obtained, washed in one stage with two phases, increasing its purity to 99.5%. The presence of magnesium benefited the boron extraction process, by inducing the “salting-out” effect [13].

Another study extracted boron from brine using 2-butyl-1-n-octanol dissolved in sulfonated kerosene, with water as a stripping agent to obtain boric acid. The process involved six countercurrent stages, with an overall yield of 98%. In the extraction stage, the salting-out effect was studied, and the presence of  $\text{AlCl}_3$  yields the best results. Thermodynamic modeling indicated that the extraction process is exothermic [14]. Researchers also investigated the recovery of boron from brines with a high sulfate concentration through a low-cost and environmentally friendly process. Magnesium removal was achieved with solid  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , followed by brine evaporation to precipitate more salts. This brine was diluted with deionized water to precipitate boron salts, primarily magnesium borates, with a yield of 80%. The process yield was influenced by the pH of the solution, and no further reagents were used [15].

Other studies have focused on recovering boron from various sources such as seawater [16], geothermal waters [17,18], ore [19,20] and tailings [21] employing different solvents and procedures [22–24]. Meanwhile, other research has targeted to recovery of lithium from wastewater containing high concentrations of boron or magnesium, using organic solvents [25,26], with the intention of retaining boron in the residue and preventing contamination of the product [27,28].

In this study, the replacement of the recirculated stream with a water stream was examined because the recirculated stream contains a significant amount of lithium that is currently being wasted. This water stream would extract the boron from the loaded organic phase and serve as an input stream for a boric acid production process. Thus, the behavior of water with a loaded organic phase was investigated to determine the optimal conditions for efficient boron re-extraction. Figure 1 shows the current process and the proposed change.



**Figure 1.** Current and proposed process for the extraction of lithium carbonate. Recirculated stream to be replaced (red) and new stream proposed (blue). The dotted line highlights the boron removal process.

## 2. Materials and Methods

### 2.1. Materials

The loaded organic phase (from solvent extraction) was provided by SQM. It is composed of a solvent and an extractant: Scaid 100, a hydrocarbon fluid (industrial grade), and Exxal 8, an isodecyl alcohol (technical grade), both purchased from Brenntag. This organic solution consists of 0.46% impurities and 0.54% boron (Table S-1 shows the full composition). The aqueous solutions used are the LBML, which has 0.99% impurities and  $5.4 \times 10^{-4}$ % boron (i.e., 5.4 mg/L B) (Table S-2 shows the full composition), and freshwater (<1% salts). Aqueous mixtures were prepared according to the LBML/freshwater volume ratios of 9/1, 4/1, 7/3, 1/1, 2/3, 3/7, 1/4 and 1/9.

### 2.2. Equipment and Software

The equilibrium pH (pH(eq)) was measured using an Orion Star A211 pH meter/oxidation–reduction potential (ORP) meter, with a margin of error of  $\pm 0.002$  for pH and  $\pm 0.2$  mV for potential. Sample homogenization was conducted using a magnetic stirrer (Scinics Multistirrer MC-303 Controller) operating at a power of 50/60 Hz and a stirring speed of 70 to 100 rpm. Additionally, a propeller stirrer (IKA RW 20 digital) with a universal speed from 60 to 2000 rpm and speed adjustment of  $\pm 1$  rpm, along with a thermostatic bath (model F25 from Julabo) with a temperature range from  $-50$  °C to  $+200$  °C were utilized. The chemical analyses were performed using inductively coupled plasma–optical emission spectrophotometer (ICP-OES), using the 249.774 nm emission line in the SQM laboratories.

The MINTEQ 3.1 software was employed for speciation analysis. It is capable of simulating the chemical composition of solutions in contact with gases, solid compounds and particle surfaces. In the MINTEQ application, the elements of the aqueous solution, specifically the LBML in this case, were selected. Furthermore, various proportions of the LBML and water in the mixture were analyzed to identify the chemical species present in the solutions.

## 3. Methodology

The stripping isotherms were determined using the following methods: The loaded organic and aqueous phases (LBML or water) were mixed in the established proportions in 30 mL decanting funnels, as shown in Table 1. The solutions were manually agitated for 5 min. Subsequently, the agitation was halted, and they were left undisturbed for another 5 min to allow for the phases (organic and aqueous) to separate. Once fully separated, the solutions were poured into separate containers and sent for chemical analysis to quantify the boron yield.

**Table 1.** Organic/aqueous (O/A) ratios used to determine stripping isotherms.

N <sup>o</sup>	O/A Ratio	Volume of Organic Phase <sup>a</sup> (mL)	Volume of Aqueous Phase (mL)
1	1/10	2.5	25
2	1/5	4.5	22.5
3	1/3	7	21
4	1/2	9	18
5	1/1	10	10
6	2/1	18	9
7	3/1	21	7
8	5/1	22.5	4.5
9	10/1	25	2.5

<sup>a</sup> Organic phase (impurities 0.46 % w/w and boron 0.54 % w/w), LBML (boron 0.0005 % w/w), ambient temperature.

For pH(eq) measurement, the samples were prepared in 30 mL beakers and stirred magnetically for 1 min; then, the pH meter was inserted. Additionally, the initial pH values of the reagents (loaded organic phase, LBML and freshwater) were recorded.

To determine the McCabe–Thiele diagram, two simultaneous re-extraction isotherm processes were performed, one with water and the other using the LBML. This aimed to establish the operating conditions, organic/aqueous (O/A) ratio and the number of stages required to maximize the amount of boric acid obtained in solution. Emulsion formation in the solutions was also examined in this analysis, aiming to identify the reason for its occurrence, which hinders the optimal extraction of boron from the organics [29].

For the re-extraction tests with the LBML, nine experiments were conducted (according to established ratios), while for the boron stripping tests with water, only seven tests were performed, excluding the 1/10 and 10/1 ratios. The equilibrium diagram was obtained following the methodology described in the literature [30–32].

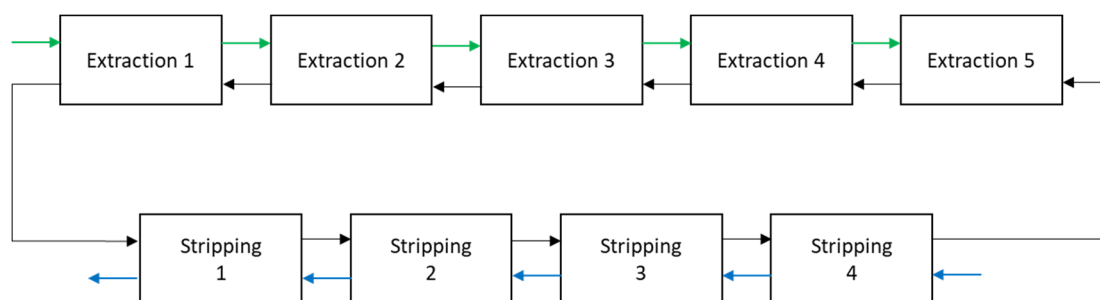
To further investigate emulsion formation in the solutions, the kinetics of boron re-extraction were examined. This involved analyzing the phase separation time and the dispersion band.

Organic continuity was measured using a solution with an O/A ratio of 2.6/1; the loaded organic phase was added and stirred at 750 rpm, and the aqueous solution (LBML, freshwater or a mixture) was added and stirred for 3 min. Stirring was then stopped and the phases were allowed to separate and settle. If a dispersion band formed, its measurement was taken, and the phases were given time to disperse and separate. Subsequently, aqueous continuity was assessed. The agitator helix was positioned in the aqueous phase of the solution, and stirring was resumed for 3 min. The time taken for phase separation and any potential formation of a dispersion band was recorded.

#### 4. Extraction Process

The extraction process applied to the brine aims to concentrate the lithium content and remove impurities, including boron. The overall process comprises five extraction stages and four stripping stages. The extractant utilized is Exxal 8, a clear, distilled, high-purity alcohol composed of primary aliphatic alcohols derived from selected olefins. The diluent used is Escaid 100, classified as a class IIIA flammable liquid with a flash point of 77 °C and a boiling point of 200 °C. The O/A ratio used in the extraction is 2.6.

The operating temperature is 22–23 °C (depending on the season), while the equilibrium pH varies between 2.85 and 2.96. The average operational concentrations of  $H_3BO_3$  in the primary process streams are as follows: organics loaded = 2.288%, organics discharged = 0.004%. The boron concentration at the inlet of the extraction process ranges from 5138 to 8059 mg/L, while the outlet concentration in the refining process is 29.6–31.0 mg/L. The LBML has a concentration of 0.003% and the high-boron mother liquor (HBML) has a concentration of 3.95%. The organic flow rate ranges from 33 to 44 m<sup>3</sup>/h, the brine flow rate ranges from 16 to 19.5 m<sup>3</sup>/h and the mother liquor flow rate ranges from 17 to 19 m<sup>3</sup>/h. To quantify the extraction, measurements were conducted using inductively coupled plasma and optical emission spectroscopy (ICP-OES) in the LBML and in the loaded organic phase, which were subsequently transformed into the HBML and unloaded organic phase, respectively. Figure 2 shows the flow of the streams in the extraction and stripping processes.



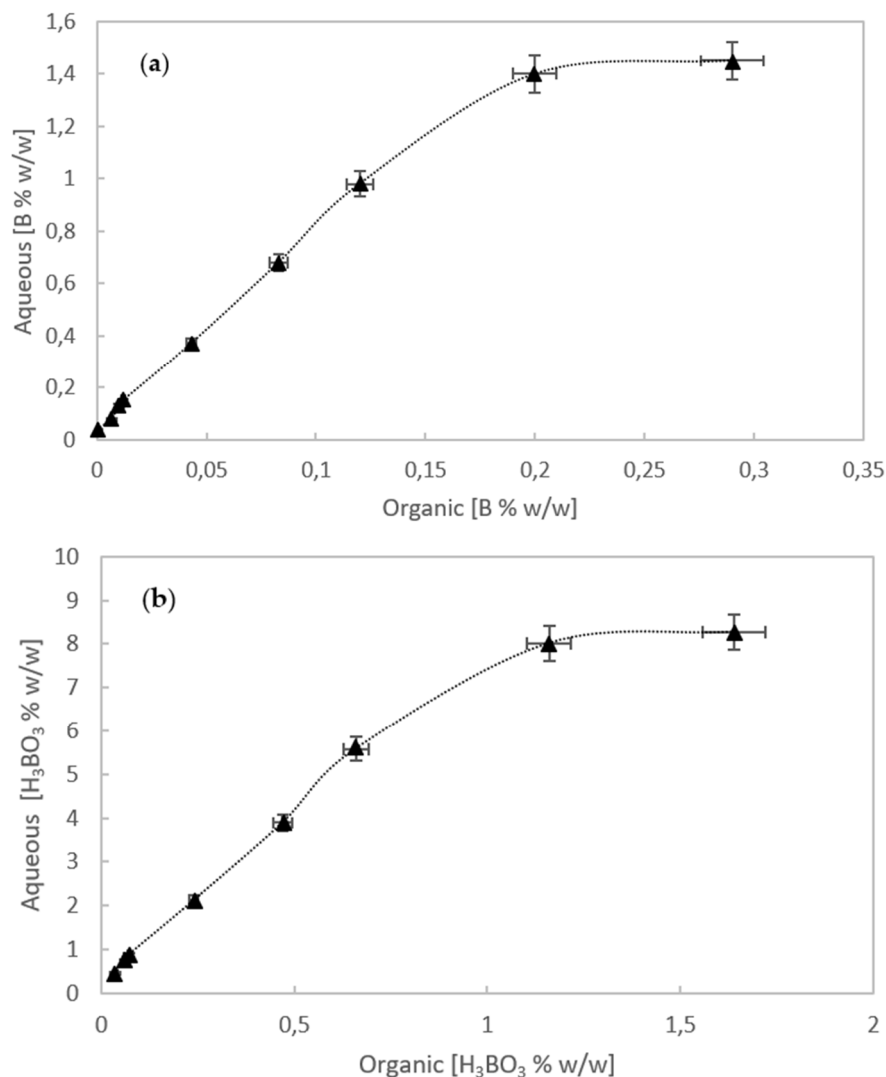
**Figure 2.** Extraction and re-extraction stages of the current process to obtain lithium carbonate. Brine stream (green), organic stream (black), mother liquor (blue).

## 5. Results

### 5.1. Stripping Isotherms for LBML

In all the experiments conducted in this study, no emulsion formation was observed after the agitation of the solution; shortly after the start of phase separation, each phase became clearly visible. The pH(eq) values of the solutions ranged between 4.18 and 9.91; additional information can be found in Tables S-3 and S-4 in the Supplementary Material.

Figure 3a,b show an increase in the percentage of boron (B) and  $H_3BO_3$  in the aqueous phase, respectively, as a result of stripping. The other elements identified in the LBML are presented in Tables S-5–S-8 in the Supplementary Material.

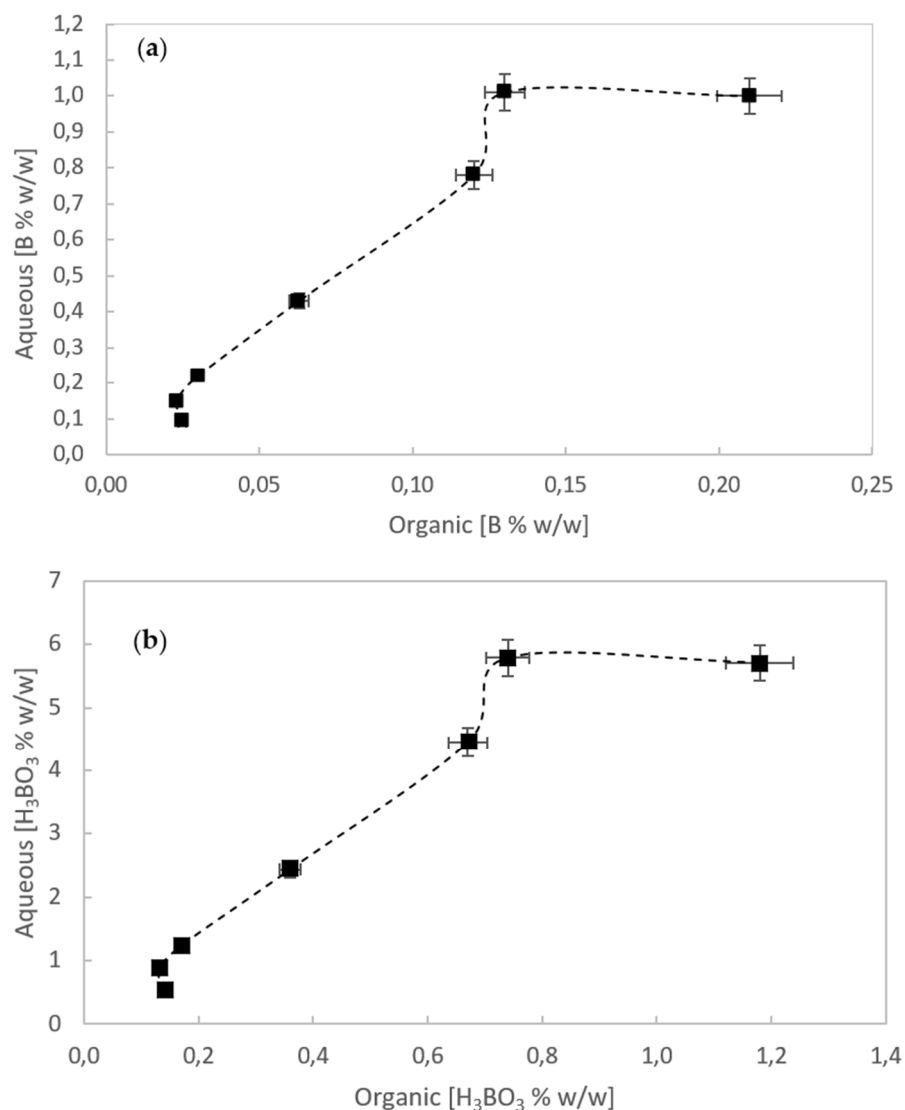


**Figure 3.** Stripping isotherms: (a) boron in the high-boron mother liquor as a function of boron in the organic phase; (b)  $H_3BO_3$  in the high-boron mother liquor versus  $H_3BO_3$  in the organic phase. The pH of the feed solution was 0.21 and tests were performed at room temperature ( $\sim 25^\circ C$ ) and O/A ratios as shown in Table 1. Data points and error bars are means and standard deviations, respectively, from duplicate experiments.

### 5.2. Stripping Isotherms for Freshwater

In these tests, the formation of an emulsion was observed after phase separation, occurring only in the tests with 1/10 and 10/1 ratios. There is a clear upward trend in the percentage of boron extracted from the organic phase versus the percentage of boron extracted from the water (Figure 4a), considering that the last two tests had a constant

concentration. By plotting the data obtained from the boron stripping, the percentage of aqueous boric acid extracted could also be obtained, as shown in Figure 4b.



**Figure 4.** Stripping isotherms: (a) boron in water versus boron in the organic phase; (b) H<sub>3</sub>BO<sub>3</sub> in water versus H<sub>3</sub>BO<sub>3</sub> in the organic phase. The pH of the feed solution was 0.21 and tests were performed at room temperature (~25 °C). Data points and error bars are means and standard deviations, respectively, from duplicate experiments.

### 5.3. pH Control

The initial pH values of the industrial samples were informed; the loaded organic phase had an initial pH of 0.21, and the LBML had an initial pH of 10.98. Figure 5 shows the behavior of pH(eq) as a function of the O/A ratios for both the LBML and water. This figure shows a tendency to decrease pH(eq), considering that the extreme points for the formation of the emulsion were not included in the water curve. It can be inferred that the formation of the emulsion would occur below 1.3 and above 6.9 on the pH scale. However, for the LBML, emulsion formation does not occur at pH(eq) values greater than 7, indicating that the chemistry of the solution significantly influences the emulsion formation, a factor analyzed in conjunction with the results of the speciation.

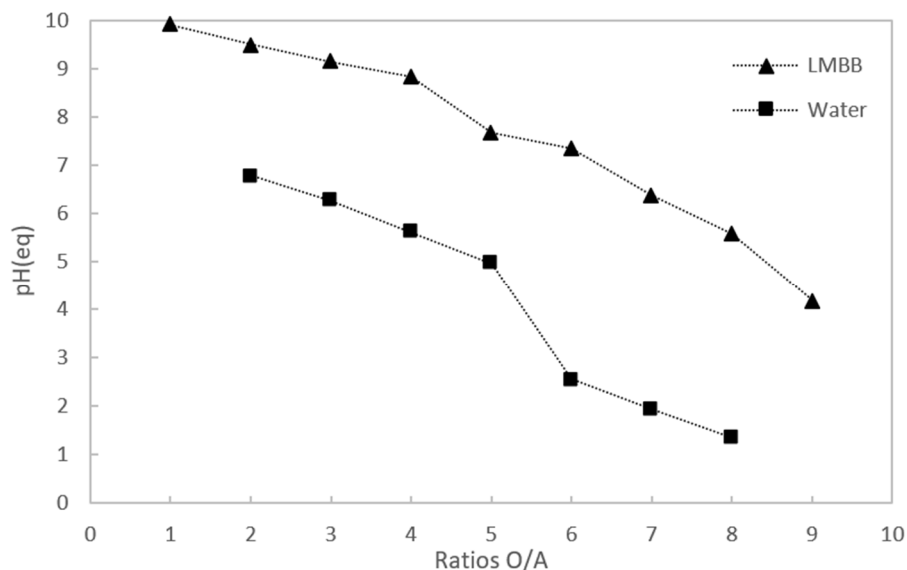


Figure 5. pH(eq) versus organic/aqueous ratio at room temperature (~25 °C).

The equilibrium pH values of the aqueous mixtures (LBML and water) were also measured. There was a clear increase in pH(eq) up to a ratio of 40/60, after which it began to decrease, as shown in Figure 6. This again indicates the predominance of certain chemical species as a function of the concentration.

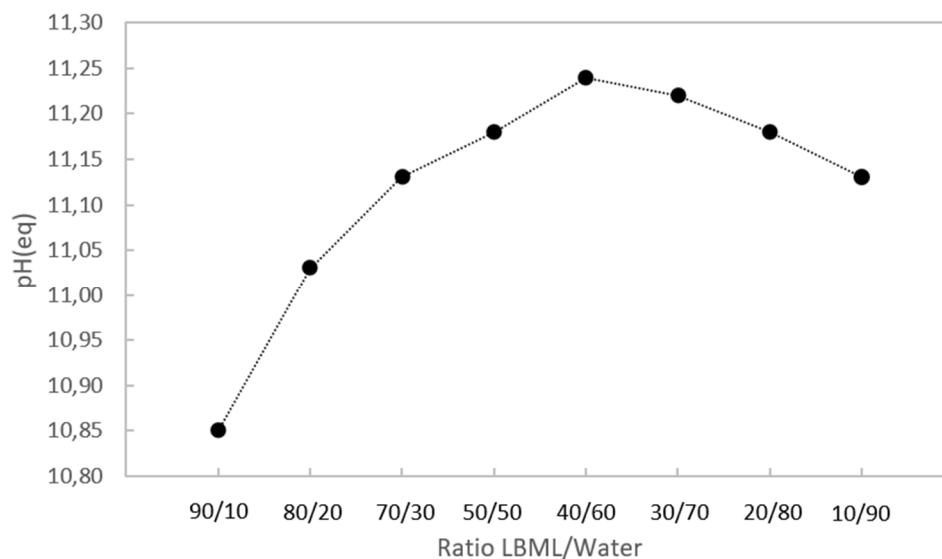


Figure 6. pH(eq) versus mixtures of aqueous phases (the low-boron mother liquor and water) at room temperature (~25 °C).

5.4. McCabe–Thiele Diagram Analysis

Figure 7 shows that when the operating straight line intercepts the stripping isotherm, two stages are obtained: a loaded organic (LO) phase enters with 0.54 % w/w B and an unloaded organic (UO) exits with 0.065 % w/w B, while the LBML enters with a concentration of 0.00054 % w/w B and exits with a concentration of 1.40 % w/w B. The slope of the operating straight line (O/A ratio) is 2.59. Figure S1 in the Supplementary Material shows a diagram of the countercurrent process.

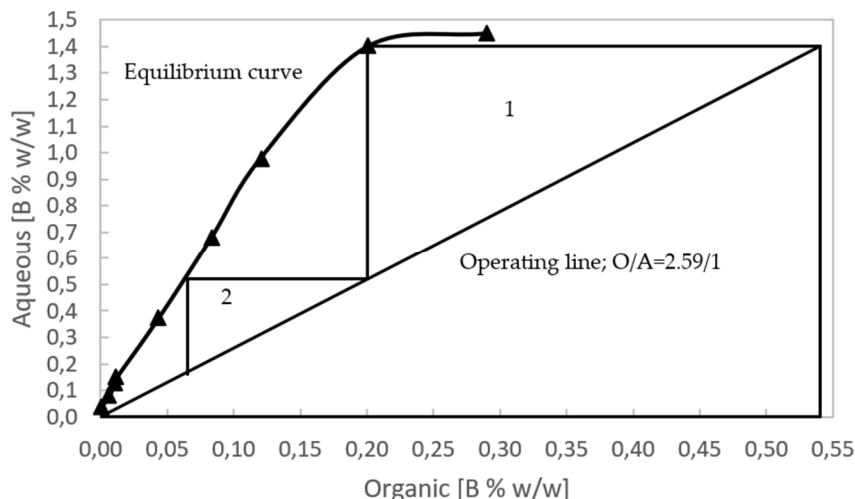


Figure 7. McCabe–Thiele diagram with low-boron mother liquor at room temperature (~25 °C).

Figure 8 shows the McCabe–Thiele diagram with water as the aqueous phase. When the horizontal line from the operating straight line intercepts the stripping isotherm, one stage is obtained. Figure S2 in the Supplementary Material shows the countercurrent process; a loaded organic (LO) phase enters with 0.54 % w/w B and an unloaded organic (UO) exits with 0.165 % w/w B, while freshwater enters with a concentration of 0 % w/w B and exits with a concentration of 0.975 % w/w B. The slope of the operating straight line (O/A ratio) is 2.60.

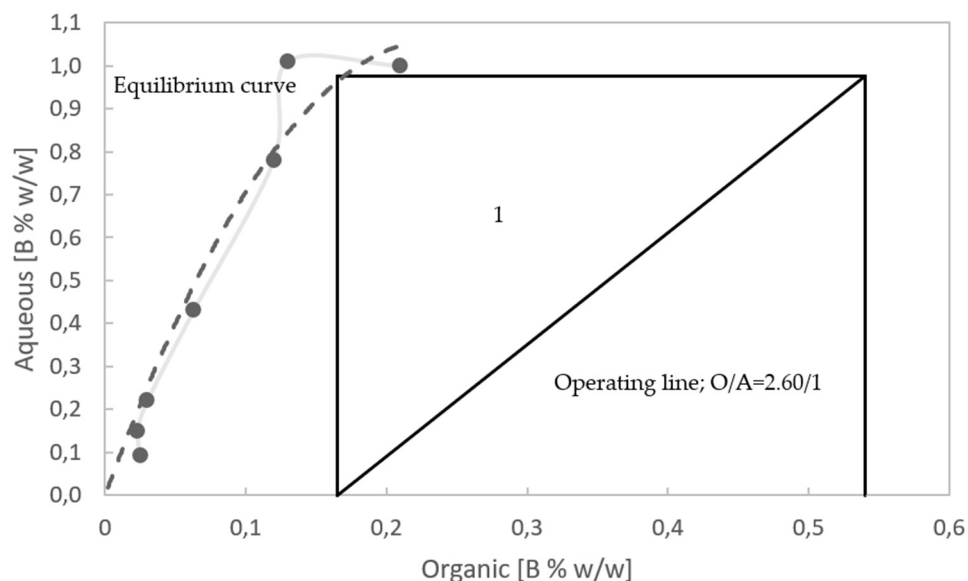


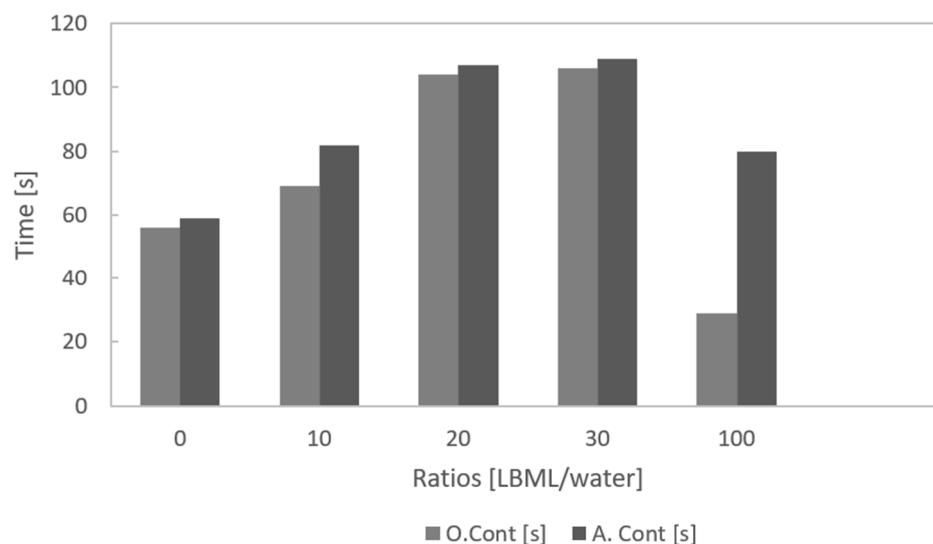
Figure 8. McCabe–Thiele diagram with water at room temperature (~25 °C). Dashed lines are guides for the eye.

Comparing both processes, with the LBML, more boron is extracted compared to the process with water, but in two stages; for the process with water, a concentration of 0.975% w/w B is obtained, while for the process with the LBML, a concentration of 1.24% w/w B is obtained. On the other hand, the countercurrent process with water forms an emulsion when it passes to stage 2 (this is discussed in the following subsection).



### 5.5. Phase Separation Time

Figure 9 shows the phase separation time in organic continuity (O. Cont) and aqueous continuity (A. Cont) for the pure aqueous solutions (water and LBML), as well as for the mixtures with LBML/water ratios of 10/90, 20/80 and 30/70.



**Figure 9.** Phase separation time in organic continuity and aqueous continuity for pure aqueous solutions (water and low-boron mother liquor) and for low-boron mother liquor/water mixtures at room temperature (~25 °C). pH values: 11.13 for 1/9, 11.18 for 2/8 and 11.22 for 3/7.

In both organic and aqueous continuity, the mixture with the longest phase separation time was that with a 30/70 ratio. Compared to the pure reagents, freshwater exhibits very similar separation times in both aqueous and organic continuity. The phase separation times for all tests are given in Table S-9 in the Supplementary Material.

The separation process with the LBML was fast, with a separation time of 29 s in organic continuity; no dispersion band was formed, but traces of the entrainment of organic matter were observed in the aqueous phase. In aqueous continuity, it took 80 s for the phases to separate. It should be noted that in this case, a small dispersion band was formed, but it separated after a few seconds, and similar to organic continuity, a greater entrainment of organic matter occurred in the aqueous phase.

The separation process with freshwater was slightly slower compared to the separation process with the LBML in the organic continuity, with a separation time of 56 s, but it was slightly faster in the aqueous continuity, with a separation time of 59 s. No dispersion bands formed in either continuity, but in the aqueous continuity, much more entrainment occurred in the aqueous phase. On the other hand, the aqueous mixture with the longest phase separation time was the mixture with a 30/70 ratio (30% LBML and 70% water), with a phase separation time in organic continuity of 106 s and in aqueous continuity of 109 s. The aqueous phase was entrained by the organic phase in both continuities (details regarding the separation times can be found in Table S-9 in the Supplementary Material).

Working with high O/A or A/O ratios leads to the use of a larger volume of solution within the process, larger reactors and a longer residence time, which slows down the stripping stage, resulting in a low concentration of boric acid [14]. By decreasing the O/A ratio using water as the stripping agent, the operating pH(eq) remains basic, base separation times are reduced and high concentrations of boric acid are obtained.

These results demonstrate that the chemical composition of the aqueous solutions has a significant influence on the phase separation time, and this composition changes in terms of the chemical species formed due to dissolutions. These changes, in turn, would influence the pH(eq) values of the solutions.

### 5.6. Speciation

Four different aqueous solutions at 25 °C were analyzed using visual MINTEQ 3.1: the LBML and mixtures with various LBML/water ratios. The results of LBML speciation at a pH(eq) value of 10.98 can be seen in Table 2. The species with the highest concentrations are  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{NaCl}_{(\text{aq})}$ .

**Table 2.** Relevant compounds of the aqueous phase analyzed by visual MINTEQ 3.1.

Species	LBML	Concentration [mol/kg]		
		10/90	20/80	30/70
$\text{Cl}^-$	1.80	$2.63 \times 10^{-1}$	$4.92 \times 10^{-1}$	$7.10 \times 10^{-1}$
$\text{NaCl}_{(\text{aq})}$	$8.84 \times 10^{-1}$	$1.58 \times 10^{-2}$	$5.28 \times 10^{-2}$	$1.09 \times 10^{-1}$
$\text{Li}^+$	$9.67 \times 10^{-2}$	$1.56 \times 10^{-2}$	$2.94 \times 10^{-2}$	$4.15 \times 10^{-2}$
$\text{LiCl}_{(\text{aq})}$	$7.31 \times 10^{-2}$	$1.45 \times 10^{-3}$	$4.79 \times 10^{-3}$	$9.75 \times 10^{-3}$
$\text{Ca}^{2+}$	$5.65 \times 10^{-5}$	$2.49 \times 10^{-5}$	$3.65 \times 10^{-5}$	$5.06 \times 10^{-5}$
$\text{CaCl}^+$	$2.12 \times 10^{-4}$	$4.84 \times 10^{-6}$	$1.30 \times 10^{-5}$	$2.85 \times 10^{-5}$
$\text{Mg}^{2+}$	$6.22 \times 10^{-5}$	$3.30 \times 10^{-5}$	$5.03 \times 10^{-5}$	$6.50 \times 10^{-5}$
$\text{MgCl}^+$	$3.69 \times 10^{-4}$	$1.02 \times 10^{-5}$	$2.83 \times 10^{-5}$	$5.79 \times 10^{-5}$
$\text{MgOH}^+$	$1.79 \times 10^{-5}$	$6.76 \times 10^{-6}$	$1.12 \times 10^{-5}$	$1.69 \times 10^{-5}$
$\text{K}^+$	$1.55 \times 10^{-2}$	$2.23 \times 10^{-3}$	$4.24 \times 10^{-3}$	$6.08 \times 10^{-3}$
$\text{KCl}_{(\text{aq})}$	$8.48 \times 10^{-3}$	$1.50 \times 10^{-4}$	$5.01 \times 10^{-4}$	$1.03 \times 10^{-3}$
$\text{Na}^+$	1.61	$2.34 \times 10^{-1}$	$4.47 \times 10^{-1}$	$6.40 \times 10^{-1}$
$\text{NaH}_2\text{BO}_3_{(\text{aq})}$	$2.41 \times 10^{-4}$	$6.19 \times 10^{-6}$	$1.96 \times 10^{-5}$	$4.08 \times 10^{-5}$
$\text{NaSO}_4^-$	$6.51 \times 10^{-4}$	$2.16 \times 10^{-5}$	$6.44 \times 10^{-5}$	$1.22 \times 10^{-4}$
$\text{SO}_4^{2-}$	$8.88 \times 10^{-5}$	$5.69 \times 10^{-5}$	$9.13 \times 10^{-5}$	$1.10 \times 10^{-4}$
$\text{H}_2\text{BO}_3^-$	$1.57 \times 10^{-4}$	$3.29 \times 10^{-5}$	$5.82 \times 10^{-5}$	$5.62 \times 10^{-7}$

Three ratios of LBML/water mixtures (10/90, 20/80 and 30/70) were analyzed at pH(eq) values of 11.13, 11.18 and 11.22, respectively. The species with the highest concentrations in these mixtures are  $\text{Cl}^-$  and  $\text{Na}^+$ . It is worth noting that if the concentrations obtained in the LBML and the mixtures are compared, the concentrations of all species tend to increase as the amount of LBML increases. Likewise, more compounds were found in lower concentrations, these are presented in Tables S-10.1–S-10.4 in the Supplementary Material.

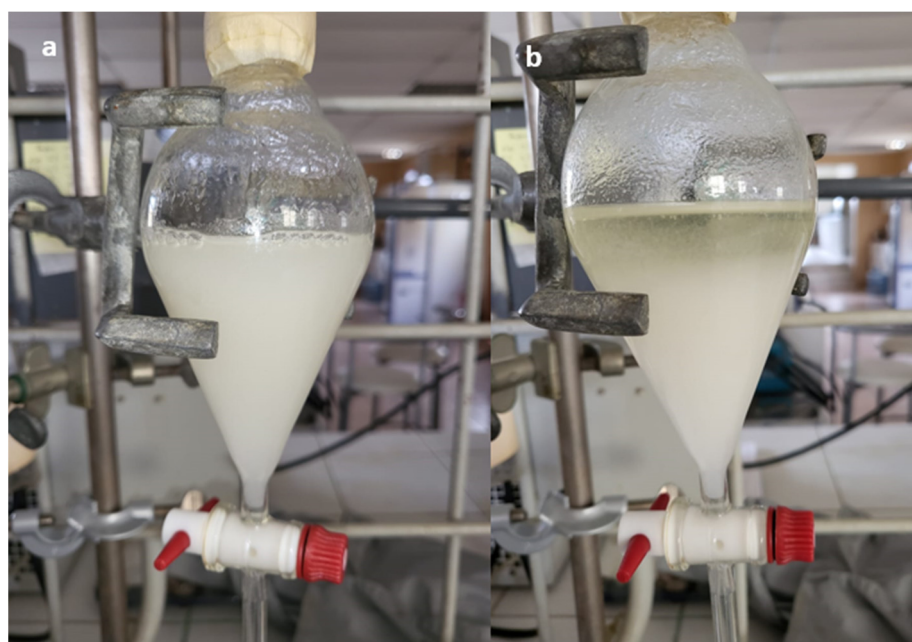
Although all the concentrations of the species in Table 2 tend to follow the same trend, the behaviors of the  $\text{H}_2\text{BO}_3^-$  and  $\text{H}^+$  species are different; their concentrations decrease for the last ratio (30/70). This may be one reason that the pH(eq) values of these three mixtures are higher than those of the LBML, and consequently, it may explain why they tend to form emulsions in the stripping stage.

To avoid the formation of emulsions, the pH was controlled, as in all the experimental processes that maintained this parameter between 1.3 and 6.9, where no emulsions were formed.

### 5.7. Process Design

#### 5.7.1. Serial Organic Discharge

A ratio of 2.6 to 1 between the loaded organic phase and water (the aqueous phase) was chosen to load the aqueous phase to the maximum capacity. In the first stage, the phases managed to separate without any difficulty, with a time of 56 s, but phase separation did not happen in the second stage because an emulsion formed. This stage was maintained for 72 h so that phase separation could be completed, but the phases only managed to separate by a few centimeters (Figure 10).



**Figure 10.** Emulsion formation: (a) phase separation time of 3 min, (b) phase separation time of 72 h.

### 5.7.2. Organic Discharge in Parallel

A four-stage parallel stripping process was carried out; water was used in the first three stages, and the fourth stage was carried out with the LBML. The concentrations obtained in the aqueous solutions are presented in Table 3, and the final aqueous output of stage 4 was 0.004% boron (0.023%  $\text{H}_3\text{BO}_3$ ). In all the stages, entrainment occurred, and the phase separation times increased in both organic and aqueous continuity, as did the pH(eq) values.

**Table 3.** Boron and  $\text{H}_3\text{BO}_3$  concentrations, phase separation times of stripping in organic continuity and aqueous continuity, and output pH(eq) values of the four-stage parallel stripping (aqueous) phases.

	B % w/w	$\text{H}_3\text{BO}_3$ % w/w	O. Cont. [s]	A. Cont. [s]	eq.pH
Stage 1	0.96	5.5	56	59	3.09
Stage 2	0.22	1.25	72	72	5.56
Stage 3	0.064	0.36	89	98	6.85
Stage 4	0.0039	0.023	189	194	10.53

Based on these results, the proposed process includes four stages that are carried out in parallel, as shown in Figure 11. Table S-11 in the Supplementary Material presents the results of the mass balance of the process at 25 °C with the respective flows and compositions of each stage.

The recovery of each stage and the overall recovery were calculated using Equation (1):

$$\%Re = \frac{C_B^A \times V_{aq}}{(C_B^A \times V_{aq} + C_B^O \times V_{or})} \cdot 100, \quad (1)$$

where %Re is the recovery percentage,  $C_B^A$  is the boron concentration in the aqueous phase and  $C_B^O$  is the boron concentration in the organic phase;  $V_{aq}$  and  $V_{or}$  are the volumes of the aqueous and organic phases, respectively.

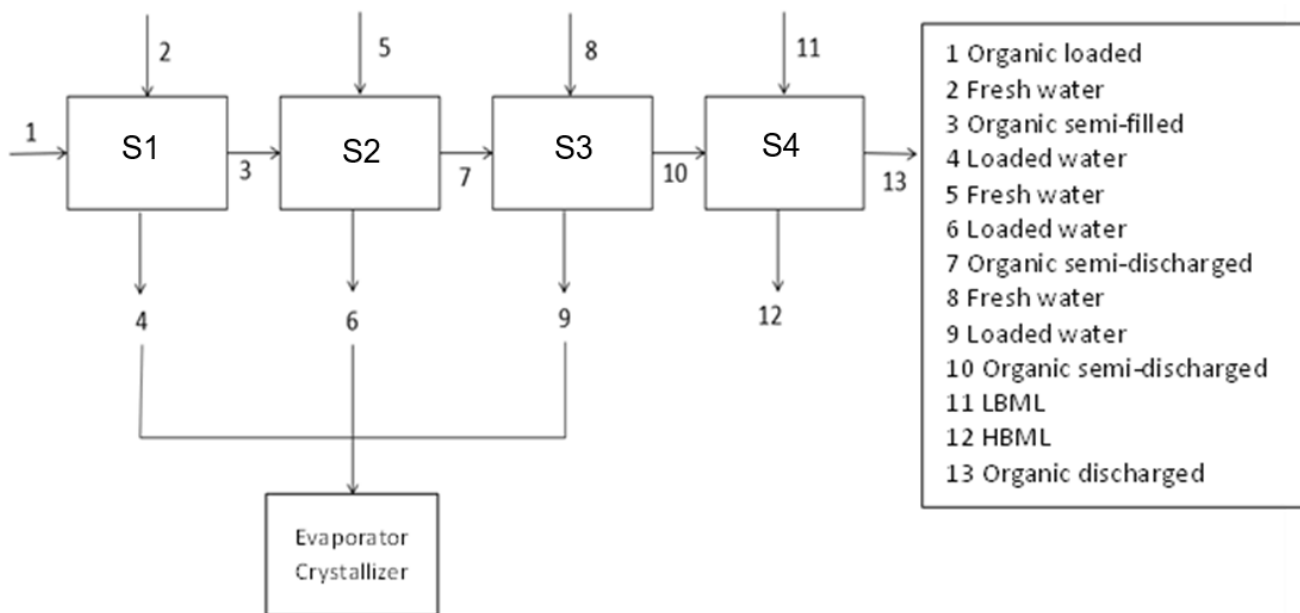


Figure 11. Proposed stripping process diagram; each  $S_i$  represents a stripping stage.

In SQM’s process plant, the recovery percentage in the first stage is 81% (information provided by the company), so the proposal to replace the LBML with water in a parallel circuit would be operationally feasible. Table 4 summarizes the results of the overall recovery and partition coefficients of the proposed process.

Table 4. Recovery (stripping) and partition coefficient (K) results of the proposed process.

	Recovery	K	B % w/w
Stage 1	68%	2.16	0.96
Stage 2	50%	0.98	0.22
Stage 3	29%	0.40	0.064
Stage 4	3%	0.03	0.004
Overall	89%	7.98	0.89

According to Peng et al. [14], similar results were obtained in the boric stripping step, where water obtained the best results (91.39%), followed by NaOH (90%), and finally HCl (89%). Kwon et al. [33] obtained high boron recovery at a basic pH (10.6) by obtaining the boron directly as a crystal using a supersaturated KOH solution; however, when water was used, at a lower pH (3.7), no crystals were obtained. This reaffirms that pH(eq) is an important operating factor during the stripping process, as it allows for the avoidance of emulsions formation and facilitates the attainment of high recovery percentages.

### 6. Conclusions

The replacement of a recirculation stream by a freshwater stream in the lithium carbonate production process has been studied to carry out the recovery of boron, one of the process impurities. The boron recovery process was carried out in four parallel stages, with a basic pH and an O/A ratio of 2.6:1, resulting in a recovery of 89%.

The pH(eq) value is one of the most important variables of the process. Through speciation analysis, it was possible to prove that species such as  $H_2BO_3^-$  and  $H^+$  influence the pH(eq) value and the formation of emulsions.

The replacement of a recirculated stream with a freshwater stream does not interfere with the current process design, as no additional stages or new pieces of equipment are required. Additionally, this would allow for the treatment of the recirculated stream in the

main lithium production process, increasing the concentration of this element, while the new stream serves as an input for the boric acid production process.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min14030265/s1>, Table S-1: Composition of the loaded organic. Analysis by ICP-OES; Table S-2: Composition of the LBML. Analysis by ICP-OES; Table S-3: pH results of LBML and fresh water; Table S-4: pH results of LBML-water mixtures; Table S-5: Chemical analysis of loaded LBML performed at SQM Company. Analysis by ICP-OES; Table S-6: Chemical analysis of the Discharged Organic for the isotherm with LMBB. Performed by SQM company. Analysis by ICP-OES; Table S-7: Chemical analysis of loaded water. Carried out by SQM company. Analysis by ICP-OES; Table S-8: Chemical analysis of the Discharged Organic for the isotherm with fresh water. Performed by SQM company. Analysis by ICP-OES; Table S-9: Phase separation time; Table S-10.1: Chemical speciation of LMBB; Table S-10.2: Chemical speciation of dilution ratio 10/90; Table S-10.3: Chemical speciation of dilution ratio 20/80; Table S-10.4: Chemical speciation of dilution ratio 30/70; Table S-11: Process mass balance; Figure S1: Stripping process using LBML; Figure S2: Stripping process using water.

**Author Contributions:** The authors would like to highlight the following contributions: Conceptualization: O.Y. and M.J.; Data curation: A.C.; Formal analysis: A.C. and Y.P.J.; Investigation: A.C. and Y.B.; Methodology: A.C.; Resources: O.Y. and M.J.; Software: A.C.; Supervision: M.J. and Y.P.J.; Validation: A.C. and Y.P.J.; Roles/Writing—original draft: Y.B.; Writing—review and editing: Y.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by SQM who presented the problem, conducted the pertinent chemical analyses and collaboration of their researchers. The APC was funded by MDPI, author voucher discount code (9f1bba58928bc3bf).

**Data Availability Statement:** The data are presented in the article and others belong to the company and are protected by industrial secret.

**Acknowledgments:** A. Cerda and Y. Jimenez thank the Department of Chemical Engineering and Mineral Processes of the Universidad de Antofagasta. A. Cerda acknowledges the infrastructure and support of the Programa de Magister en Ciencias de la Ingeniería, Mención Ingeniería de Procesos de Minerales of the Universidad de Antofagasta. The authors thank SQM for financial and technical support. Y. Barrueto is grateful for the support of the Universidad Técnica Federico Santa María for the support.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Mermer, C.; Şengül, H. Addressing Potential Resource Scarcity for Boron Mineral: A System Dynamics Perspective. *J. Clean. Prod.* **2020**, *270*, 122192. [[CrossRef](#)]
2. Garcés, I.; Chong, G. Minerales de boro de yacimientos chilenos. características, usos, mercado y aplicaciones. *Innov. Año* **1993**, *6*, 23–36.
3. Lin, J.Y.; Shih, Y.J.; Chen, P.Y.; Huang, Y.H. Precipitation Recovery of Boron from Aqueous Solution by Chemical Oxo-Precipitation at Room Temperature. *Appl. Energy* **2016**, *164*, 1052–1058. [[CrossRef](#)]
4. Kluczka, J.; Pudło, W.; Krukiewicz, K. Boron Adsorption Removal by Commercial and Modified Activated Carbons. *Chem. Eng. Res. Des.* **2019**, *147*, 30–42. [[CrossRef](#)]
5. Lin, J.Y.; Mahasti, N.N.N.; Huang, Y.H. Recent Advances in Adsorption and Coagulation for Boron Removal from Wastewater: A Comprehensive Review. *J. Hazard. Mater* **2021**, *407*, 124401. [[CrossRef](#)] [[PubMed](#)]
6. Bin Darwish, N.; Kochkodan, V.; Hilal, N. Boron Removal from Water with Fractionized Amberlite IRA743 Resin. *Desalination* **2015**, *370*, 1–6. [[CrossRef](#)]
7. Kabay, N.; Yilmaz, I.; Yamac, S.; Samatya, S.; Yuksel, M.; Yuksel, U.; Arda, M.; Sağlam, M.; Iwanaga, T.; Hirowatari, K. Removal and Recovery of Boron from Geothermal Wastewater by Selective Ion Exchange Resins. I. Laboratory Tests. *React. Funct. Polym.* **2004**, *60*, 163–170. [[CrossRef](#)]
8. İpekçi, D.; Kabay, N.; Bunani, S.; Altıok, E.; Arda, M.; Yoshizuka, K.; Nishihama, S. Application of Heterogeneous Ion Exchange Membranes for Simultaneous Separation and Recovery of Lithium and Boron from Aqueous Solution with Bipolar Membrane Electrodialysis (EDBM). *Desalination* **2020**, *479*, 114313. [[CrossRef](#)]

9. Orce Schwarz, A.M.; Valdez, S.K.; Flores, H.R. Eliminación de Boro de Soluciones Salinas Por Extracción Líquido-Líquido. *Rev. Argent. Ing.* **2019**, *13*, 94–100. Available online: <https://ri.conicet.gov.ar/handle/11336/120508> (accessed on 15 June 2023).
10. Kelly, J.C.; Wang, M.; Dai, Q.; Winjobi, O. Energy, Greenhouse Gas, and Water Life Cycle Analysis of Lithium Carbonate and Lithium Hydroxide Monohydrate from Brine and Ore Resources and Their Use in Lithium Ion Battery Cathodes and Lithium Ion Batteries. *Resour. Conserv. Recycl.* **2021**, *174*, 105762. [[CrossRef](#)]
11. Tran, T.; Luong, V.T. Lithium Production Processes. In *Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 81–124. [[CrossRef](#)]
12. Guo, J.; Yang, Y.; Gao, X.; Yu, J. Boron Extraction from Lithium-Rich Brine Using Mixed Alcohols. *Hydrometallurgy* **2020**, *197*, 105477. [[CrossRef](#)]
13. Zhang, R.; Xie, Y.; Song, J.; Xing, L.; Kong, D.; Li, X.M.; He, T. Extraction of Boron from Salt Lake Brine Using 2-Ethylhexanol. *Hydrometallurgy* **2016**, *160*, 129–136. [[CrossRef](#)]
14. Peng, X.; Li, L.; Shi, D.; Zhang, L.; Li, H.; Nie, F.; Song, F. Recovery of Boric Acid from Salt Lake Brines by Solvent Extraction with 2-Butyl-1-n-Octanol. *Hydrometallurgy* **2018**, *177*, 161–167. [[CrossRef](#)]
15. Peng, J.; Bian, S.; Zhang, B.; Dong, Y.; Li, W. Research on Boron Recovery from Sulfate-Type Saline Lakes with a Novel Dilution Method. *Hydrometallurgy* **2017**, *174*, 47–55. [[CrossRef](#)]
16. Kim, K.C.; Il Kim, N.; Jiang, T.; Kim, J.C.; Kang, C.I. Boron Recovery from Salt Lake Brine, Seawater, and Wastewater—A Review. *Hydrometallurgy* **2023**, *218*, 106062. [[CrossRef](#)]
17. Mott, A.; Baba, A.; Hadi Mosleh, M.; Ökten, H.E.; Babaei, M.; Gören, A.Y.; Feng, C.; Receptoğlu, Y.K.; Uzelli, T.; Uytun, H.; et al. Boron in Geothermal Energy: Sources, Environmental Impacts, and Management in Geothermal Fluid. *Renew. Sustain. Energy Rev.* **2022**, *167*, 112825. [[CrossRef](#)]
18. Seval, K.; Onac, C.; Kaya, A.; Akdogan, A. Separation of Boron from Geothermal Waters with Membrane System. *Membranes* **2021**, *11*, 291. [[CrossRef](#)]
19. Huang, L.; Lai, H.; Lu, C.; Fang, M.; Ma, W.; Xing, P.; Li, J.; Luo, X. Enhancement in Extraction of Boron and Phosphorus from Metallurgical Grade Silicon by Copper Alloying and Aqua Regia Leaching. *Hydrometallurgy* **2016**, *161*, 14–21. [[CrossRef](#)]
20. Qin, S.; Yin, B.; Zhang, Y.; Zhang, Y. Leaching Kinetics of Szaibelyite Ore in NaOH Solution. *Hydrometallurgy* **2015**, *157*, 333–339. [[CrossRef](#)]
21. Liu, Y.; Shi, P.; Chao, Q.; Jiang, M. Efficient Acid Leaching of High-magnesium Boron Tailings and the Low Cost Recovery of Siliceous Residues with Good Adsorption Capacity. *Hydrometallurgy* **2022**, *209*, 105827. [[CrossRef](#)]
22. Jiang, Z.; Zhang, Z.; Xia, B.; Xiong, S.; Yang, L.; Li, Z. Mechanism of Boric Acid Extraction by Trioctylamine and Tartaric Acid. *Sep. Purif. Technol.* **2024**, *331*, 125597. [[CrossRef](#)]
23. Yu, T.; He, R.R.; Zhang, X.; Liu, J.X.; Kou, B.; Zhang, X.F.; Qu, C.T.; Huang, Y. Factors Influencing the Removal of Boron from Fracturing Fluid Flowback by Chemical Oxidative Precipitation. *J. Inst. Eng. (India) Ser. E* **2022**, *103*, 219–226. [[CrossRef](#)]
24. Chruszcz-Lipska, K.; Winid, B.; Madalska, G.A.; Macuda, J.; Łukańko, Ł. High Content of Boron in Curative Water: From the Spa to Industrial Recovery of Borates? (Poland as a Case Study). *Minerals* **2021**, *11*, 8. [[CrossRef](#)]
25. Çelebi, E.E.; Öncel, M.S.; Kobya, M.; Bayramoğlu, M. Extraction of Lithium from Wastewaters Using a Synergistic Solvent Extraction System Consisting of Mextral EOL and Cyanex 923. *Hydrometallurgy* **2019**, *185*, 46–54. [[CrossRef](#)]
26. Xiang, W.; Liang, S.; Zhou, Z.; Qin, W.; Fei, W. Extraction of Lithium from Salt Lake Brine Containing Borate Anion and High Concentration of Magnesium. *Hydrometallurgy* **2016**, *166*, 9–15. [[CrossRef](#)]
27. Wang, H.; Zhong, Y.; Du, B.; Zhao, Y.; Wang, M. Recovery of Both Magnesium and Lithium from High Mg/Li Ratio Brines Using a Novel Process. *Hydrometallurgy* **2018**, *175*, 102–108. [[CrossRef](#)]
28. Liu, X.; Lu, Q.; Zhou, Q.; Chen, P.; Li, K. Bisulfite-Activated Permanganate Oxidation plus Coagulation as a Pretreatment of SWRO Desalination Lines to Enhance Boron Rejection. *Sep. Purif. Technol.* **2023**, *308*, 122959. [[CrossRef](#)]
29. Rydberg, J. *Solvent Extraction Principles and Practice, Revised and Expanded*. Rydberg, J., Ed.; CRC Press: Boca Raton, FL, USA, 2004; ISBN 9780203021460.
30. Nozari, I.; Azizi, A. An Investigation into the Extraction Behavior of Copper from Sulfate Leach Liquor Using Acorga M5640 Extractant: Mechanism, Equilibrium, and Thermodynamics. *Min. Metall. Explor.* **2020**, *37*, 1673–1680. [[CrossRef](#)]
31. Parhi, P.K.; Park, K.-H.; Kim, H.-I.; Park, J.-T. Recovery of Molybdenum from the Sea Nodule Leach Liquor by Solvent Extraction Using Alamine 304-I. *Hydrometallurgy* **2011**, *105*, 195–200. [[CrossRef](#)]
32. Vahidi, E.; Rashchi, F.; Moradkhani, D. Recovery of Zinc from an Industrial Zinc Leach Residue by Solvent Extraction Using D2EHPA. *Miner. Eng.* **2009**, *22*, 204–206. [[CrossRef](#)]
33. Kwon, T.; Hirata, M.; Sakuma, S.; Hano, T.; Yamagishi, T. Continuous Recovery of Boron from Wastewater with a Diol. *Solvent Extr. Ion Exch.* **2005**, *23*, 391–400. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.