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Koivisto, ES; Reuter, T; Zevenhoven, R

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# Performance Optimization of Bipolar Membrane Electrodialysis of Ammonium Sulfate/Bisulfate Reagents for CO<sub>2</sub> Mineralization

Evelina S. Koivisto,\* Tobias Reuter, and Ron Zevenhoven

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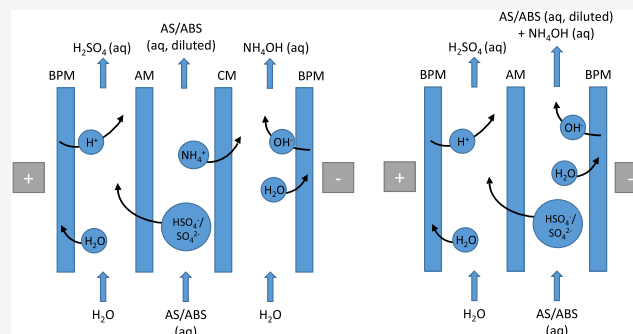
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**ABSTRACT:** This paper reports on tests performed with the dual aim of minimizing the energy use (kilojoules per kilogram) and maximizing the conversion rate (kilograms per hour) of bipolar membrane electro dialysis (BPMED) for the regeneration of chemicals needed for the effective scale-up of the accelerated CO<sub>2</sub> mineralization route developed at Åbo Akademi University (ÅA). The performance of two- and three-compartment stacks was compared with ammonium sulfate (AS) and ammonium bisulfate (ABS) as the input product feed, yielding sulfuric acid and aqueous ammonia, respectively, as the final products. It was shown that a two-compartment stack is more efficient with regard to energy use (i.e., electricity consumption), with values in the range of 3630–4844 kJ/kg of AS or ABS, compared to the three-compartment stack requiring 5102–7223 kJ/kg of AS or ABS. A maximum conversion rate of ~0.13 kg/h was achieved with the two-compartment stack. We also concluded that approximately 25% of the energy needed for the process may give off heat, depending primarily on the voltage applied to the membrane stack. A two-compartment stack will require fewer membranes, which is an obvious benefit in terms of maintenance and cost. Furthermore, we concluded that AS provides a more efficient conversion than ABS, when considering both energy use and the amounts of the solution that need to be recycled in the BPMED step.

**KEYWORDS:** mineral carbonation, bipolar membrane electro dialysis, ammonium hydrogen sulfate, ammonia, ÅA route



## 1. INTRODUCTION

Research into carbon capture, storage, and usage potential via accelerated mineral carbonation has been undertaken during the past two decades at Åbo Akademi University (ÅA).<sup>1–5</sup> An overview of global research within this field was published recently, with a particular focus on progress toward economically viable deployment of mineral carbonation achieved over the past 5–10 years. That report gives a strategic overview of the future potential and opportunities for CO<sub>2</sub> mineralization and assesses the challenges for scaling up the laboratory bench-scale work that has been done worldwide, using a range of different approaches.<sup>6</sup>

This study presents results from tests performed with the aim of optimizing both energy (i.e., electricity) use and conversion rate when using bipolar membrane electro dialysis (BPMED) for the regeneration of chemicals required for the accelerated mineral carbonation route developed at ÅA. The ÅA mineral carbonation process is initiated by grinding of magnesium silicate rock and leaching in ammonium bisulfate (ABS) and/or sulfuric acid solutions followed by separation of insoluble matter (i.e., silicates). This is in turn followed by carbonation of the magnesium sulfate (MS) leachate (with the option of precipitating any desirable metallic elements before carbonation), during which ammonium sulfate (AS) is

obtained. The solution pH plays an important role in all steps of the process (leaching, precipitation, and carbonation), and carefully regulating the concentrations of ammonia and sulfuric acid/ABS solutions is important to keep the volumes of chemicals to a minimum and to achieve optimal leaching and carbonation results. One critical aspect in the scale-up of this process using the larger volumes and at rates of material flow of several kilograms per second required for commercially viable industrial uptake is the efficient regeneration of chemical reagents.

Regeneration of the chemicals needed in the mineral carbonation route can be accomplished in several ways by applying BPMED electro dialysis (see Figure 1 for two options). Either part of the ABS (first requiring mixing of H<sub>2</sub>SO<sub>4</sub> and AS) can be transported to a BPMED unit, which separates the ABS to produce NH<sub>4</sub>OH and H<sub>2</sub>SO<sub>4</sub> (Figure 1a).

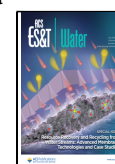
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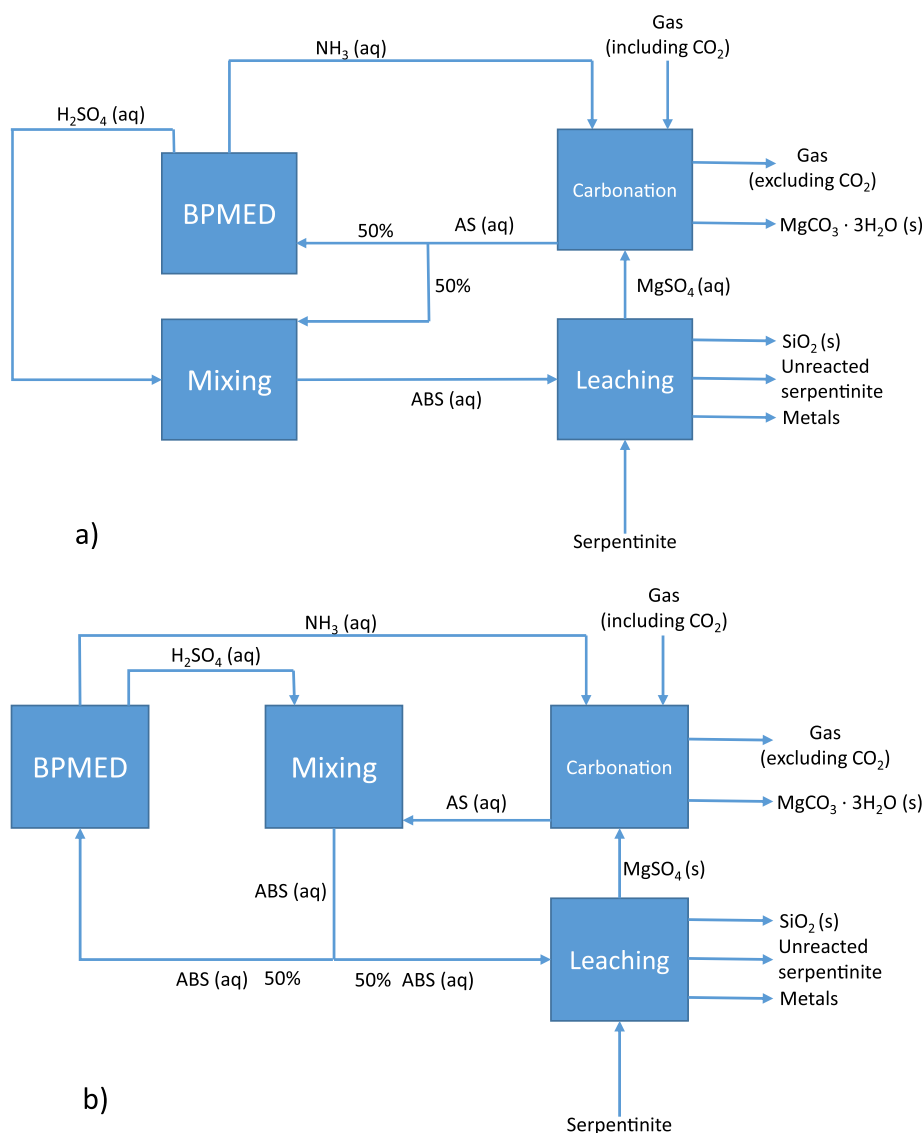
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**Figure 1.** Wet “AA route”, including extraction and carbonation in aqueous solutions at low temperatures and BPMED for regeneration of ABS. (a) Production of ammonia and sulfuric acid solutions from ABS solutions. (b) Production of ammonia and sulfuric acid solutions from AS solutions.

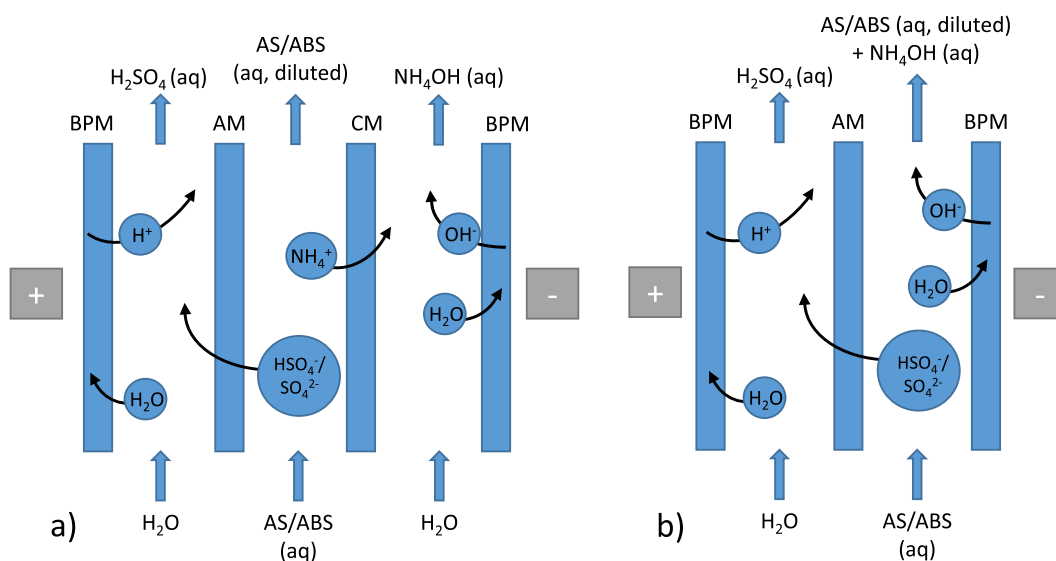
In addition, AS from the carbonation step can also be separated directly (Figure 1b), producing aqueous ammonia and sulfuric acid in the BPMED unit, as well. The magnesium sulfate solution obtained (after leaching of the rock and removal of dissolved matter and, in addition, recovery of desirable metallic elements) reacts with  $CO_2$  and aqueous  $NH_3$  (which gives the necessary alkalinity) to form (hydrated) magnesium carbonates and ammonium sulfate (AS), respectively. Following carbonation, the solution pH equals  $\approx 10$ , resulting in a surplus of AS rather than ABS. The process will therefore need a mixing step after regeneration during BPMED to regenerate the AS back to ABS for subsequent use in the process (Figure 1a). Alternatively, AS could be mixed with a sulfuric acid solution obtained from the BPMED process and ABS solutions could be treated in the BPMED unit instead of AS solutions (Figure 1b). If AS is allowed to react with  $H_2SO_4$ , ABS is obtained (at low pH ABS will be dominant instead of AS) according to



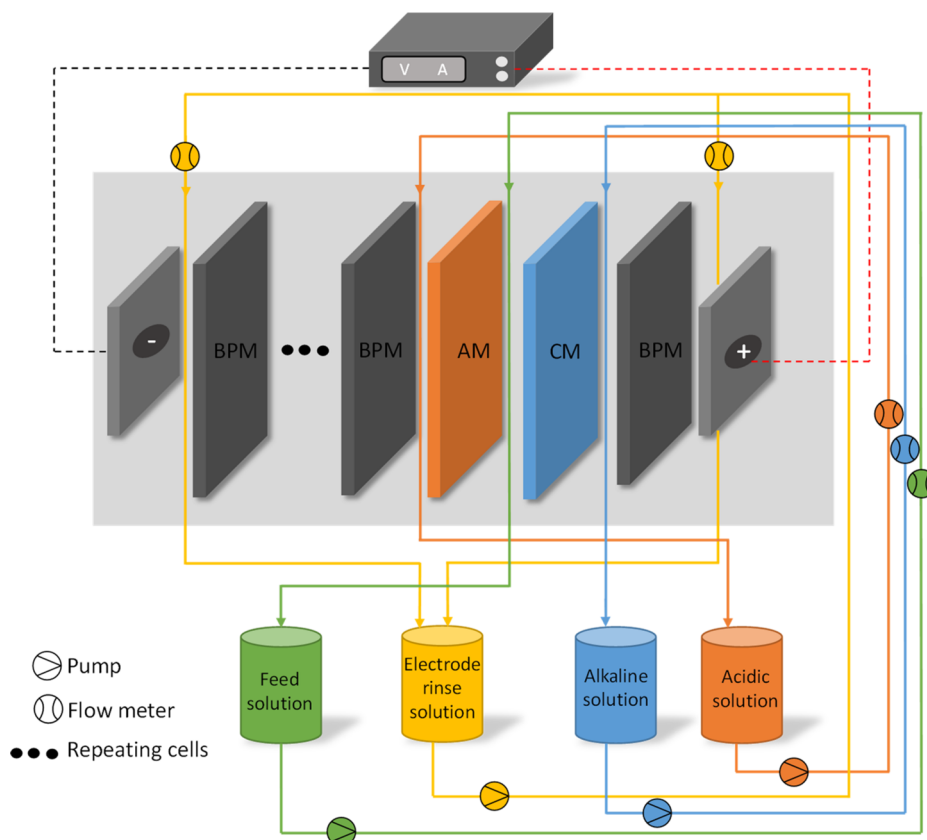
The mixing step after the BPMED step also means that only half of the AS solution obtained after leaching in the BPMED unit must be treated (Figure 1a); this contrasts with the other option (Figure 1b) in which AS is mixed with sulfuric acid from BPMED to enable separation by BPMED of the ABS solution instead.

The aim of this study was to ascertain the feasibility of separating AS or ABS and to optimize the energy use (kilojoules per kilogram of salt) and conversion rate (kilogram of salt per hour) of the separation process for a given available membrane surface.

Anionic (AMs), cationic (CMs), and bipolar membranes (BPMs) are typically used in BPMED setups. These are used in various combinations to form a BPMED cell. While the AM and CM allow anions and cations, respectively, to pass through, the BPM consists of a combined anionic and cationic membrane. Because of the functional groups in such membranes, only positively charged ions can penetrate the anionic layer in a bipolar membrane, while only negatively charged ions can penetrate the cationic layer, thus resulting in the bipolar membrane rejecting all ions.<sup>7</sup> However, it must be



**Figure 2.** Schematics of (a) a three-compartment BPMED setup and (b) a two-compartment BPMED setup showing one repeating cell. The ratio between  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  depends on pH and whether AS or ABS is used as the starting solution (shown as AS/ABS in the schematics).



**Figure 3.** Schematic illustration of the setup used to describe the flows in the three-compartment stack. For the two-compartment setup, the principal is the same; however, the alkaline solution route is then not in use, and the cationic membranes are not present.

pointed out that co-ionic transport across the anionic and cationic membranes can occur. Ideally, electrical repulsion would exclude the transport of ions having the same charge as the functional groups in the membrane, but in reality, some of the co-ions will be transported across the membrane. This will have an adverse effect on separation efficiency and lead to impurities in the final process streams (i.e., an acid and a base when BPMs are applied).<sup>8</sup>

The working principle of BPM is that water dissociates into  $\text{H}^+$  and  $\text{OH}^-$  ions in the interface layer between the AM and the CM. These leave the interface layer through opposite membranes, transporting electric charges and producing an acid and a base on either side of the BPM. Water dissociation is possible only where an AM is facing the anode and a CM faces the cathode.<sup>11</sup> The current density and voltage play a major role in the efficiency of the BPMED process. An

Table 1. Starting Parameters of Tests Performed in a Three-Compartment BPMED Stack<sup>a</sup>

test no.	volume (product, base, or acid) (dm <sup>3</sup> )	cell no.	input electricity	initial product solution	initial base solution
1	4	7	24 V	0.5 M ABS	water and 1 g of AS
2	2	7	24 V	0.5 M AS	water and 0.5 g of AS
3	2	7	24 V	0.5 M ABS	water and 0.5 g of AS
4	2	7	24 V	0.5 M ABS	water, 0.5 g of AS, and 10 g of MS (35 min before the end)
5	2	7	24 V	0.1 M ABS and an addition every 10 min until 0.5 M	water and 10 g of MS
6	2	7	18 V	0.5 M AS	water and 10 g of MS
7	3	9	24 V	0.5 M AS	water and 0.75 g of AS
8	3	9	24 V	0.5 M ABS	water and 3 g of AS
9	3	9	4 A	0.5 M AS	water and 3 g of AS
10	3	9	24 V	0.5 M AS and 0.57 M AA	water and 3 g of AS
11	3	9	24 → 30 V	1.0 M AS	water and 3 g of AS
12	3	9	30 → 24 V	1.0 M AS	water and 3 g of AS
13	3	9	24 → 30 V	1.0 M ABS	water and 3 g of AS

<sup>a</sup>The initial acid solution at the start was water. AA indicates an aqueous ammonia solution.

increased current density implies greater transport of charges in a shorter time, thus increasing the production capacity. However, it is possible that an increased current density will also result in increased electricity consumption, and it is therefore important to determine the optimal electrical operating conditions.

Several different arrangements of BPMED have been tested previously, which use ammonium sulfate as input species.<sup>9–12</sup> With regard to the separation of ABS, however, there are almost no publications available, except for work published by the authors of this paper.<sup>13,14</sup> Direct CO<sub>2</sub> capture in the BPMED unit using processes that include the precipitation of carbonates inside the BPMED unit has also been investigated.<sup>15,16</sup> Such precipitation is avoided in the mineral carbonation route presented here.

## 2. MATERIALS AND METHODS

**2.1. BPMED Setup.** In this study, a three-compartment BPMED configuration was used first and later a two-compartment BPMED configuration was tested and compared. Simple schematics of these are shown in Figure 2.

Acid/base production or recovery from salt can be carried out in a three-compartment setup (Figure 2a). A salt solution is fed through the middle compartment, located between an AM and a CM. Water or water with added salt is initially fed through the compartments on either side. When an electric current is applied, positively charged ions in the salt solutions are transported across the CM and the negatively charged ions across the AM. The OH<sup>−</sup> and H<sup>+</sup> ions combine with the transported ions to form a base and an acid, respectively, in the compartments on either side of the salt solution compartment. This is the most commonly used BPMED configuration.<sup>17</sup>

The two-compartment stack (Figure 2b) consists of two bipolar membranes and one anionic membrane forming one cell. Here, ions migrate from one solution to produce a pure acid solution (or base, if the anionic membrane is replaced with a cationic membrane) and a solution of a salt and a base (or acid). The two-compartment stack is more suitable for solutions having low conductivity, or rather to avoid the formation of such solutions. For example, when a low-conductivity solution is generated in the base (or acid) compartment of a three-compartment stack, this limits the

current density in the entire stack. However, in a two-compartment stack, the input salt increases the solution conductivity. This configuration requires fewer membranes and one fewer process stream compared to the three-compartment setup, which makes it potentially cheaper.<sup>7</sup> The main reason why the two-compartment stack was studied here is that aqueous ammonia, which represents the base solution, has very low conductivity, which adversely affects the separation efficiency.

The experiments were carried out in a Eurodia SED 3 pilot unit. The unit consisted of a metallic frame, a membrane stack, four 5 L tanks made of polypropylene, five flowmeters, four pumps, an electrical cabinet and piping, valves, and fittings (see Figure 3 for a simple sketch of the apparatus and system). Furthermore, a Microlab MX 50V-25A dc power supply was used to provide electricity to the stack. High-mechanical strength anionic and cationic Neosepta-Tokuyama Corp. membranes were used, as well as bipolar membranes from the same manufacturer. The membranes used give an active area of 2 dm<sup>2</sup>/cell. Flow rates of 20 dm<sup>3</sup> h<sup>−1</sup> cell<sup>−1</sup> were applied in all tests, in accordance with instructions from the manufacturer of the pilot unit and the membrane stack. Spacers (thickness of 0.75 mm) separated the membranes. Initially, nickel electrodes were used, but these were later exchanged for DS (dimensional stability) electrodes. WTW pH/Cond 3320 meters equipped with WTW SenTix pH electrodes and WTW TetraCon 325 standard conductivity measuring cells were used, recording and storing data every 30 s. The pH meters were calibrated using two-, three-, or four-point calibration, using buffer solutions with pH values of 1, 4, 7, and 10 prior to each test run.

Before each experiment, the stack and storage vessels were rinsed with RO/electro-deionized water until a conductivity of <100 μS/cm was reached in all streams. The electrode rinse solution was 4 dm<sup>3</sup> of a 0.5 M AS solution unless otherwise specified. The laboratory temperature was 22 °C, with temperatures of the solutions tested increasing sometimes ≤35 °C for some of the tests, as reported below.

The streams will hereafter be termed the product, acid, base, and electrolyte streams. The product stream refers to the stream that contains the salt that is to be separated; the acid and base streams contain the produced sulfuric acid and

aqueous ammonia, respectively, while the electrolyte stream contains the electrode rinse solution.

**2.2. Chemical Reagents.** Ammonium sulfate [Honeywell Fluka/Sigma-Aldrich (Merck),  $\geq 99\%$ ], ammonium bisulfate (Thermo Scientific, extra pure),  $\text{NH}_4\text{OH}$  (Honeywell Fluka, 25%  $\text{NH}_3$  basis), and magnesium sulfate (VWR Chemicals, 100%) were used.

**2.3. Experimental Parameters.** Numerous different starting parameters were used in the experiments. These are listed in Table 1 (three-compartment stack) and Table 2 (two-

**Table 2. Starting Parameters of Tests Performed in a Two-Compartment BPMED Stack with Seven Repeating Cells**

test no.	volume (product or acid) ( $\text{dm}^3$ )	voltage (V)	initial product solution	initial acid solution
14	2	16	0.5 M AS	$\text{H}_2\text{O}$
15	2	12	1.0 M AS	$\text{H}_2\text{O}$
16	2	16	1.0 M AS	$\text{H}_2\text{SO}_4$ (pH 0.9)
17	2	18	1.0 M AS	$\text{H}_2\text{O}$

compartment stack). A small amount of chemicals was added to almost all of the base solutions according to Tables 1 and 2 to increase the conductivity at the start of each experiment. Experiments were conducted only once in this study (i.e., no exact duplicate experiments) because tests using slightly different starting settings consistently gave different results, as expected. For test 4, the first 50 min was conducted under conditions identical to those of test 3: this showed an average difference of 1.1% (for the electric current vs time). See Figure SII-1 for these results.

Table 3 shows parameters for four experiments carried out to investigate how the presence of AS or ABS as the starting solution affects the energy use and conversion rate of BPMED.

**Table 3. Experimental Parameters of Comparable AS and ABS Experiments<sup>a</sup>**

test no.	volume (product or base) ( $\text{dm}^3$ )	voltage (V)	initial product solution	initial base solution
3 = ABS-1	2	24	0.5 M ABS	0.5 g of AS
2 = AS-1	2	24	0.5 M AS	0.5 g of AS
18 = ABS-2	2	24	0.1 M ABS	water
19 = AS-2	4	24	0.1 M AS and 0.005 M MS	$\text{NH}_4\text{OH}$ (pH 9)

<sup>a</sup> $\text{NaOH}$  solutions (1 N) were used as electrode rinse solutions for tests ABS-2 and AS-2.

To determine the overall (electrical) energy used for electro dialysis (joules per kilogram of salt), the following equation was used:

$$E = \frac{\int_0^t U \cdot I \, dt}{nc_0V/M} \quad (1)$$

where  $U$  (volts) is the potential decrease (voltage) across the membrane stack,  $I$  (amperes) is the electric current,  $t$  (seconds) is the time,  $n$  is the conversion level (percent),  $c_0$  (moles per cubic decimeter) is the salt concentration at the start of the experiment,  $V$  (cubic decimeters) is the volume of

the salt solution, and  $M$  is the molar weight (kilograms per mole).

To determine the conversion level, the electrical conductivity of the salt solution was measured. The concentration was then determined from this conductivity, with a calibration curve for either AS or ABS (see Figures S12-1 and S12-2). The concentration was then compared to the initial concentration to determine the conversion according to

$$n = \left(1 - \frac{c}{c_0}\right) \times 100\% \quad (2)$$

where  $c$  is the concentration (moles per cubic decimeter). The calibration curve for ammonium sulfate was used for the calculations of the tests performed with the two-compartment stack because the contribution of ammonia produced to the conductivity of the ammonium sulfate solution may be neglected.

The current efficiency ( $C_E$ ) was determined by the ratio of the current effectively used for salt separation through the stack and the total current through the stack, which is calculated according to

$$C_E = \frac{FzV\Delta C}{NIt} \quad (3)$$

where  $F$  is Faraday's constant (96485 C/mol),  $z$  is the ion valence,  $V$  (cubic decimeters) is the solution volume,  $\Delta C$  is the change in concentration (moles per cubic decimeter),  $N$  is the number of cell pairs,  $I$  (amperes) is the current through the stack, and  $t$  (seconds) is the time.<sup>18</sup> The change in volume ( $V$ ) between the time intervals was considered to be very small and therefore neglected in the calculations. Because the current varied while the voltage was kept constant,  $C_E$  was calculated for time intervals (here the time between readings) and an overall  $C_{E(\text{tot})}$  was calculated according to

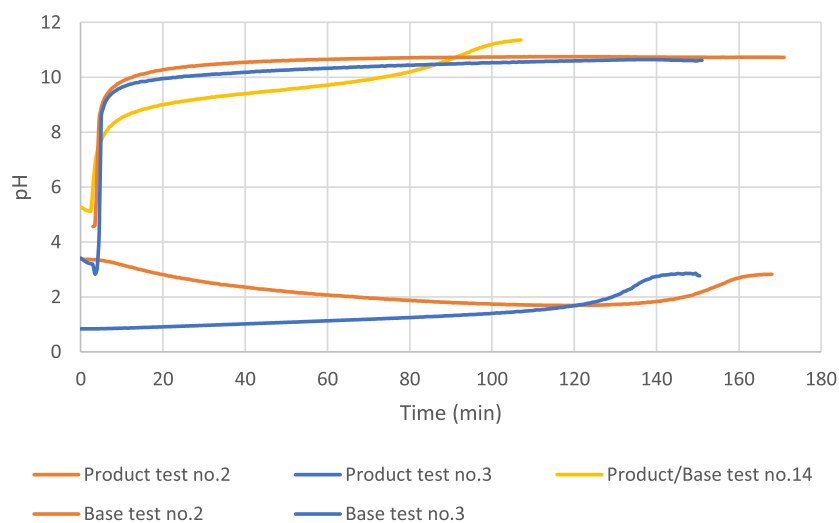
$$C_{E(\text{tot})} = \frac{\sum C_E \Delta t}{t_{\text{tot}}} \quad (4)$$

An estimate of how much heat per second ( $\dot{Q}$ ) the pumps generated was calculated according to

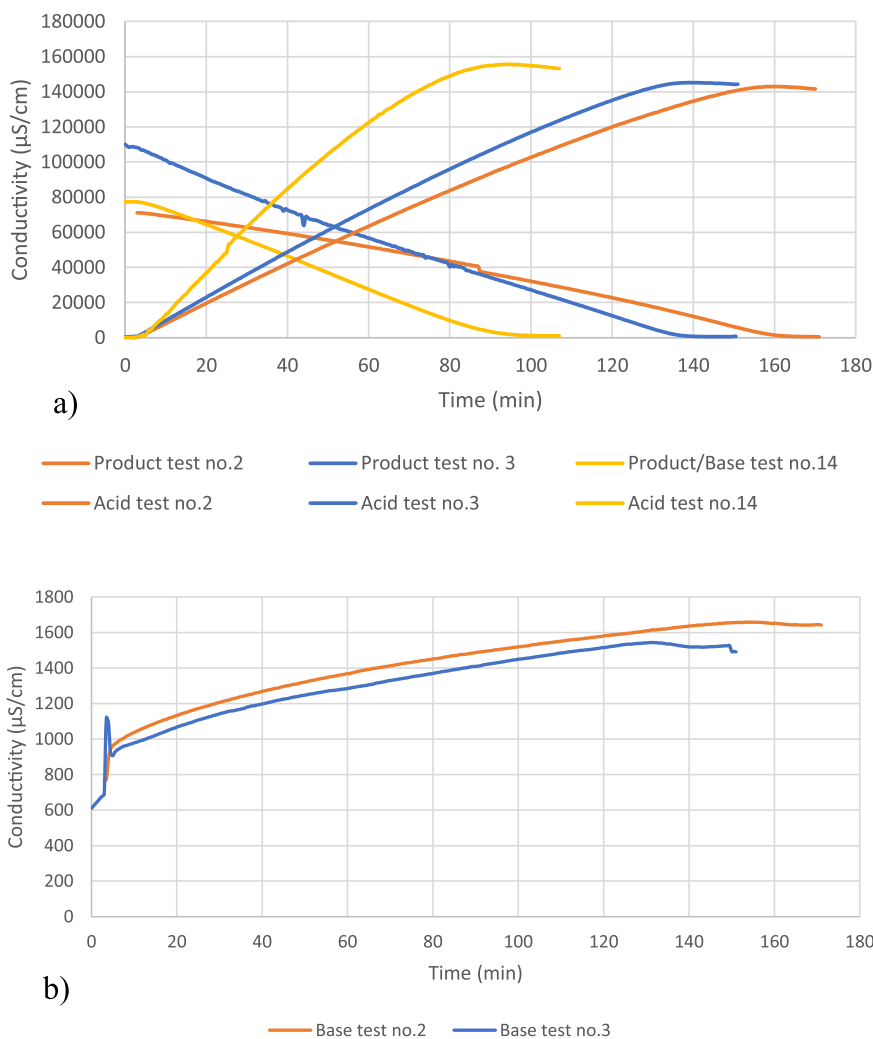
$$\dot{Q} = \frac{\int_{T_0}^{T_1} c_p m \, dT}{t} \quad (5)$$

where  $T_0$  and  $T_1$  (degrees Celsius) are the initial and final temperatures, respectively,  $c_p$  ( $4.18 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1}$ ) is the specific heat capacity for water,  $m$  (kilograms) is the mass that is heated, and  $t$  (seconds) is the experimental time.

Because the BPMED unit is not heat insulated, significant heat loss to the laboratory (with an ambient temperature of  $\sim 22.5 \text{ }^\circ\text{C}$ ) can be expected. Furthermore, higher stream temperatures lead to an increased heat loss while the ambient temperature was practically constant and the temperature difference increased. Hence, these calculations can be used only as a rough estimate of heat production in the membrane stack. By using eq 5 and via comparison of the heat generated by the pumps (determined from tests without electricity input for electro dialysis) with the heat generated in the experiments, an estimation of the proportion of the total electricity use that results in heat generation could be obtained.



**Figure 4.** Comparison of pH vs time for three tests in base and product solutions.

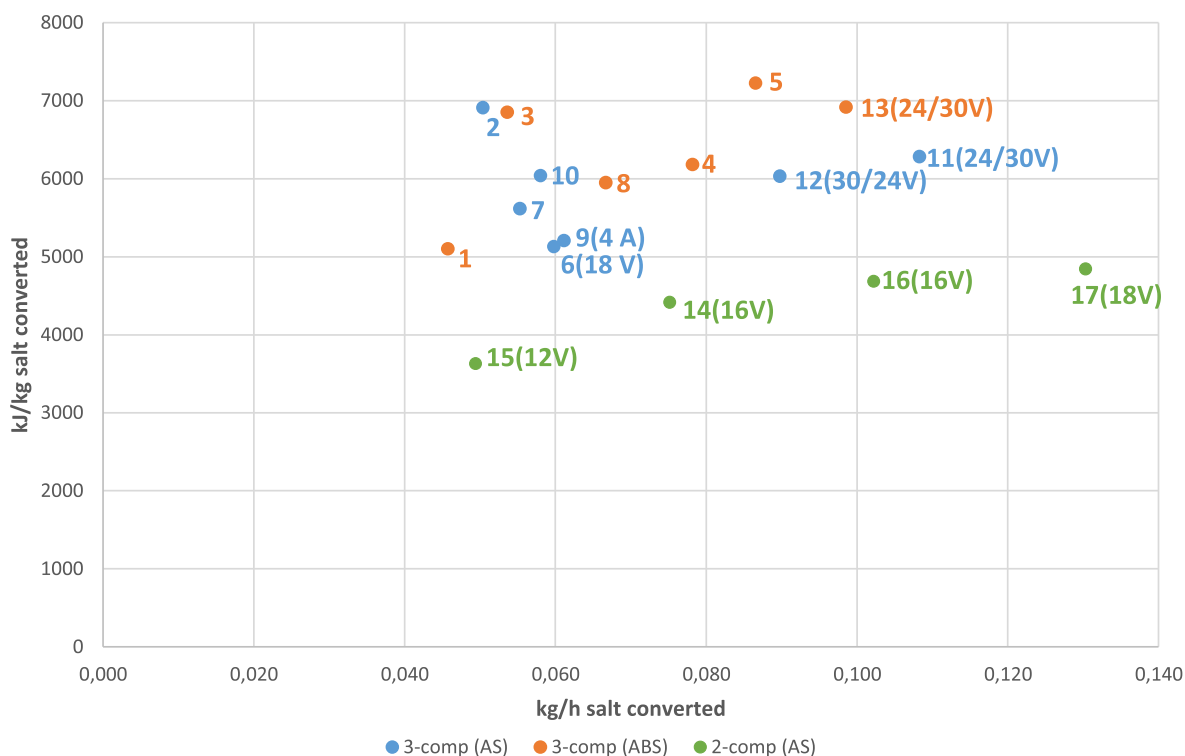


**Figure 5.** Conductivity vs time for three tests in (a) product and acid and (b) base solutions.

### 3. RESULTS AND DISCUSSION

**3.1. pH and Conductivity.** The pH and conductivity of the product, acid, and base were measured for the three-compartment stack, while for the two-compartment stack, these were measured in the product, acid, and electrode rinse

solutions. Figures 4 and 5 show typical results with respect to pH and conductivity from measurements from three tests (see tests 2 and 3 in Table 1 and test 14 in Table 2). Tests 2 and 3 were performed in a three-compartment stack, while test 14 was performed in a two-compartment stack, thus giving a



**Figure 6.** Energy use vs salt conversion rate of tests in two- and three-compartment stacks with either AS or ABS as the initial product stream. Tests at 24 V unless otherwise indicated. Tests 1–3 used Ni electrodes, tests 4–17 DSE electrodes, tests 1–3 and 14–17 seven cells, and tests 7–13 nine cells.

combined product/base process solution (see Figures 4 and 5). It is obvious that the separation became much faster upon application of a two-compartment stack. The pH of the ammonia (base) solution also reached a somewhat higher value with the two-compartment stack. Tests 2 and 3 were performed at 24 V, while test 14 was performed at 16 V ( $2/3$  of 24 V) because the number of membranes in the two-compartment stack was only  $2/3$  of that in the three-compartment stack. The voltage per membrane thus remained the same. It was nevertheless observed that even if the applied voltage was lower in the two-compartment stack the separation became faster.

The conductivity curve for the base solution in Figure 5a shows that the ammonia solution has a higher conductivity than the expected value of 1.2 mS/cm,<sup>19</sup> which indicates leakage of co-ions over the cationic membranes. The conductivity of the base solution was much lower than that of the product and acid solutions, so to increase the initial conductivity of the base solution, 0.5 g of AS was added. This can also partly explain why the conductivity in the end became higher. The transport of unwanted ions is a possible side effect of electrodialysis. Rottiers et al.<sup>8</sup> found that co-ionic transport is largely dependent on concentration differences and that an increasing current density does not significantly influence co-ion flux. This implies that a high current density is beneficial for the process, with the transport of “wanted” ions then overwhelming that of “unwanted” ones. On the contrary, the use of low-concentration solutions is also an effective way to suppress co-ion fluxes.

The importance of the regeneration of ammonia by BPMED is crucial for the CO<sub>2</sub> mineralization process favored in these investigations. Ammonia is required first for adjusting the pH of the solution after initial leaching of the rock to liberate and

separate metals (Fe, Ni, Al, etc.) by precipitation of hydroxides at weakly alkaline pH ( $\approx 8.5$ ) and thereafter for the carbonation step (pH  $\approx 10$ ). Therefore, it is necessary to reach a sufficiently high concentration of the ammonia solution to ensure a sufficiently high pH in the carbonation step. However, studies have shown that membrane resistance increases when the conductivity of the surrounding solutions becomes low, and because ammonia is a weak base, it will lead to a relatively high membrane resistance. Geise et al.<sup>20</sup> studied the effect of solution concentration differences on bipolar membranes. When using NaCl solutions with concentrations of 1 and 0.1 mol/dm<sup>3</sup> on either side of the membrane, it was shown that membrane resistance increased by 13–15 times compared to that of NaCl solutions with concentrations of 1 mol/dm<sup>3</sup> on either side of the membrane. This drastic increase in membrane resistance becomes very important when producing weak acids or bases, such as ammonia, as these have low conductivities even at high concentrations and limit the current density in the stack.

The pH values in the acid solutions at the end of the three tests presented above were recorded as pH  $\approx 0.5$ . Taking into consideration the 0.5 M concentration of sulfate in the initial solutions, we should have been able to reach a pH value of 0.29 for sulfuric acid with maximum conversion. The trend of reaching a higher pH than theoretically predicted was seen in most tests. One reason for this may be the co-transport of ions to the acid solution. A buffer effect will occur, for example, if NH<sub>4</sub><sup>+</sup> ions are transported to the acid solutions together with HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions. The pH meters were calibrated to only pH 1, which can also partly explain the measured deviation from the expected values. Another factor that should be considered is the possibility that leakage of protons from the



**Table 4. Salt Conversion Rates and Electricity Consumption per Mass Product Salt Transferred for Comparable AS and ABS Experiments in Table 3, Conversions, Final Temperatures, and Overall Average Current Efficiencies for the Tests**

test no.	salt conversion (kg/h)	electricity consumption per salt converted (kJ/kg)	conversion (%)	temperature at the end (°C)	$C_{E(\text{tot})}$ (%)
3 = ABS-1	0.054	6851	99.40	36.6	0.381
2 = AS-1	0.050	6906	98.08	35.8	0.633
18 = ABS-2	0.045	5695	92.67	27.8	0.675
19 = AS-2	0.041	6288	89.47	28.6	0.778

acid compartment has occurred, which also would limit the pH decrease.

**3.2. Two-Compartment versus Three-Compartment Stacks.** A summary of the results from the tests listed in Tables 1 and 2 is presented in Figure 6; the numbers in Figure 6 refer to these respective tables. There is a clear difference in energy (electricity) use between the test results using a three-compartment stack (blue and orange) and a two-compartment stack (green). The tests performed in the two-compartment stack were more efficient with regard to energy use in the range from 3630 to 4844 kJ/kg of AS or ABS compared to the three-compartment stack, requiring 5102–7223 kJ/kg of AS or ABS. The highest conversion rates (kilograms of salt per hour separated) are also reached using a two-compartment stack. The difference between using AS and ABS as the product feed with respect to energy use or conversion rate in the three-compartment stack is not as clear, but a trend with AS resulting in lower energy use can be seen. Test points not marked with additional information in Figure 6 were performed at 24 V throughout the entire test.

While the two-compartment stack resulted in lower energy use, it is also obvious from Figure 2 that the two-compartment stack will require one-third less membranes because the cationic membranes can be left out (i.e., no separation of  $\text{NH}_4^+$  ions is needed because it stays in the product solution).

Tests 11–13 were run at 24 and 30 V, by starting with a higher voltage and ending with a lower voltage (30 and 24 V, respectively), or vice versa (24 and 30 V, respectively). Figure 6 indicates that the overall energy use (kilojoules per kilogram of salt) reaches a slightly lower value in the case in which a higher voltage was applied from the start.

Little difference was detected between tests in which seven and nine cells were used considering energy use. More tests would be needed to allow further conclusions to be drawn regarding the effect of the number of repeated cells (thus also the total membrane area).

**3.3. Differences between Using AS and ABS as the Initial Product Stream.** Both AS and ABS were used as product solutions in the three-compartment stack to compare their behavior as possible input salt solutions to be separated using BPMED. Both routes in Figure 1 may be feasible, and thus, investigating which one is most beneficial regarding electricity use for a given conversion throughput per amount of cells is essential for evaluating the process energy demand. BPMED tests with comparable experimental initial parameters are listed in Table 3.

Considering the results of the BPMED experiments in Table 4, it seems that both AS and ABS give similar results for both (time-averaged) salt conversion and electricity consumption when using similar experimental parameters. The electricity use per kilogram of salt, when AS is used as the product solution, is slightly higher, and the conversion rate of the product salt is slightly lower. However, considering the process

routes in Figure 1, it is apparent that, if AS is used, only half of the molar amount needs to be separated compared to ABS. Examining the conversion rate and energy use in Figure 6 suggests that AS is the more beneficial product substance, also because electricity consumption is more than halved, and the conversion rate is more than double than that of ABS. Altogether, a process route that uses BPMED for conversion of AS solutions uses less energy and is faster than if ABS solutions are processed. Furthermore, the overall average current efficiency [ $C_{E(\text{tot})}$ ] is higher for the tests in which AS was used. Thus, using AS is more energy efficient. Investigating how input concentrations affect energy use in more detail is recommended for future work.

**3.4. Minimum Reaction Energy versus Heat Consumption.** Another comparison that is useful when determining the efficiency of the process is the ratio between the energy needed for the process and the thermodynamic minimum for the conversion reaction. HSC 5.1 (Outokumpu Research Oy, 2002) Gibbs energy minimization software was used to determine the minimum reaction energy.<sup>21</sup>  $\text{NH}_4\text{OH}$  does not exist as a discrete substance but further reacts with water to form dissolved molecular ammonia, ammonium ions, and hydroxyl ions, in a ratio that depends on solution concentrations and pH (and temperature). The minimum reaction energy is dependent on this ratio, and while an exact value cannot be readily determined for the reaction, two limiting values can be obtained. The energies will be compared to minimum reaction energies at 25 °C because the experimental solution temperatures varied roughly between 20 and 40 °C. When converting reaction energies to kilojoules per kilogram, we obtained the following values: ABS, 607.09 and 984.18 kJ/kg (lower and upper, respectively); AS, 1217.25 and 1874.20 kJ/kg (lower and upper, respectively).

The energy use curves presented in Figure 6 show that a significantly larger amount was needed for the separations, varying between 3629 and 7224 kJ/kg of input salt. This can partly be explained by heat generation during the process. Upon examination of heat generation in the BPMED process, it is important to determine how entropy is generated, because heat in the membrane stack is synonymous with entropy.<sup>22</sup> Therefore, the heat generated by the circulation pumps was measured while the electro dialysis electricity was switched off. These values were compared to the heat generated in the membrane stack during operation for 3 dm<sup>3</sup> tests at 24 V and 4 A. See also the starting parameters for tests 7–9 in Table 1. The calculations indicate that up to nearly 25% of the electricity use resulted in heat generation in the stack. The real value is likely higher, because a higher temperature also results in the faster transfer of heat to the surroundings. Regardless of this, fluid flow resistance losses affect BPMED performance considerably in terms of energy use. See Figure S13-1 for temperature curves compared to heat generated by pumps.

**3.5. Magnesium Sulfate.** Magnesium sulfate was added to the base solution in tests 4–6 (see Table 1) to investigate whether the conductivity could be significantly increased and thus improve the separation rate and efficiency. The stack was washed with an acidic solution after the tests, and magnesium was found in all process solutions, including the electrolyte solution. This presumably indicates that some leakage of magnesium from the base compartment to the acid, product, or electrolyte compartments had occurred. The pH was also increased to 12.5 in a sample of the base solution after the test, and no magnesium hydroxide was found to precipitate. This also indicates that either magnesium was transported into other compartments or precipitation occurred inside the stack. Fortunately, no precipitation was observed during the test, nor was poorer performance noticed. Increasing the conductivity of the base solution by addition of magnesium sulfate should therefore be done with care.

## 4. CONCLUSIONS

Optimization of the throughput of ammonium sulfate and ammonium bisulfate in BPMED, producing sulfuric acid and aqueous ammonia, was investigated using two- and three-compartment membrane stacks, respectively. Particular attention was paid to the energy (electricity) input requirements and separation rates for recovering ABS for the ÅA mineral carbonation route by feeding AS into the BPMED unit. Comparing results obtained with AS and ABS as respective input salt solutions leads to the conclusion that the AS solution is the preferred feed to the BPMED. Upon comparison of the results from the tests performed in the two- and three-compartment stacks, we also concluded that applying a two-compartment stack gives a lower electricity consumption. An additional benefit with the two-compartment setup is that the product solution is converted into an alkaline ammonia solution while ammonium sulfate/bisulfate is contributing to a higher conductivity when compared to a system using a three-compartment stack, in which ammonium will become the only species contributing to the (inherently low) conductivity. Even where 100% conversion of AS or ABS is not attained (i.e., the base solution contains ammonium sulfate and ammonia), it is still possible to reuse the obtained ammonia solution in the presented mineral carbonation route because the process solution itself will contain some ammonium sulfate when it enters the carbonation step. More work is needed to investigate the limiting factors for reaching a pH closer to the theoretical values in terms of the acid and base solution. Further work is also required with regard to the presence of magnesium in the BPMED separation process. Elemental analyses could also be performed in future studies to gain knowledge about the purity of the obtained acid and base solutions. The cationic membranes can be replaced with monovalent cationic membranes to keep  $Mg^{2+}$  ions separated from  $NH_4^+$ , thus preventing them from entering the base solution and causing precipitation. This applies to the three-compartment stack. All tests in this study were performed with a flow rate of  $20 \text{ L h}^{-1} \text{ cell}^{-1}$ , but it is suggested that future work should investigate further the effect of the flow rate.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.3c00028>.

Experiments under similar initial conditions (Figure SI1-1), calibration curves for ammonium sulfate and ammonium bisulfate of conductivity versus concentration (Figures SI2-1 and SI2-2), and temperature curves compared to heat generated by pumps (Figure SI3-1) (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

**Evelina S. Koivisto** – Laboratory of Process and Systems Engineering, Åbo Akademi University, FI-20500 Turku, Finland; [orcid.org/0000-0003-1122-8257](https://orcid.org/0000-0003-1122-8257); Email: [evelina.koivisto@abo.fi](mailto:evelina.koivisto@abo.fi)

### Authors

**Tobias Reuter** – Laboratory of Process and Systems Engineering, Åbo Akademi University, FI-20500 Turku, Finland

**Ron Zevenhoven** – Laboratory of Process and Systems Engineering, Åbo Akademi University, FI-20500 Turku, Finland; [orcid.org/0000-0002-1031-5861](https://orcid.org/0000-0002-1031-5861)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsestwater.3c00028>

### Author Contributions

The manuscript was written through contributions of all authors. Experiments were conducted by T.R. and E.S.K. E.S.K. wrote the first draft of this paper. R.Z. acted as the supervisor, participated in several of the experiments, edited the language, and checked the manuscript and secured project funding. All authors have given approval to the final version of the manuscript. All authors performed part of the calculations after individual tests. CRediT: **Evelina Koivisto** conceptualization (equal), data curation (equal), formal analysis (equal), investigation (equal), methodology (equal), software (equal), visualization (equal), writing-original draft (lead); **Tobias Reuter** conceptualization (equal), data curation (equal), formal analysis (equal), investigation (equal), methodology (equal), software (equal), visualization (equal); **Ron Zevenhoven** conceptualization (equal), data curation (equal), formal analysis (equal), funding acquisition (lead), investigation (equal), methodology (equal), project administration (lead), resources (lead), software (equal), supervision (lead), visualization (equal), writing-original draft (supporting).

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### Notes

The authors declare no competing financial interest.

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