The efficient conversion of $\text{K}_2\text{SO}_4$ from $\text{Na}_2\text{SO}_4$ by continuous electrodialysis metathesis process

Jie Liu$^{a,b,c,*}$, Dandan Li$^a$, Fan Xu$^a$, Junsheng Yuan$^{a,b,c,*}$, Zhiyong Ji$^{a,b,c}$, Yingying Zhao$^{a,b,c}$, Fei Li$^{a,b,c}$, Xiaofu Guo$^{a,b,c}$, Shizhao Wang$^a$

$^a$School of Chemical Engineering, Hebei University of Technology, Tianjin, China, emails: liuji@hebut.edu.cn (J. Liu), jsyuan2012@126.com (J. Yuan)
$^b$Hebei Collaborative Innovation Center of Modern Marine Chemical Technology, Tianjin 300130, China
$^c$Engineering Research Center of Seawater Utilization, Ministry of Education, Tianjin 300130, China

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Abstract

A continuous electrodialysis metathesis (EDM) process for converting $\text{Na}_2\text{SO}_4$ to high-value $\text{K}_2\text{SO}_4$ fertilizer was proposed and investigated in this paper. After 6 h, a stable production could be obtained. The concentration of $\text{K}_2\text{SO}_4$ output could be as high as 0.683 mol/L, with a purity of 93.4%–96.5%. The specific energy consumption was 166–300 kWh/ton $\text{K}_2\text{SO}_4$, and the current efficiency was 74.7%–84.5%. Meanwhile, the concentration of by-product $\text{NaCl}$ could also reach 2.226 mol/L. The results showed that the effects of stack voltage, feed flowrate, feed concentration, and temperature were similar to those occurring in the normal electrodialysis process. There was a restriction relation between the ions from the two desalination compartments, due to the Donnan equilibrium and electrostatic effect. Therefore, a mole ratio of 1:2 between $\text{Na}_2\text{SO}_4$ and $\text{KCl}$ in feed solutions would be of benefit for the synthesis process. An EDM process combined with reverse osmosis and vapor mechanical recompression was proposed and evaluated. The result of the economic evaluation showed that gross profit by converting the $\text{Na}_2\text{SO}_4$ wastewater to $\text{K}_2\text{SO}_4$ is nearly 475.13 CNY/ton.

Keywords: Electrodialysis metathesis; $\text{Na}_2\text{SO}_4$, $\text{K}_2\text{SO}_4$; Continuous operation

1. Introduction

$\text{K}_2\text{SO}_4$ is the basic raw material for the preparation of various potassium salts such as $\text{K}_2\text{CO}_3$, $\text{K}_2\text{S}_2\text{O}_8$, etc. In agriculture, it is a common chlorine-free high-quality potassium fertilizer, which has no harm to chloride-sensitive crops and soil [1–3]. In medicine, it is a very valuable inorganic salt and was used to test serum protein. Therefore, the preparation of $\text{K}_2\text{SO}_4$ is very important. The traditional synthesis methods of $\text{K}_2\text{SO}_4$ mainly include the Mannheim method, mirabilite conversion method, ammonium sulfate conversion method, gypsum conversion method [4,5] and membrane separation method [1]. However, these methods have disadvantages such as high energy consumption, low product purity, complex operation and high production cost. Electrodialysis metathesis (EDM) can recombine the ions from different solutions to synthesize new compounds [6], the generated solutions are also concentrated. At present, the EDM technology is not only applied to the zero-discharge desalination of groundwater and brackish water [7–9] and the recovery of organic acids [10–12], but also successfully applied to the production and synthesis of inorganic salts [13], organic compounds [14], ionic liquids [15] and explosives [16], providing a new way for the synthesis of substances.
EDM technology has great application prospects in the preparation of inorganic salts, especially potassium salts, due to its advantages of environmental-friendly, low cost, and non-formation of double salt [17,18]. Sharma et al. [19] converted KCl to KNO₃ by EDM with an energy consumption of 0.82 kWh/kg and current efficiency of 83%. Jaroszek et al. [20] investigated the KNO₃ synthesis process by EDM. The highest concentration of KNO₃ could be 2.55 M and the highest purity was 99%. These results indicate that EDM technology is an alternative way to produce high-quality potash fertilizer. In the process of synthesis of potassium fertilizer by EDM, the main factors that affect the process of electrodialysis are current density, concentration and type of raw materials. Trivedi et al. [21] found when the molar ratio of raw materials (Na₂SO₄ and KCl) was 1:1, the applied voltage was 1.5 V/pair, the impurity content in K₂SO₄ was 1.16% and concentration and purity reached their maximum level. Zhang et al. [22] found that when the molar ratio of (NH₄)₂SO₄ to KCl was slightly higher than the theoretical molar ratio, the complete conversion of KCl to K₂SO₄ could be ensured, and the final concentration of K₂SO₄ could be increased by reducing the volume of the initial K₂SO₄ solution. Han et al. [23] investigated the effect of cation types on the synthesis of K₂SO₄, the orders of energy consumption Eᵢ and cations impurity Wi in the product were C₄MgSO₄ > E₆Na₂SO₄ > E₆(NH₄)₂SO₄ and W₄NH₄ > W₆Na > W₆Mg₄ while (NH₄)₂SO₄ was regarded as the suitable sulfate source. The economic evaluation result showed that the production cost of synthetic K₂SO₄ was 537.1 $/ton. The properties of the ion exchange membrane also influence the process index and product quality of electrodialysis metathesis. Pisarska [24] used Neosepta AMX type anion membrane and Nafion 423 type anion membrane to synthesize K₂SO₄ through EDM. The results showed that the current efficiency was up to 94% and the impurity content in the product was only 0.2%.

Most of the above researches is carried out in batch operation mode, which is unsuitable for industrial continuous processes. Therefore, a continuous EDM process was proposed in this paper. Various operating conditions, such as membrane stack voltage, feeding flow rate, concentration, were investigated in detail. Changes in water permeability were also investigated because water permeability due to transmembrane concentration differences dilutes product concentration. Then, a possible EDM process combined with reverse osmosis (RO) and MVR was proposed to realize the conversion and reclamation of Na₂SO₄ and the economic value was evaluated as well.

2. Materials and methods

2.1. Membrane stack and configuration

The stack configuration used to synthesize K₂SO₄ by EDM is shown in Fig. 1. KCl and Na₂SO₄ solutions are fed into the membrane stack. K⁺ and Na⁺ penetrate through the cation exchange membrane, while SO₄²⁻ and Cl⁻ permeate through the anion exchange membrane driven by the electric field force. Then, K₂SO₄ and NaCl are synthesized in adjacent compartments, respectively [Eq. (1)]. Commercial homogeneous ion exchange membranes (Type II, Fujifilm Co., Ltd., Japan) are used, and the membrane properties given by the supplier are shown in Table 1.

$$Na_2SO_4 + 2KCl \rightarrow K_2SO_4 + 2NaCl \tag{1}$$

2.2. Experimental conditions

The schematics of the continuous EDM experimental setup are shown in Fig. 2. The Na₂SO₄ and KCl solution tanks are named as desalination compartments 1 (D₁) and 2 (D₂), and the K₂SO₄ and NaCl solution tanks are named as concentration compartments 1 (C₁) and 2 (C₂), respectively. A 30 g/L Na₂SO₄ solution is used as the electrode solution. The solutions in the five tanks were fed to the compartments of the membrane stack at a fixed flow rate (D₁, D₂, C₁, and C₂ solution: 2 L/min, electrode solution: 1.5 L/min) by pumps and back to the tanks. Na₂SO₄ and KCl solutions were fed to D₁ and D₂, respectively, as raw materials, whose concentration and the flow rate was investigated. The production of K₂SO₄ and NaCl solutions and desalinated Na₂SO₄ and KCl solutions were obtained from the overflow pipes of the four tanks, respectively. The deionized water was pumped to the C₂ to avoid the formation of K₂SO₄ crystal, whose flow rate was investigated as well. The temperature of the solution in this experiment is controlled by coiled pipes immersed in the tanks, connected to a water bath. All the reagents used in the experiments were analytically pure.

2.3. Analysis and calculation methods

Materials from C₁, C₂, D₁, D₂ were sampled and analyzed per hour, and the current, voltage, and production volume were recorded. SO₄²⁻ was measured by EDTA complexometric titration method (Standardization Administration of P.R. China, GB/T 13025.8-2012, ‘General Test Methods for Salt Industry – Determination of Sulfate’), Cl⁻ was measured by silver nitrate titration method (ASTM D912-12, ‘Standard Test Methods for Chloride Ion In Water’), and K⁺ was measured by sodium tetraphenylborate quaternary ammonium salt capacity method (Standardization Administration of P.R. China, GB/T 6549-2011, ‘potassium chloride’), while
the concentration of Na\(^+\) was calculated based on the charge conservation principle. The permeate flux of ions \(J_{\text{ion}}\), water permeate flux \(J_{\text{Wi}}\), energy consumption \(W\), current efficiency \(\eta\), purity \(P\) are important evaluation indicators, with formulas reported hereinafter.

The permeate flux of ions (\(J_{\text{ion}}\)) is expressed in mol/(m\(^2\) h) and calculated as:

\[
J_{\text{ion}} = \frac{\int_{t_{i-1}}^{t_i} c dt \times (V_i + V) + (C_i - C_{i-1}) \times V_i}{N \times s \times t}
\tag{2}
\]

where \(t\) is the time interval between two samplings, 1 h; \(i\) is the sample serial number; \(V\) is the volume of solution that overflows from the concentration tank at No. \(i\) hour, L; \(V\) is each sampling volume, 0.02 L; \(C\) is the ion concentration in the concentration tank at No. \(i\) hour, mol/L; \(V_c\) is the volume of the concentrated tank, 1.367 L; \(N\) is the number of membrane group, 10; \(s\) is the active membrane area, 0.0198 m\(^2\).

The total water permeate flux (\(J_{\text{Wi}}\)) is expressed in mol/(pair m\(^2\) h) and calculated as:

\[
J_{\text{Wi}} = \frac{\rho_{i, C_1} \times V_{i, C_1} - V_{i, C_2} \times \int_{t_{i-1}}^{t_i} c dt \times 174 - V}{18 \times N \times s \times t}
\tag{3}
\]

\[
J_{\text{Wi}} = \frac{\rho_{i, C_2} \times V_{i, C_1} - V_{i, C_2} \times \int_{t_{i-1}}^{t_i} c dt \times 58.5}{18 \times N \times s \times t}
\tag{4}
\]

where \(J_{\text{Wi}}\) and \(J_{\text{Wi}}\) are the total water permeate fluxes to \(C_1\) and \(C_2\) from both membranes forming the compartment, respectively; \(\rho_{i, C_1}\) and \(\rho_{i, C_2}\) are the densities of the overflow solution in No. \(i\) hour, g/L; \(V_{i, C_1}\) and \(V_{i, C_2}\) are the volumes of overflow solutions, L; \(V\) is the mass of deionized water replenished in \(C_1\) per hour, g; 174 is the molar mass of K\(_2\)SO\(_4\), g/mol; 58.5 is the molar mass of KCl, g/mol.

The density of K\(_2\)SO\(_4\) and NaCl could be calculated by Eqs. (5) and (6), respectively, which were obtained by fitting the experimental data of standard solutions and their density:

\[
\rho_{K_2SO_4} = 0.7 C_{K_2SO_4} + 995.1 \left(35.4 \text{ g/L} \times C_{K_2SO_4} < 122.0 \text{ g/L}\right)
\tag{5}
\]

\[
\rho_{NaCl} = 0.7 C_{NaCl} + 1,002.2 \left(10.7 \text{ g/L} \times C_{NaCl} < 155.7 \text{ g/L}\right)
\tag{6}
\]

The specific energy consumption producing one ton of solid (\(W\)) was calculated as:

\[
W = \frac{U \times I \times t \times 10^3}{C \times V \times M}
\tag{7}
\]

It is expressed in terms of the amount of salt dissolved in the solution, kWh/ton; \(U\) is the stack voltage, V; \(I\) is the current, A; \(t\) is the time, 1 h; \(C\) is the product concentration of NaCl or K\(_2\)SO\(_4\), mol/L; \(V\) is the overflow production volume of NaCl or K\(_2\)SO\(_4\) in 1 h, L; \(M\) is the molar mass of K\(_2\)SO\(_4\) or NaCl, g/mol.

The current efficiency (\(\eta\)) of NaCl or K\(_2\)SO\(_4\), %, was calculated as:

\[
\eta = \frac{C \times V \times F \times z \times 100}{N \times I \times t}
\tag{8}
\]

where \(C\) is the product concentration of NaCl or K\(_2\)SO\(_4\), mol/L; \(V\) is the overflow production volume of NaCl or
K\textsubscript{2}SO\textsubscript{4} in 1 h, L; \( F \) is the Faraday constant, 96,485 C/mol; \( z \) is the ionization valence.

Finally, the purity of production \((P)\) was expressed in \% and calculated as:

\[
P = \frac{C \times M}{\sum C_i \times M_i} \times 100 \tag{9}
\]

where \( C \) is the concentration of the pure product, mol/L; \( C_i \) is the concentration of each component in the mixture, mol/L; \( M \) is the molar mass of each component in the mixture, g/mol.

3. Results and discussion

3.1. Effect of the stack voltage

The effect of membrane stack voltage was investigated under the following conditions: the flow rate of Na\textsubscript{2}SO\textsubscript{4} and KCl feed to \( D_1 \) and \( D_2 \) tanks were 30 mL/min, the concentration of Na\textsubscript{2}SO\textsubscript{4} was 0.25 mol/L, the concentration of KCl was 0.5 mol/L, the flow rate of deionized water feed to \( C_1 \) tank was 7 mL/min, and the experimental temperature was 25°C.

3.1.1. Permeate flux of ions and water

The electric potential is the main force driving the mass transfer in the electrodialysis process, so all of the ions’ permeate flux increased as the voltage increased, as shown in Fig. 3a. The increases of \( J_{SO_4^-} \) and \( J_{Cl^-} \) slowed down at high values of stack voltage because the concentration of K\textsubscript{2}SO\textsubscript{4} in \( C_1 \) was nearly close to saturation. The current also increased with the increase of voltage, as shown in Fig. 4a. C\textsubscript{Na} was slightly larger than C\textsubscript{K} in the same compartment (C\textsubscript{1}). This is mainly related to a tiny amount of other ions simultaneously present into C\textsubscript{1} [25], as the selectivity of the ion exchange membrane is smaller than 100%. The same holds for C\textsubscript{K} and C\textsubscript{SO\textsubscript{2}^-} in C\textsubscript{2}. The primary ‘impurity’ ions in C\textsubscript{1} and C\textsubscript{2} were Cl\textsuperscript{−} and K\textsuperscript{+}, respectively, as shown in Fig. 4b. But their concentrations were smaller than 10% concerning the concentration of the primary ions. The migration of impurity ions is mostly related to the properties of ions and membrane, so the increase of voltage has little effect on the product purity: that of K\textsubscript{2}SO\textsubscript{4} was about 95% and that of NaCl was about 93%.

The current efficiency for K\textsubscript{2}SO\textsubscript{4} case was about 80%, and the one for NaCl case was about 68%. Both of the efficiencies were substantially not affected by voltage, as shown in Fig. 5. Actually, the current efficiency slightly increased with the increase of voltage, because the current efficiency is related to the selective transmittance of the ion exchange membrane. The higher the voltage, the greater the driving force of ion migration across the membrane in

![](image_url)

Fig. 3. The variation of permeate flux of ions and water under different voltages. (a) The permeate flux of ions and water under different voltages and (b) The molar concentration ratio and current under different voltages.
the desalination compartments, and the lower the concentration of the desalination compartments. The selective transmittance of the membrane increases with the decrease of the concentration of the solution, so the current efficiency slightly increases. The voltage applied on the stack is the main source of energy consumption, so the specific energy consumption increases with the increase in voltage. The energy consumption for K$_2$SO$_4$ case increased from 167 to 304 kWh/ton, and the energy consumption for NaCl case increased from 296 to 487 kWh/ton.

3.2. Effect of feed flow rate and concentration of the raw solution

The EDM process could be considered to be a kind of metathesis reaction using ion-exchange membrane. Therefore, the mole ratio of reactants will also affect its process similar to the ordinary metathesis reaction. In the continuous EDM process, the amount of reactants is the product of flow rate and concentration of raw solution feed to $D_1$ and $D_2$ (Na$_2$SO$_4$ and KCl). Therefore, the effect of flow rates of raw solution feed to $D_1$ and $D_2$ with a constant ratio of 1:1, was investigated under the following conditions: voltage = 11 V, the concentration of Na$_2$SO$_4$ = 0.25 mol/L, the concentration of KCl = 0.5 mol/L. And the effect of feed concentration was investigated under the following conditions: Na$_2$SO$_4$ and KCl concentration ratio kept at 1:2, the flow rate of Na$_2$SO$_4$ and KCl = 30 mL/min. In these experiments, the flow rate of deionized water feed to $C_1$ was 7 mL/min, and the experimental temperature was 25°C.

3.2.1. Permeate flux of ions and water

The concentration difference across the membrane is the resistance to the ion mass transfer in the electrodialysis process. When the solution feed flowrate or concentration is increased, the ion permeates flux increases, and the reverse diffusion decreases. All of these are beneficial to the increase of ions concentration in $C_1$ and $C_2$ (Fig. 7).

3.2.2. Ion concentration and energy consumption

The increase of feed flowrate and concentration decreases the concentration difference across the membrane, so the ion permeates flux increases, and the ions ‘reverse diffusion’ decreases. All of these are beneficial to the increase of ions concentration in $C_1$ and $C_2$ (Fig. 7).
The relationship between ions concentration and feed flow rate is approximately linear. However, improving the flow rate and concentration has little effect on the purity of the product. The purity of K$_2$SO$_4$ was about 95%, and the purity of NaCl was about 93%.

From Fig. 8a, increasing the feed flowrate has almost little effect on both current efficiency and specific energy consumption. The high concentration of output and the lower mass transfer resistance also lead to a slight decline in the specific energy consumption for NaCl and K$_2$SO$_4$ cases, as shown in Fig. 8b.

3.3. Effect of operating temperature

3.3.1. Permeate flux of ions and water

The effect of temperature was investigated under the following operating conditions: the flowrate of Na$_2$SO$_4$ and KCl feed to $D_1$ and $D_2$ was 30 mL/min, the concentration of Na$_2$SO$_4$ was 0.25 mol/L, the concentration of KCl was 0.5 mol/L, the flowrate of deionized water feed to $C_1$ was 0.225 mL/min. As the temperature rises, the solute diffusion coefficient increases, and the solution viscosity decreases, phenomena favoring ions migration [26]. As a result, the permeate flux of ions shown in Fig. 9 increases with increasing temperature. The temperature has also a positive impact on the total water permeate flux, as shown in Fig. 9.

3.3.2. Ion concentration and energy consumption

The increase of ion permeates flux was smaller compared to the one of water when the temperature was increased, so the concentration of Na$^+$ and Cl$^-$ in $C_2$ decreased, as shown in Fig. 10. As the concentration of osmotic water flux only accounts for 14% of the replenishment of deionized water, the concentration of K$^+$ and SO$_4^{2-}$ in $C_2$ was little affected by temperature. The purity of NaCl slightly decreased from 94.3% to 92.6%. This indicates that high temperatures would increase the permeation of co-ions. The current efficiency of the product is shown in Fig. 11 and slightly increased with temperature. The current efficiency for K$_2$SO$_4$ case increased from 74.6% to 79.3%, and the current efficiency for the NaCl case increased from 68.7% to 72.4%. Specific energy consumption slightly decreased with temperature: for K$_2$SO$_4$ case, it decreased from 296.5 to 283.7 kWh/ton; for NaCl case, it decreased from 479.3 to 452.4 kWh/ton. This may be explained as the mass transfer is enhanced at higher temperatures.

3.4. Process and economy analysis for EDM industrial application

When high concentration K$_2$SO$_4$ and NaCl solutions are generated in the EDM process, diluted KCl and Na$_2$SO$_4$ solutions are also produced as a by-product. An integrated process combining RO, EDM and MVR is proposed in this paper to realize the industrial production from Na$_2$SO$_4$ to K$_2$SO$_4$. The diluted by-products from EDM could be concentrated by RO. The industrial EDM application is shown in Fig. 12. The Na$_2$SO$_4$ solution and the KCl solution are fed to the EDM system. The high concentration K$_2$SO$_4$ and NaCl solutions are evaporated and crystallized through MVR, respectively. The diluted Na$_2$SO$_4$ and KCl solutions
are concentrated to get the same concentrations as in the feeding solution (Na$_2$SO$_4$: 0.25 mol/L, KCl: 0.5 mol/L). The Na$_2$SO$_4$ solution from 1$^\#$ RO is mixed with Na$_2$SO$_4$ raw solution, then the mixed solution is fed to the EDM system. Similarly, the KCl solution from the 2$^\#$ RO is mixed with KCl raw solution and then fed to the EDM system. At the same time, desalinated water is generated from RO and MVR.

A process yielding 1 ton/h K$_2$SO$_4$ is analyzed to evaluate the economic value of this EDM-RO-MVR integrated process, as shown in Table 2. The data of EDM was calculated based on a condition of the previous study (membrane stack voltage: 11 V, freshwater feed to K$_2$SO$_4$: 7 mL/min, the concentration of Na$_2$SO$_4$: 0.25 mol/L, concentration of KCl: 0.5 mol/L, feeding flowrate of Na$_2$SO$_4$: 30 mL/min, feeding flowrate of Na$_2$SO$_4$: 30 mL/min).

Based on these data, the economic value of this process was estimated, and the results are shown in Table 3. The total economic value could be calculated as follows:

\[ E_{\text{tot}} = E_p - C_m - C_e \]

where \( E_{\text{tot}} \) is the gross profit, \( E_p \) is the profits from sales, \( C_m \) is the material consumption cost and \( C_e \) is the electricity consumption cost. The price of material, production and electricity was inferred from the domestic market of China in June 2020, and the values are expressed in the Chinese Yuan. The electric consumption of EDM is 315 kWh, according to Fig. 5. The electric consumption of RO was calculated by a design software of DuPont (WAVE, version 1.77) [27]. The energy consumption for the evaporation of 1-ton water was reported to be about 20–39 kWh/ton [28], and 30 kWh/ton was therefore chosen in this evaluation. The gross profit by converting the Na$_2$SO$_4$ wastewater to K$_2$SO$_4$ is nearly 475.13 CNY/ton.

The energy consumption in the EDM system will be obviously reduced when membrane stack with larger size and more membrane pairs are used in the industrial process, which will lead to higher profit. At the same time, this estimation is only based on the simple connection of EDM, RO and MVR to prove its possibility. Optimization of the operation conditions of these three processes should be carried out, which could also further reduce the consumption costs of the whole integrated process.
4. Conclusions

A continuous EDM process for high-value conversion of Na$_2$SO$_4$ was proposed in this paper, and the effects of stack voltage, feed flowrate, feed concentration, deionized water flow rate and temperature for the low concentration Na$_2$SO$_4$ EDM process were investigated. A stable production could be obtained after 5–6 h in this continuous process. The concentration of K$_2$SO$_4$ in the produced stream could be as high as 0.683 mol/L, and that of NaCl could reach 2.226 mol/L. The purity of NaCl was 92.2%–94%, and the current efficiency was 61.2%–73.6%. The purity of K$_2$SO$_4$ was 93.4%–96.5%, and the current efficiency was 74.7%–84.5% in this case. The specific energy consumption for NaCl and K$_2$SO$_4$ production are as low as 295.8 and 166.6 kWh/ton, respectively. Thank you for your careful guidance. Compared with the reported synthesis of K$_2$SO$_4$ by EDM, this paper adopts continuous experiments and proposes a process combining RO, EDM and MVR, which

![Graph](image)

Fig. 11. The variation of specific energy consumption and current efficiency under different temperatures.

![Diagram](image)

Fig. 12. Possible process for EDM industrial application.

Table 2

Properties data of each stream in the analyzed integrated process (stream number refers to Fig. 12)

<table>
<thead>
<tr>
<th>No.</th>
<th>Name</th>
<th>Flowrate (m$^3$/h)</th>
<th>Concentration (mol/L)</th>
<th>Solute (ton/h)</th>
<th>H$_2$O (ton/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na$_2$SO$_4$ solution</td>
<td>22.989</td>
<td>0.250</td>
<td>0.816</td>
<td>22.855</td>
</tr>
<tr>
<td>2</td>
<td>KCl solution</td>
<td>22.989</td>
<td>0.500</td>
<td>0.856</td>
<td>22.631</td>
</tr>
<tr>
<td>3</td>
<td>Na$_2$SO$_4$ mixed solution</td>
<td>25.830</td>
<td>0.250</td>
<td>0.917</td>
<td>25.680</td>
</tr>
<tr>
<td>4</td>
<td>KCl mixed solution</td>
<td>25.830</td>
<td>0.500</td>
<td>0.962</td>
<td>25.427</td>
</tr>
<tr>
<td>5</td>
<td>Feeding water</td>
<td>3.446</td>
<td>/</td>
<td>/</td>
<td>3.446</td>
</tr>
<tr>
<td>6</td>
<td>Concentrated K$_2$SO$_4$ solution</td>
<td>10.263</td>
<td>0.560</td>
<td>1.000</td>
<td>10.023</td>
</tr>
<tr>
<td>7</td>
<td>Concentrated NaCl solution</td>
<td>6.180</td>
<td>1.860</td>
<td>0.672</td>
<td>5.953</td>
</tr>
<tr>
<td>8</td>
<td>Diluted Na$_2$SO$_4$ solution</td>
<td>16.519</td>
<td>0.043</td>
<td>0.101</td>
<td>16.484</td>
</tr>
<tr>
<td>9</td>
<td>Diluted KCl solution</td>
<td>24.493</td>
<td>0.058</td>
<td>0.106</td>
<td>24.919</td>
</tr>
<tr>
<td>10</td>
<td>Na$_2$SO$_4$ solution from 1$^{st}$ RO</td>
<td>2.841</td>
<td>0.250</td>
<td>0.101</td>
<td>2.825</td>
</tr>
<tr>
<td>11</td>
<td>KCl solution from 2$^{nd}$ RO</td>
<td>2.841</td>
<td>0.500</td>
<td>0.106</td>
<td>2.797</td>
</tr>
<tr>
<td>12</td>
<td>Freshwater from 1$^{st}$ RO</td>
<td>13.659</td>
<td>/</td>
<td>/</td>
<td>13.659</td>
</tr>
<tr>
<td>13</td>
<td>Freshwater from 2$^{nd}$ RO</td>
<td>22.122</td>
<td>/</td>
<td>/</td>
<td>22.122</td>
</tr>
<tr>
<td>14</td>
<td>K$_2$SO$_4$ solid production</td>
<td>/</td>
<td>/</td>
<td>1.00</td>
<td>/</td>
</tr>
<tr>
<td>15</td>
<td>NaCl solid production</td>
<td>/</td>
<td>/</td>
<td>0.672</td>
<td>/</td>
</tr>
</tbody>
</table>
is more suitable for industrial production. Economic evaluation results show that the production cost of synthetic K$_2$SO$_4$ is 2818.99 CNY/ton, which is cheaper than 537.1 $/ton [23]. Following your advice, these have been added to the manuscript. More, in particular, it was observed that:

- The stack voltage is the main driving force of ions migration during the electrodialysis metathesis process; the higher the voltage, the higher the permeate flux of ions and water, and the concentration of ions in the product.
- The concentration and flow rate of the feed solution and the deionized water flowrate could affect the electrodialysis metathesis process by changing the concentration of the desalination compartments. The optimal molar ratio Na$_2$SO$_4$:KCl was 1:2, resulting in a satisfying mass transfer process because the mass transfer of ions was also restricted by ‘recombined’ ions (Na$^+$ and Cl$^-$, K$^+$ and SO$_4^{2-}$).
- The higher temperature could induce a greater permeate flux of ions and water in the product, and a lower concentration of NaCl. Increasing the temperature has a great influence on the concentration of osmotic water flux.
- The product purity and current efficiency are mainly determined by the migration of impurity ions, which are greatly affected by the selectivity and permeability of the ion exchange membrane. Therefore, these factors had little influence in this case. The energy consumption was positively affected by stack voltage, and little influenced by other factors.

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**References**


**Table 3**

<table>
<thead>
<tr>
<th>Consumption</th>
<th>Specific value (CNY/ton)</th>
<th>Total value (CNY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.816 ton/h</td>
<td>599</td>
</tr>
<tr>
<td>KCl</td>
<td>0.856 ton/h</td>
<td>1,900</td>
</tr>
<tr>
<td>H$_2$O/preparing KCl solution</td>
<td>22.631 ton/h</td>
<td>5</td>
</tr>
<tr>
<td>H$_2$O/feeding to K$_2$SO$_4$</td>
<td>3.446 ton/h</td>
<td>5</td>
</tr>
<tr>
<td>EDM</td>
<td>315 kWh/h</td>
<td>0.7</td>
</tr>
<tr>
<td>1’ RO</td>
<td>9.6 kWh/h</td>
<td>0.7</td>
</tr>
<tr>
<td>2’ RO</td>
<td>15.5 kWh/h</td>
<td>0.7</td>
</tr>
<tr>
<td>1’ MVR</td>
<td>308 kWh/h</td>
<td>0.7</td>
</tr>
<tr>
<td>2’ MVR</td>
<td>185 kWh/h</td>
<td>0.7</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>1 ton/h</td>
<td>2,800</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.672 ton/h</td>
<td>350</td>
</tr>
<tr>
<td>H$_2$O/1’ RO</td>
<td>13.659 ton/h</td>
<td>5</td>
</tr>
<tr>
<td>H$_2$O/2’ RO</td>
<td>22.122 ton/h</td>
<td>5</td>
</tr>
<tr>
<td>H$_2$O/1’ MVR</td>
<td>10.023 ton/h</td>
<td>5</td>
</tr>
<tr>
<td>H$_2$O/2’ MVR</td>
<td>5.953 ton/h</td>
<td>5</td>
</tr>
<tr>
<td><strong>Gross profit</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is more suitable for industrial production. Economic evaluation results show that the production cost of synthetic K$_2$SO$_4$ is 2818.99 CNY/ton, which is cheaper than 537.1 $/ton [23]. Following your advice, these have been added to the manuscript. More, in particular, it was observed that:

- The stack voltage is the main driving force of ions migration during the electrodialysis metathesis process; the higher the voltage, the higher the permeate flux of ions and water, and the concentration of ions in the product.
- The concentration and flow rate of the feed solution and the deionized water flowrate could affect the electrodialysis metathesis process by changing the concentration of the desalination compartments. The optimal molar ratio Na$_2$SO$_4$:KCl was 1:2, resulting in a satisfying mass transfer process because the mass transfer of ions was also restricted by ‘recombined’ ions (Na$^+$ and Cl$^-$, K$^+$ and SO$_4^{2-}$).
- The higher temperature could induce a greater permeate flux of ions and water in the product, and a lower concentration of NaCl. Increasing the temperature has a great influence on the concentration of osmotic water flux.
- The product purity and current efficiency are mainly determined by the migration of impurity ions, which are greatly affected by the selectivity and permeability of the ion exchange membrane. Therefore, these factors had little influence in this case. The energy consumption was positively affected by stack voltage, and little influenced by other factors.

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[27] https://www.dupont.com/water/resources/design-software.html