

Article

Application of Electrodialysis to Production of High-Purity Perrhenic Acid

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Abstract: Laboratory tests were conducted for the production of high-purity perrhenic acid using a membrane technique—electrodialysis. Four solutions were used in the tests: diluate, concentrate, anolyte, and catholyte. The experiments were carried out in a two-stream system. The influence of basic process parameters, including the flow rate of process streams or current density, on the purity of the obtained perrhenic acid were examined. Electrodialysis was also carried out as part of this research, aiming to concentrate the perrhenic acid >100 g/dm³. The concentrate solution obtained in the concentration tests, with a concentration of 148.7 g/dm³ HReO₄ and 530 mg/dm³ NH₄⁺, was then sent to the purification process using the electrodialysis method. The purification process was carried out until the concentration of NH₄⁺ ions was <100 mg/dm³ in the concentrate. Finally, perrhenic acid was obtained with the following composition: 169.7 g/dm³ HReO₄ and 70 mg/dm³ NH₄⁺. Based on this research, a technological scheme for producing high-purity HReO₄ by electrodialysis was developed.

Keywords: electrodialysis; membrane techniques; perrhenic acid



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1. Introduction

Electrodialysis is an advanced separation technology that uses an electric current to move ions through semi-permeable membranes. This process is commonly used in industry to desalinate water, concentrate solutions, and recover valuable ingredients [1–3]. In electrodialysis, the solution is often placed between a cation-exchange membrane (permitting only positive ions) and an anion-exchange membrane (permitting only negative ions). Under the influence of an electric current, these ions are attracted to the electrodes with the opposite charge, passing through the appropriate membranes, which effectively separates them from the solution [4–7]. Bipolar membranes are also used in electrodialysis processes [8]. Bipolar membranes are a particular type of membrane that can conduct cations and anions, making them extremely useful in electrodialysis processes. They are composed of two layers: a combined cation-selective membrane (with built-in functional groups with a negative electric charge) and an anion-selective membrane (with built-in functional groups with a positive electric charge) [9]. A schematic diagram of a bipolar membrane is shown in Figure 1. Bipolar membranes are a crucial element in reverse electrodialysis and bipolar membrane electrodialysis, which are technologies that enable even

greater control over the separation process. Thanks to their unique ability to conduct both types of ions, bipolar membranes can open new opportunities for industry in efficient and sustainable resource management [10]. The electro dialysis process is highly efficient and technologically sustainable, making it an attractive option for many industrial applications.

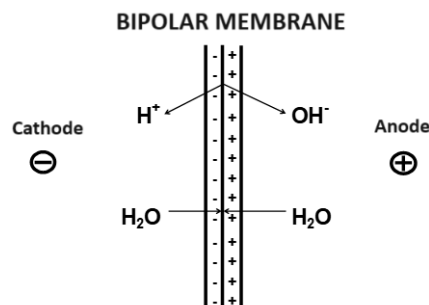


Figure 1. Schematic diagram of a bipolar membrane.

The electro dialysis process can be used to produce perrhenic acid, which is a secondary market product produced from rhenium [11]. However, a critical aspect is the selection of appropriately selective and durable membranes tailored to specific needs [12–14]. One of the known methods for the electro dialytic production of perrhenic acid is a process carried out in a seven-chamber reactor, where MA-40 anion exchange and MK-40 cation exchange membranes are installed alternately [15]. However, this method has disadvantages. The first requirement is that multiple ion-exchange membranes are needed to construct a single-membrane cell [16–19]. Additionally, it is recommended to regularly remove the acid from the concentration chamber so that the HReO_4 concentration does not exceed $>200 \text{ g/dm}^3$ [20,21]. When the concentration exceeds this value, both the selectivity and strength of the membranes used decrease significantly, which leads to a reduction in the transport of ReO_4^- ions through the membrane and a reduction in the efficiency of the process [22]. Moreover, the authors should have focused on analyzing the impurities in the obtained HReO_4 concentrate. Therefore, it is important to conduct additional research in this area to ensure the highest quality of the final product [23–26].

The method proposed in this article offers significant improvements in the production of perrhenic acid. The main advantage is the ability to produce high-purity perrhenic acid (less than $<100 \text{ ppm}$ of impurities) with a concentration of $>100 \text{ g/dm}^3 \text{ HReO}_4$. This method, based on a two-stage electro dialysis process, allows for the concentration of perrhenic acid that is $>100 \text{ g/dm}^3$ and its purification from potential impurities and ammonium ions. This approach is more effective and efficient compared to the methods mentioned above. Overall, the proposed solution offers significant improvements in efficiency, final product purity, and purification capabilities, making it an attractive choice for producing perrhenic acid.

This paper is centered on laboratory experiments aimed at producing high-purity perrhenic acid. A series of tests were conducted using the electro dialysis process, which involved four solutions: a diluate, a concentrate, an anolyte, and a catholyte. These investigations provided insights into how key process parameters—such as the flow rates of process streams, current densities, and concentrations of individual solutions—affect the purity of the resulting perrhenic acid. The objective of these tests was to identify the most optimal parameters for the electro dialysis process to yield high-purity perrhenic acid. Subsequent steps involved concentrating the perrhenic acid to a level exceeding 100 g/dm^3 , followed by a purification process to remove any impurities, which primarily include ammonium ions (NH_4^+). The culmination of this research was the development of a technological blueprint for the production of high-purity HReO_4 .

2. Materials and Method

Trials in double-flow system (Figure 2) were performed using electrolysers PC Cell ED 640 04 (Figure 3), supplied by PCCell (Heusweiler, Germany), which enables use of 5 sets of membranes in a package, with 3 membranes of size 110×110 mm in each set, with active surface area of a membrane of 64 cm^2 (PCCell, Heusweiler, Germany). Additionally, a peristaltic pump with 4 working heads (Masterflex, Gelsenkirchen, Germany), 4 tanks for circulating solutions, power supply UTP3705S (Uni-T, Garwolin, Poland), 4 magnetic mixers with heating mode (IKA, Warsaw, Poland), and 5 pH meters (Endress+Hauser, Wroclaw, Poland) were used.

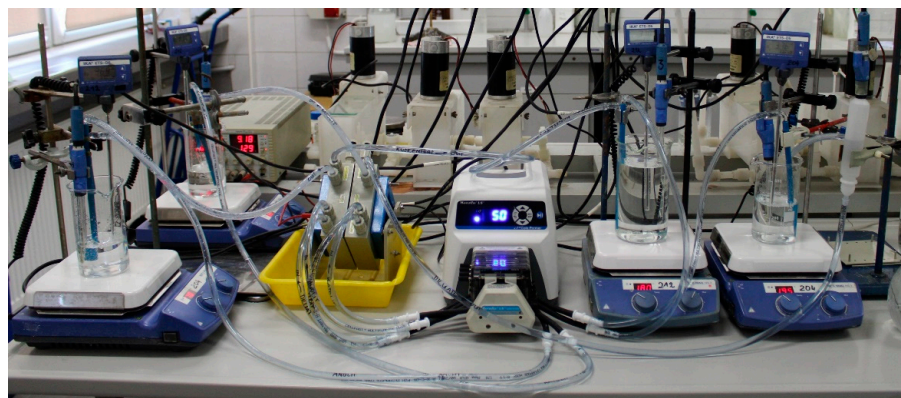


Figure 2. Set for electro dialysis test.

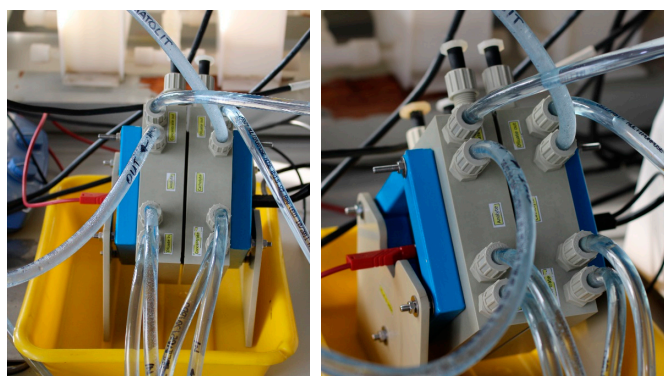


Figure 3. Electro dialyser PC Cell ED 640 04.

Temperature and pH of circulating solutions were continuously measured using pH meters from Endress+Hauser and electrodes CPS41D-7BC2B1, combined with recording system, in ten-second intervals. Four types of solutions with a set concentration were used: concentrate—perrhenic acid with a concentration of $40 \text{ g/dm}^3 \text{ HReO}_4$, the diluate—ammonium perrhenate with a concentration of $25 \text{ g/dm}^3 \text{ NH}_4\text{ReO}_4$ (INNOVATOR sp. z.o.o., Gliwice, Poland), the catholyte—perrhenic acid with a concentration of $30 \text{ g/dm}^3 \text{ HReO}_4$, and the anolyte—perrhenic acid—with a concentration of $30 \text{ g/dm}^3 \text{ HReO}_4$. This perrhenic acid was obtained from secondary raw materials—superalloy scrap waste—generated during previous projects realized in Łukasiewicz—IMN. The concentrate was enriched and concentrated in the ReO_4^- ions from a second solution—diluate. Catholyte and anolyte were circulating solutions, in which cathode and anode were immersed. Process solutions were pumped by peristaltic pumps. This research used three types of membranes: bipolar PC bip, cation-exchange PC SK, and anion-exchange PC SA.

The membranes used for testing were characterized by low electrical resistance, high selectivity, and good chemical and mechanical resistance. Generally, the effect of ionoselectivity of membranes depends on the positively or negatively charged compounds built

into their structures, which attract ions with varying strengths (allowing them to be transported through the membrane) or repel them (causing separation of the solution) [27,28]. Their mutual exclusion causes the problem of selecting the optimal parameters for ion exchange membranes. An example is the degree of cross-linking of the polymer on which the membrane is based; its increase improves mechanical strength while increasing electrical resistance. The increasing density of functional groups in the membrane matrix results in lower electrical resistance. Still, at the same time, the tendency of the membrane to swell increases, and its mechanical stability decreases. This makes it necessary to select the appropriate membrane for a specific need. The characteristics of the ion-exchange membranes used in these studies are presented in Table 1.

Table 1. Characteristics of ion-exchange membranes used in research.

Membrane	Type	Resistant Electric, $\Omega \cdot \text{cm}^2$	Interchangeable Capacity, eq/g	Maximum Temperature Process, $^{\circ}\text{C}$	Thickness, μm	Resilience Mechanical, kg/cm^2	H ₂ O Content in a Dry State, %
PC bip	bipolar cation exchanger	<3	-	40	200–350	-	-
PC SK	strongly acidic anion exchanger	~2.5	3	50	100–120	4–5	~9
PC SA	strongly basic anion exchanger	~1.8	0.7–1.2	60	100–110	4–5	~14

Each of process streams were continuously mixed in buffer tank and temperature-stabilized by the heating elements of magnetic mixers, with thermocouples immersed in solutions. This allowed us to keep temperature constant within whole electrolysers and circulating solutions. The procedure of electro dialysis was as follows: all solutions were heated to 35 $^{\circ}\text{C}$ prior to pumping to electrolysers, a stack of ion-selective membranes and sheet spacers was prepared, and then they were placed in the electrolysers. Scheme of the electrolysers construction with the membrane assembly in double-flow system is presented in Figure 4, with the ion flow in double-flow system in Figure 5.

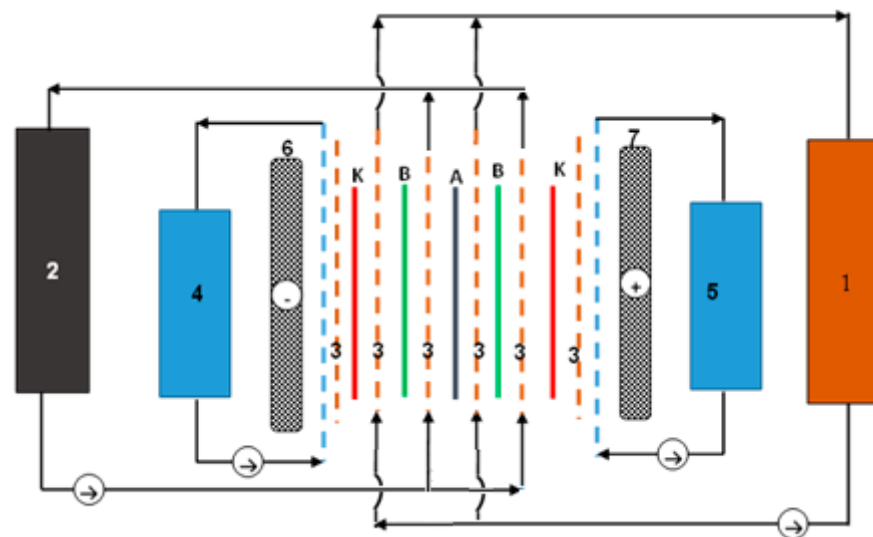


Figure 4. Scheme of the electrolysers construction: 1—concentrate flow; 2—diluate flow; 3—spacer; 4—catholyte flow; 5—anolyte flow; 6—cathode; 7—anode; A—anionite membrane; K—cationite membrane; and B—bipolar membrane.

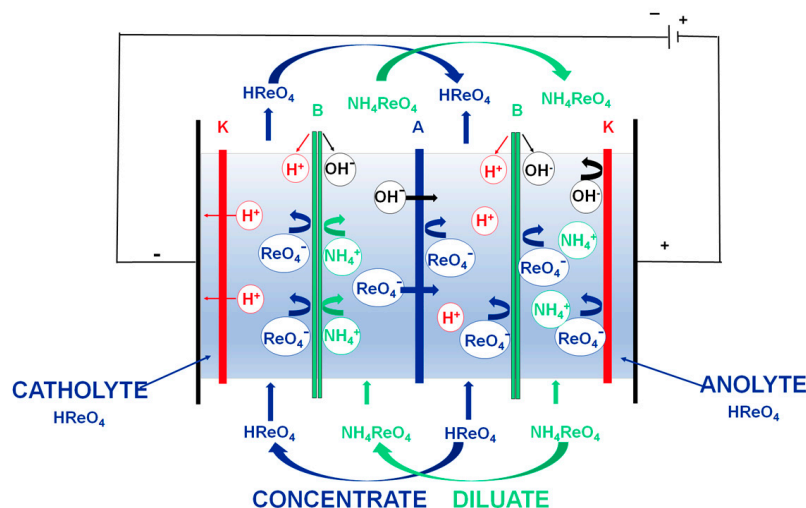


Figure 5. Ion flow in double-flow system.

Initial samples were collected after entire deaeration of system and flow stabilization. The process was started when power supply was turned on, and set current intensity was chosen, which was kept constant during the process. Samples were collected periodically from all or selected streams. Voltage and temperature were monitored as well. The final point was the moment when pH reached 10.6 in diluate, satisfying depletion of ReO_4^- ions to $<1 \text{ g/dm}^3$ (process efficiency $> 90\%$) and/or when a sudden and significant increase in voltage occurred. The solution’s volume was measured and samples were collected. Each test was performed three times. A statistical analysis was conducted and standard deviations were plotted on the charts.

Process efficiency was calculated from Equation (1):

$$W = \frac{C_0 - C_1}{C_0} \cdot 100\% \quad (1)$$

where C_0 and C_1 are the concentration of diluate at the beginning and at the end of process in mol/dm^3 .

3. Results and Discussion

Within these experiments:

- The effect of the flow intensity of process streams through an electrolysers, including the current density and concentration of selected process streams on the purity of the produced perrhenic acid, were examined;
- Trials for the production of perrhenic acid, with a concentration of $>100 \text{ g/dm}^3$ using electro dialysis, were performed;
- Purification of the produced perrhenic acid, with the use of electro dialysis, was performed.

3.1. Flow Intensity

One of the examined parameters was the flow intensity of the process streams through the electrolysers. Tests were performed with set values of $0.75 \text{ dm}^3/\text{h}$, $3.0 \text{ dm}^3/\text{h}$, $4.5 \text{ dm}^3/\text{h}$, $5.0 \text{ dm}^3/\text{h}$, and $7.0 \text{ dm}^3/\text{h}$, keeping a constant current density of 300 A/m^2 , and a temperature of $35 \text{ }^\circ\text{C}$. The initial volumes of the concentrate, diluate, catholyte, and anolyte were 0.35 dm^3 each. Electro dialysis was carried out until the diluate pH value reached a minimum of 10.6—this meant that the ReO_4^- ions in the diluate were depleted—while the current voltage was monitored. After completing the tests, the following process durations were recorded and are presented in Table 2.

Table 2. Influence of flow intensity of process streams on the duration of electro dialysis.

Flow Intensity of Streams, dm ³ /h	Electrodialysis Time, h
0.75	5.0
3.0	1.4
4.5	1.6
5.0	1.2
7.0	1.8

At the lowest stream flow rate—0.75 dm³/h—the electro dialysis time was as long as 5 h, while for the remaining samples, it was less than 2 h. Figure 6 shows the concentration values of the perrhenic acid and ammonium ions in the concentrates, obtained after electro dialysis, depending on the flow rate of the process streams used.

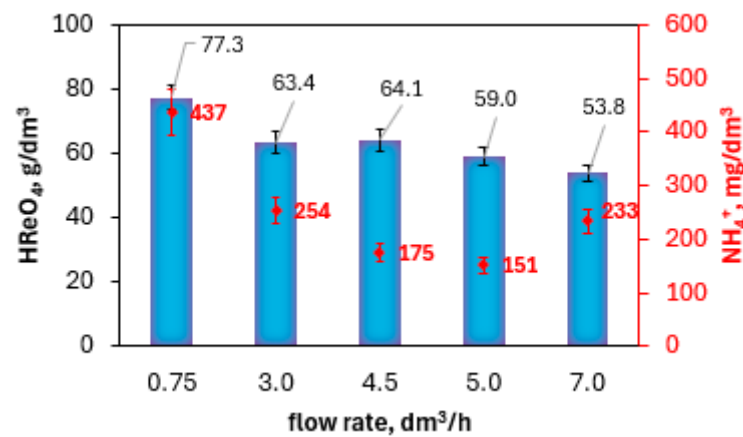


Figure 6. Concentration of perrhenic acid in produced concentrates and concentration of ammonium ions with respect to flow intensity of process streams.

As the initial concentration of the perrhenic acid in the concentrate was 40 g/dm³, a significant increase in Re, up to 77 g/dm³, can be observed. The bigger the flow intensity of the process streams, the lower the contamination with ammonium ions (the exception is 7 dm³/h) and the lower the rhenium increase in the concentrate. The amount of migrating ammonium ions depends on the time of electro dialysis and the flow intensity of the process streams. The lowest level of contamination of the concentrate with NH₄⁺ ions (151 mg/dm³) was found at the flow intensity of 5 dm³/h. The process efficiency in all five electro dialysis experiments was above 90%. Consequently, the most favorable flow intensity was said to be in the range of 3.0–4.5 dm³.

3.2. Current Density

The next parameter tested was current density. While designing an electro dialysis process, special attention should be paid to limiting current density, which is the maximum current that can be passed through a given membrane without a visible increase in the electrical resistance of the system or deterioration of the current efficiency. The ions responsible for current transport through the membrane are almost entirely removed from the solution layer directly adjacent to the membrane on the diluate side. It is necessary to use a higher voltage to maintain a constant current with the increased electrical resistance of the solution. When there are no ions to transport the current, the reverse transport of anions through the cation-exchange membrane begins. The next stage is the decomposition of water molecules into H⁺ and OH⁻ ions, which serve as charge carriers and cause direct changes in the pH. These phenomena are undesirable and reduce the efficiency of the process. Four different current density values were used in the tests: 150, 200, 250, and 300 A/m². In these experiments, a solution of NH₄ReO₄, with about a concentration of 25 g/dm³, was used as the diluate, and the temperature of all the solutions was maintained

at 35 °C. The flow rate of the process streams through the electrolysers was set at 3.0 dm³/h. And similarly to before, electro dialysis was carried out until the pH of the diluate reached at least 10.6. The times of each process vs. the applied current densities are presented in Table 3 .

Table 3. Time of each electro dialysis process vs. applied current densities.

Current Density, A/m ²	Electro dialysis Time, h
150	2.0
200	1.8
250	1.6
300	1.4

The higher the current density used, the shorter the electro dialysis process time. The concentration of the perrhenic acid and ammonium ions in the produced concentrates after electro dialysis vs. the current densities are presented in Figure 7.

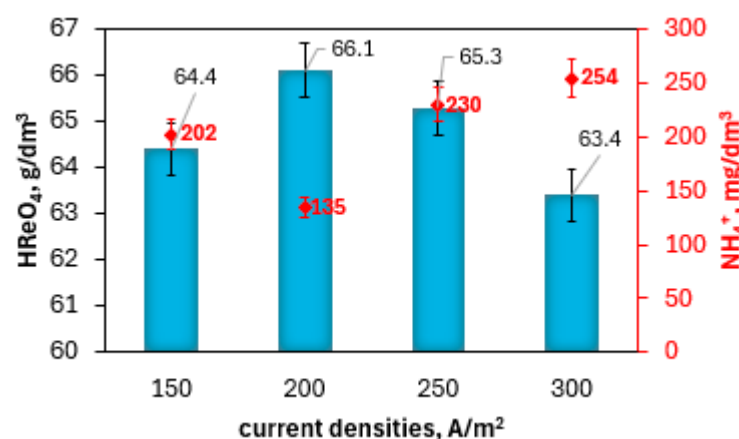


Figure 7. Concentration of perrhenic acid and ammonium ions in produced concentrates after electro dialysis vs. current densities.

As a result, an increase in the concentration of HReO₄⁻ was observed in all concentrates up to ~65 g/dm³. The lowest concentration of NH₄⁺ ions (135 mg/dm³) was obtained at 200 A/m². The concentration of ammonium ions in other trials was >200 mg/dm³. The change in the perrhenic acid concentration in both the anolyte and catholyte and the rhenium in the diluate, both before and after the process for all four attempts, are presented in Table 4.

Table 4. The change in perrhenic acid concentration in anolyte and catholyte and rhenium in diluate, both before and after process, for all four attempts.

Current Density, A/m ²	Anolyte HReO ₄ , g/dm ³		Catholyte HReO ₄ , g/dm ³		Diluate Re, g/dm ³	
	Before	After	Before	After	Before	After
150		34.4		31.6		0.35
200	30.0	30.9	30.0	29.1	17.5	0.20
250		31.4		28.7		0.12
300		30.5		28.9		0.14

Based on the data in the Table 4, the following trends can be noticed:

- In the anolyte, regardless of the current density, the concentration of the perrhenic acid increases after the end of the electro dialysis process;

- In the catholyte, the concentration of the perrhenic acid increases after the electro dialysis process at a current density of 150 A/m² while for the densities of 200, 250, and 300 A/m², it decreases;
- In the diluate, the rhenium concentration drops below 0.50 g/dm³ for all current densities after the electro dialysis process is completed.

The process efficiencies in all electro dialysis experiments reached above 90%. It was determined that the most favorable current density value is 200 A/m².

Applications of New Kind of Diluate for Different Current Densities

There were also tests with varied initial concentrations of particular process streams. The combined anolyte and catholyte from the previous trials was used as a diluate. Prior to electro dialysis, the following concentrations were found: Re—25.6 g/dm³ and NH₄⁺—123 mg/dm³. Regarding the anolyte, catholyte, and concentrate, the same set, as previously described, was used: concentrate—40 g/dm³ HReO₄, catholyte—30 g/dm³ HReO₄, and anolyte—30 g/dm³ HReO₄. The temperature was at 35 °C and the flow intensity was 3.0 dm³/h. The current density used was varied: 150, 200, and 300 A/m². The tests were carried out until the pH value was reached—10.6 in the diluate—while the current voltage was monitored simultaneously. The time need to finish each process vs. the current densities is presented in Table 5.

Table 5. Electro dialysis time vs. current densities in trials with new combined diluate.

Current Density, A/m ²	Electro dialysis Time, h
150	1.6
200	2.1
300	3.6

With the increase in current density, the electro dialysis process time increases from 1.6 h for 150 A/m² to 2.1 h for 200 A/m² and up to 3.6 h for 300 A/m². Figure 8 shows the concentration values of the perrhenic acid and ammonium ions in the obtained concentrates after electro dialysis, depending on the current density used and using a new type of diluate.

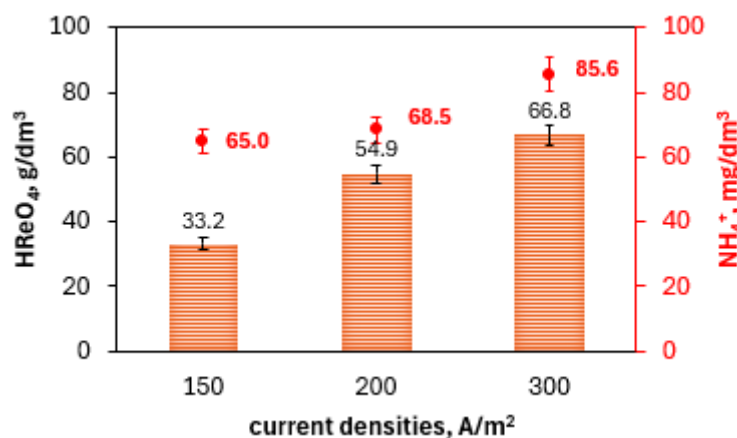


Figure 8. Concentration of perrhenic acid and ammonium ions in concentrates after electro dialysis vs. applied current densities, with a use of a new feed (combined).

The analysis of the obtained results satisfied that the higher current density, with a new feed (Re—25.6 g/dm³, and NH₄⁺—123 mg/dm³), the higher the concentration of the perrhenic acid in the produced concentrate. Moreover, the increase in the current density results in an increase in the contamination of the concentrate with ammonium ions. The relationship between the electro dialysis time and the applied current densities, with a use of a new feed, is presented in Figure 9.

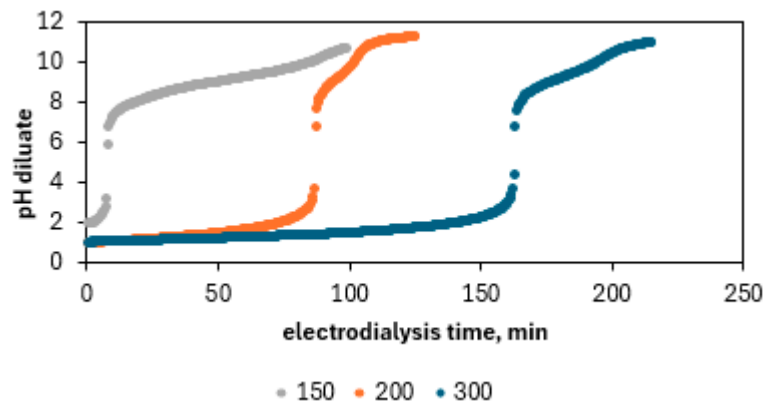


Figure 9. Relation between electrodiolysis time and applied current densities with a use of a new feed.

It appears that increases in the current density result in increased electrodiolysis times, ranging from 1.6 h at 150 A/m² (gray line), to 2.1 h at 200 A/m² (orange line), and up to 3.6 h at 300 A/m². The phenomena of a sudden change in the diluate pH to ~8 was observed later when a higher current density was used.

3.3. Concentration and Purification of Perrhenic Acid >100 g/dm³

Attempts were made to concentrate perrhenic acid in a double-flow stream and were realized in five cycles. In each of them, a new portion of the diluate—with ammonium perrhenate as a source of ReO₄⁻ ions—was used. When the pH of the diluate achieved a value of 10.6, the ReO₄⁻ depleted solution was rejected and a new one was used. The entire process took a total of 8 h. The relationship between the change in the HReO₄ concentration in the concentrate and the pH of the diluate during the electrodiolysis process is presented in Figure 10.

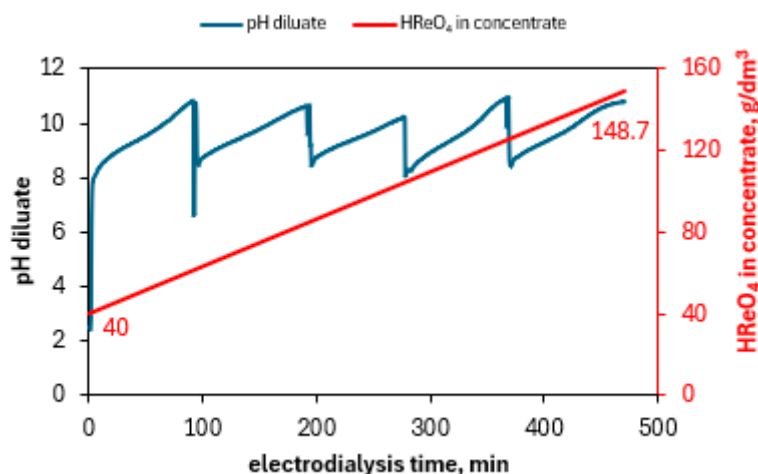


Figure 10. Change in HReO₄ concentration in the concentrate and pH of the diluate in a 5-cycle extended electrodiolysis process.

The whole process took 8 h across five cycles, which allowed us to increase the concentration of the concentrate from 40 g/dm³ to 148.7 g/dm³ HReO₄, while simultaneously contaminating it with NH₄⁺ ions up to a concentration of 530 mg/dm³. In all cycles, the process efficiency was above 90%. Despite the contamination with ammonium ions, the concentrates were successfully enriched in rhenium, lowering the rhenium amount in the diluates from 17.5 g/dm³ to <1.0 g/dm³ Re. The produced concentrate, with a concentration of 148.7 g/dm³ HReO₄ and 530 mg/dm³ NH₄⁺, was electrodiolatically purified to lower the concentration of NH₄⁺ to <100 mg/dm³. It was used as the diluate in the next stage. The purification was performed at 200 A/m², with a flow rate of 3.0 dm³/h,

a temperature of 35 °C, and a time of 8 h. The applied method allowed us to produce a concentrate with concentrations of 169.7 g/dm³ HReO₄ and 70 mg/dm³ NH₄⁺. Based on this, a technological scheme for perrhenic acid production, with a concentration of >100 g/dm³ and a high purity, was developed (Figure 11).

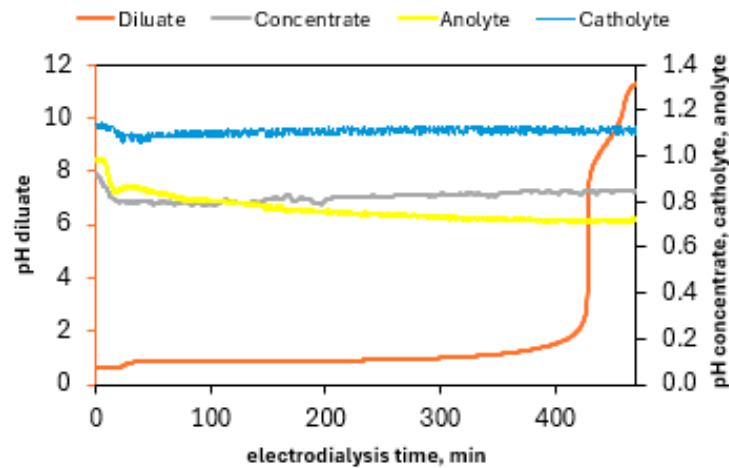


Figure 11. Change of pH of all process streams during the electrolytic purification process.

The electro dialytic method used to purify the perrhenic acid made it possible to obtain a concentrate with the following composition: 169.7 g/dm³ HReO₄ and 70 mg/dm³ NH₄⁺. On this basis, a technological scheme (Figure 12) was developed for obtaining high-purity perrhenic acid with a concentration of >100 g/dm³.

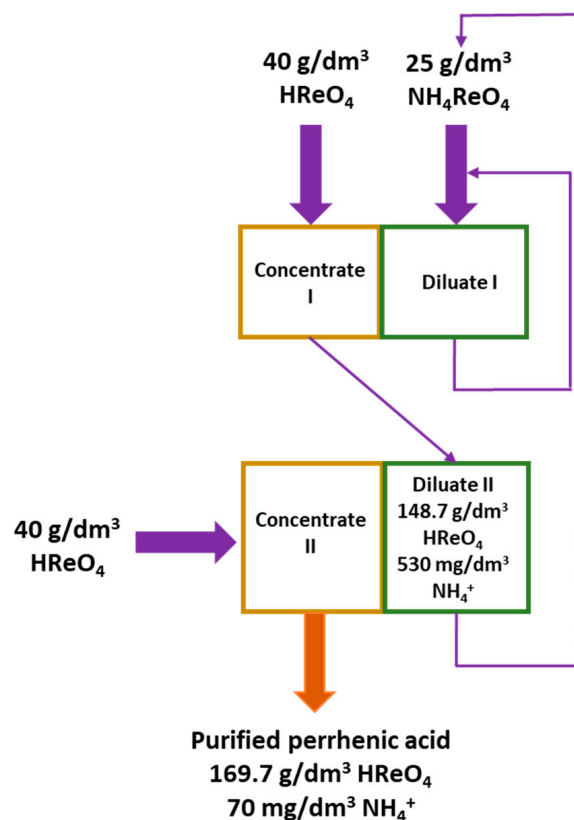


Figure 12. Technological scheme for production of high-purity perrhenic acid.

The proposed technological scheme consists of two successive electro dialysis processes. In the first stage, the HReO₄ solution should be used as the feed in the Concentrate I stream

and the NH_4ReO_4 solution should be used in the Diluate I stream. During this process, an HReO_4 solution with a concentration of $\sim 150 \text{ g/dm}^3$ is obtained in the Concentrate I stream and the Diluate I stream is depleted of ReO_4^- ions. The exhausted Diluate I stream can be returned to the process and used to dissolve a new portion of ammonium perrhenate. In the second stage, a fresh solution of 40 g/dm^3 HReO_4 should be used as the feed in the Concentrate II stream, and the perrhenic acid solution obtained in the first stage should be used as the feed in the Diluate II stream. During this stage, a solution of $\sim 170 \text{ g/dm}^3$ HReO_4 is obtained in the Concentrate II stream, and the exhausted Diluate II stream containing most of the impurities can be returned to the first stage and serve as a base for the preparation of the input to the Diluate I stream. The process parameters are a temperature of $35 \text{ }^\circ\text{C}$, current density of 200 A/m^2 , and flow rate of process streams through the electrolyser of $3.0 \text{ dm}^3/\text{h}$. After working on the system for a long time, it is necessary to determine the moment for removing part of the solution to remove the accumulating impurities.

4. Conclusions

Laboratory tests were conducted for the production of high-purity perrhenic acid using a current membrane technique—electrodialysis—in a two-stream system. A stack of cation-exchange, anion-exchange, and bipolar membranes, as well as sheet spacers, were selected to perform these experiments. The most favorable parameters of the electrodialysis process for obtaining high-purity perrhenic acid were determined, such as the temperature, current density, flow rate, and concentrations of individual process streams. It was determined that the most favorable flow rate of the process streams through the electrodialyser is $3.0\text{--}4.5 \text{ dm}^3$. The most favorable current density value is 200 A/m^2 and the process temperature is $35 \text{ }^\circ\text{C}$. It is also possible to use a diluate with an initial concentration of 25.6 g/dm^3 of rhenium and 123 mg/dm^3 of ammonium ions without any visible deterioration of the process efficiency or the purity of the obtained HReO_4 concentrate.

Finally, high-purity perrhenic acid (containing $<1 \text{ ppm Ca}$, $<10 \text{ ppm K}$, $<1 \text{ ppm Mg}$, $<1 \text{ ppm Cu}$, $<1 \text{ ppm Na}$, $<1 \text{ ppm Mo}$, $<1 \text{ ppm Ni}$, $<1 \text{ ppm Pb}$, $<1 \text{ ppm Fe}$, $<1 \text{ ppm Co}$, and $<1 \text{ ppm Zn}$) with a rhenium concentration of $>100 \text{ g/dm}^3$ was obtained in the electrodialysis process with an efficiency of $>90\%$. A two-stream system using three ion-exchange membranes was employed to develop a technological scheme consisting of two successive electrodialysis processes. In the first stage, perrhenic acid is produced from a solution of ammonium perrhenate. The obtained acid is cleaned of potential impurities and ammonium ions in the second stage.

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