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Performance evaluation of diaphragm electrolysis cell for alkali production

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ABSTRACT

Seawater desalination technology is important for solving water shortage problems. RO desalination is the most frequently used process for obtaining fresh water from salt water. Electrolysis is also one way of reusing the enriched brine. Alkali-activated products can be made by producing NaOH after electrolysis. There are three kinds of brine electrolysis methods including diaphragm, membrane, and mercury methods. This study was conducted using a 200 mL electrolysis diaphragm cell. Tedlar bags were used in order to gather gases such as Cl_2, O_2, and H_2. The head was less than 10 mm when a diaphragm with a 10 μm pore size was used. The data in this study was collected to analyze the relationships between concentration, chloride removal, and current density (CD). Our results showed that pore size influenced the head at the anode. Chloride removal was not high even when a high CD was applied. When the CD was 200 mA/cm^2, the maximum NaOH concentration was 1.85%. However, the NaOH concentration was just 1.5% at 100 mA/cm^2. The correlation coefficient was also more than 0.99 at a 200 mA/cm^2 CD. The applied high CD at the diaphragm cell was unstable because it caused high temperature. The high CD caused the head of the reactor to be higher. Thus, the diaphragm cell could not be operated anymore. The sensitivity analysis results showed that control of the flow rate was more efficient than control of the CD.

Keywords: Alkali production; Chlor-alkali; Diaphragm; Electrolysis; Enrichment brine

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1. Introduction

Seawater desalination technology is an important technology for solving the problem of water insufficiency. Desertification has occurred in dry weather regions due to many factors, particularly climate change and human activity. Desertification leads to a loss in economic productivity and influences ecosystems by causing changes in soil, plants and other biotic components such as bio-geochemical and hydrological processes [1]. Presently, the demand for fresh water dramatically exceeds the water supply. This situation has created an urgent need for an integrated water resource management strategy, which must focus on nonconventional water resources, namely sea water desalination and wastewater reuse

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[2]. Countries located in the Middle East, which have low precipitation and dry climates, have met this challenge by producing fresh water using desalination technology [3]. Industries throughout the world continue to grow and demand ever more water. Therefore, desalination of seawater has been considered an attractive and logical method for making pure water to meet the demands [4]. Reverse osmosis (RO) desalination is the most frequently applied desalination process to obtain fresh water. Also, RO systems driven by gas and steam turbines have a lower cost than other alternatives [5].

Electrolysis is one way to reuse enrichment brine produced as a byproduct of the RO process. Methods involving diaphragms, membranes, and mercury can also be used. In the chlor-alkali process, NaCl is electrolytically decomposed using a direct current to generate a sodium hydroxide solution, chlorine gas, and hydrogen gas [6]. Diaphragm cells have two significant drawbacks. First of all, diaphragm cells consume more energy than other methods. Secondly, diaphragm cells result in side effects from asbestos, which is conventionally used to construct the diaphragm. Asbestos causes asbestosis, lung cancer, and mesothelioma [7]. However, polytetrafluoroethylene (PTFE) filters can be used today. One of the reasons why diaphragm cells are used is that membrane cells are more complex than diaphragms in the operation of preconditioning processes like fine purification. However, diaphragm cells require precipitation and filtration in previous steps [8]. Mercury cells are excluded from this study because mercury cells cause the discharge of mercury into the air, and these impurities can have a negative influence on water. Diaphragms in such a system have been intensively studied using different materials like PTFE [9]. A diaphragm is used to separate the two compartments within the cell. Hydrogen ions and hydroxide ions are generated by splitting of water that migrates to the anode and cathode, respectively [9]. Eqs. (1)–(3) that govern the chlor-alkali process are shown below:

$$\text{Anode: } 2\text{Cl}^-_{(\text{aq})} \rightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^- \tag{1}$$

Here, Cl_2 gases are produced at the anode.

$$\text{Cathode: } 2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})} + 2\text{OH}^- \tag{2}$$

Here, H_2 gases are produced at the cathode.

$$\text{Overall: } 2\text{NaCl}_{(\text{aq})} = 2\text{NaOH}_{(\text{aq})} + \text{H}_{2(\text{g})} + \text{Cl}_{2(\text{g})} \tag{3}$$

Because the NaCl content in the water is high, NaOH is produced as a result of the chemical reaction at the diaphragm cell. At the anode, chloride ions are converted to gaseous chlorine. In the general process of water electrolysis, hydrogen ions move toward the cathode, whereas hydroxide ions move toward the anode. The cathode compartment is fed with brine, and the brine is reduced to gaseous hydrogen and hydroxide ions. Because the sodium hydroxide concentration increases in the anode chamber, the NaOH can be concentrated in the cathode cell by introducing oxygen and water [10]. Therefore, NaOH can be produced during operation of the electrolysis cell.

The main purpose of the present study is to evaluate how current density (CD) and hydraulic retention time (HRT) affect the diaphragm cell. The effects of CD and HRT on total chlorine, NaOH concentration, current efficiency, chloride removal, voltage, and temperature are also discussed.

2. Materials and methods

2.1. Chemicals and materials

To make the artificial brine, sodium chloride (NaCl 99.5%, produced by Samchun company, Republic of Korea) was used to make a 66.67 (g/L) sodium chloride solution. All solutions were prepared using deionized water, and the experiments were carried out at room temperature. The electrode area in the cells was 20.7 cm^2, and the cell volume was 200 mL. The electrolytic cell was made of a parallelepiped acrylic resin to observe whether the head changed or not. A power supply (DCS55–55E, Sorensen) was used (0–55 V, 0–55A) in order to measure the electric power consumption and CD (mA/cm^2). Omnipore PTFE filters were used to measure the head in the diaphragm cell (hydrophilic 90 mm white, plain 0.45 μm, JHWP09025; 1 μm, JAWP09025; 5 μm, JMWP09025; 10 μm, JCWP09025; thickness 85 μm, Merck Millipore, Germany). A peristaltic pump (No. 77200-60, Easy-load II, Cole-Parmer Instrument Co.) and tubing (96410-25, Master flex) were used in order to regulate the flow of the brine. Finally, Tedlar bags (CEL Scientific Corp., 10 L) were used in order to collect Cl_2, O_2 and H_2 gases produced at the cathode and anode [11].

2.2. Experimental setup

The diaphragm cell apparatus is shown in Fig. 1. The reactor was 5 cm long, 4 cm high, and 10 cm thick with an acrylic thickness of 1.5 cm. A PTFE filter was

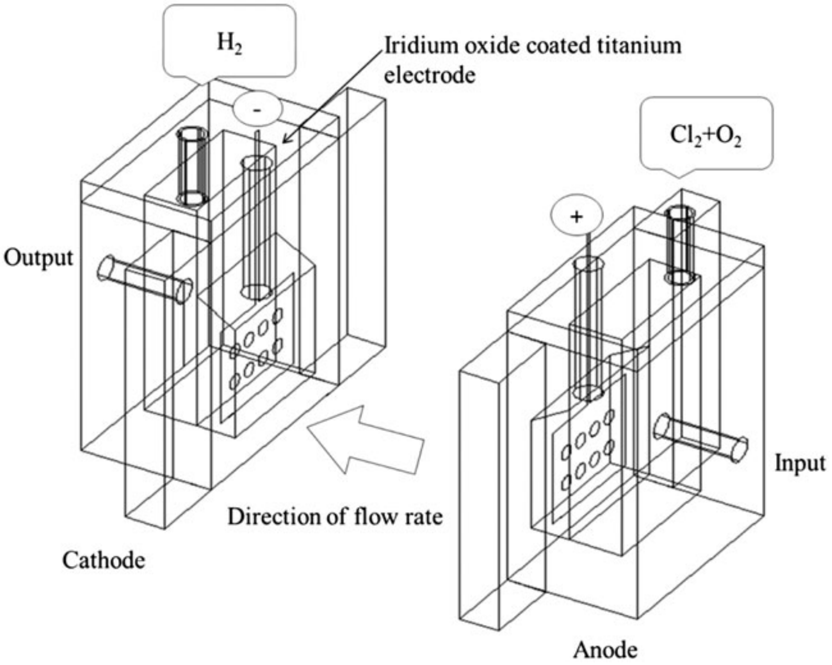

Fig. 1. Schematic diagram of electrolysis using diaphragm.

symmetrically set up in the center of the diaphragm cell, and the electrode gap was 1 cm. The inlet water flowed toward the anode. At the same time, the water drained slowly because the pores of the filter became blocked. Therefore, a differential head occurred between the anode and cathode. Before starting electrolysis, the artificial brine was moved toward the diaphragm cell. Vent lines were tightly connected to prevent gas leakage.

2.3. Analytical methods

All samples were taken at the end of the electrolysis reactor, and gas samples were taken from the Tedlar bags. To measure the hydroxide ion concentration in the sample, the solution was titrated with diluted 0.1% hydrochloric acid (HCl 35.0–37.0%, produced by Junsei) using phenolphthalein. A spectrophotometer (HACH model DR-2800) was used in order to analyze total chlorine content, chloride ion content, sulfate content, and hardness (Mg, Ca) in the electrolyzed solution. The electric conductivity was measured using an Orion 013010MD conductivity meter (Thermo Scientific, USA). Gas detecting tubes (Gastech, No. 31B for oxygen; No. 8HH for chlorine; No. 30 for hydrogen) were used to measure concentrations of specific species in the produced gas. The current efficiency was calculated using the equation shown below, which is based on Faraday's law.

$$\text{Effective current } (I_E) = \frac{(C_{\text{in}} - C_{\text{out}}) \times z \times V \times F}{t \times M} \tag{4}$$

Here, C_{in} and C_{out} are the input and output concentrations (mg/L), z is the valence number of the ion, V is the volume of the reactor (L), and t is the electrolysis time (minutes). F is Faraday's constant (96,485 C/mol), I_E is the current efficiency, and M is the molar mass (g/mol).

Hydraulic conductivities were calculated using Darcy's law shown in Eq. (5) where the permeability area was 25 cm^2.

$$Q = K \times A \times (H_1 - H_2)/L \tag{5}$$

Here, H_1 and H_2 are the differential head (cm) between the cathode cell and anode cell. Q (cm^2/s) is the conductivity, K (cm/s) is the hydraulic permeability, A (cm^2) is the area, and L (cm) is the length of the flowing solution.

3. Results and discussion

3.1. Effect of pore size

Fig. 2 shows that head can be influenced by the pore sizes of the membranes in the reactor. As shown,

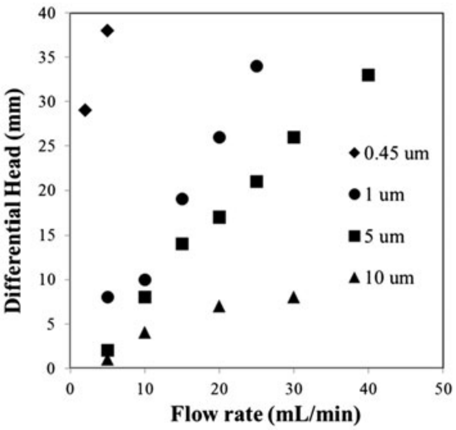

Fig. 2. Relationship between differential head and flow rate for different pore sizes.

the maximum head was 38 mm when a 0.45 μm filter was used in the reactor because the permeability resistance was higher. In contrast, the head was less than 10 mm when a diaphragm with a 10 μm pore size was used. Therefore, the pore size was influenced by the head. The trends in Fig. 2 were almost straight lines. The results can be used to define the appropriate pore size, which we believe is 1–10 μm for flow rates from 10 to 20 mL/min.

Fig. 3 shows the relationship between hydraulic conductivity and diaphragm pore size. The correlation coefficient when fitting the data to Eq. (5) was 0.95. This result implies that head can be controlled by adjusting the flowing quantity. In other words, the head can be predicted at each flow rate and each pore size.

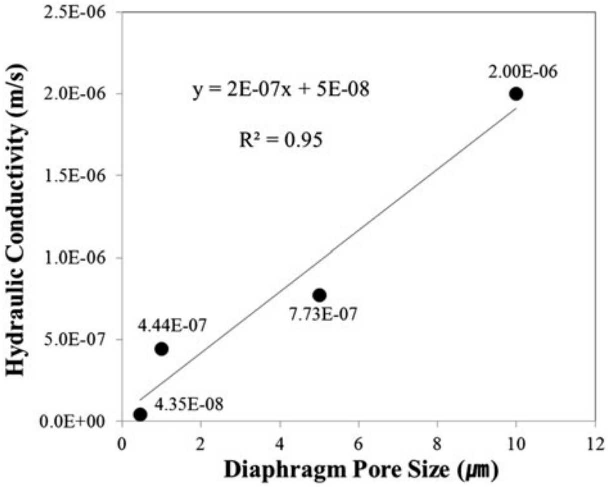

Fig. 3. Relationship between hydraulic conductivity and diaphragm pore size.

3.2. Effect of NaOH concentration and removal of chloride ions by CD

We performed a variety of experiments to analyze what relationships exist between concentration, chloride removal and CD. Two types of correlations were expected based on the chloride removal results. An increase in chloride removal (by conversion of chloride ions to chlorine gas) occurred at CD values sufficient for chloride removal. Specifically, removal of chloride ions increased as the CD increased, indicating an inverse relationship between CD and chloride ion removal [7]. After water flowed from the anode to the cathode, hydroxide ions were produced in the solution. Then, hydroxide ions moved toward the anode because of a concentration difference (diffusion). Chloride ions were converted to chlorine gas during electrolysis. When the CD increased, the chloride removal rate also increased. However, the temperature of the reactor was also higher, and thus the CD increased as well.

Fig. 4 shows the relationship between rate constant of chloride removal and the applied electric current, which was 4.16, 6.24, or 8.32 *A*. As shown, the rate constant of chloride also increased from 0.26–0.36 to 0.38–0.57 and to 0.64, respectively, with these changes in applied current. This result shows that the rate constant of chloride increased for high electric currents.

3.3. Effects of flow rate on NaOH production

Fig. 5 shows an exponential relationship between flow rate and NaOH concentration in the effluent at each CD. NaOH concentration was directly controlled by changing the flow rate at a particular CD. The maximum NaOH concentration was just 1.5% at 100 mA/cm^2. However, it was more than 2% when the CD was at 200 mA/cm^2. Electrical efficiency

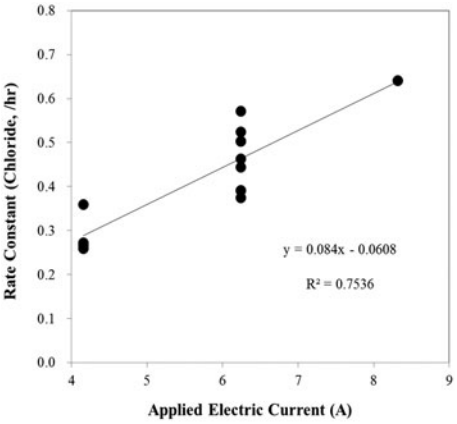

Fig. 4. Change in rate constant of chloride as a function of the applied electric current.

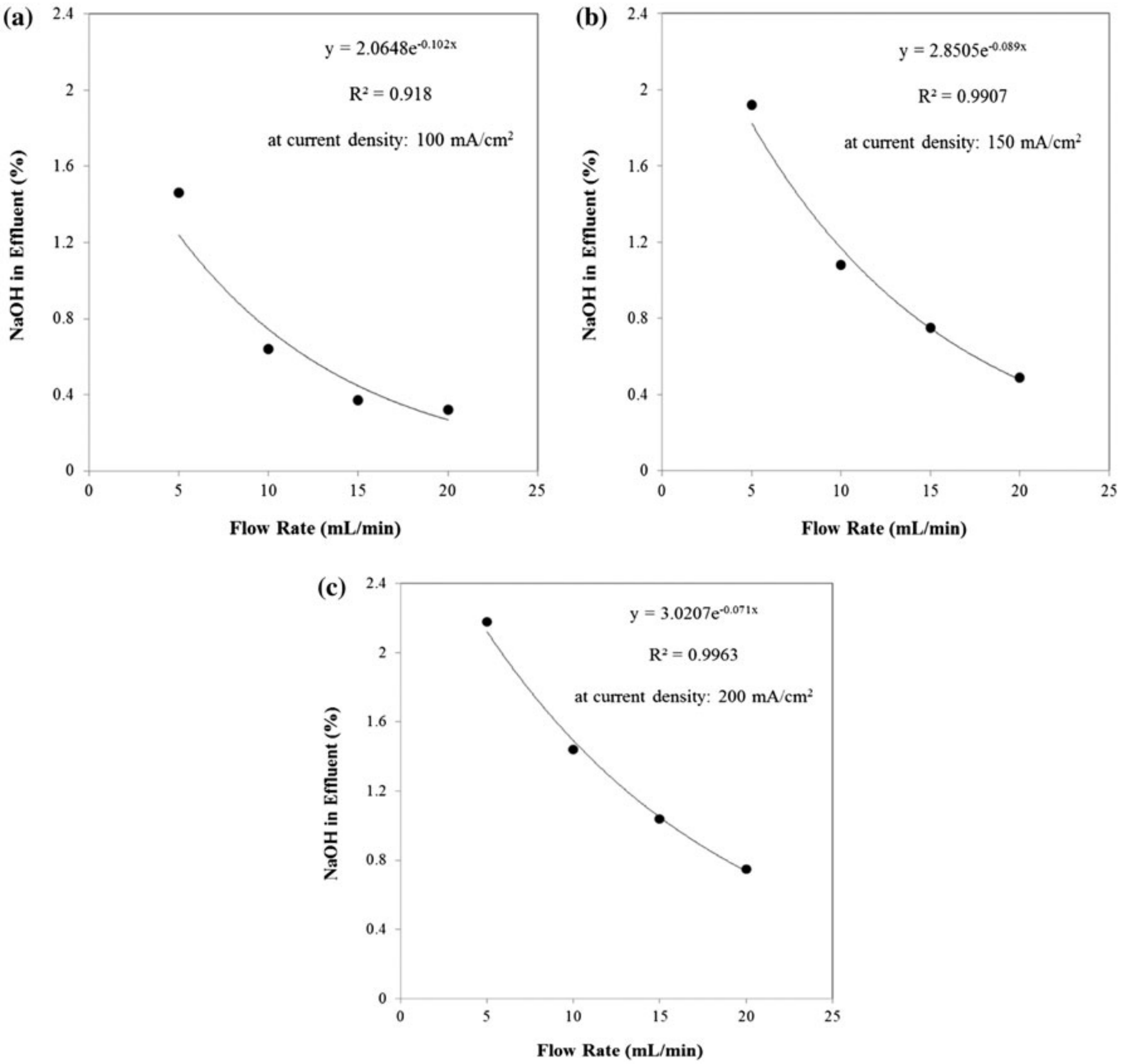

Fig. 5. Variation in NaOH concentrations as a function of flow rate by changing Current density such as 100 (a), 150 (b), and 200 mA/cm^2 (c).

decreased when the CD was high because of excessive heat emission. NaOH concentration gradually decreased while operating at high flow rates such as 10, 15, and 20 mL/min. NaOH concentration seemed to increase when the flow rate was low. The correlation coefficient for an exponential fit of the data was >0.99 at 200 mA/cm^2. The most important observation from Fig. 5 was that the CD and flow rate were absolutely the main factors for producing high concentrations of NaOH.

3.4. Sensitivity analysis

Fig. 6 show the results of a sensitivity analysis. When HRT doubled, the chloride removal efficiency and NaOH concentration increased by 58.1–67.9%, respectively. In contrast, chloride removal and NaOH concentration increased by 88.2 and 42.0%, respectively, due to changes in CD. However, the temperature increased for higher current densities. An increase in temperature would melt an acrylic reactor if it was over 90℃. Furthermore, the increased voltage caused excessive power consumption. According to the reported study, high temperature water electrolysis was required less energy to reach any given CD as compared to a low-temperature process [12]. Previous work reported tests that were conducted to investigate the electrochemical features and characteristics of high temperature steam electrolysis, which is as an efficient process [13]. However, increased voltage

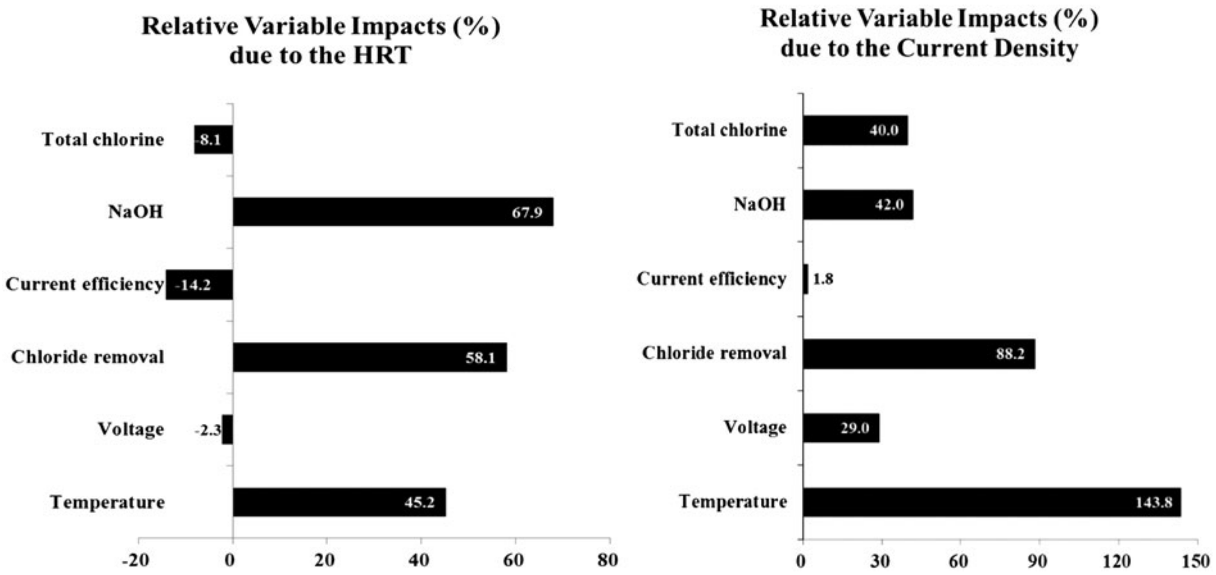

Fig. 6. Sensitivity analysis of the diaphragm cell by regulating HRT and CD.

caused excessive power consumption. Therefore, an efficient method is necessary to regulate HRT, and one of the main purposes of this work was to produce a high NaOH concentration. The results in Fig. 5 imply that increasing HRT was more efficient than increasing CD in diaphragm type chlor-alkali cell operation.

4. Conclusion

Many studies were conducted to determine the benefit of high temperature. In spite of many advantages, a high applied CD in the diaphragm cell resulted in unstable conditions because it resulted in high temperature. One of the reasons why high CD caused problems was that it resulted in high head in the reactor. The diaphragm cell could not be operated after brine overflowed in the diaphragm cell. This also led to a large power consumption because the main purpose of this study was to improve NaOH production by recycling enrichment brine. In other words, the cost of maintaining a high voltage was higher than the benefit of increasing the NaOH concentration. Variation of CD is therefore not a viable solution for producing high NaOH concentrations. Regulation of flow rate showed more efficient cell operation than regulation of CD.

Acknowledgment

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