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Characteristic analysis of a diaphragm electrolysis reactor with different electrode materials and concentrated degrees of brine

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ABSTRACT

The current demand for drinking water is rapidly exceeding the water supply. Desalination is one effective way to solve the worldwide water shortage. However, disposal of concentrated brine depends on discharge through oceans and evaporation ponds. Electrolysis is one of the solutions to address discharge of concentrated brine. Electrolysis is mainly categorized into mercury, diaphragm, and membrane types. Diaphragm type electrolysis was adopted here and was applied to a 200 mL reactor. A 10 μm pore size filter was used, and the head was <8 cm. The data in this study were collected to evaluate NaOH concentration, Cl^- removal, and current efficiency (CE) by changing the concentrated degree and electrode material. When changing the concentrated brine to degrees of raw, triple, and quintuple, NaOH concentration was 1.6%, 2.3%, and 2.8% and Cl^- removal was 75%, 39%, and 28%, respectively. These tendencies were caused by decreasing internal resistance. CE was inversely proportional to temperature, caused by ion quantity. Because iridium has a lower electrical resistivity than ruthenium, electrical resistivity has a decisive effect on electricity consumption. When highly concentrated brine was used in electrolysis, around 3% NaOH alkaline water was produced. Because of the thermal resistance of reactor in acrylic, the maximum temperature of operating reactor was until 90°C. Current density can be higher in the reactor if brine concentration is higher. The right options for catalyst material selection depend on the designated purpose of the catalyst material.

Keywords: Chlor-alkali process; Concentrated brine; Electrolysis; Diaphragm cell

1. Introduction

Currently, the demand for freshwater is rapidly exceeding the supply because of population growth and global warming. To produce freshwater, many countries are trying to develop desalination processes in attempt to solve the worldwide water shortage. A number of countries have been conducting desalination projects.

According to a previous paper, countries located in the Middle East, which receive little precipitation and have dry climates, have tried to develop desalination technology to overcome the water shortage [1]. The process of seawater reverse osmosis (SWRO) is effective to get the freshwater. However, SWRO system demands to high electricity cost to operate the SWRO process. Nowadays, pressure-retarded osmosis (PRO) is tried to develop in order to decrease the electricity price. PRO process is basically generated power generation by osmotic pressure between seawater and freshwater. Therefore, PRO system is contributed to electricity cost savings for operating an SWRO plant [2,3].

Disposal of concentrated brine currently is only achieved through discharge into oceans or use of evaporation ponds. Discharge into the sea is not good for the environment as the brine can disrupt the circumlittoral ecosystem. According to another study, a desalination plant in Libya has continuously discharged 17,778 ppm of sodium and >30,000 ppm of chloride [2]. Also, many kinds of toxic substances can be present in concentrated brine. According to a previous study, this disposal problem is expected to augment the general growth

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predictions of greater than 200% increase in desalination capacity of the Mediterranean region [4].

Electrolysis is one possible solution to address discharge of concentrated brine because alkaline water can be utilized additional value by mixing with industrial by-product. In association with sodium hydroxide solution, alkali activated slag can be used to make precast pavers [5]. Electrolysis processes are categorized as mercury, diaphragm, or membrane process. Table 1 shows the characteristics of these different electrolysis processes. Ruthenium and iridium electrodes have been generally important for water treatment technology because they are corrosion-resistant and produce a low over-potential for manufacturing chlorine gas [6].

According to Table 1, low purity NaOH and chlorine gas are produced in the operation of diaphragm type electrolysis. However, it is effective to defect blockage filter and economic cost. Thus, our study chose the diaphragm type electrolysis process for analysis. Platinum, ruthenium, and iridium are the main components used to perform electrolysis or the manufacture of alkaline solution. The dimensionally stable anode (DSA) was the early material used for the anodes of the diaphragm cells. However, the cost of electricity must be considered when using magnetite, and graphite became the primary anode material starting in the 1970s [9]. Therefore, DSA electrodes which are made of ruthenium and iridium is not only electric efficiency but also economic efficiency. To perform a fundamental analysis, the chemical reaction formulas are used [1,6].

Anode: $2Cl^- \rightarrow Cl_{2(g)} + 2e^-$ (Cl_2 gases are produced at the anode) (1)

Cathode: $2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-$
(H_2 gases are produced at the cathode) (2)

Overall: $2NaCl_{(aq)} = 2NaOH_{(aq)} + H_{2(g)} + Cl_{2(g)}$ (3)

The main purpose of this study is to determine the DSA electrode that produces the best NaOH concentration and electricity consumption (EC).

2. Materials and methods

2.1. Chemicals and materials

To manufacture artificial brine, sodium chloride (NaCl 99.5%, produced by Samchun Company, Republic of Korea), magnesium chloride ($MgCl_2$ 97.0%, produced by Junsei Company, Japan), and sodium sulfate (Na_2SO_4 anhydrous, produced by Millipore Corporation, Germany) were used according to the ASTM D1141 standard. All solutions were prepared using deionized water. To accomplish a precipitation reaction, sodium hydroxide (NaOH 93%, produced by Showa Company, Japan) and sodium carbonate (Na_2CO_3 99.5%, produced by Sigma-Aldrich Company, USA) were used. Porous hydrophilic polytetrafluoroethylene (PTFE) filters were used to measure the head in the diaphragm cell (JMWP09025; 10 μm, thickness: 85 μm produced by Merck Millipore, Germany) [10]. The electrode area in the cell was 23.02 cm^2, and the volume of each cell was 200 mL. A power supply (DCS55-55E, Sorensen) was used (0–55 V, 0–55 A) to measure the EC (W) and current density (mA/cm^2). A peristaltic pump (No. 77200-60, Easy-load II, Cole-Parmer Instrument Co.) and tubing (96410-25, Master flex) were used to adjust the flow rate of artificial brine by connecting with input side.

2.2. Experimental setup

The diaphragm reactor was 5 cm long, 4 cm height, and 10 cm thickness, 1.5 cm of which was made of acrylic. Fig. 1 is

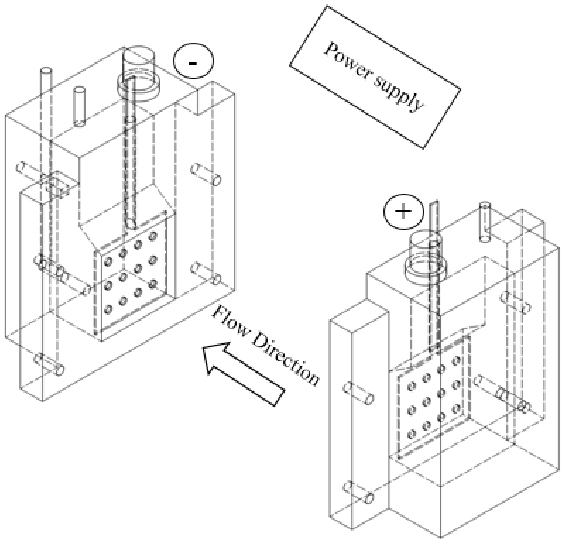

Fig. 1. Schematic diagram of electrolysis based on a diaphragm reactor.

Table 1
Typical characteristics of chlor-alkali electrolysis processes such as mercury, diaphragm, and membrane types [7,8]

	Mercury	Diaphragm	Membrane
Advantages	• High purity NaOH • High purity Cl_2 and H_2 gases	• Low quality requirements of brine • Low electric consumption	• No use of asbestos or mercury • High purity NaOH
Disadvantages	• Costly environmental protection • Expensive cell operation	• Low purity NaOH • Low chlorine quality	• High purity brine required • High cost of membrane
NaOH concentration	50 wt%	10–12 wt%	30–35 wt%
Environmental problem	Mercury discharge	Asbestos problem	None
Brine pretreatment method	Simple	Simple	Complex

a schematic diagram of the reactor. Acrylic material was used to create the reactor, and the vent line was tightly sealed to prevent gas leakage and reactor blockage [1].

A PTFE filter was installed in the center of the cell, and the gap diameter of the electrode was 1 cm. The inlet water flowed toward the anode, where it was drained off so that the pores of the filter were not clogged. DSA electrode was 48 mm long, 48 mm height, and contained 12 holes in order to create a larger cross-sectional area (Wesco Electrode Company, Republic of Korea). Titanium plate electrodes coated with 3 μm RuO_2 and IrO_2 were used in each cell. Finally, the electrolytic cell was made of a parallelepiped acrylic resin to observe head change. Therefore, a differential head was produced between the anode and cathode. Before starting electrolysis, the artificial brine was moved toward the diaphragm cell [1].

2.3. Analytical methods

The method was performed as in a previous paper [1]. To measure the hydroxide ion concentration in the sample, the solution was titrated with diluted 0.1% hydrochloric acid (HCl 35.0%, produced by Junsei) using phenolphthalein. To analyze chloride, total chlorine, and hardness, a spectrophotometer (HACH model DR-2800) was used with the electrolyzed solution. The electrical conductivity was measured using an Orion 013010MD conductivity meter (Thermo Scientific, USA). The current efficiency was calculated using the equation shown below, which is based on Faraday's law.

$$\text{Current efficiency } (I_E) = \frac{\left(C_{\text{in}} - C_{\text{out}}\right) \times z \times V \times F}{t \times M} \tag{4}$$

where C_{in} and C_{out} are the input and output concentrations (mg/L), respectively, z is the valence number of the ion, V is the volume of the reactor (L), and t is the operation time of the reactor (min). F is Faraday's constant (96,485 C/mol), I_E is the current efficiency, and M is the molar mass (g/mol) [1].

3. Results and discussion

3.1. Performance changes according to concentration degree

Fig. 2 shows that NaOH concentration is influenced by Cl^- removal. The maximum NaOH concentration was 1.6%, 2.3%, and 2.8% for the raw, triple, and quintuple degrees of brine concentration, respectively. Electrical conductivity continuously increased until 40 min and was stable thereafter. NaOH concentration was directly proportional to electric conductivity. Because of generated chlorine gas at the anode cell, sodium ions can be combined with hydroxide ions to produce highly concentrated alkaline solution. In other words, production of hydroxide has an effect on the electrical conductivity.

Fig. 3 shows the temperature of the reactor and current efficiency (CE) at different times. The maximum temperature of the reactors was 88°C, 57°C, and 49°C when using

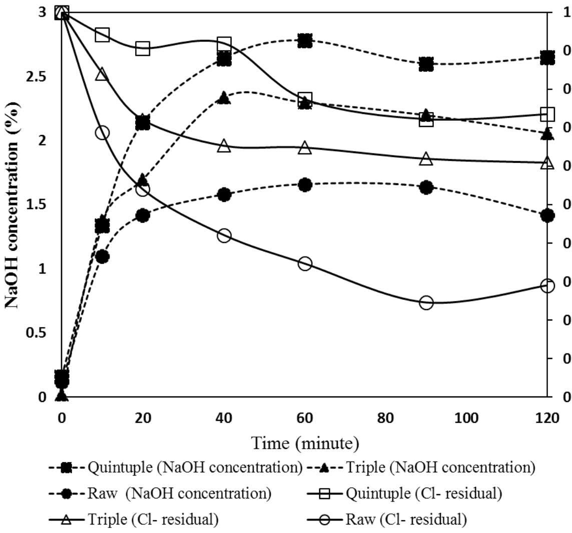

Fig. 2. Changes in NaOH concentration and Cl^- removal according to time.

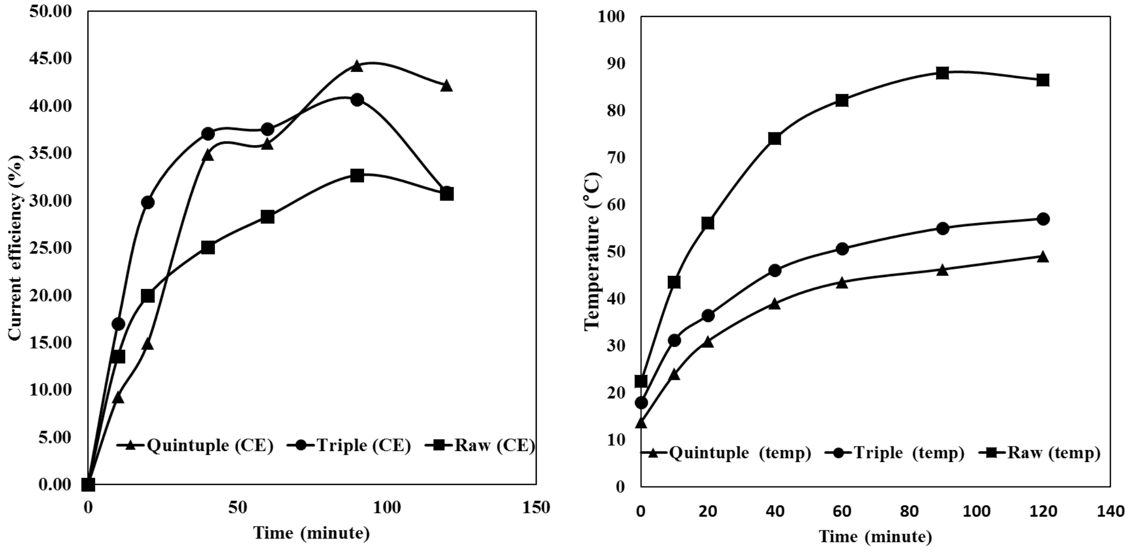

Fig. 3. Changes in temperature on the reactor and current efficiency according to time.

raw, triple, and quadruple degrees of brine concentration, respectively, and the maximum CE was 32.7%, 40.7%, and 44.2%. CE was inversely proportional to temperature. These tendencies were caused by the different resistances of the brine. Resistance was lower with higher brine concentration because of the increased quantity of ions.

3.2. NaOH concentration change according to electrode material

Fig. 4 demonstrates the relationship between EC and NaOH concentration. EC is generally related to current density [11]. According to the paper, generation NaOH concentration and chlorine gas is related with rate determining step. It means because of the rate determining step is different from each other; the mechanism of chlorine occurrence quantities can be different by the differential materials [12,13].

Fig. 5 presents EC based on changes in chloride removal. The maximum chloride removal in the reactors was 38%, 18%, 32%, and 28%, respectively, for Ir/Ir, Ru/Ti, Ru/Ru, and Ir/Ti. According to a previous paper, the IrO_2 electrode has higher efficiency than the RuO_2 electrode with regard to chlorine evolution based on the measurement of total active chlorine concentration after electrolysis of chloride solutions [6]. The IrO_2/Ti electrode is the best catalyst with regard to EC, as shown in Table 2. One of the reasons why electrical resistivity has a decisive effect on EC is that iridium has a lower electrical resistivity than ruthenium (ruthenium: 71 nΩ·m, iridium: 47.1 nΩ·m at 0°C). Resistivity indicates titanium has the lowest electrical conductivity among these three materials, so electrodes that did not include ruthenium or iridium did not show good chloride removal or electrical efficiency.

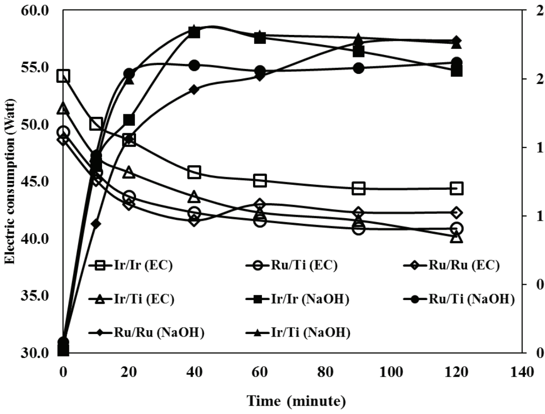

Fig. 4. Performance changes in electricity consumption (EC) and NaOH concentration with time (Ir: IrO_2-coated titanium, Ru: RuO_2-coated titanium, and Ti: uncoated titanium).

3.3. Economic analysis of concentrated brine electrolysis

To perform an economic evaluation, the following equation was used [14]:

$$\mathrm{Ig} = \mathrm{Cr} + \mathrm{Ir} + T + E \tag{5}$$

where Cr is the capital repayment; Ir is the return on investment; and *E* is the expenses.

$$\mathrm{T}\left(\text{tax payment}\right) = \frac{t}{1-t}[C_r - D_t + I_r(1 - \frac{i_D r_D}{i}) \tag{6}$$

where t is the tax rate and D_t is the depreciation for tax purposes.

Table 2 presents data on the cost of electrolysis according to diaphragm type. The prices in the chart were calculated when purchased wholesale which are consist of more than 10 pieces of DSA electrodes and 20 reactors. The reason why 2.55 g/L of sodium carbonate was included by the concentrated brine was that we have considered with molar ratio by conducting precipitation process. The decision of sodium carbonate quantity was for multiple brines. The diaphragm prices were estimated from the Omnipore website. Because this study recycled material from the alkaline tank to the sedimentation tank to aid in the settling of sedimentation through the sodium hydroxide ions present in the alkaline water, NaOH solution did not need to be added. Finally,

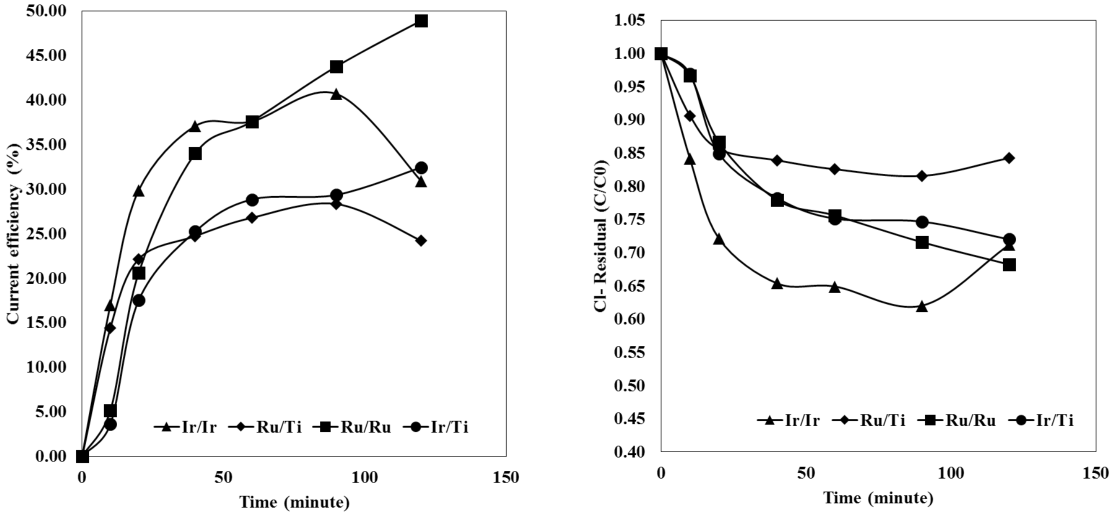

Fig. 5. Changes in chloride removal and CE by electrode material.

Table 2
The cost of electrolysis by diaphragm type

Capital investment costs (except power supply)				
Diaphragm	DSA electrode	Reactor	Supplement and installation fee (10%)	Total
11,300 KRW	60,000 KRW	60,000 KRW	15,000 KRW	146,300 KRW
Operating cost (for 1 year of 24 h operation)				
Electricity (a)		–52,560 KRW	(0.06/cell + 0.02/pump) kW × 24 h × 75 KRW/kWh^{a} × 365	
Coagulant (b)		–3,290 KRW	2.55 g/L × 6.6 L × 540 KRW/kg^{b}/1,000/0.99 × 365	
Concentrated brine		Free		
NaOH (c)		64,020 KRW	0.0084 kg × 24 h × 870 KRW/kg^{c} × 365	
Total		8,190 KRW	(c) – {(a) + (b)}	

Note: Site fee, power supply, and personnel expenses are excluded from the chart.
[a] The average price of Korea Electric Power (average of industrial service, A type).
[b] 99% sodium carbonate, Korea Price Research Center (June, 2015).
[c] Industrial caustic soda (98%), Korea Price Research Center (June, 2016).

the prices of the electrode materials were estimated based on the use of iridium oxide-coated titanium for the anode cell and uncoated titanium for the cathode cell.

4. Conclusion

The experimental results with regard to the best method according to electrode type are as follows:

- EC: $IrO_2/IrO_2 > RuO_2/RuO_2 > IrO_2/Ti > RuO_2/Ti$.
- NaOH concentration: $RuO_2/RuO_2 > IrO_2/Ti > RuO_2/Ti > IrO_2/IrO_2$.
- Chloride removal: $IrO_2/IrO_2 > RuO_2/RuO_2 > IrO_2/Ti > RuO_2/Ti$.

If DSA price and EC are considered, the IrO_2/Ti electrode should be chosen. On the other hand, RuO_2/RuO_2 should be chosen if prioritizing chloride removal and reactor stability. When the electrode is coated with ruthenium or iridium, the production cost was doubled compared with the uncoated titanium electrode. Otherwise, ruthenium is better to choose for electrolysis if the prices of ruthenium and iridium are considered. Iridium is approximately 20 times as expensive as ruthenium. To confirm a stable performance of NaOH concentration, twice hydraulic retention time (2 HRT) has to be maintained the volume of the reactor. Therefore, the present experiment was conducted for at least 100 min because the volume of the reactor was 200 mL. When highly concentrated brine was used in electrolysis, around 3% NaOH alkaline water could be produced. Because of the thermal resistance of reactor in acrylic, the maximum temperature of operating reactor was until 90°C. As a result, current density can be higher in the reactor if the brine concentration is higher. The options for catalyst material selection depend on the designated purpose of the catalyst material.

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