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Effects of Operating Conditions on Improving Alkali and Electrical Efficiency in Chlor-Alkali Diaphragm Cell

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The concentrated brine from seawater desalination plants is generally discharged directly to the sea. To reuse brine, diaphragm type chlor-alkali experiments were carried out to make alkaline solution and gases. For this purpose, a rectangular acrylic reactor, 66.5 g/L of sodium chloride solution, a PTFE hydrophilic filter as asbestos free diaphragm, and IrO_2 coated titanium net or plate electrode were used. The experimental results show that sodium hydroxide concentration and chloride removal increased with higher current density, and had inverse linear correlations to the increasing flow rate. The theoretical maximum sodium hydroxide concentration in effluent was estimated as 4.06%. Chloride removal and electric conductivity have a linear correlation with the sodium hydroxide concentration in effluent. Hydroxyl ion production was affected by the surface area of electrode per unit volume and by diaphragm pore size. Back-migration of hydroxyl ions from the cathode to anode is the major reason for side-reactions that cause low faradaic efficiency, including oxygen production in the anode compartment. Over 99% pure hydrogen was produced in the cathode compartment, and the current efficiency of hydrogen production was calculated as 92 - 99%.

Keywords: Chlor-alkali, diaphragm cell, electrolysis, sodium hydroxide, synthetic brine

1. INTRODUCTION

Seawater desalination is one effective way to solve the worldwide water shortage. Many countries depend on seawater desalination technology to overcome natural fresh water shortages [1]. Acute water shortages have stimulated the investigation and application of various approaches to seawater desalination. The market for seawater desalination technology grows rapidly and is expected to double to the multibillions in the next few decades [2]. However, concentrated brine is produced during desalination processes. For coastal desalination plants, the most practical, easiest, and cheapest method of brine disposal is to discharge it into the sea. Other brine disposal methods may significantly add to the cost of the desalination process. However, brine disposed of in the sea likely has detrimental effects on the marine and benthic environment [3, 4].

This study applied an electrochemical method called the chlor-alkali process to reuse brine by producing alkaline effluent and gases. The chlor-alkali technique is applied via three methods involving mercury, diaphragm, or membrane. Among these techniques, the diaphragm method produces a more dilute and slightly impure alkali solution compared to other methods but it does some advantages. The diaphragm method operates at lower voltage than mercury cells, is free from mercury discharge problems, and requires less pure brine than membrane cells that reducing the burden of brine pre-treatment. Based on these advantages, the diaphragm process is used in 41% of cases worldwide. It has been the dominant process since the 1970s in the U.S., and in Brazil it accounts for 72% of chlor-alkali technique [5, 6]. The reactions that generally occur in the chlor-alkali process are shown below.

(At the anode)

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{(side reaction)} \quad (2)$$

(At the cathode)

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

Once the diaphragm itself is not a fully effective separator, it is subject to back-migration or transportation of hydroxyl ions from the cathode to the anode compartment [7]. Back-migration decreases system efficiency due to secondary reactions. Hypochlorite ion and hypochlorous acid are rapidly formed by hydrolysis due to an acid-base equilibrium.

(At the bulk solution)

$$Cl_2 + OH^- \Leftrightarrow HOCl + Cl^- \quad (4)$$

$$HClO \Leftrightarrow ClO^- + H^+ \quad (5)$$

The following chemical and electrochemical reactions describe the unwanted formation of chlorate and oxygen as side reaction [8, 9].

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O \quad \text{(with heat)} \quad (6)$$

$$Cl^- + 3H_2O \rightarrow ClO_3^- + 6H^+ + 6e^- \quad \text{(direct oxidation at the anode)} \quad (7)$$

$$2HClO + ClO^- \Leftrightarrow ClO_3^- + 2H^+ + 2Cl^- \quad \text{(slow chemical reaction)} \quad (8)$$

$$6ClO^- + 3H_2O \rightarrow 4Cl^- + 6H^+ + 1.5O_2 + 6e^- + 2ClO_3^- \quad (9)$$

Chlorine is formed in the anode reaction and is subsequently used for industrial purposes or water disinfection. Hydrogen is produced in the cathode reaction. Though the alkaline effluent produced in the cathode compartment generally has a harmful effect on water, it is a potential material as alkali activator that can be used to make geopolymers in further research. For successful application of an alkali activator, at least several percent of hydroxyl ion is needed in solution.

The main purpose of this study was to evaluate which operating factors affect cell performance and electrical efficiency in the chlor-alkali diaphragm cell using continuous experiments. Synthetic brine, which has a relatively low concentration, was used to compare with the general chlor-alkali researches. Current density, flow rate, electrode and diaphragm parameters were experimentally studied in a lab scale experiment. The hydrophilic PTFE filter was used to prevent asbestos release to environment, a potential problem with diaphragm cells. The gases produced are also discussed in this paper.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

To create the synthetic membrane distillation brine, 66.5 grams of sodium chloride (guaranteed reagent, Junsei, Japan) was used per liter, because the concentration of brine is usually double or close to double that of natural seawater [4]. A divided symmetric filter-press type of electrolytic cell was made by a rectangular parallelepiped acrylic resin, and effective total cell volume was 180 to 450 mL. A power supply (DCS55-55E, Ametek, USA) was used to apply constant currents to the electrolytic cell and measure cell voltages at the same time. Netting or plate shaped titanium electrodes coated with 3 μm of IrO_2 (Wookyoung Electrolysis System, Korea) were used as electrodes (surface area: 20.8 and 47 cm^2, respectively), and the gap between the electrode and diaphragm was 5 mm. Two different porosity hydrophilic PTFE (polytetrafluoroethylene) filters (pore sizes: 5 and 10 μm, thickness: 85 μm, Merck Millipore, Germany) were used as a non-asbestos diaphragm to separate the electrolytic compartments. A small porous hydrophilic filter helps brine flow from the anode to the cathode compartment without mixing. A peristaltic pump (Easy-load® II, Cole-Parmer) and silicon tubing (Masterflex®, Cole-Parmer) were used to feed the brine solution uniformly. To collect and analyze gases produced at each compartment, 10 L of tedlar bag (CEL Scientific, USA) was used. To prevent safety accidents caused by chlorine leakage, all experiments were carried out in a fume hood and a movable air purifier (TOGA-M01, GTSciEN, Korea) was used. All aqueous solutions were prepared using deionized water, and the experiment was conducted at room temperature.

2.2. Experimental procedures and analytical methods

The diaphragm and electrodes were installed symmetrically in the middle of the electrolytic cell. Brine was continuously fed to the anode compartment at constant volumetric flow and percolated through the diaphragm to the cathode compartment due to the force of the hydraulic head. During cell operation, hydroxyl ions were produced and chloride was gradually depleted. To prevent unwanted gas mixing between hydrogen and chlorine, the diaphragm was always maintained under the solution surface. Without a diaphragm, the hydrogen and chlorine would spontaneously ignite. The hydroxyl ion and chlorine would react to form sodium hypochlorite with further reaction to produce sodium chlorate. Electrolyzed brine was obtained at the end of the cathode compartment, and the gases were obtained from the tedlar bag at each compartment. Silicon pads were used at every connecting part to prevent gas leakage.

To analyze the sodium hydroxide produced in electrolyzed brine, titration was carried out immediately after a sample was obtained using 0.1% of hydrochloric acid and phenolphthalein solution. A spectrophotometer (DR-2800, HACH) was used to analyze chloride ion and free chlorine (hypochlorous acid plus hypochlorite ion), and a conductometer (Orion 013010MD, Thermo Scientific) was used to measure the electric conductivity of electrolyzed brine. The chlorine, oxygen, hydrogen, and chlorine dioxide content of collected gas was measured using gas detection tubes (Gastech, Japan). The temperature inside the reactor was monitored by glass thermometers.

Two types of current efficiency were calculated based on Faraday's law of electrolysis and hydrogen production at the cathode compartment. The equations used to calculate current efficiencies are as follows.

Current efficiency based on chloride removal

$$= \frac{\left(Cl^{-}_{in} - Cl^{-}_{out}\right) \times z \times Q \times F}{M \times I \times 60 \times 1000} \times 100 \ \textbf{(\%)} \tag{10}$$

Where Cl^{-}_{in} and Cl^{-}_{out} are the input and output concentrations of chloride ion (mg/L), z is the valency number of ions in the substance, Q is flow rate (L/min), F = 96,485 (C/mol) is the Faraday constant, M is the molar mass of the substance (g/mol), and I is the actual current applied at the electrolytic cell (ampere, C/sec).

Current efficiency based on hydrogen production at the cathode compartment

$$= \frac{V_{produced}}{V_m} \times \frac{T_0}{T} \times \frac{2N_A}{C \times I \times 3600} \times 100 \ \textbf{(\%)} \tag{11}$$

Where $V_{produced}$ is gas volume produced from the cathode compartment (L/hr), V_m = 22.414 (L/mol) is the molar volume of a gas at standard temperature and pressure, T_o = 273 (K) is standard temperature, T is room temperature (K), $N_A = 6.022 \times 10^{23}$ (1/mol) is the Avogadro constant, C is Coulomb, which is equal to the charge of approximately proton number of electrons (6.241×10^{18} /C), and I is the actual current applied at the electrolytic cell (ampere, C/sec). Laboratory pressure was assumed to be standard pressure (1 atm).

3. RESULTS AND DISCUSSION

3.1. Effectiveness of current density and flow rate to sodium hydroxide concentration in effluent

As the current density increased, sodium hydroxide production increased and chloride ion decreased accordingly. Figure 1A shows variation of sodium hydroxide concentration in effluent and chloride removal at different current densities from 100 to 200 mA/cm^2. The maximum sodium hydroxide concentrations were 1.49%, 1.76%, and 1.85% while chloride removal was 29%, 36%, and 51% with 100, 150, and 200 mA/cm^2 current density, respectively. Less increased sodium hydroxide concentration in higher current density is likely due to increasing diffusion from the cathode to the anode. However, chloride ions ware removed more in higher current density.

Figure 1B represents a correlation between sodium hydroxide concentration in effluent and flow rates. The sodium hydroxide concentration in effluent was inversely correlated to increasing flow rate. In higher flow rates, hydrogen ions in the anode compartment migrate to the cathode compartment more quickly and then neutralize hydroxyl ions in the cathode [10]. In terms of temperature control, flow rate is a main factor in the chlor-alkali process. In low flow rates, the heat caused by electric currents through the diaphragm and electrolyte raises cell temperature. If the temperature rises to 95 - 100 degrees Celsius, electrolysis will be unstable because water boils leading to low performance efficiency. Considering the production of effluent as alkali solution, the optimal hydraulic retention time is 10~20 minutes at each compartment.

The calculated current efficiencies based on chloride removal were 62.7%, 48.7%, and 56.7% with 100, 150, and 200 mA/cm^2 current density, respectively. Current efficiency was generally better than in lower current density secondary to increased loss of hydroxyl ions from the cathode compartment due to migration through the diaphragm [11].

3.2. Variation of sodium hydroxide concentration in effluent according to chloride removal and electric conductivity

Chloride ion was converted to chlorine, hypochlorous acid, and hypochlorite ion during electrolysis. Chloride ion showed a linear relationship with sodium hydroxide concentration in effluent within a range of 0-70% chloride removal. Figure 2 shows the electric conductivity and the linear correlation between sodium hydroxide concentration in effluent and chloride removal. From figure 2A, the theoretical maximum sodium hydroxide concentration in effluent was estimated as 4.06% if all chloride ions are removed. The slope will be changed according to the initial brine concentration. This means that the alkali concentration that can be produced is changed depending on the intensity of electrolyte. Figure 2B also shows linearly proportional tendencies between sodium hydroxide concentration and electric conductivity. This is because hydroxyl ions produced by electrolysis in the cathode compartment have higher ionic conductance than other ions, such as sodium or chloride. In this respect case, electric conductivity can be used as an alkali indicator for the chlor-alkali process in unchangeable influent brine conditions.

3.3. Effectiveness of electrode and diaphragm related to sodium hydroxide concentration in effluent

Figure 3 shows the sodium hydroxide concentration in effluent and chloride removal according to electrode and diaphragm conditions. The electrode surface can directly affect the kinetics of electrolysis. Thus, the cell performance of different net- and plate-shaped Ti/IrO$_2$ paired electrodes was evaluated.

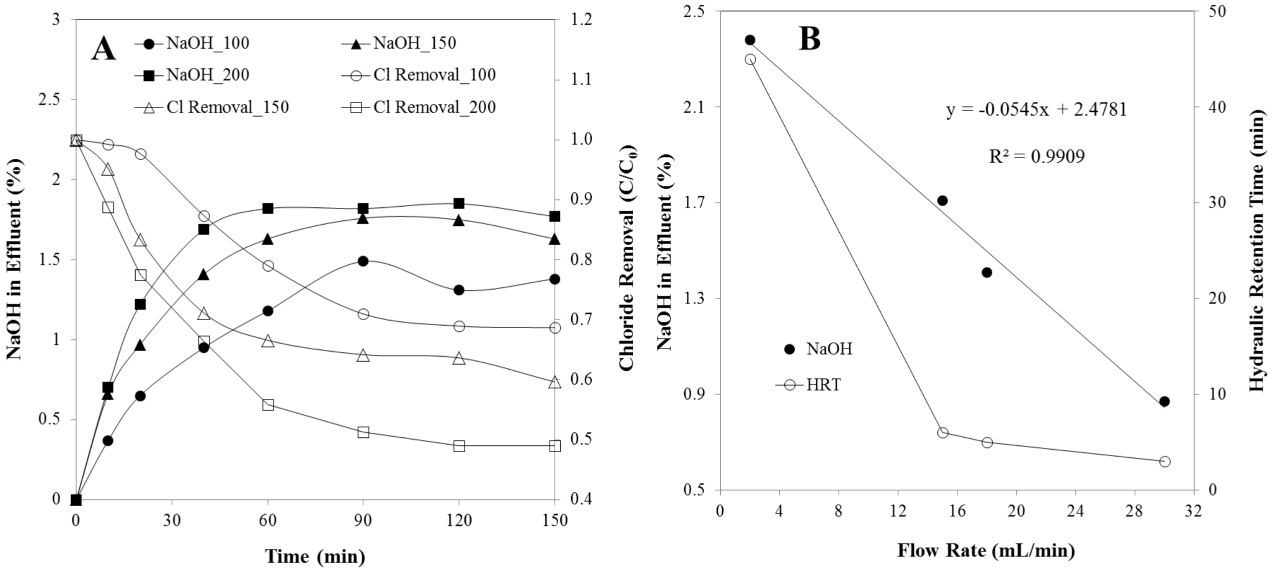

Figure 1. Variation of sodium hydroxide concentration in effluent (%) and chloride removal (C/C_0) at different current densities of 100, 150, and 200 mA/cm^2 and 45 minutes of hydraulic retention time with net type electrode (A). Correlation between sodium hydroxide concentration in effluent (%) at different flow rates from 2 to 30 mL/min, which can be converted 45 to 3 minutes of hydraulic retention time at each compartment, and 150 mA/cm^2 of current density with plate type electrode (B).

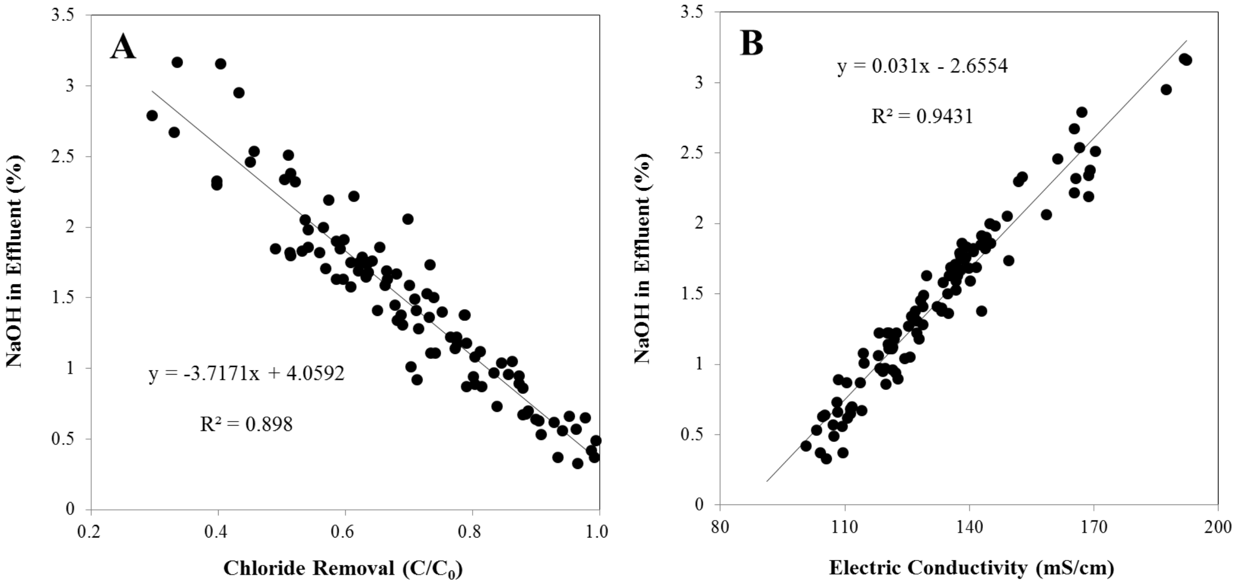

Figure 2. Correlation between variation of sodium hydroxide concentration in effluent (%) and chloride removal (C/C_0)(A), and sodium hydroxide concentration in effluent (%) and electric conductivity (mS/cm) during the entire experiment (B).

The plate-shaped electrode was 2.2 times larger than the net-shaped electrode. As figure 3A shows, the maximum sodium hydroxide concentration in effluent was 3.2% and chloride removal was 70% with the plate-shaped electrode. However, the maximum sodium hydroxide concentration in effluent was 1.5%, while chloride removal was 29% with the net-shaped electrode condition. With those conditions, current efficiencies based on chloride removal were calculated 62.7% and 22.6%, respectively.

Results indicate that a larger electrode surface area per unit volume is better for the production of hydroxyl ions with the same current density. However, current efficiency drops off due to high current consumption.

Figure 3B confirms increased sodium hydroxide concentration in the effluent and chloride removal though the diaphragm pores were smaller. A smaller diaphragm pore size is expected to reduce back-migration of hydroxyl ions from the cathode compartment. Through this feature, it is postulated that hydroxyl ions in the effluent will increase. However, prior to the selection of smaller diaphragm pore size, expected hydraulic head and percolation rate should be considered to operate cell appropriately or not.

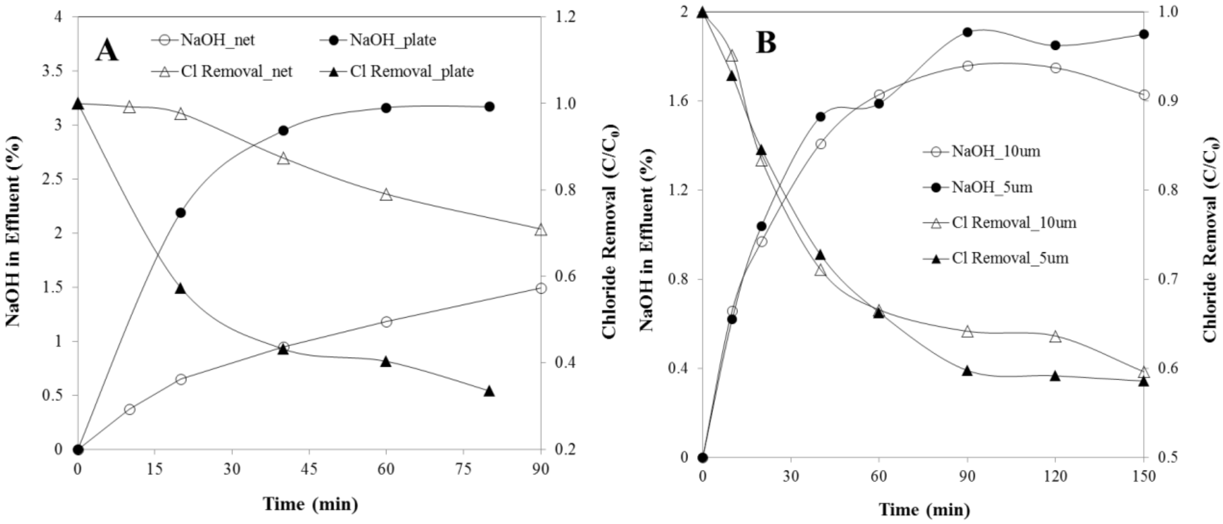

Figure 3. Variation of sodium hydroxide concentration in effluent (%) and chloride removal (C/C_0) at different electrode conditions of net-type and plate-type with 100 mA/cm^2 current density (A). Different diaphragm pore conditions of 10 μm and 5 μm with 150 mA/cm^2 current density (B). Hydraulic retention time was 45 minutes at each compartment in all experiments.

3.4. Production of secondary compound and gas

Chloride ions in the brine are converted to various chlorine compounds during electrolysis and hydrolysis (Equations. 4-9). In this study, it is postulated that most chlorine compounds in effluent are hypochlorite ion because the end product is strongly alkaline electrolyzed water. Furthermore, there is no organic material in the synthetic brine. As current density increases, hypochlorite production also increases due to rising temperature.

Figure 4 shows the linear correlation between temperature and hypochlorite ion identified in this study. The presence of chlorate in the effluent is expected due to high cell temperature. With high temperature, hypochlorite tends to chemically decompose to chlorate, as shown in the following equation [6].

$3ClO^- \rightarrow ClO_3^- + 2Cl^-$ (12)

According to this side-reaction, both higher temperature and hypochlorite concentration promote chlorate production and may cause low faradaic efficiency by chloride reproducing. Thus low operating temperatures close to room temperature are helpful in avoiding the generation of secondary compounds such as chlorates [12].

In the chlor-alkali process, chlorine and hydrogen gas production in the anode and cathode compartments are generally proportionate to the current applied. Oxygen production is thermodynamically favored over chlorine [13]. To prevent oxygen production, IrO_2 covered titanium was used as one of the chlorine production anodes [14, 15]. Indeed, chlorine was seldom produced when another anode such as platinum was used. Although an iridium coated titanium electrode was used, there was maximum 40% oxygen in the produced chlorine gas. Back-migration of hydroxyl ions from the cathode compartment is one major reason for oxygen production in the anode compartment. If pH rises due to back-migration of hydroxyl ions, thermodynamic oxygen production is favoured at the anode compartment through electrolytic decomposition of water and chlorine disproportionation to hypochlorous acid [16]. Once chlorine is converted to hypochlorous acid, it may decompose to form oxygen in a chemical reaction of the bulk solution.

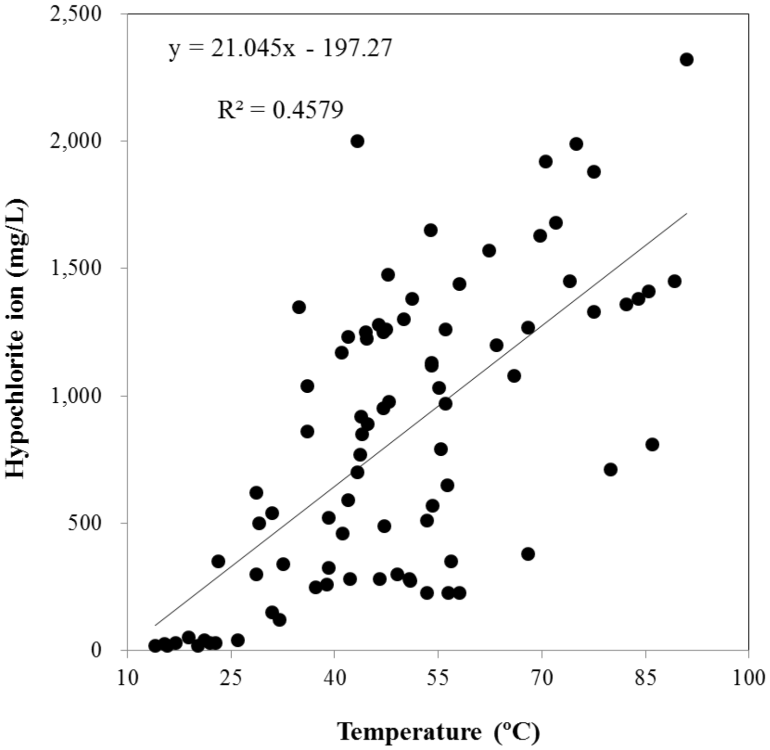

Figure 4. Correlation between chlorine compounds in effluent (mg/L) and cell temperature (°C) during the entire experiment.

$2HClO \rightarrow O_2 + 2HCl$ (13)

$2ClO^- \rightarrow O_2 + 2Cl^-$ (in higher pH at hydroxyl front-acid interface) (14)

However, over 99% pure hydrogen was produced in the cathode compartment and the current efficiency of hydrogen production was calculated as 92 - 99%. The results demonstrate that most generated electrons generated in the anode were used to produce hydrogen gas in the cathode.

4. CONCLUSIONS

Synthetic brine was electrolyzed in a diaphragm chlor-alkali process in this study. Experimental results show that the chloride was gradually removed from brine and then sodium hydroxide was produced in the effluent. In higher current density, hydroxyl ion diffusion increased from the cathode to the anode. The sodium hydroxide concentration in the effluent and the flow rate had an inverse linear correlation because of hydrogen ion migration from the anode compartment. Chloride removal and electric conductivity have a linear correlation with sodium hydroxide concentration in the effluent. The electrode surface area per unit volume and diaphragm pore size also affected hydroxyl ion concentration. Side-reactions related to hypochlorite and chlorate production may result in low faradaic efficiency. Back-migration of hydroxyl ions from the cathode to the anode is a major reason for oxygen production in the anode compartment. Precipitation of magnesium and calcium hydroxides on the cathode side of the diaphragm may cause blocking problems since real brine has a high concentration of hardness. Thus, brine pre-treatment is required when using real brine for long-term operations, especially in a diaphragm process.

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