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양이온교환막 전해조의 최적화 연구

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The optimization of an ion exchange membrane cell

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Introduction

In recent years the electrolytic production of chlorine, caustic soda and hydrogen has been shifted from diaphragm process or mercury process to the cation exchange membrane process due to many benefits.

In a chlor-alkali process, there is a trade-off between operating and fixed capital costs. The rate at which a cell produces chlor-alkali products can be increased by increasing the rate at which electrical energy is applied to the cell. The cell size needs to be determined to produce a fixed quantity of products. This means that the size depends on the applied electrical energy. Reducing the cell size(fixed capital investment) causes the increasing power requirements(operating cost).

Chlor-alkali processes are operated under various conditions due to changes such as the electric cost, low or high current density and power interruption. The major goal is to produce the desired amount of the product at the lowest power consumption and to operate for the longest possible period without the replacement of membrane, gasket or electrode.

The optimization problems in electrolytic process are classified into three categories.

1. At design stage, the optimization problem is to find the optimal size to maximize the profit.
2. At operation stage, the optimization problem is to find the optimal operating condition under fixed capacity.
3. Another optimization problem is to find the optimal replacement time of membrane, anode and cathode.

There have been few studies on an electrochemical cell including chlor-alkali cell in the literature. The present work attempts to optimize the electrolytic cell of ion exchange membrane cell for the production of chlorine and caustic soda. An accurate model can predict the performance for most parameters. Studies can be performed to determine when to replace cell components.

Chlor-alkali cell modelling [1,2,3,4]

The general type of the cell is the filter-press type. The cell model is based on the concept of CSTR(a continuous stirred tank reactor). Models of electrolytic cells generally include non-linear algebraic equations.

Material Balanoe

The main reactions in the chlor-alkali cell are :

$2\ NaCl \rightarrow 2Na^+ + Cl^- + 2e$ (at anode) and $2\ H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (at cathode)

At steady state, the material balance on a CSTR gives

$J_i = J_i'' - J_i'$, where J is the rate of production of species i(mole/time) in the CSTR and superscript ′ and ″ mean the outlet and inlet molar flowrate of species j, respectively. The material balance is set up for the production of chlorine, oxygen, hydrogen, vaporized water, sodium ion and water molecules across the membrane.

Energy Balance

Heat requirement during the cell operation is:

$q = \Delta H + \frac{E \cdot I\ 3600}{4.18}$, where q is the rate of heat flow into the cell, E is the cell voltage and ΔH is the enthalpy difference between inlet and outlet streams.

Voltage Balance

Cell voltage is taken into account the overpotential of anode and cathode, the concentration polarization, the ohmic resistances of electrolyte with bubble effects from cell geometry and membrane. The cell voltage for operating conditions is :

$E = E_o + \eta_a - \eta_c - (IR)_a - (IR)_c - (IR)_m$, where E_o is the decomposition voltage. E_o is expressed by the Nernst equation. η_a is the anodic overpotential of low oxygen anode(DSA type), oxygen anode, η_c is the cathodic overpotential on activated cathode in concentrated caustic soda solution, $(IR)_a$ is the voltage drop in the solution of anolyte between membrane and electrode, $(IR)_c$ is the voltage drop in the solution of catholyte between membrane and electrode, $(IR)_m$ is the voltage drop of membrane.

Experiments[5,6,7]

Ti coated with Ru-Ti-Ir mixture was used as the low oxygen anode. Ni coated with Ni-Ru mixture was used as the activated cathode. Each electrode was made by the thermal decomposition of precious metal salts. The overpotential of anode , cathode and used electrode are measured by Potentiostat. Fig.1 shows the cylindrical laboratory cell for testing the performance of the cell component. Fig.2 shows the commercial cell to test the performance of the cell, and measure the void fraction. Saturated brine(300 g NaCl/ℓ) and demineralized water were fed into a cell by pumps. The brine was made of vacuum from Akzo company and was purified only by a chelate resin(CR-10). Electrolysis condition is as follows: Temperature 85℃, Current density varied, Depleted brine concentration 210 NaCl gr/ℓ, Caustic soda condition 33% NaOH.

Results and discussion

A lab scale cell is used for testing the performance of the membrane under the varied conditions and the variation of cell voltage with time using low oxygen anode and activated cathode. Commercial cells have maximum void fraction above 0.1 of dimensionless height. It is possible to consider average void fraction as maximum void fraction. Above these data are input to cell modeling.

Fig.3 shows the performance of the cell model to predict the performance of the cells with large size and lab scale size cell. The line shows the predicted values and points the experimental values. Predicted values show a good fit with experimental data in both cases : lab electrolyzer and commercial electrolyzer. The difference between the cell voltage values of the lab scale cell and the commercial cell is derived from the bubble dynamics.

As operating time elapses, the voltage across the membrane changes. Fig.4 shows the changes of the cell voltage with time. Current efficiency is also an important factor affecting the power consumption. Fig.4 shows the current efficiency of the production of caustic soda and the decrease of the current efficiency as the operating time elapses.

The optimization problem was solved by using the program GMS. Initial guesses represent the starting point for searching the optimum. Many starting points were tried and several local maxima were found. The best has the lowest total annual cost.

Problems P_1 and P_2 have been run to analyze the effect on the total annual cost. Fig. 5 shows current density effects on the total annual costs. Current density is the primary optimization variable. Fig. 6 shows the optimal current density for the different values of the membrane cost and the electric cost while holding the other operating variables constant.

Problem P_3 is to find the optimal replacement time of the membrane, anode and cathode. To analyze the performance changes of the membrane, the historical operating data such as shown in Fig.4 are necessary. From the operating data, the decline rate of current efficiency and increasing rate of membrane voltage drop, anode potential and cathode potential are the inputs to problem 3.

If the membrane cost and the electric cost are changed, the optimal replacement time is changed as shown in Fig.7.

Acknowledgement

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Literature cited

[1] J.H. Austin and M. Esayian, Paper Presented at the 165th Meetings of the Electrochem Soc., Cincinati, Ohio, May, 6-11, 1984

[2] R.R. Chandran and D.T. Chin, 'Reactor anylis of a chlor-alkali membrane cell', Electrochem. Acta. 31, 1, 1986, pp 39-50.

[3] B.V. Tilak, S.R. Fitzerald and C.L.Hoover 'Estimation of current efficiency in ion-exchange membrane chlor-alkali cell', J of Applied Electrochemistry, 18, 1988, pp 699-704.

[4] B.V. Tilak, S.D. Fritts, J of Applied Electrochemistry 122, 1992, pp 675-697.

[5] Dupont materials, 1990

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[7] Sangbong Moon, KP 82100

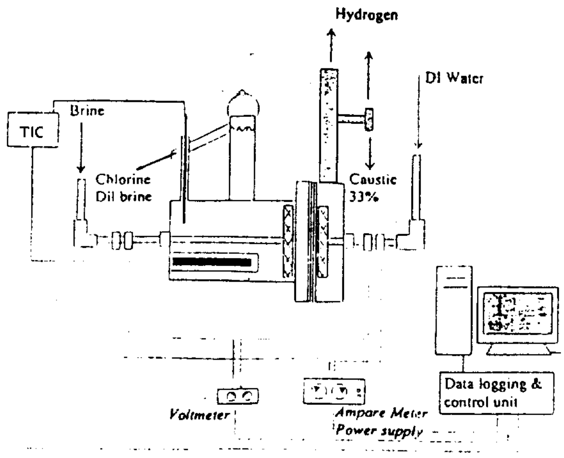


Fig. 1 The cylindrical laboratory cell

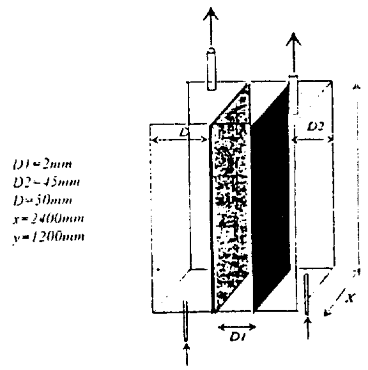
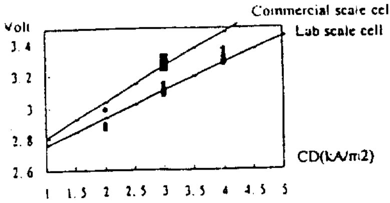


Fig. 2 The commercial cell



Plant X
Active Area: 2.88 m2, Membrane:N90209
Feed Brine:25%,Weak Brine:18%,NaOH %:33%
LCA(Low oxygen anode),Activated Cathode

Fig. 3 The performance of the cell model

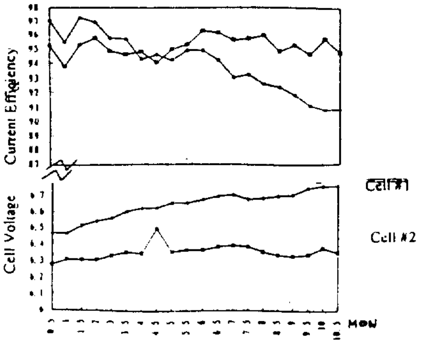


Fig. 4 The changes of the membrane potential and efficiency with time

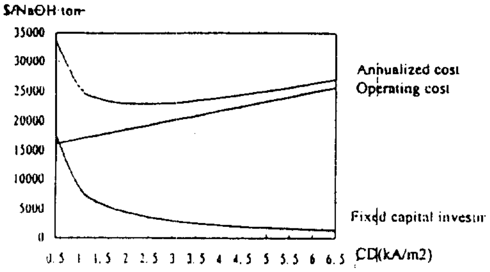


Fig. 5 Current density effects on annualized costs

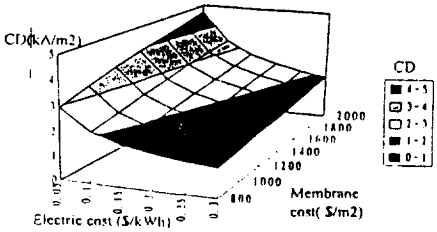


Fig. 6 The optimal current density according to membrane cost and electric cost

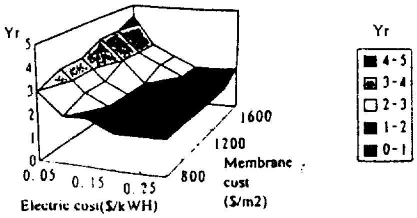


Fig. 7 The optimal replacement time