Operational and Performance Optimisation of an Expanded Area Diaphragm Cell

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Abstract

The basic parameters and relevant design criteria needed for the optimisation of any electrochemical cell operation were identified and applied in this work. Experimental studies, modelling, simulation, analysis of variance (ANOVA) with Bonferroni-Holm Posthoc statistical parametric test and performance characterisation were carried out with a Sliding Cathode Diaphragm Cell (SCDC). An Expanded Area Diaphragm Cell (EADC) was later used to evaluate improved electrolytic cell operating characteristics, performance and productivity optimisation based on inferences from the SCDC operation. The operational voltage, height of anolyte and electrode areas were the parameters carefully varied for the SCDC operation. Well established inferential results from the SCDC with good insight into the production of caustic soda, prompted the theoretical optimization, fabrication and optimum operation of the EADC with output and performance that compared favourably with some industrial cells. With the operation of the EADC at close numerically estimated optimised values, the EADC current efficiency was improved over that of the SCDC to a value of 95%. The outcome of the work could further pave way for the design of more improved electrolytic cell types and/or methodology.

Keywords: ANOVA, Caustic soda, efficiency, electrochemical cell, modelling.

1.0 INTRODUCTION

Electrochemical processing is very complex and results in many different phenomena occurring simultaneously. The ability of an engineer to predict an optimal configuration for a system represents a central goal of science and engineering practice. Even with the most up to date technologies in the caustic soda / chlorine facilities, the cost of electricity alone accounted for about 60% of the variable production cost (Delfrate and Schmitt, 2010). Ohm (2007) pointed out that since energy suppliers' prices cannot be influenced, the better option of reducing energy consumption is by sustainable ways in which one can optimise an electrochemical process.

The productivity of any cell can be increased as the current density is increased, up to a value of current density beyond, which the system seems to be mass transfer limited. This limit could depend on some factors like temperature, fluid velocity, nature of the electrode surfaces and the on-set of unwanted side reactions. Practically, definite optimal values of these parameters must be carefully determined for any electrochemical cell processing. To maximise the performance of electrochemical cells, three basic parameters affecting process economics have been suggested for optimization (Keating and Sutlic, 1979). These include the electrical current efficiency, cell voltage and electrical current density. The electrical current efficiency depends on a large number of factors such as mass transport and kinetics of other competing processes (Selman, 1983). It seems that if overall cell voltage is kept to a minimum, power costs may be reduced significantly for an electrochemical processing facility.

It had been suggested that the electrolytic process industry will be moving steadily toward the use of improved optimisation techniques as tools in process evaluation and process design according to Westerberg (1981). As pointed out by Alkire and Stadtherr (1983), the main value of most optimisation studies is not always in the specific numerical results but, rather in the awareness, which is achieved through subtle interactions within the system. As a result one's intuition is prepared to operate at a higher level of insight. In the formulation of a model for optimisation, it is important first to define the objective of the optimisation study and to anticipate the kind of answers which are to be sought. It is equally relevant to recognize restrictions which might limit the freedom of action of one's attempts for optimization.

As concerted efforts in this field grows, Joudaki *et al*. (2010) and Joudaki *et al*. (2011) have investigated new electrodes and process parameters to overcome some disadvantages to increase efficiency in caustic soda chlor-alkali cells performance evaluation. The effects of various operating parameters on some variables such as cell voltage, current efficiency and so on for some electrochemical cells had been reported separately by Shojaikaveh *et al*. (2009) and Jalali (2009). Energy loss in an electrochemical diaphragm cell process had been studied by Lima *et al*. (2010). Shojaikaveh and Ashrafizadeh (2010) have also worked on the prediction of cell voltage and current efficiency in a laboratory scale chlor-alkali cell. The possibility of producing caustic soda directly from solar powered electrolytic diaphragm cells, with the possibility of designing better cells in future had been reported (Olufemi *et al*., 2012).

Though the philosophy of electrochemical process development is that one should start out with a definite preliminary choice of the cell type and capacity as documented by Selman (1983). It is evident that some processes might have to be re-optimised to new variables and constraints, while other entirely new technologies might emerge as probable solutions.

In this study, a qualitative and quantitative evaluation, experimental investigation, mathematical modelling and optimisation into the characteristic performance of a Sliding Cathode Diaphragm Cell (SCDC) was carried out so as to properly define and attain good controlled electro-hydrodynamic conditions of the cell. The sliding cathode feature of the cell was to permit easy maintenance and cell operation. Operational and performance evaluation of the SCDC was useful in fabricating, operating, evaluating, modelling and optimisation of an Expanded Area Diaphragm Cell (EADC) to exhibit performances comparable to some industrial cells.

2.0 METHODOLOGY

2.1 Operation of the Sliding Cathode Diaphragm Cell (SCDC)

A fabricated Sliding Cathode Diaphragm Cell (SCDC) was used to produce caustic soda, hydrogen and chlorine from 25 wt. % NaCl solution. The basic feature of the SCDC is shown in **Figure 1**. The details of the experimental procedure followed for the SCDC operation had been reported (Olufemi, 2008, Olufemi *et al.,* 2010). Values of d.c. open circuit voltage applied were 11.2, 14.0, 16.8, 19.6 and 22.4 V respectively, designated as V1, V2, V3, V4, and V5 for a run per time. The various anolyte heights used were 0.4, 0.5, 0.6, 0.7 and 0.8 m respectively for a run per time; designated as H1, H2, H3, H4 and H5. A particular voltage was used in conjunction with a particular anolyte height and with a particular electrodes area for a run, while monitoring other measurable variables. For all these measurements taken, the anode area was varied one after the other as 0.0092, 0.0184, 0.0276, 0.0368 and 0.046 m^2, while the cathode area was varied as 0.009, 0.018, 0.027, 0.036 and 0.045 m^2 respectively. The anode and cathode pairs were designated as SC1, SC2, SC3, SC4 and SC5 respectively.

2.2 Description and Application of Relevant Parameters and Design Criteria for the Optimisation of the Expanded Area Diaphragm Cell (EADC)

The fabrication and operation of an improved EADC was achieved by making use of the results observed in the operation of the SCDC, as well as considering relevant parameters and design criteria. To optimise the basic parameters, emphasis was placed on the following design criteria relating directly to the design of any electrolytic cells' hardware (Keating and Sutlic, 1979):

2.2.1 Overall Fluid Distribution

For all cell banks, the parallel flow arrangement was used. In the parallel flow arrangement, net heat build-up was kept to a minimum because the electrolyte path was shorter. Also, the resistivity of the electrolyte was lower due to ease of release of gas bubbles into the outlet stream. Finally, there was lower pressure drop across the cell banks.

2.2.2 Fluid Distribution in a Cell

Uniform distribution of electrolyte within the cells was ensured to eliminate stagnant zones. This was done to minimise concentration polarisation, side reactions, low current efficiency and high electrode over voltages. It was achieved by proper design and fabrication of distribution ports in a cell, increasing the outlet flow ports and utilising gravity to sweep product by running electrolyte from top to bottom. The highest anolyte height of 0.8 m was used for optimisation as in the case of the SCDC operation.

2.2.3 Electricity Utilisation

Effective usage of electricity was made possible by minimising ohmic losses and power losses. These was achieved by making all electrical connections to be as short as possible, minimising contact resistances by using spring connectors and keeping the anode to cathode gap as short as possible (one centimetre) due to the resistance of the electrolyte solution.

2.2.4 Electrode Surface Area to Cell Volume Ratio

This ratio was increased as much as possible. The anode surface area of the EADC was increased by a factor of twelve, while the cathode surface area was increased by a factor of four over the areas used for the SCDC. The new cell volume was also increased over that of the SCDC by a factor of four. This was because the anodes have the tendency to wear off with usage at very high current densities and voltage. The electrode active surface area was increased so as to allow effective contact with the electrolyte by increasing the number of electrodes.

2.2.5 Critical Component Selection

The electrodes used have adequate electrical and thermal conductivity, good mechanical properties, corrosion resistance and low cost. The separator used has low ohmic resistance, low resistance to plugging, dimensional stability, useful life and low cost. Selected cell components were able to withstand the electrochemical reaction and operating conditions.

2.2.6 Materials of Construction

Material properties, useful life, availability and cost are prime factors in the selection of materials of construction for the electrolyser. Materials that were chosen have their coefficients of thermal expansion as low as possible. Differential expansion was allowed for in the design. Materials chosen also have moderate weight, easily machined and inert to the process fluids and solids.

2.2.7 Assembly and Maintenance

The cell banks were easy to assemble and maintain. Leakages were reduced by minimising the number of sealing surfaces. The design was good because it allowed very low shut-down period for abrupt maintenance when there is operational problem and therefore, ensuring maximum profitability.

2.2.8 Operating Conditions

The operating conditions for the EADC were chosen in such a way that the maximum working pressure, temperature, voltage, current and current densities of the cell were not exceeded. This was because throughout the period of operation, there was no failure of any of the cell components, unlike the SCDC operation at above 16.8 V and 21 A. All the seals, electrodes and other cell components remained intact.

Based on the outcome of the parametric studies of the SCDC, the EADC was fabricated and operated with the same procedure for starting the SCDC and operated continuously for 14 days using 16.8 V designated as V3, anolyte height of 0.8 m designated as H5 and a cathode area of 0.18 m^2 designated as SC5.

2.3 Electrochemical Mathematical Model Description

The caustic soda formation electrochemical reactions can be expressed as in Eqs. 1 to 5:

$$NaCl\,(aq) \rightleftharpoons Na^+ + Cl^- \qquad (1)$$

$$H_2O\,(aq) \rightleftharpoons H^+ + OH^- \qquad (2)$$

At the cathode hydrogen gas is given off as follows:

$$2H^+ + 2e^- \longrightarrow H_2\,(g) \qquad (3)$$

At the anode, chlorine gas is evolved according to the following reaction:

$$2Cl^- \longrightarrow Cl_2\,(g) + 2e^- \qquad (4)$$

The activities of Eqs. 3 and 4 enables a concentration of sodium ions (Na^+) and hydroxyl ion (OH^-) in the catholyte solution to form sodium hydroxide as follows:

$$Na^+ + OH^- \longrightarrow NaOH\,(aq) \qquad (5)$$

The chlor-alkali electrolytic processes operate primarily under charge transfer control according to Pletcher and Walsh (1990). This means that electrodes, separators, inter electrode gap and cell geometry are very important parameters.

The basic features of the SCDC and EADC are shown in **Figures 1 and 2** respectively. The spatial arrangement of the anode, anolyte height, diaphragm and cathode with the direct current (d.c) source for the SCDC and EADC are shown in **Figure 3**.

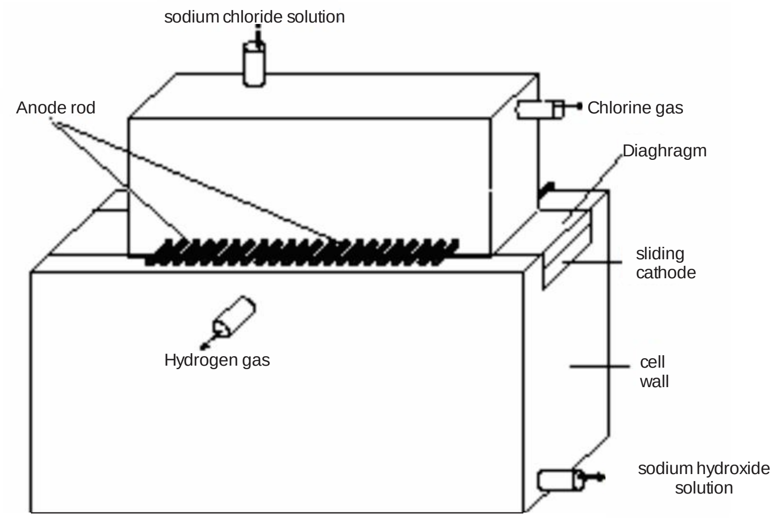

Figure 1: Basic Features of the SCDC (Olufemi, 2008)

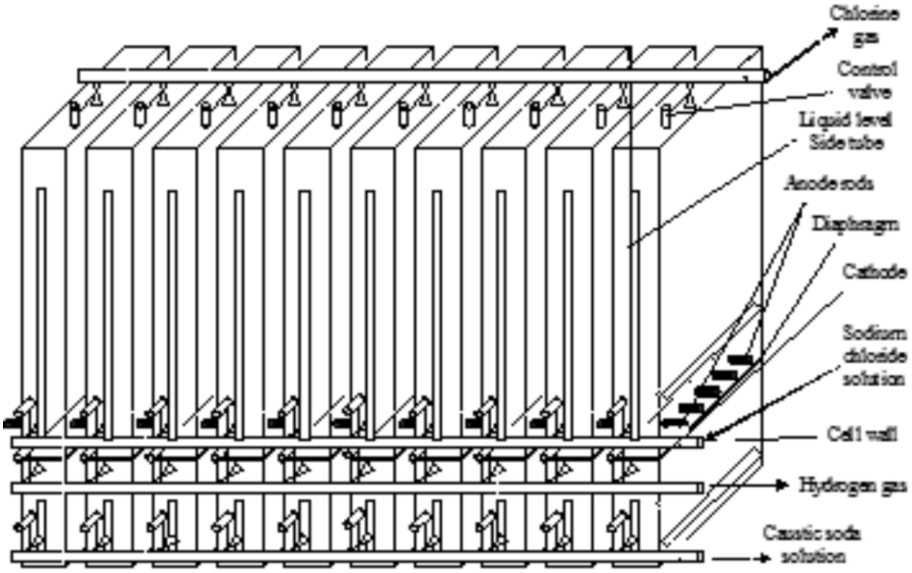

Figure 2: Basic features of the EADC (Olufemi, 2008)

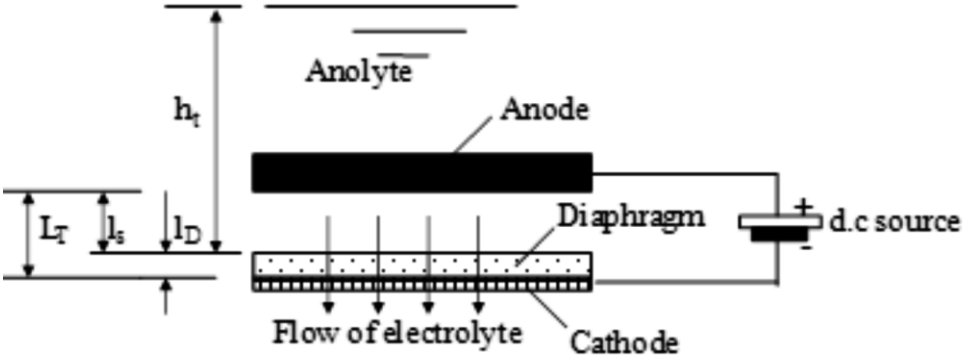

Figure 3: SCDC and EADC spatial arrangement of the anode, anolyte height, diaphragm and cathode (Olufemi et *al.,* 2010)

The expressions for the modelled volumetric flow rate of electrolyte through the diaphragm, modelled variation of the anolyte temperature with time, modelled current based on the Tafel approximation and temperature dependency had been reported (Olufemi, 2008; Olufemi *et al.*, 2010), and need not be repeated here.

By using the Geometrically Dependent Operational Current Effectiveness (GDOCE) also known as the modeled current efficiency (η_{MD}), which gives the constructive portion of the current density available for the desired reaction, the modeled mass flow rate of caustic soda per unit time, which is to be optimised is given as Eq. 6 (Olufemi, 2008; Olufemi *et al.*, 2010):

$$\dot{m}_{MS} = \frac{I_{MD}\eta_{MD}e_{WS}}{N_A z} = \frac{(V-2.3+\eta_A-\eta_C)\eta_{MD}e_{WS}}{\left[\frac{\pi D_P^2\varepsilon^3(P_O-P_L)}{144\Lambda(1-\varepsilon)^2\tau\mu}\left(\frac{l_s}{l_D}+1\right)+R_m\right]N_A z} \qquad (6)$$

In order to optimally predict the best values of the independent variables in Eq. 6 for the EADC operation, it is important to formulate an objective function of the mass flow rate and maximize it in terms of important variables. Using the Tafel approximation (Olufemi, 2008; Olufemi *et al.*, 2010), Eq. 6 can be expressed as:

$$\dot{m}_{MS} = \frac{\left(V-2.3+a_A+b_A\log\left(\frac{I_{MD}}{A_A}\right)-a_C-b_C\log\left(\frac{I_{MD}}{A_C}\right)\right)\eta_{MD}e_{WS}}{\left[\frac{\pi D_P^2\varepsilon^3(P_O-P_L)}{144\Lambda(1-\varepsilon)^2\tau\mu}\left(\frac{l_s}{l_D}+1\right)+R_m\right]N_A z} \qquad (7)$$

P_O - P_L can be expressed in terms of the hydrostatic head of anolyte and anolyte temperature.

From Perry (1997), ρ_{EL} can be expressed as in Eq. 8:

$$\rho_{EL} = \left(-0.5731T_f\right)+1356.3 \qquad (8)$$

Therefore,

$$P_O - P_L = \rho_{EL}gh_t = (1356.3 - 0.5731T_f)gh_t = 13305.3h_t - 5.622h_tT_f \qquad (9)$$

From experimental investigation as will be shown later, the height of anolyte (h_t) favours both the optimal electrical power utilisation and productivity. Hence its maximum allowable value was used in the optimisation. The anolyte viscosity can also be expressed in terms of the temperature from Perry (1997) as in Eq. 10:

$$\mu = 0.451\exp\left(-0.018T_f\right) \qquad (10)$$

By substituting Eqs. 8 to 10 into Eq. 7, with the mean Tafel constants and rearranging, it follows that:

$$\dot{m}_{MS} = \frac{40\eta_{MD}\left(V-2.3+0.1145+0.088\log\left(\frac{I_{MD}}{0.552}\right)-0.2585-0.12\log\left(\frac{I_{MD}}{0.18}\right)\right)}{\left[\frac{5.73\times10^7}{0.485T_f-119.79}+7.72\times10^7\right]} \qquad (11)$$

where $A_D = 0.192$ m^2, $l_D = 0.003$ m, $l_S = 0.01$ m, $\varepsilon = 0.253$, $e_{WS} = 40$ kg kmol^{-1}, $\tau = 3.272$, $h_t = 0.8$ m, $N_A = 6.02205 \times 10^{26}$ kmol^{-1} and $z = 1.60219 \times 10^{-19}$ C.

The constraints of the objective function are given as: $\eta_{MD} \leq 1$, $V \geq 11.2$ V, $V \leq 22.4$ V, $I_{MD} \times V \leq 750$ W, and $T_f \geq 301$ K. The fourth constraint limits the available electrical power to 750 W, which was the range of the power supply unit used. Therefore, the four variables to be optimally determined are applied voltage (V), operating current (I_{MD}), current efficiency (η_{MD}), caustic soda mass flow rate $(\dot{m}_{MS})$ and anolyte operating temperature (T_f). Experimentally only the applied voltage was pre-determined, but the other variables attained various values as the electrochemical operation progressed.

3.0 RESULTS AND DISCUSSION

For a non-isothermal, unsteady state operation of the cell until steady state is achieved, a Computer Electrochemical Simulation Programme (ELCHESIM) was written to coordinate the various simulation equations and relationships (Olufemi, 2008; Olufemi *et al.*, 2010). The Productivity Optimisation Objective Function in Equation (11) is a non-linear equation, which was solved with the MPL for Windows 4.2 Optimization software, Maximal Software Inc., Copyright 1988 – 2007. The software utilised the Lipschitz-Continuous Global Optimizer (LGO) for the nonlinear optimization. According to Pinter (2007), a practically important point to emphasize is that a specialized model structure is not assumed or exploited by LGO. All the analysis of variance (ANOVA) and Bonferroni-Holm Posthoc parametric test statistical computation presented in this work were carried out with the aid of Daniel’s XL Toolbox Version 5.09 © 2008 - 2013 software. The simulation of the current, current efficiency, final anolyte temperature and catholyte volumetric flow rate had been reported (Olufemi, 2008; Olufemi *et al.*, 2010), and will not be repeated here. Since the mass flow rate is being optimized in this work, the simulation result is presented.

3.1 Effect of Voltage and Cathode Area on Mass Flow Rate of Caustic Soda

The mass flow rate of caustic soda increased as the operational voltage and area increased as shown in **Figure 4**. The higher the voltage and cathode area, the higher the mass flow rate of caustic soda produced, for the anolyte height H5 considered. Higher area and voltage increased reactivity of electrolyte within the diaphragm making them more available for electrochemical reaction. Percentage deviation of simulated from experimental data was between -5.26 and +4.76 %. There existed a significantly statistically wide variation between the experimental mass flow rates at various cathode areas and voltages at the 95% confidence interval, as the Fisher’s F which is ratio of the variance between groups to the variance within groups had a value of 72.00 and the probability factor P, which must be less than 0.05 was less than 1.655E-09 in the ANOVA analysis. The F and P values implied a strong dependence of mass flow rates on voltage and cathode area. In **Table 1**, the Bonferroni-Holm Posthoc parametric tests for various parameters are presented.

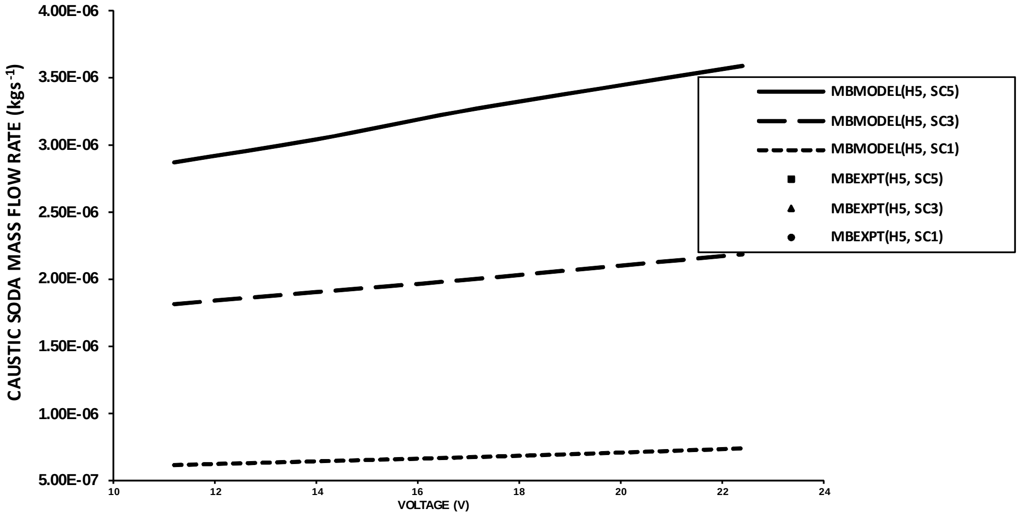

Figure 4: Variation of caustic soda mass flow rate with voltage at different cathode areas

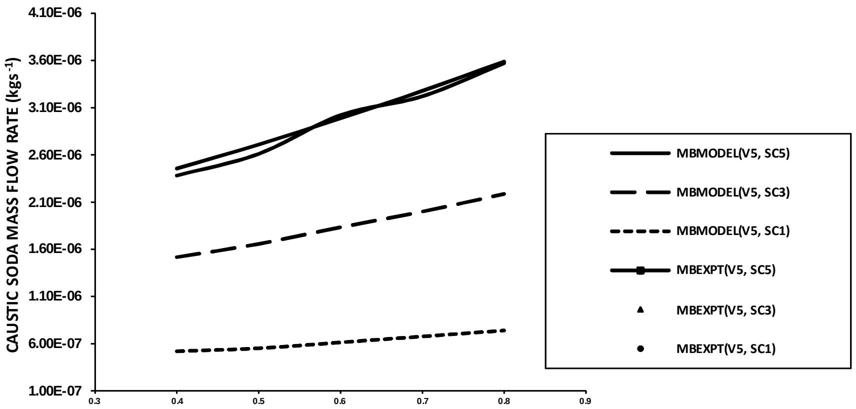

Figure 5: Variation of caustic soda mass flow rate with anolyte height at different cathode areas

Table 1: Bonferroni-Holm Posthoc parametric tests for experimental mass flow rates and voltages at various cathode areas

Data Group 1	Data Group 2	Critical P Value	Actual P value	Significance
MBEXPT(H5, SC5)	MBEXPT(H5, SC1)	8.333E-03	9.7850E-08	Significant
MBEXPT(H5, SC3)	MBEXPT(H5, SC1)	1.000E-02	1.7636E-07	Significant
V	MBEXPT(H5, SC1)	1.250E-02	2.8511E-05	Significant
V	MBEXPT(H5, SC3)	1.667E-02	2.8511E-05	Significant
V	MBEXPT(H5, SC5)	2.500E-02	2.8511E-05	Significant
MBEXPT(H5, SC5)	MBEXPT(H5, SC3)	5.000E-02	3.7832E-05	Significant

3.2 The Effect of Anolyte Height and Cathode Area on Caustic Soda Mass Flow Rate

Figure 5 showed the dependence of caustic soda mass flow rate on height of anolyte and cathode area. The mass flow rate increased with increase in cathode area and height of anolyte at the voltage V5 considered. Higher anolyte heights resulted in more electrolytes passing through the diaphragm, and higher cathode area implied that more electrolytes would be converted at the cathode. Percentage deviation of simulated from experimental data was between -4.27 and +5.90 %. Also, a statistically wide variation existed between the experimental mass flow rates, anolyte heights and cathode areas at the 95% confidence interval, as the F ratio had a value of 72.00 with $P < 1.655E-09$ in the ANOVA analysis. As for the voltages also, the data groups are 4, while the numbers of data are 20. The F and P values established the strong experimental dependencies of experimental parameters. In **Table 2**, the Bonferroni-Holm Posthoc parametric tests are presented.

Table 2: Bonferroni-Holm Posthoc parametric tests for experimental mass flow rates and anolyte heights at various cathode areas

Data Group 1	Data Group 2	Critical P Value	Actual P value	Significance
MBEXPT(V5, SC3)	MBEXPT(V5, SC1)	8.3333E-03	2.2111E-06	Significant
MBEXPT(V5, SC5)	MBEXPT(V5, SC1)	1.0000E-02	5.2360E-06	Significant
H (m)	MBEXPT(V5, SC1)	1.2500E-02	2.8511E-05	Significant
H (m)	MBEXPT(V5, SC3)	1.6667E-02	2.8512E-05	Significant
H (m)	MBEXPT(V5, SC5)	2.5000E-02	2.8512E-05	Significant
MBEXPT(V5, SC5)	MBEXPT(V5, SC3)	5.0000E-02	1.3449E-03	Significant

3.3 Summary and Application of SCDC Simulation Studies for EADC Optimisation

From the outcome of some of the simulation results presented (Olufemi, 2008; Olufemi *et al.*, 2010), as well as those presented in **Figures 4 and 5**, it could be inferred that higher cathode area will probably increase the current, current efficiency, caustic soda mass flow rate, catholyte volumetric flow rate and decrease electrolyte temperature. Too high temperature is not desirable because it caused melting of seals and components, electrolyte leakages which could result in electric shock and intermittent shut-downs. Voltage must be moderate, as too high voltage led to reduced current efficiency, caused too high temperature, leakages, material losses and energy wastage. The height of anolyte used seemed to be adequate at the maximum height of 0.8 m, as average current and efficiency seems to be more controlled by area than height of anolyte. The ANOVA and Bonferroni-Holm Posthoc parametric tests showed the statistical significance of the experimental data as very highly reliable in the cell operation, which can be employed as a tool for optimization.

As a result, an Expanded Area Diaphragm Cell was fabricated, operated and optimised with better output. The maximum cathode current efficiency obtained with the SCDC was 65.67 %, while that obtained with the EADC was 95.00 %. The EADC experimental operational and performance information are given as follows:

Operating time = 14 days = 1,209,600 s
Open circuit d.c. voltage = 16.8 V (Average of 11.2 and 22.4 V)
Inlet temperature of anolyte = 301 K
Anolyte height = 0.8 m
Cathode electroactive area = 0.18 m^2

The predicted numerical optimisation results are as follows: $\dot{m}_S$ = 1.003 x 10^{-5} kgs^{-1}, V = 22.4 V, I_{MD} = 33.48 A, η_{MD} = 1.00 and T_f = 309.12 K, Number of iterations = 25320, Solution time = 0.88 s.

The experimental operational and performance results are as follows: $\dot{m}_{OB}$ = 8.19 x 10^{-6} kgs^{-1}, V = 16.8 V, I_{OB} = 20.8 A, η_{OB} = 0.95 and T_f = 306.00 K

These results confirmed that the cell was practically operated as closely as possible to the predicted optimum operating conditions. There was a need in carefully realising the optimal values experimentally because the numerical optimisation technique might not reveal the ruggedness of some of the interactions taking place within and outside the cell as electrochemical operation progresses. It was observed experimentally for the SCDC operation that voltages above 16.8 V gave current above 21 A. This current value damaged some of the electrical and electronics components, caused excessive high temperatures that melted connectors and wires and caused electrolyte leakages that could lead to electric shock and rapid wearing of the anodes. All these problems hindered smooth operation of the SCDC and hence its performance. It was better to operate the cell at a safe moderately lower voltage and current density that will greatly prevent any unwanted side reactions as well as other hazard either to any of the cell components, supporting facilities or personnel as it was done in the case of the EADC operation.

These results depict that the EADC is very durable and the operating conditions are selected in such a way as to ensure optimum performance and cell durability. These results show a considerable improvement over that of the SCDC because of the size factor, carefully selected operating conditions and operating time. The current efficiency was improved by about 145 % over that of the SCDC. The EADC performance in **Table 3** was compared with some industrial cells as documented from Olufemi (2008).

Table 3: Comparison of Some Industrial Cells with EADC Operation

Measured Parameter	Industrial Cells				EADC
	MDC-29	MDC-55	H-2A	H-4	
Anodic current density (kAm^{-2})	1.21	1.37	1.11	1.24	0.04
Current efficiency (%)	96.5	96.5	93.0	93.8	95.0
Active anode area / Cell volume (m^{-1})	4.737	4.458	3.947	3.775	3.594
Yield (Kg NaOH / kg NaCl input)	0.6598	0.6598	0.6359	0.6414	0.6496

4.0 CONCLUSION

From the results obtained, with a proper implementation of the basic parameters and design criteria necessary for the optimisation of electrochemical cells, the optimal operating condition for the cell design can be determined between operating at higher voltages, which enhanced the production of more caustic soda and operating at lower voltages, which enhanced the cell efficiency. This was depicted by modelling, simulation and optimisation. The ANOVA and Bonferroni-Holm Posthoc parametric tests showed the importance of the SCDC experimental data as very highly reliable and a good tool for optimization. The closeness between the theoretical optimum values and experimental values is a reflection of the technical and engineering judgements involved in optimising the EADC operation with comparable high yield. An important issue worthy of note is the insight gained in the optimum cell operation, without resulting to trial and error procedure, rule of the thumb or wastage of time, energy and resources. There is still room for development and improvement, but the outcome of this present work can be utilised for improved cell design, operation and performance.

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REFERENCES

Alkire, R. C and Stadtherr, M., (1983). Optimisation of Electrolytic Cells and Processes, *AIChE Symposium Series*, 229 **(79)**: 135-141.

Delfrate, A. and Schmitt, C., (2010). Integration of Fuel Cells Systems into Chlor Alkali Plants: The Chlorine Industry Perspective, *Proceedings of the 18th World Hydrogen Energy Conference 2010 - WHEC 2010*, 427 – 432.

Jalali, A. A., F. Mohammadi, F., and Ashrafizadeh, S. N., (2009). Effects of process conditions on cell voltage, current efficiency and voltage balance of a chlor-alkali membrane cell, *Desalination*, 237**(1-3):**126 – 139.

Joudaki, E., Farzami, F., Mahdavi, V. and Hashemi, S. J. (2010). Performance Evaluation of Oxygen-Depolarized Cathode with PtPd/C Electrocatalyst Layer in Advanced Chlor-Alkali Cell. *Chem. Eng. Technol*., 33: 1525–1530.

Joudaki, E., Hashemi, S. J., Mohammadi, F., Yousefi, A. and Eivazkhani, M. (2011). Oxygen reduction electrode in advanced chlor-alkali with ruthenium as electro-catalyst., *Can. J. Chem. Eng*., 89: 197–201.

Keating, K. B. and Sutlic, V. D., (1979). The Cost of Electrochemical Cells, *AIChE Symposium Series*, 185 **(75):** 76-88.

Lima, P. R., Mirapalheta, A., Henrique dos Santos Andrade, M., Vilar, E. O., and Tonholo, J. (2010). Energy loss in electrochemical diaphragm process of chlorine and alkali industry–A collateral effect of the undesirable generation of chlorate, *Energy*, 35**(5):**2174-2178.

Ohm, C., (2007). Innovative Chlorine Production - Increasing Energy Efficiency, http://www.press.bayer.com/baynews.nsf/id/F9D7D38D, 1-10 Accessed: April 24, 2007.

Olufemi, B. A. (2008). “Characterisation of Locally Produced Diaphragm Cells for the Production of Caustic Soda”, Ph. D. Thesis, University of Lagos, Akoka, Lagos, Nigeria.

Olufemi, B. A, Kehinde, A. J and O. Ogboja (2010). Non-Isothermal Operational Simulation of Caustic Soda Production Electrolysers for Improved Performance. *Journal of Engineering Research*, 3**(15):** pp. 50 - 64.

Olufemi, B. A., Ozowe, W. and Afolabi, K., (2012). Operational Simulation of Solar-Powered Variant-Diaphragm Cells for Caustic Soda Production. *Journal of Energy Technologies and Policy*, The International Institute for Science, Technology and Education (IISTE), 32-43.

Perry, J. H. and Chilton, C. H., (1997). Chemical Engineers Handbook, 7th Ed., McGraw Hill Book Company, pp. 50-400.

Pinter, J. D., (2007). Nonlinear Systems Modelling and Optimization Using AIMMS/LGO, http://www.aims.com/aims/download/solvers/ aimms_lgo_shortpaper.pdf, 1-4. Accessed: March 5, 2007.

Pletcher, D. and Walsh, F. C., (1990). Industrial Electrochemistry, 2nd ed., Chapman and Hall, London, Great Britain, 79-81.

Selman, J. R., (1983). Dimensional Analysis and Scale-up of Electrochemical Reactors, *AIChE Symposium Series*, 183 **(79):** 101- 110.

Shojaikaveh, N., Mohammadi, F. and Ashrafizadeh, S. N, (2009). Prediction of cell voltage and current efficiency in a lab scale chlor-alkali membrane cell based on support vector machines, *Chemical Engineering Journal*, 147**(2):**161 - 172.

Shojaikaveh, N., and Ashrafizadeh, S. N., (2010). Development and comparison of non-parameter regression methods for prediction of cell voltage and current efficiency in a lab scale chlor-alkali membrane cell. *Desalination and Water Treatment*, 14**(1-3):**135 - 145.

Westerberg, A. W., (1981). Optimization in computer aided design, *Proceedings of Conference on Computer-Aided Chemical Process Design, A.I.Ch.E.,* N.Y, 28-29.

NOMENCLATURE

a_A = *Anodic Tafel constant (V)*
a_C = *Cathodic Tafel constant (V)*
A_A = *Area of anode* (m^2)
A_C = *Area of cathode* (m^2)

A_D = Cross-sectional area of diaphragm (m^2)
A_T = Total area of electrodes (m^2)
b_A = Anodic Tafel constant (V)
b_C = Cathodic Tafel constant (V)
C_{OS} = Concentration of caustic soda in catholyte (M)
d, D = Diameter (m)
D_P = Pore Diameter (m)
D_T = Denominator (Ohm)
e_{WS}, e_{WE} = Equivalent weight. (kg kequiv.$^{-1}$), (kg kmol^{-1})
F = Faraday's Constant (Cmol^{-1}), Fisher's Constant
g = Acceleration due to gravity (ms^{-2})
h_t = Height of anolyte (m)
i_A = Anodic current density (Am^{-2})
i_C = Cathodic current density (Am^{-2})
IMODEL, I_{MD} = Modelled current (A)
IEXPT, I_{OB} = Observed current (A)
I_{th} = Theoretical current required (A)
k = Average electrolyte specific conductivity (Ohm^{-1}m^{-1})
l_D = Length or thickness of diaphragm (m)
l_S = Distance between electrodes (m).
MBEXPT, $\dot{m}_{OS}$ = Observed mass flow rate of caustic soda (kgs^{-1})
MBMODEL, $\dot{m}_{MS}$ = Modelled mass flow rate of caustic
n = Number of electrons transferred.
N_A = Avogadro's number (mol^{-1})
P = Pressure (Nm^{-2}), Probability Factor
P_O, P_L = Pressure (Nm^{-2})
R = Resistance (Ohm)
R_m = Miscellaneous resistance (Ohm)
t = time (s)
T = Temperature (K)
TFEXPT, T_f = Final temperature of electrolyte (K)
T_{fm} = Mean film temperature of anolyte case wall (K)
V = Voltage (V)
$\dot{V}_D$ = Modelled volumetric flow rate of catholyte (m^3s^{-1})
VDEXPT, $\dot{V}_{OB}$ = Observed volumetric flow rate of catholyte (m^3s^{-1})
z = Electron Charge (C), (As).
ε = Porosity
η = Overvoltage (V)
ρ = Resistivity (Ohm.m), Density (kgm^{-3})
τ = Shear Stress (Nm^{-2}), Tortuosity factor
ν = Velocity (ms^{-1})
Λ = Equivalent conductivity of electrolyte (ohm^{-1} m^2 equiv^{-1})
Λ_O = Equivalent conductivity of electrolyte at reference temperature (ohm^{-1} m^2 equiv^{-1})
σ = Stefan Boltzman constant (Wm^{-2}K^{-4})
ρ = Resistivity (Ohm.m)
ρ_{EL} = Density of electrolyte (kgm^{-3})
κ_T = Specific conductance of electrolyte at temperature T (ohm^{-1} m^{-1})
ε_W = Emissivity of anolyte case wall
η_{MD} = Modelled cathodic current efficiency
EFEXPT, η_{OB} = Observed or experimental cathodic current efficiency.