ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 9, September 2016

Modified Industrial Chlor Alkali Process for Reduction in Power Consumption

Abhishek Sinha, Anurag Ranjak

Department of Chemical Engineering, Indian Institute of Technology, Delhi, India

Abstract: Chlor-alkali process, being the second most widely used process, has a very high value of power consumption all over the world. In these experiments, we tried to relate this value of power consumption to some of the Donnan potential and process conditions, and tried to capture the impact of varying these parameters, like temperature difference across the electrolytes, concentration of the electrolytes and tried to reduce this value of power consumption. Finally, we also applied di-electrophoresis over the electrodes, so as to enhance the surface area for ion transfer, resulting in decreased resistance. A total of 4 sets of experiments, with multiple runs, were performed to capture this behavior and it was found that the outcome was optimum when the temperature of NaCl side was 5 K more than the other chamber, with the value of Donnan potential being reduced significantly. Also, the Donnan potential was minimum when NaCl concentration was 4 M. Di-electrophoresis produced optimum results for frequencies 50 Hz and 100 Hz. After all these, a combined experiment, with optimized process conditions and di-electrophoresis, was performed and the obtained result proved that the final Donnan potential value was actually around 12% less than that for a normal chlor-alkali process at lab scale, hence implying significant reduction in power consumption. This significant reduction in power consumption can have some serious economic impact on this process being carried out at large-scale.

Keywords: Chlor-alkali process, Di-electrophoresis, Power consumption.

I. INTRODUCTION

Industrial Chlor-Alkali process is the second most widely used process in the industries. It is the primary mode for producing Chlorine gas and Caustic Soda (NaOH). The process involves electrolysis of Sodium Chloride which can be replaced by Calcium and Potassium salts (in which case, Calcium and Potassium alkali are formed, respectively).
Three types of cells are used to carry-out the process:

- Membrane Cell (most common)
- Diaphragm Cell
- Mercury Cell (Castner-Kellner Method)

Chlor-Alkali process has a high energy consumption, resulting from the high resistance inside the cell (the electrolytes, the electrodes and the membrane). For example, the energy consumption in the Chlor-Alkali industry was over 4 billion kWh per year in West Germany in 1985. And as the energy consumption depends on Voltage applied (direct proportionality), which in turn is directly proportional to Resistance across the cell (Ohm’s law, for constant current), energy consumption depends directly on the resistance across the cell.

Now across the cell, as there is continuous movement of ions from one chamber to the second, resistance keeps on decreasing and so does the voltage, until it attains a settled value. It is this settles voltage and settled resistance which helps to determine the power consumption in the process. The settled electric potential is called **Donnan Potential**, which will be explained in detail in the experimental process.

The objective of this experiment was to reduce the power consumption in the process, which required reduction in resistance across the cell and reduction in the Donnan potential. The primary source of resistance to the flow of ions is the bubbles which get accumulated over the electrodes and thus reduce the surface area for current to flow. Di-electrophoresis is a method which is used to remove these non-polar bubbles, which in turn increases the surface area of electrodes on which ions accumulate, and thus decreasing the resistance to electron flow. Donnan potential depends on parameters such as the temperature difference across the chambers, concentration of the electrolytes, etc. Varying these parameters will give different value of Donnan potential for different combinations. Di-electrophoresis and the variation of Donnan potential will be explained in detail in the Experimental Process.

In this experiment, we tried to reduce the power consumption of a Membrane Cell with Sodium Chloride as the electrolyte by performing Di-electrophoresis and varying the parameters on which Donnan potential depends.

II. MATERIALS REQUIRED

Plexi-Glass cell was designed and manufactured by the vendor. Electrodes were made using graphite sheet, steel plate and mesh and copper wire, partly coated with insulating element like adhesive. Other materials like dosing pumps, power source, NaCl powder, NaOH pellets, alternating signal generator, 2 thermocouples, pH electrodes, connecting wires, multi-meter, tapes, adhesives and copper wire were required to perform experiments in different runs.

III. EXPERIMENTAL SET-UP

Cell:

A cuboidal structure made of plexi-glass which was internally divided into two compartments, each containing one vent on top face, one on bottom and one on side face. The bottom vents were used to inflow the solutions into the cell and the top vents were used for outflow of reacted (solution + gas) mixture. Side faces of each compartment had openings for inserting wires which connected electrodes to power generator.

- Both the bottom vents of the cell, used for inflow of solutions, was connected through **pipes** to a **dosing pump** each. Dosing pump's function was to draw the solution from its vessel and pump it into the cell.
- Both the top vents were connected through pipes to the same vessel which contained the original solution, thus making it a continuous process.
- Aqueous Sodium Chloride was the electrolyte used in anodic compartment. In cathode compartment, instead of water, which is used in normal chlor-alkali process, a very dilute solution of sodium hydroxide was used, with the purpose of instantiating the process.

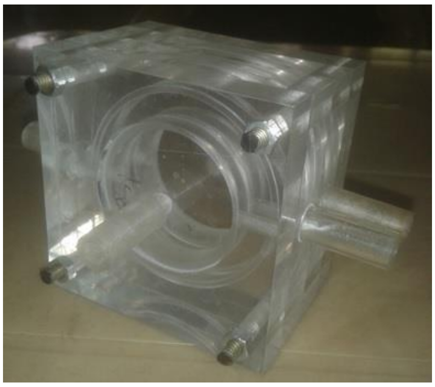

Figure 1: Chlor-alkali cell used to conduct the experiments. Two vents on the right and left side are the ones used for inflow and outflow of solutions in the compartment. The vents on front and back walls are used for electrodes.

Different types of electrodes were used for specific purpose and these were connected to the **DC meter**, which provided necessary current for the process to occur. In case of di-electrophoresis, side vents were also used to connect the probes to the **signal generator**, which provided alternating current of necessary frequency.

Electrodes

Different types of electrodes used were:

Anode:

1. For performing normal chlor-alkali process, chlor-alkali using temperature difference and chlor-alkali for concentration difference, graphite sheet was used as anode. Insulated copper wire was used to connect the sheet to DC meter. The part of the copper wire which was in contact with electrolyte was insulated using araldite and feviquik in order to avoid preferential reaction on the copper surface. For connecting the wire and graphite sheet, steel plate was used upon which, copper wire was welded. The purpose of using steel plate was increasing the contact area so as to reduce electrical resistance.
2. Another choice was a similar type anode. Only difference was in the contacting. Instead of steel plate, copper wire was directly inserted into the sheet from one of its side faces.
3. A more acceptable option for anode was using graphite as a whole instead of steel plate and copper wire. Only graphite was in contact with electrolyte and hence there was no chance of preferential reaction on copper surface which was the possible reason for error in previous two cases. And since only graphite was used, there was no chance of gapping and hence electrical resistance was minimal.
4. For the experiments involving di-electrophoresis, electrode of case 3 was used with some modifications. 2 small probes were placed on the top and bottom face of the graphite sheet, making sure that the probes are not in direct contact with the graphite sheet and then the probes were connected to AC signal generator. For electrochemical reactions, DC source is needed and hence, chlor-alkali reaction would not occur on the probes and this is why they are separated from graphite sheet. Also, for di-electrophoresis, variable electric field is required, which is generated by AC source (and not with DC source), and so, bubbles would be removed using probes only.

Cathode:

1. For cathode, mesh steel was used which was connected to DC meter using copper wire similar to that in the case of anode. Copper in contact with electrolyte was insulated using araldite and feviquik.
2. Another option for cathode was using whole of mesh steel instead of copper wire to be contacted with electrolyte. This was more conductive electrically as compared to previous case.

Membrane:

Current generation techniques produce Cl_2 and NaOH/KOH from the electrolysis of brackish water utilizing a Nafion membrane between half-cells, which was also used in these sets of experiments. Prior to the utilization of Nafion, industries used mercury containing sodium amalgam to separate sodium metal from cells or asbestos diaphragm to take into consideration exchange of sodium particles between half cells.

The membrane permits sodium particles to exchange from one cell to the next with negligible electrical resistance. The membrane is likewise strengthened with extra films to avert gas item blending and minimize back exchange of Cl^- and OH^- particles.

IV. EXPERIMENTAL PROCESS

Membrane Chlor-Alkali Cell

This is the most common type of chlor-alkali cell which involves electrolysis of aqueous sodium chloride in a membrane cell. Saturated brine is passed into the first chamber of the cell where the chloride ions are oxidized at the anode, losing electrons to become chlorine gas.

At the cathode, the positive hydrogen ions pulled from water molecules are reduced by the electrons produced by the electrolytic current, to hydrogen gas, releasing hydroxide ions into the solution. The ion-permeable ion exchange membrane at the center of the cell allows the sodium ions (Na+) to pass to the second chamber where they react with the hydroxide ions to produce caustic soda (NaOH). The reaction thus, at anode and cathode becomes:

At Anode

$$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$$

At Cathode

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$

And the overall reaction across the cell becomes

$$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$$

A membrane cell is used to prevent the reaction between the chlorine and hydroxide ions. If this reaction were to occur the chlorine would disproportionate to form chloride and hypochlorite ions:

$$Cl_2 + 2OH^{-} \rightarrow Cl^{-} + ClO^{-} + H_2O$$

Above about 333 K, chlorate can be formed

$$3Cl_2 + 6OH^{-} \rightarrow 5Cl^{-} + ClO_3^{-} + 3H_2O$$

Because of the corrosive nature of chlorine production, the anode (where the chlorine is formed) must be made from a non-reactive metal such as titanium, whereas the cathode (where hydroxide forms) can be made from a more easily oxidized metal such as nickel. In the performed experiment, anode was made from graphite, and mesh steel was used as cathode.

In the membrane cell, the anode and cathode are separated by an ion-permeable membrane. Saturated brine is fed to the compartment with the anode (the anolyte). A DC current is passed through the cell and the NaCl splits into its constituent components. The membrane passes Na+ ions to the cathode compartment (catholyte), where it forms sodium hydroxide in solution. The membrane allows only positive ions to pass through to prevent the chlorine from mixing with the sodium hydroxide. The chloride ions are oxidized to chlorine gas at the anode, which is collected, purified and stored. Hydrogen gas and hydroxide ions are formed at the cathode.

Di-Electrophoresis

Di-electrophoresis (or DEP) is a phenomenon in which a force is exerted on a dielectric particle when it is subjected to a non-uniform electric field. This force does not require the particle to be charged. All particles exhibit di-electrophoretic activity in the presence of electric fields. However, the strength of the force depends strongly on the medium and particles' electrical properties, on the particles' shape and size, as well as on the frequency of the electric field. Consequently, fields of a particular frequency can manipulate particles with great selectivity. This has allowed, for example, the separation of cells or the orientation and manipulation of nanoparticles and nanowires. Furthermore, a study of the change in DEP force as a function of frequency can allow the electrical properties of the particle to be elucidated.

Now one of the primary reasons for high power consumption in chlor-alkali process is the accumulation of gas bubbles on electrode surface. Now the bubbles reduce the surface area for reaction and current to pass, so as we remove the accumulated bubbles, we increase the surface area and reduce the resistance for current flow and hence reduce the power consumption. So, we use this phenomenon of di-electrophoresis for this purpose.

Donnan Potential

Donnan potential appears as a result of Donnan equilibrium, which refers to the distribution of ion species between two ionic solutions separated by a semipermeable membrane or boundary. The boundary layer maintains an unequal distribution of ionic solute concentration by acting as a selective barrier to ionic diffusion. Some species of ions may pass through the barrier while others may not. The solutions may be gels or colloids as well as ionic liquids, and as such the phase boundary between gels or a gel and a liquid can also act as a selective barrier. Electric potential arises between two solutions is called Donnan potential.

In chlor-alkali cell, the semi-permeable transfer of ions from one chamber to another results in continuous decrement of cell resistance and hence cell potential. At certain value, the cell potential stabilizes and this potential is called Donnan potential which is the potential difference between the two chambers of the cell. Power consumption in the chlor alkali process is directly proportional to the value of Donnan potential and hence, lower the value of Donnan potential, lower is the power consumption, which is the AIM of the experiment.

V. PROCEDURE

Among the many ways described to reduce the power consumption, the following 3 were performed during experiment:

- Temperature difference across the chamber
- Different concentrations of the solutions in both chambers
- Di-electrophoresis in anode compartment

The basic procedure was same as normal chlor-alkali process with slight changes according to the 3 parts (temperature difference, concentration difference and di-electrophoresis) as mentioned below:

- For Temperature Difference: The experiment was carried out with different temperatures of the 2 chambers and the Donnan potential was measured as a function of temperature difference.
- For Concentration Difference: The experiment was carried with different concentrations of the solutions in anode chamber and cathode chamber and Donnan potential was measured with different solution concentrations.

For Di-electrophoresis: Experiment was performed using a modified anode as described before, at different frequencies of AC Current and variation of Donnan potential was again studied.

VI. OBSERVATIONS

Normal Chlor-alkali process (Set 1)

The process was conducted at 1 M concentration of NaCl and 30% by weight concentration of NaOH to begin with. A current of 1 A was passed through the set-up, and this whole experiment was performed at a room temperature of 35.4^o C. For the process at this normal condition, OCV at the beginning and the end of experiment was 0.4 V and 1.3 V respectively. A stable voltage of 3.1 V was established between the two chambers, after which the experiment was terminated.

With temperature difference (Set 2)

Experiments were conducted at concentrations similar to those mentioned in the previous case, viz. 1 M NaCl and 30% by weight NaOH, with 0.1 A current flowing through the circuit. However, the temperature of both the chambers were varied with the difference $T_{NaCl} – T_{NaOH}$ being constant throughout the experimental run. This value, termed as δT, was varied from -15 K to +15 K, wherein the temperature of one of the chambers was kept at room temperature, whereas the second chamber's temperature was varied using a heating source over the solution tank. Starting OCV was almost similar in every case (0.3 V), except for the case of $\delta T = 15$ K, where the starting OCV was 0.6 V. Open Circuit Voltage (OCV) at the end of the experimental run was 1.3 V in all the cases. Though the final stable voltage ranged between 2.8-3.1 V, the least potential difference was found to be in case of 5 K temperature difference, where the voltage was 2.8 V.

With concentration difference (Set 3)

For experiments at different concentrations, only the concentration of NaCl solution was varied from 0.5 M to 5 M (0.5 M, 1 M, 2 M, 4 M and 5 M), whereas NaOH concentration was kept at a constant value of 30% by weight. OCV at the beginning of the experiment was least for 4 M NaCl solution, 0.2 V, whereas for all the other cases, it was 0.3 V for all the others. Ending OCV was 1.2 V for 0.5 M and 4 M cases, and it was 1.3 V for all the other cases. Stable voltage was the least for 4 M NaCl case, which valued 2.8 V, while for all other cases, it varied up to 3.1 V.

With di-electrophoresis (Set 4)

For the case of di-electrophoresis, a normal experimental set-up, with NaCl and NaOH concentration same as in the first case, was used for these set of experiments. In order to conduct di-electrophoresis, an alternating current with peak voltage of 2 V was applied across the probes, and the frequencies for different runs were 10 Hz, 50 Hz and 100 Hz, respectively. Starting OCV for all the cases was 0.4 V and end OCV was almost around 1.5 V. Stable voltage at the end of the experiments was 3.0 V for 10 Hz, 2.9 V for 50 Hz and 2.9 V for 100 Hz, which was slightly lower than the potential in normal case, which was 3.1 V.

Optimized case (Set 5)

Two final experiments were conducted with all the optimized parameters from the previous runs, i.e. temperature difference of 5 K, NaCl concentration of 4 M and di-electrophoresis frequencies of 50 and 100 Hz respectively. OCV for both these experiments were measured to be 0.3 V at the beginning and 1.4 V at the end. The final voltage was found to be 2.7 V for both the cases, which is significantly lower than the normal value of 3.1 V. Though there might be some variation in the value of stable voltage, but the variation smaller than the least count of the instrument, and hence both the values came out to be same.

VII. RESULT AND DISCUSSIONS

1. Temperature Difference of 5 K was optimum in experiment of varying temperature difference (Set 2). Although, there was a decrease in Donnan Potential for all the cases where temperature differed as compared to normal case, but the decrease was greatest in the case of difference of 5 K. As we increase the temperature on NaCl compartment ($\delta T > 0$), there is more mobility on NaCl side, and hence ions transfer at faster rate through the membrane and so, there is less net resistance and hence less stable voltage. On increasing the temperature on NaOH side ($\delta T < 0$), there is more mobility of ions on NaOH side and there is slight decrease in Donnan Potential, but there is no change in rate of transfer of positive ions through the membrane and the ions diffuse through the membrane at similar rate as in normal case but as soon as they reach the second side, they get carried away faster, which leaves the surface of membrane in contact with NaOH vacant. As a result, there is net decrease in Donnan Potential, but not to that amount as compared to the case of $\delta T > 0$ where the reduction was more due to faster rate of transfer of ions resulting in lesser resistance. But, in case of $\delta T > 0$ also, the Donnan Potential attains a minima and if we keep on increasing the temperature of NaCl, there is heat transfer across the membrane and hence, the hydroxide ions on the other side also get excited and produce more resistance to current flow as a result of which, Donnan Potential increases at high temperatures.

   If we have a look at the Open Circuit Voltage (OCV), the starting OCV decreases as the stable voltage decreases. However, the final OCV remains almost the same in every case which signifies that given two solutions of similar concentrations, the distribution of ions (or number of ions present in each compartment) will be same after a saturation point and hence the open circuit voltage will be the same. The starting OCV decrement shows that there is not a uniform distribution of ions in the chamber which is explained by the result of mobility raised due to high temperature. As the ions get mobilized, they go on having a random motion and do not participate in contributing for the OCV.

2. Solutions of 4 M NaCl and 30% by wt. NaOH was the optimum case which reduced the stable voltage to significant amount (Set 3). Although there was slight decrease in all the cases where NaCl molarity was increased and there was decrease with decrease in NaCl concentration. As we increase the concentration of NaCl, the flux of sodium ion transfer increases but it also increases the molecules in the compartment, which results in resistance to current flow. So, the net effect on stable voltage is the net result of these two effects. At very high concentration of NaCl, the number of molecules is so high that there is increase in resistance and hence, the stable voltage increases. In case of very low NaCl concentration, although there is less number of molecules but as the flux for sodium ion transfer is very less, value of stable voltage again increases. This shows that there is a certain value of NaCl concentration at which Donnan Potential attains a minima and in our case, this minima is attained at NaCl concentration of 4 M.

   Studying the behavior of OCV shows that the starting and final OCV changes as the concentration of NaCl is varied. This is again a result of varying number of molecules present in the compartment which varies the starting OCV, more the number of molecules, more is the OCV. In case of final OCV, if we have more number of molecules, more will be the transfer of these molecules through the membrane, as a result of which, more will be the difference in the charged species present on both sides and hence, more will be the OCV.

3. In case of di-electrophoresis (Set 4), there was a decrease as we increase the frequency of current because as we increase the frequency, current changes its direction more often and electric field changes direction faster due to which, bubbles are forced to move at a faster rate. However, there was a constancy seen after 50 Hz which can be answered as a result of saturation. At certain high frequency, all the removable bubbles are removed from the

surface and after this, if we keep on increasing the frequency, there is no more removable bubble available on the surface and hence there is no further decrease in voltage seen.

As for the case of Open Circuit Voltage (OCV), the initial solution in every case is the same and present in same conditions. There is no difference in number of molecules or the mobility of ions due to which, the initial OCV comes out to be almost same for every case. But as we apply di-electrophoresis on NaCl side, there will be more surface area for the anode reaction, which signifies that there is more and faster consumption of chloride ions or more production of sodium ions. And more the production more is the transfer. Hence, there is an increase in production of hydroxide ions. Now as there is more number of ions on one side (hydroxide) and less number of ions on other side (chloride, because more of it is reacted), OCV increases with frequency. But similar explanation can be given for a stable value after certain frequency that at a certain frequency, all the chloride available for reaction will be reacted and hence, after this frequency, there will be no change in the OCV, it will stay at the stable value.

4. In case of experiments for Set 5, it can easily be said that all the optimized parameters contribute to lower the Donnan potential, though the reduction is not a linear addition of reduction in individual cases. Also, since even in this case, the stable voltage value was same, nothing can be said as whether it was a result of saturation, or there would be a further reduction upon increasing frequency to a very high value.

VIII. CONCLUSION

1. As we increase the temperature difference (TNaCl –TNaOH), there is a decrease in Donnan Potential which attains a minima at certain temperature difference and after this minima, again increases. For negative temperature difference, there is only a slight decrease in this voltage.
   OCV initially in this case depends on the mobility of ions and hence changes similar to the stable voltage. The final OCV is the same in every case which shows similar distribution of ions in the 2 chambers after a long time of reaction.
2. As we increase the concentration on NaCl side, stable voltage drops initially but again increases as we keep on increasing the concentration.
   In this case, OCV depends directly on the number of molecules present before and after the reaction on each side and increases as the difference of charged species present on both side increases.
3. If we apply di-electrophoresis either on one or both of the electrodes, there is a decrement in stable voltage up to a certain frequency after which it stays at a particular value even on increasing the frequency of alternating current.Open Circuit Voltage follows a similar but opposite trend and decreases as to a certain value and then stays at that value.
4. The power consumption in chlor-alkali process, as already said, depends on the value of stable voltage and in each of the previous cases, there is an optimum point when there is a minima of this voltage attained. Hence, we can say that we can reduce the power consumption in Chlor-Alkali process by either varying creating temperature difference among the 2 chambers, varying the molarity of one or both of the species or by applying di-electrophoresis on one or both sides, or by using a combination of 2 or all 3 of them together.

REFERENCES

[1] TF O'Brien, TV Bommaraju, F Hine, “Handbook of Chlor-Alkali Technology” Vol. 1, 2007.
[2] DL Caldwell, MJ Hazelrigg, MO Coulter, “Modern Chlor-Alkali Technology” Modern Chlor-Alkali Technology, 1980.
[3] SS Madaeni, V Kazemi, “Treatment of saturated brine in chlor-alkali process using membranes. Separation and Purification Technology, Vol. 61, Issue 1, pp. 68-74, 2008.

[4] F Hine, M Yasuda, T Yoshida, "Studies on the Oxide-Coated Metal Anodes for Chlor-Alkali Cells" Journal of The Electrochemical Society, Vol. 124, Issue 4, pp. 500-505, 1977.
[5] K Sollner, "Ion exchange membranes". Annals of the New York Academy of Sciences, Vol. 57, Issue 3, pp. 177-203, 1953.
[6] Y Tanaka, SH Moon, VV Nikonenko, T Xu, "Ion-exchange membranes". International Journal of Chemical Engineering, 2012.
[7] Y Ogata, T Kojima, S Uchiyama, M Yasuda, F Hine, "Effects of the Brine Impurities on the Performance of the Membrane-Type Chlor-Alkali Cell". Journal of the Electrochemical Society, Vol. 136 Issue 1, 91-95, 1989.
[8] M Seko, "The ion-exchange membrane, chlor-alkali process". Industrial & Engineering Chemistry Product Research and Development, Vol. 15, Issue 4, 286-292, 1976.
[9] MP Hughes, R Pethig, XB Wang, "Dielectrophoretic forces on particles in travelling electric fields". Journal of Physics D: Applied Physics Vol. 29, Issue 2, pp. 474, 1996.
[10] GH Markx, R Pethig, "Dielectrophoretic separation of cells: continuous separation". Biotechnology and bioengineering, Vol. 45, Issue 4, pp. 337-343, 1995.
[11] H Strathmann, L Giorno, E Drioli E, "Introduction to membrane science and technology". Weinheim: Wiley-VCH, Vol. 544, 2011.