



STUDIES ON THE PRODUCTION OF CAUSTIC SODA USING SOLAR POWERED DIAPHRAGM CELLS

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ABSTRACT

An experimental study was performed using an array of solar panels to power asbestos and non-asbestos diaphragm type electrolytic cells whose anodes consisted of carbon rods and cathodes made up of stainless steel plate for the electrolysis of a 25% w/w sodium chloride solution, with the aim of producing caustic soda. The asbestos and non-asbestos diaphragms served to hinder the formation of unwanted substances as well as permit reasonable production of the desired products. Quantitative analysis showed that the quantity and concentration of caustic soda produced varied with the current and voltage obtained from the solar panels which were dependent upon the intensity of the sun on any particular day and the length of time the panels were exposed to sunlight. The asbestos and non-asbestos diaphragm cells exhibited various characteristic performances, which is a reflection of their design, fabrication, composition and operation parameters. The non-asbestos diaphragm cell showed similar trend with the conventional asbestos diaphragm cell performances indicating higher yield of caustic soda per d.c Watt. The research served as an encouraging inquisitive foundation into the possibility of producing caustic soda directly from solar powered electrolytic diaphragm cells in comparison with present conventional modes of electrochemical production.

Keywords: caustic soda, asbestos, diaphragm cells, solar, catholyte, non-asbestos, energy.

INTRODUCTION

The electrochemical production of caustic soda from brine in the chlor-alkali industry, with chlorine and hydrogen as the by-products is one of the leading industrial production processes in the chemical industry. According to Alkire and Braatz (2004), electrochemical processes provide the only commercially viable means for the production of caustic soda, chlorine and some chemical products. Chlorine and/or caustic soda is involved directly or indirectly in the manufacture of about 70 percent of all chemical products (Ohm, 2007).

The chlor-alkali process is the most economically important electrosynthetic process (Minteer, 2002). The chlor-alkali (also called "chlorine-caustic") industry is one of the largest electrochemical technologies in the world. It is an energy intensive process and is the second largest consumer of electricity (2400 billion kWh) among electrolytic industries. In 2006, about 84% of the total world chlorine capacity of about 59 million metric tons was produced electrolytically using diaphragm and membrane cells, while about 13% was made using mercury cells (Tilak *et al.*, 2007). The diaphragm cell alone accounted for about 62% production (Tilak *et al.*, 2007).

According to Ohm (2007), a typical world-scale chloralkali-electrolysis plant produces above 1,000 tons of caustic soda a day. For this it consumes a shipload of salt (about 1,700 tons) and enough electricity to power a town in Germany with 130,000 inhabitants. The threat of inadequate electrical power has resulted in much effort toward reducing electrical power consumption. Power consumption accounts for approximately 60 to 70% of the total cost of industrial chlor-alkali production (Minteer, 2002; Patel, 2009). In addition, the power supply is highly unreliable, with frequent fluctuations, resulting in lower

operational efficiency and higher input cost. Another inputs cost such as gas and petroleum fuel for running the captive power plant are rising steadily and do not show any signs of reduction in the near future. Cheap availability of gas is also a major concern.

Although the process chemistry of the chlor-alkali electrolytic production of caustic soda is simple to understand, the design and operational issues are vastly complex (Gunatillaka and Achwal, 2003). This particular area of production has witnessed, and is still witnessing drastic changes in the methods of production, all of which are directed towards achieving better ways of production in terms of yield, economics, operation, instrumentation, durability, environmental suitability and improvement on equipment design. Recently, low energy consumption in chlor-alkali cells using oxygen reduction electrodes was investigated by Kiros and Bursell (2008). A novel electrolytic cell which reduced power consumption by 91% was recently developed with significantly superior kinetics, selectivity and efficiency compared to the traditional types of chlor-alkali cells for the production of caustic soda (Minteer, 2002). The effect of magnetic field in chlor-alkali cells performance was also studied by Minteer and Burney (2005). Performance and durability enhancement was investigated for another chlor-alkali cell recently by Ichinose *et al.*, (2004). Application of simulation results as well as relevant parameters and design criteria in the electrochemical industry for the operation of an Expanded Area Diaphragm Cell (EADC) for the electrochemical production of caustic soda with some results similar to what is obtainable in the industry was carried out recently (Olufemi, 2008).

In view of the above areas of concern, the chlor-alkali sector which is a basic driver of the economy has to play a pro-active role in optimizing energy efficiency and



reducing wastage. Among the various strategies aimed to meet energy demand, efficient use of energy and its conservations emerges out to be the least cost option. Energy Conservation assumes special significance due to the limited availability of energy, and heavy dependence on imports for this purpose. Hence, all attempts should be made to make efficient use of energy possible, so as to keep operational cost down and attain sustainability in a global competitive environment.

Against this back drop of high energy saving potential and its benefits, Bureau of Energy Efficiency has been established in some countries. Under the provisions of this statute, they are responsible for laying down standards and implements policy and programmes pertaining to energy conservation. In energy conservation conscious countries, Energy Conservation Acts (ECAs) has specified the list of energy intensive industries and establishments as designated consumers. Chlor-alkali is one of such industry. Such designated consumers will have to carry out certain mandatory functions such as appointing designated energy managers, get energy audit conducted at regular intervals, implement techno-economically viable recommendations, comply with fixed norms of specific energy consumption and submit to the designated authority periodic reports on steps taken by them. The chlor-Alkali industry has to aggressively pursue the energy conservation agenda - not so much for meeting any lofty social obligation, but to ensure its own survival and growth. Members of the chlor-alkali industry can adopt several such strategies. Reduced energy-consuming chlor-alkali process and solar power derived energy is a good recommendation for the process.

This work is set-out to study and put forward successful implementation of techno-economically viable recommendations in the chlor-alkali industry. The possibility of this is to be explored by theoretical investigation and experimental demonstration of the usage of solar powered electrolytic asbestos and non-asbestos diaphragm cells for the production of caustic soda.

EXPERIMENTAL

The experimental set up consisted of electrochemical cells with anolyte and catholyte compartments, graphite anodes, stainless steel cathodes, array of solar panels producing electric current, a voltmeter, an ammeter, a charge controller and ducts used to collect products of electrolysis. Additional apparatus employed in the preparation of 25% w/w brine and 2.78M HCl for titration were; volumetric flask, a measuring cylinder, an electronic weighing balance, a stirrer, distilled water and crystalline sodium chloride. Apparatus involved in the titration were beakers, retort, burette, conical flask, and pipette. A total of 6 hours electrolysis time was taken for each daily run, with the open and closed cell voltages and current taken at hourly intervals for three days a week. Inlet temperature of brine was 313K for all runs, while the final is about 315K for all runs. Asbestos plate (85% cement and 15% chrysolite asbestos) and non-asbestos plate (85% cement, 7.5% PVC and 7.5% Silica), were

separately prepared, and were subsequently adhered to the cathode plate, for use as diaphragms to aid the comparative study. Figure-1 shows the schematic electrochemical operational diagram.

Solar modules were firmly fixed in place, in a manner suitable to withstand all expected loads. The modules were mounted with the orientation and tilt angle required for optimum performance. Its location was selected to have direct access to sunlight from 0900 to 1500 hours GMT. The tilt angle was maintained at 20 degrees to the horizontal, with modules facing south in the northern hemisphere or north in the southern hemisphere as the case may be.

During installation of the modules, so as to avoid the destruction of the solar cells, bypass diodes and junction box, the correct polarity was observed and blocking diodes were used to prevent reversal flow of current to the panels. Positive wire from modules was connected to the positive terminal of the charge controller and negative wire from the modules was connected to the negative terminal of the charge controller. Positive wire from the charge controller was connected to the cell anode and negative wire from the charge controller was connected to the cell cathode. Insulated copper wire was used to connect the panels in parallel to the charge controller and cells.

The voltage supply from the panels was suitable to drive the electrochemical reaction and overcome circuit resistances. The theoretical decomposition voltage needed is 2.3V. The parallel array of the solar panels used has an average open circuit voltage of about 18.4V. The open circuit voltage was taken at the beginning of each run on a daily basis, and each cell was operated for three days a week for a total of five weeks. The products generated were chlorine gas, hydrogen gas and caustic soda solution. It was observed that after the second day of operation, a sizeable quantity of liquor had been produced and consistent production followed thereafter. Electrolytic product was consequently withdrawn from the cathodic end of the electrolytic cell.

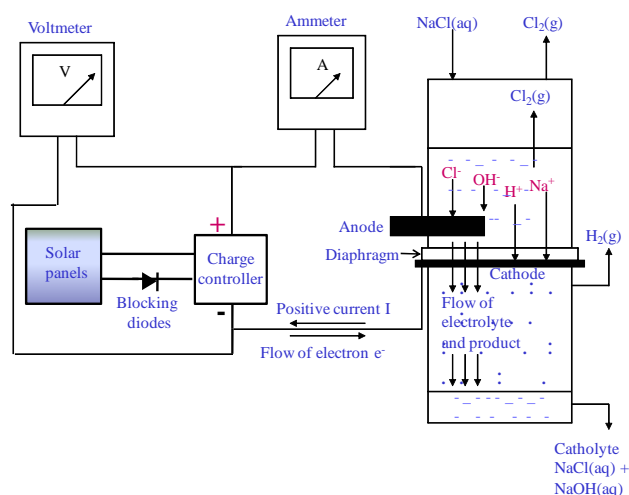


Figure-1. Schematic electrochemical operational diagram of solar powered diaphragm cells.



RESULTS AND DISCUSSIONS

It was observed for both cell types and for all operations that the open circuit voltage was always greater than the cell voltage at loading. This was because of the fact that loading caused a drop in potential, in addition to the effect of the charge controller on the cells also. The charge controller was needed to regulate the amount of current entering into the cell, and also to prevent the backward flow of electricity from the cell to the solar panels as a result of the electrochemical potential generated in the cell by reason of the electrochemical reactions. Furthermore, it was observed that the amount of electricity generated by the solar panels varied with the intensity of the sun on each particular day. The highest voltage was observed for the hottest day and vice-versa. The values of current, mass flow rate, efficiency and so on obtained for the two cells closely resemble the range obtained for diaphragm cells operated by stepped down a.c to d.c rectified power supply from mains (Olufemi *et al.*, 1999; 2000, 2008).

Figure-2 shows the variation of average current with average voltage for the asbestos and non-asbestos diaphragm cells. Higher currents and voltages were observed for the asbestos diaphragm cells. The two cells confirmed the ohmic direct proportional relationship that current increases linearly with voltage. The non-asbestos seems to have a higher operational electrical resistance with respect to the present operation.

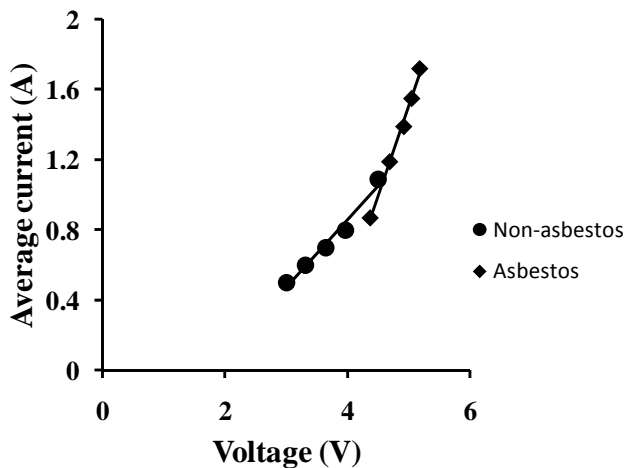


Figure-2. Variation of current with voltage for the asbestos and non-asbestos diaphragm cells.

In Figure-3, the molar concentration of caustic soda in the catholyte products of the two cells is shown to increase with average cell current. The non-asbestos diaphragm cell produced more concentrated solutions relatively than the asbestos diaphragm cell with respect to the present electrochemical operation. Despite the fact that the non-asbestos cell operated at a lower electrical current than its counterpart, it still produced more concentrated products. The non-asbestos diaphragm cell seems to be better in the production of more concentrated product in this regard. The reason may be due to the fact that the non-

asbestos diaphragm is less permeable than the asbestos diaphragm resulting in relatively higher residence time of the reacting species at the electrodes. This means that conversion will be higher per unit space volume of cell.

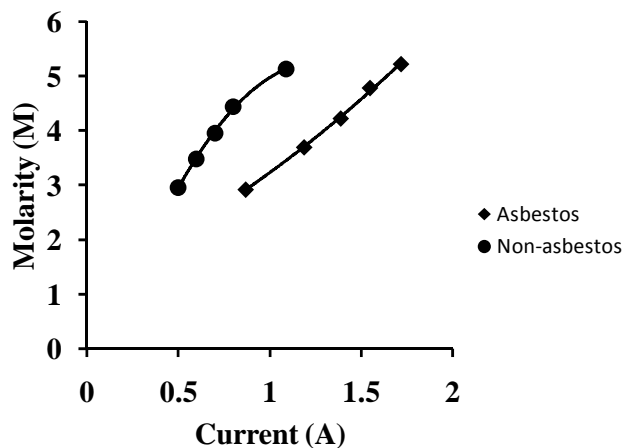


Figure-3. Variation of concentration with current for the asbestos and non-asbestos diaphragm cells.

Variation of the mass flow rate of caustic soda produced for the two cells with average operational current is plotted in Figure-4. As expected from the previous plot, the asbestos diaphragm cells resulted in higher mass flow rate than the non-asbestos cell. This follows directly from the fact that the asbestos diaphragm is more permeable in the present operation. However it can be observed in the two cells that the mass flow rate increased to a maximum value and then declined. This means that operation at too high current values can lead to energy wastage if not controlled. This is a subject of optimum cell design and optimum cell operation.

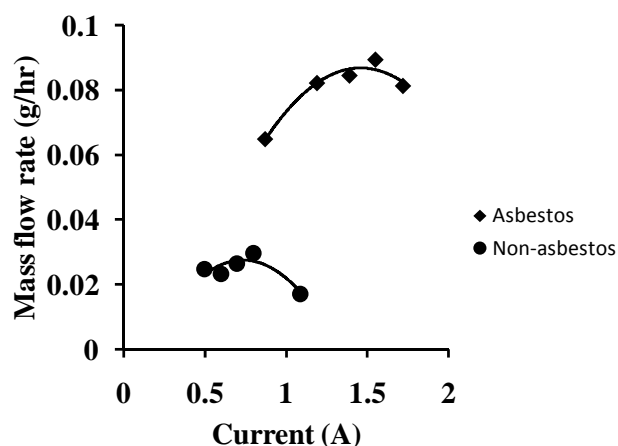


Figure-4. Variation of mass flow rate with current for the asbestos and non-asbestos diaphragm cells.

Figure-5 shows the variation of average current efficiency with operational voltage. As it can be deduced from the operation of the two cells, too high voltages above the theoretical decomposition voltage leads to reduction in efficiency, there by resulting in more energy



wastage. The asbestos diaphragm cells recorded higher current efficiencies with respect to the present operational procedure. The less permeable nature of the non-asbestos diaphragm may be responsible for its lower current efficiency relative to its counterpart.

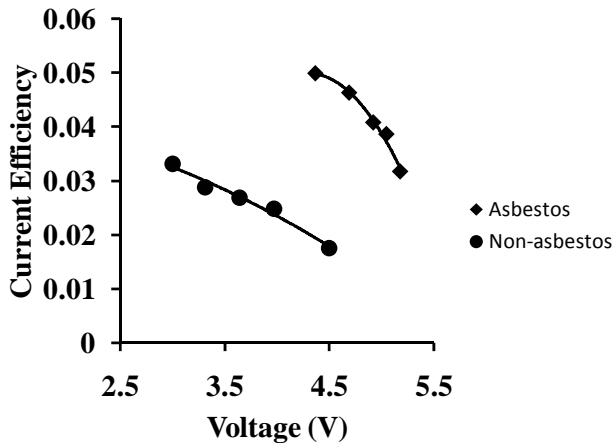


Figure-5. Variation of current efficiency with operational voltage for the asbestos and non-asbestos diaphragm cells.

The yield (kg NaOH / kg NaCl input) increased with voltage in Figure-6, with that of the non-asbestos cell indicating higher yield with respect to voltages applied. This showed the possibility of improving the yield of caustic soda produced with increased operational voltages for the cells.

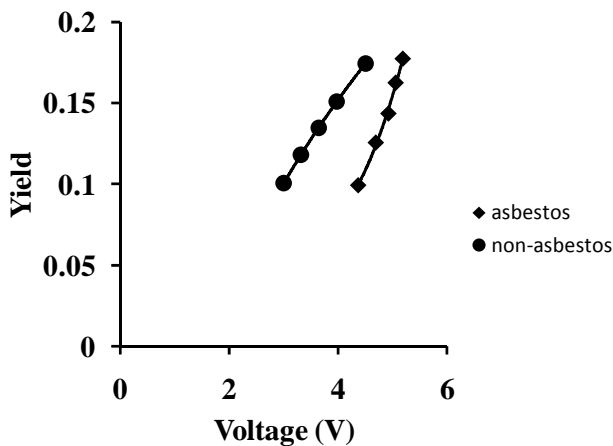


Figure-6. Variation of yield with operational voltage for the asbestos and non-asbestos diaphragm cells.

In Figure-7, the non-asbestos cell showed a better yield per d.c Watt than the asbestos diaphragm cell. This indicated that the non-asbestos cell in the present operation produced more desired product than the asbestos cell at corresponding

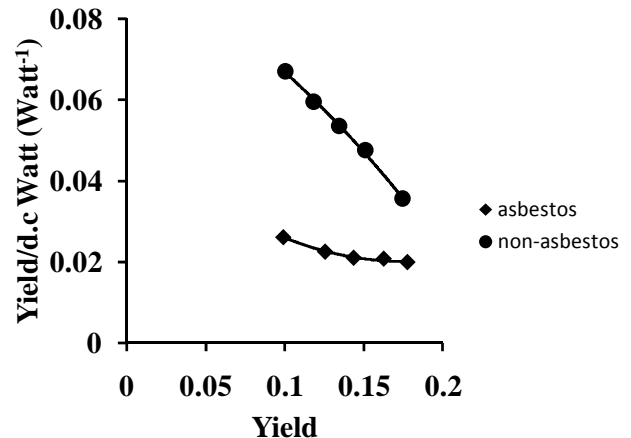


Figure-7. Variation of yield with yield /d.c Watt for the asbestos and non-asbestos diaphragm cells.

electrical d.c power supplied. The yield /d.c Watt is a good indication of the electrical power effectiveness of substance producing electrochemical cells.

In Figure-8, the variation of the specific electrical energy requirement for the production of caustic soda with respect to operating voltage is shown. It can be deduced that the specific electrical energy needed to produce 1 kg of caustic soda decreased with operating voltage for the two cells. The specific energy required decreased with increasing cell voltage for the two cells. From the plot, the specific energy required by the non-asbestos diaphragm cell for corresponding voltages with that of the asbestos diaphragm cell seems to be lower. This is a strong indication that if improved upon, the non-asbestos diaphragm cell has a higher capability of producing more caustic soda for the same electrical energy supplied with its asbestos counterpart. In simple terms, the non-asbestos diaphragm cell produced more caustic soda for the same applied potential difference than the asbestos diaphragm cell in the present operation. In comparison with industrial cells, the specific energy required by commercial diaphragm cells approximately varies from 1.38×10^7 to 2.03×10^7 J/kg, with current densities ranging between 900 to 2600 A/m² (Worell *et al.*, 2000; Tilak *et al.*, 2007). The two laboratory scale cells presented here required higher specific energy per kilogram of caustic soda produced in the present operation. The current densities employed in the solar powered cells ranged from 52.08 to 179.17 A/m², which is relatively lower to commercial diaphragm cells current densities. This is likely to be the reason for the relatively higher specific energy required per kilogram of caustic soda produced. Appropriate scale-up and optimization techniques of the solar powered cells could make the values comparable.

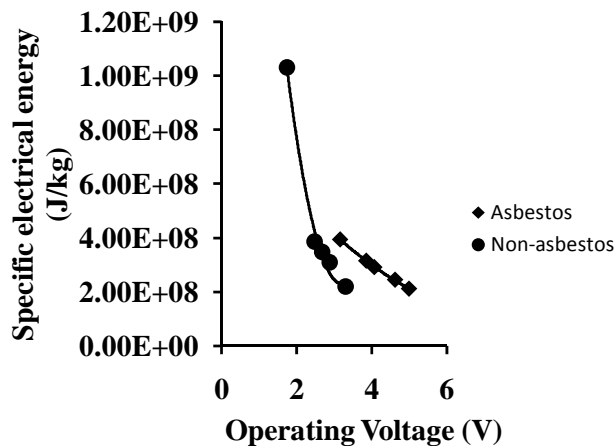


Figure-8. Variation of specific electrical energy with operational voltage for the asbestos and non-asbestos diaphragm cells.

CONCLUSIONS

From the results obtained by the cell operations, it can be reasonably concluded that a solar powered diaphragm cell is capable of producing caustic soda of specification closely equal to those produced by conventionally powered diaphragm cells of similar scale, as long as the solar panels are capable of generating enough voltage to overcome cell and circuit resistance by situating it in an appropriate location, installing them correctly, and completing the circuit as required. The advantages of the present work are that the cells can be operated without the use of conventional electric power, since the only energy required comes directly from the sun. Also the operation can be a very compact process that fits into a small area or can be scaled up to the required size depending on the capacity of production. The process promised to be very economical and very flexible in terms of expansion. The operation is environmentally friendly, because the only form of energy required is solar. The disadvantages of the operation are that it is not highly efficient after sunset and during rainfall. Also, production is not constant but depends on the sun's intensity.

On comparison of the types of diaphragms used, the non-asbestos diaphragm seems to be more preferred, because its yield and productivity is comparatively better to that of the asbestos diaphragm. It could also be less harmful compared to the carcinogenic nature of asbestos.

With further research on appropriate scale-up and optimization techniques, solar powered cells could possibly match commercial scale conventional cells in certain performances. The maximum current density employed was 179.17 A/m^2 for the two cells combined together. This is low compared with those employed in conventional commercial diaphragm cells which in many cases range from 900 to 2600 A/m^2 (Worell *et al.*, 2000; Tilak *et al.*, 2007). However, a very important factor which the solar powered cells are expected to achieve is to have a high output of material for little input of material and energy, which is the recent trend in the chlor-alkali

industry, according to Minter (2002) and Sugiyama *et al.*, (2003).

Above all, this direct solar energy powered means of producing caustic soda with electrochemical cells could be a very commercially viable project in areas where the power situation is epileptic, erratic and undergoing reforms, considering the fact that those areas might need to have abundant sunlight for better part of the year.

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