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### Preliminary Analysis of Fuel Cell Derived Technologies Applied to Energy Conservation in the Chlor-alkali Industry

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PRELIMINARY ANALYSIS OF FUEL CELL DERIVED TECHNOLOGIES APPLIED TO ENERGY CONSERVATION IN THE CHLOR-ALKALI INDUSTRY

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ABSTRACT

In this work we investigated the application of four fuel cell derived technologies for energy conservation in the chlor-alkali industry. They include: (1)  $H_2$ - $Cl_2$  fuel cell (HCLFC), (2) electrochemical concentrator (ECC), (3) alkaline  $H_2$ - $O_2$  fuel cell (AFC), and (4) air depolarized chlor-alkali cell (ADCAC). We have developed performance models for the various fuel cell derived systems and combined them with an economic model to predict the benefits of a particular technology to the chlor-alkali process. The results of a differential net present value economic analysis conducted for each of these technologies is presented and discussed. All the fuel cell derived technologies investigated exhibit potential for significant energy savings in the chlor-alkali industry. Our economic analysis indicates that the commercial attractiveness for the above technologies is in the order:  $CAC + HCLFC > CAC + ECC > CAC + ECC + AFC > CAC + AFC > ADCAC$ . Increasing the lifetime of the gas diffusion electrodes and minimizing the cost of the electrochemical modules appear to be the major challenges impeding the speedy implementation of the fuel cell derived technologies in the chlor-alkali industry.

1. INTRODUCTION

The chlor-alkali industry is one of the major electrochemical industries. It produces over 10 million tons of chlorine and 11 million tons of caustic soda annually in the U.S. The industry is very energy intensive and consumes 27,000 MW-hr of electricity and  $80 \times 10^{12}$  Btu's of steam annually.<sup>1</sup> Hence, development and implementation of any technology to reduce the electrical and/or

thermal energy requirements of the chlor-alkali process would have a significant impact on the nation's energy usage.

Previously, fuel cells were considered for their energy conserving potential at chlor-alkali facilities.<sup>2</sup> Others have investigated the specific application of alkaline fuel cell<sup>3</sup> and proton exchange membrane fuel cell<sup>4</sup> technology to the chlor-alkali process. Both the electricity and heat produced by the various fuel cells was used to reduce the net energy consumption of the chlor-alkali process. High strength caustic membranes are another alternative in reducing the energy requirements of the membrane chlor-alkali process.<sup>5</sup>

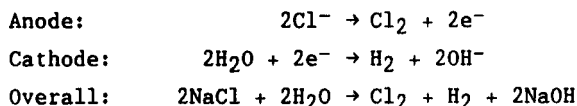
Fuel cell derived technologies offer the potential for significant energy savings in the chlor-alkali industry. We are investigating four specific technologies for application in the chlor-alkali industry: (1)  $H_2$ - $Cl_2$  fuel cell,<sup>2</sup> (2) electrochemical concentrator,<sup>6</sup> (3) alkaline fuel cell, and (4) air-depolarized chlor-alkali cell.<sup>7</sup> All these technologies are based on the efficient use of or elimination of the  $H_2$  by-product produced in the chlor-alkali cell.

The  $H_2$ - $Cl_2$  fuel cell consumes a fraction of the by-product hydrogen and chlorine to produce hydrochloric acid while cogenerating electricity. The electrochemical concentrator consumes the by-product hydrogen and oxygen from air to concentrate the caustic soda from 30 wt% to the 50 wt% commercial product while cogenerating electricity. The alkaline fuel cell consumes the by-product hydrogen and oxygen from air to generate electricity. The air depolarized chlor-alkali cell replaces the hydrogen evolving cathode with an oxygen consuming cathode and lowers the electricity requirements of the process. All the above technologies offer significant potential for energy conservation in the chlor-alkali process. In addition, all the technologies utilize gas diffusion electrodes derived from fuel cell technology.

## 2. ENERGY SAVING FUEL CELL DERIVED TECHNOLOGIES

### Membrane Chlor-Alkali Cell

Figure 1 is a schematic of a membrane chlor-alkali cell. A cation exchange membrane separates the anode and cathode compartments. In the anolyte compartment  $NaCl$  is electrolyzed to produce  $Cl_2$  and in the catholyte compartment water is reduced to produce  $OH^-$  and  $H_2$ . The  $Na^+$  ions are transported from the anode to the cathode compartment to form  $NaOH$ . Hence, the products of the overall process are  $Cl_2$ ,  $NaOH$  and  $H_2$ . For every ton of  $NaOH$  produced, 0.88 tons of  $Cl_2$  and 0.025 tons of  $H_2$  are produced. The electrode reactions are given by:



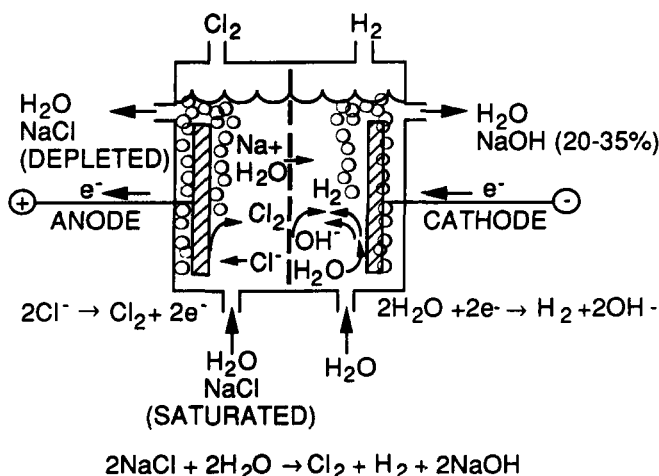
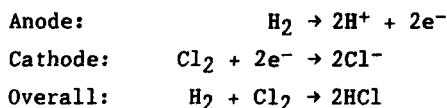


Fig. 1. Schematic of Membrane Chlor-Alkali Cell

The typical operating current density and cell voltage for the membrane chlor-alkali cell is 3.5 kA/m<sup>2</sup> and 3.3V, respectively. The electrical energy consumed by the process is 2150 KWhr per metric ton of caustic. The concentration of the caustic (NaOH) in the exit catholyte stream is typically around 30 wt%. To reduce shipping costs, the caustic is concentrated to 50 wt% commercial product using thermal evaporators. The thermal energy required for raising steam to drive the evaporators is obtained by burning conventional fossil fuels or by burning part or all of the hydrogen by-product.

#### Membrane Electrolysis Cell and HCl Fuel Cell

In the HCl fuel cell, part of the hydrogen and chlorine produced in the chlor-alkali cell is consumed to produce hydrochloric acid while cogenerating d.c. electricity (see Figure 2). The fuel cell electrode reactions are:



The electrodes are porous gas diffusion electrodes and PSI has successfully developed high performance hydrogen and the chlorine electrodes for use in the HCl fuel cell.

The benefits associated with the HCl fuel cell technology are: (1) generation of d.c. electric power for use in the chlor-alkali process, and (2) synthesis of high purity HCl. HCl is used for brine acidification and is currently either purchased or produced by burning the chlorine and hydrogen. By producing the HCl in a cogenerating fuel cell, the negative free energy change of the

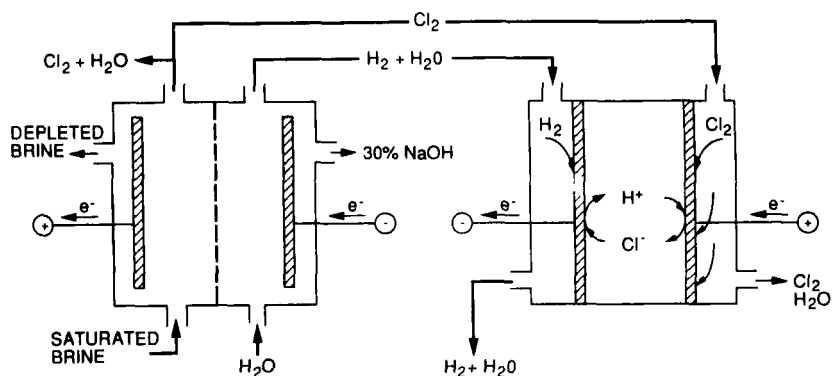
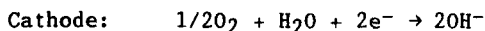
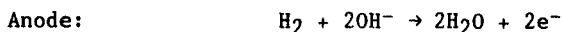


Fig. 2. Schematic of Membrane Electrolysis and HCl Fuel Cell

reaction is recovered as d.c. electric power rather than lost as waste heat.

#### Membrane Electrolysis Cell and Electrochemical Concentrator

A schematic of the electrochemical concentrator coupled to the chlor-alkali cell is shown in Figure 3. In this process, caustic soda (30 wt%) from the electrolysis cell enters the anode and cathode compartments of the membrane alkaline fuel cell. By-product hydrogen gas from the electrolysis cell and oxygen from air react at the gas diffusion anode and cathode, respectively. The individual electrode reactions are given below:



Due to the presence of the cation selective membrane, sodium ions flow from the anode to the cathode compartment. The consumption of water and generation of hydroxyl ions at the cathode combined with the selective transport of sodium ions from the anode to cathode compartment result in increasing the sodium hydroxide concentration in the cathode compartment. Conversely, the generation of water at the anode and the depletion of sodium ions through membrane transport, result in diluting the anolyte stream.

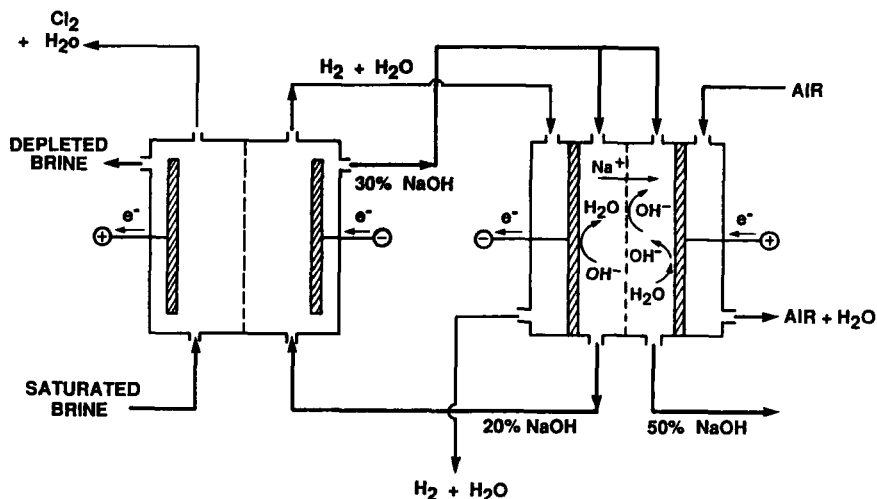


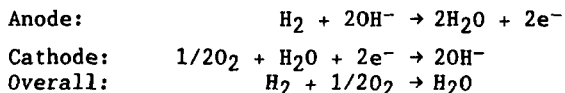
Fig. 3. Schematic of Membrane Electrolysis Cell Coupled to Electrochemical Concentrator

we have also successfully tested several advanced cation selective membranes for use in the electrochemical concentrator.<sup>8</sup>

The benefits offered by this technology are twofold: (1) elimination of thermal evaporators for caustic concentration, thereby help save thermal energy requirements of the process, (2) cogenerate d.c. electricity which can be used in the electrolysis process and thereby help save electrical energy.

#### Membrane Electrolysis Cell and Alkaline Fuel Cell

Figure 4 shows the membrane electrolysis cell coupled to an alkaline fuel cell. The chemical energy of the hydrogen by-product of the chlor-alkali cell is directly converted into electrical energy by electrochemically reacting it with oxygen in the fuel cell. The individual electrode reactions are given below:



#### Air-Depolarized Chlor-Alkali Cell

In this technology, the hydrogen evolving cathode in a conventional membrane cell is replaced with a oxygen consuming electrode (see Figure 5). The individual electrode reactions and the overall cell reaction is given below:

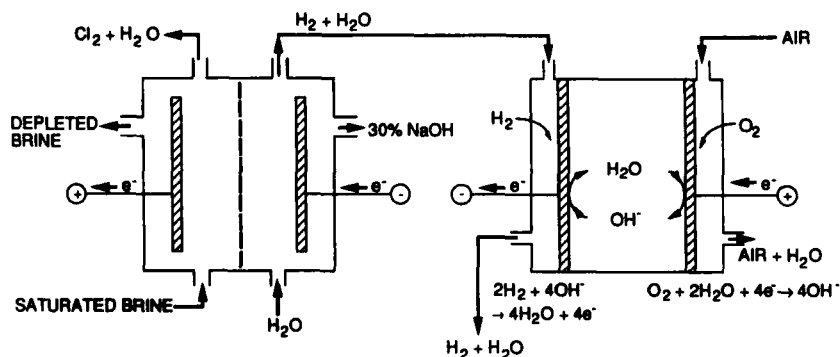


Fig. 4. Schematic of Membrane Electrolysis Cell and Alkaline Fuel Cell

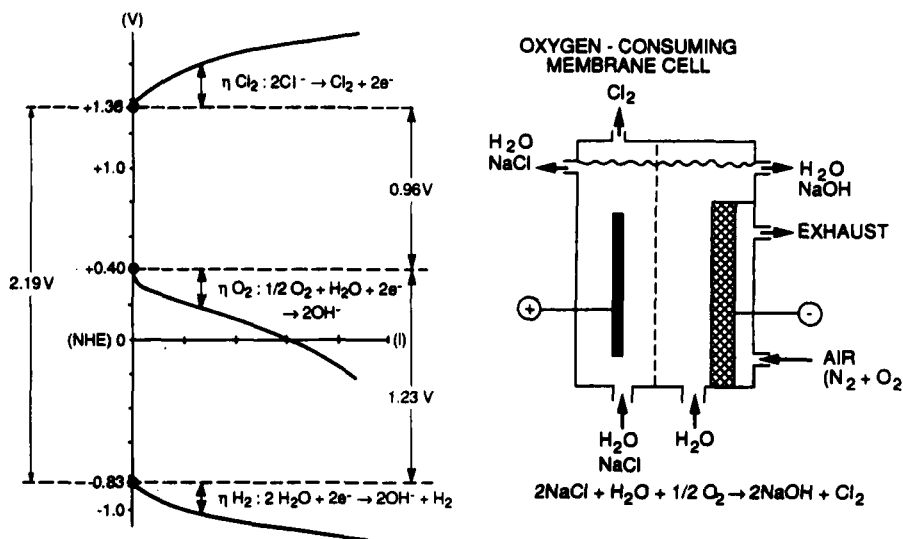
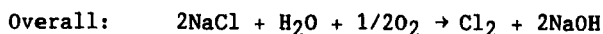
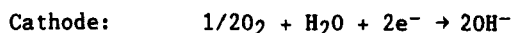


Fig. 5. Schematic of Air Depolarized Membrane Electrolysis Cell



The cathode is actually a gas diffusion fuel cell electrode exposed to oxygen on one side and the electrolyte on the other side. The electroactive species, namely  $\text{O}_2$  and  $\text{H}_2\text{O}$ , diffuse into the electrode matrix and undergo reduction to produce  $\text{OH}^-$ .

The thermodynamic reversible potential of the oxygen consuming cathode in the air depolarized cell is 1.23V more positive than the hydrogen evolving cathode in the conventional chlor-alkali cell.

Hence, even after including the overpotential losses at the cathode the cell voltage of the air-depolarized chlor-alkali cell is significantly lower than the cell voltage of the conventional chlor alkali cell and thereby reduces the energy requirements of the chlor-alkali process.

### 3. ELECTRODE AND MEMBRANE DEVELOPMENT

The success of the fuel cell derived technologies for energy conservation in the chlor-alkali industry depends on the performance of the electrodes and membranes. The electrodes are porous gas diffusion electrodes exposed to gas on one side and electrolyte on the other. The electrocatalyst is comprised of small particles of platinum or gold (25 to 100Å) supported on high surface area carbon. The performance of the electrocatalyst is affected by the choice of carbon support, choice of catalyst, mechanism of catalyst dispersion, catalyst particle size/surface area and catalyst loading. The electrocatalyst is then blended with a hydrophobic binder (e.g., Teflon), formed, and sintered to yield the electrodes. The binder content, sintering temperature, catalyst loading and thickness also affect the performance of the electrodes.<sup>9</sup>

In Figure 6, we present the polarization data for oxygen reduction in 30 wt% caustic at 75°C using Au/C electrocatalyst.

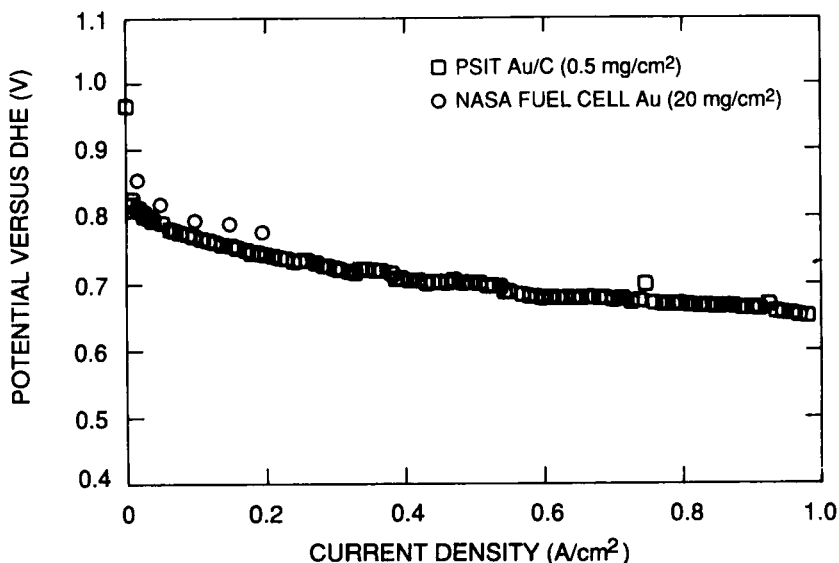


Fig. 6. Oxygen Reduction Polarization Data for PSI Au/C Electrode in 30 wt% NaOH at 75°C

Details on the preparation of the catalyst and electrode fabrication procedure are given elsewhere.<sup>10</sup> The catalyst loading is  $0.5 \text{ mg/cm}^2$ . The data is in close agreement with the unsupported gold electrocatalyst used in the NASA fuel cell. The above gold electrode can be used in the electrochemical concentrator, alkaline fuel cell or the air depolarized chlor-alkali cell. In Figure 7 we present the data for the chlorine reduction electrode in 3M HCl at room temperature. The best performance was obtained with 10 percent Pt/Ketjen electrode with a catalyst loading of  $0.5 \text{ mg/cm}^2$ . The chlorine electrode potentials are considerably higher than the oxygen electrode suggesting that the HCl fuel cell will deliver more power at the same current density than the alkaline fuel cell.<sup>11</sup>

In Figure 8 we present the polarization data for hydrogen oxidation in 30 wt% caustic at  $75^\circ\text{C}$ . The electrode is made up with a Pt/C electrocatalyst and will be used as the anode in the alkaline fuel cell and the electrochemical concentrator. In Figure 9 we present the anode data for the HCl fuel cell in 3M HCl at room temperature.

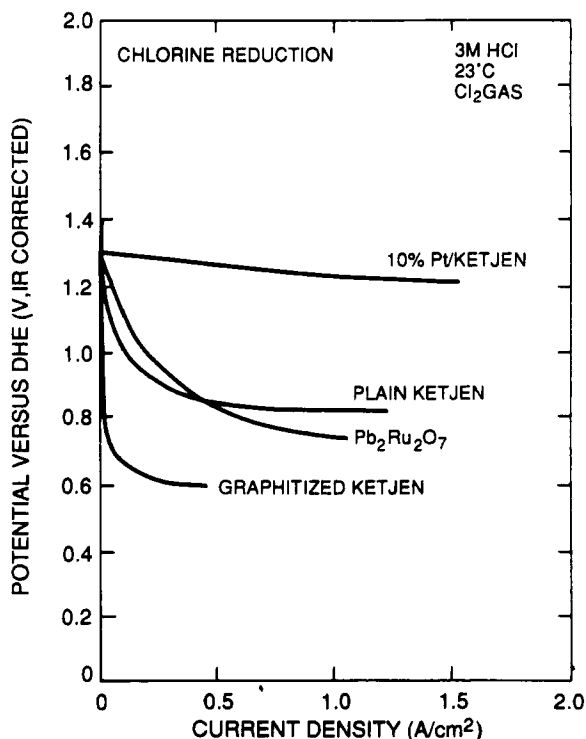


Fig. 7. Chlorine Reduction Polarization Data in 3M HCl at  $23^\circ\text{C}$  with (a)  $\text{CO}_4\text{-Pt/Ketjen}$ , (b) Plain Ketjen, (c)  $\text{Pb}_2\text{Ru}_2\text{O}_7$ , and (d) Graphitized Ketjen Electrode

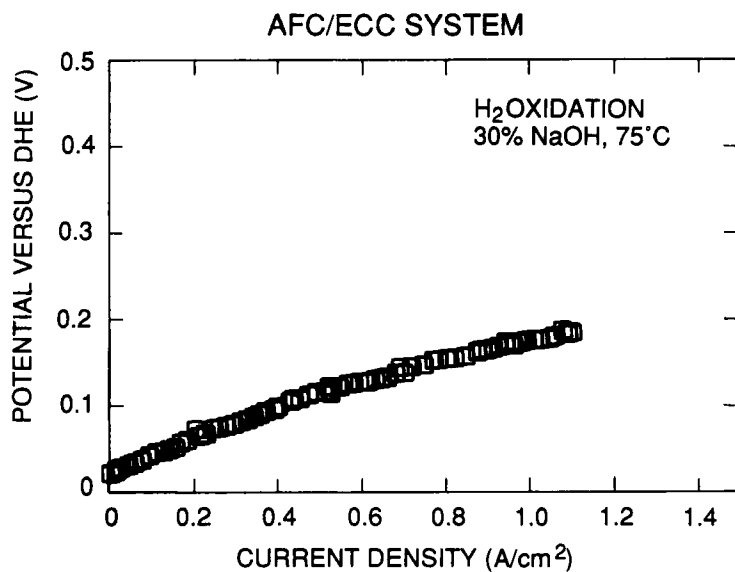


Fig. 8. Polarization Data for H<sub>2</sub> Oxidation in 30 wt% Caustic at 75°C

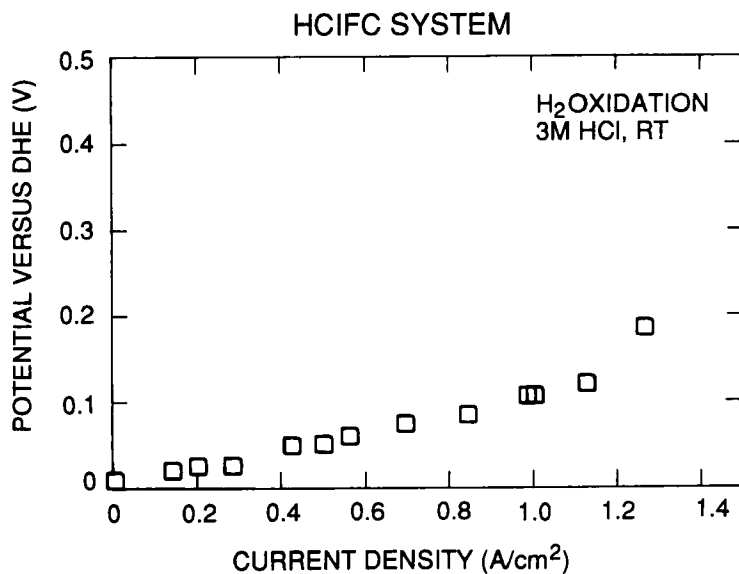


Fig. 9. Polarization Data for H<sub>2</sub> Oxidation in 3M HCl

In collaboration with duPont, we have tested several advanced developmental membranes for use in the electrochemical concentrator. Specifically we measured the electrical conductivity and the transport number (both the sodium transport and water transport) for these membranes in different environments of interest to the electrochemical concentrator.<sup>12</sup> Also we have developed special membrane coatings on electrodes for Cl-tolerance in HCl fuel cell applications.<sup>13</sup>

#### 4. FUEL CELL DERIVED TECHNOLOGY PERFORMANCE ESTIMATES

Using the data for hydrogen oxidation and chlorine reduction in HCl acid media, we estimate that the HCl fuel cell will generate 45 KWhr of d.c. electricity per metric ton of caustic and co-produce the HCl required for the acidification of brine in the chlor-alkali process.

We estimate the electrochemical concentrator to concentrate the caustic from 30 wt% to 50 wt% consuming only 45 percent of the hydrogen produced in the chlor-alkali cell. Additionally, the electrochemical concentrator will produce 202 KWhr of d.c. electricity per metric ton of caustic.<sup>14</sup>

Using the electrode performance data for oxygen reduction and hydrogen oxidation in alkaline electrolyte and all the hydrogen by-product, we estimate the alkaline fuel cell to produce 463 KWhr of d.c. electricity. The alkaline fuel cell also has the advantage of being an add-on technology without disrupting the operation of current membrane chlor-alkali process.

The HCl fuel cell, the electrochemical concentrator and the alkaline fuel cell may be integrated with the chlor-alkali cell. Figure 10 shows the schematic of such an integrated process with the chlor-alkali cell coupled to the HCl fuel cell, electrochemical concentrator and the alkaline fuel cell. In this process based on a metric ton of caustic, 45 percent of the hydrogen is used in the concentrator to concentrate the caustic from 30 to 50 wt% cogenerating 202 KWhr of d.c. electricity; 50 percent of the hydrogen is consumed in the alkaline fuel cell to produce 255 KWhr of d.c. electricity and the remaining hydrogen is consumed in the HCl fuel cell to produce hydrogen chloride required for brine acidification cogenerating 45 KWhr of d.c. electricity. The advantages offered by this process are: (1) elimination of evaporators reducing thermal energy requirements of the chlor-alkali process, (2) more efficient use of hydrogen by-product to cogenerate/generate d.c. electricity in the fuel cells, and (3) synthesis of high purity HCl for brine acidification. These technologies also share common module designs which facilitates the engineering design and development of these technologies.

Using the oxygen reduction data we calculate that the electrical energy requirements of the air-depolarized chlor-alkali cell at an operating current density of 3.5 kA/m<sup>2</sup> is only 1713 KWhr per metric ton of caustic.

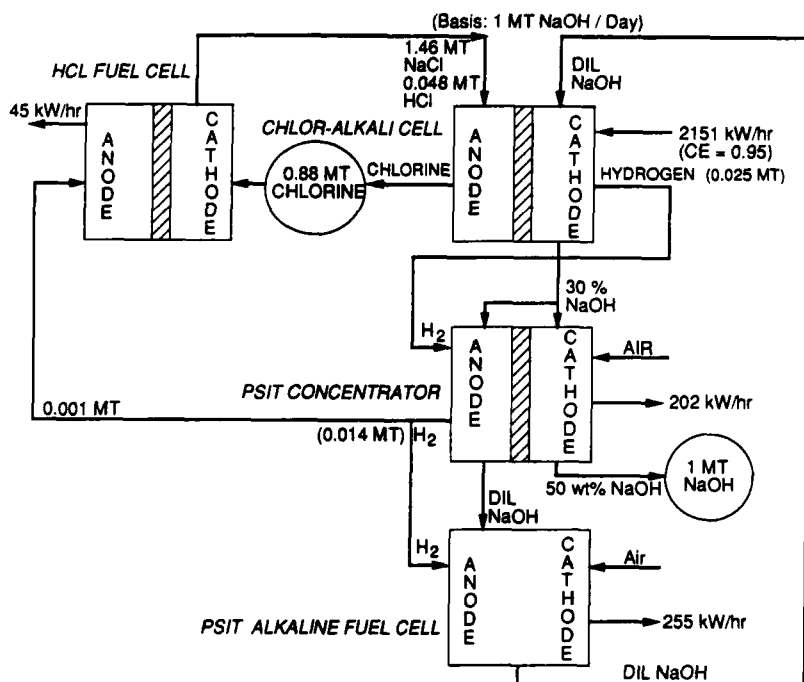


Fig. 10. Schematic of Chlor-Alkali Cell, Electrochemical Concentrator, Alkali Fuel Cell, and HCl Fuel Cell

In summary, the salient features of the above mentioned technologies are: (1) the HCl fuel cell will produce the HCl required for brine acidification consuming 5 percent of the chlorine and hydrogen and generating 45 KWhr/MT NaOH, (2) the electrochemical concentrator will concentrate the caustic to 50 wt% consuming 45 percent of the hydrogen and cogenerating 202 KWhr/MT NaOH, (3) the alkaline fuel cell will generate 463 KWhr/MT NaOH consuming all the hydrogen, and (4) the air-depolarized chlor-alkali cell will save 438 KWhr/MT NaOH eliminating the hydrogen by-product. Depending on the plant location and the demand for hydrogen or chlorine, any one or combination of the fuel cell derived technologies described above can be used to conserve energy in the chlor-alkali process.

## 5. ECONOMIC ANALYSIS

Using the above performance estimates, we conducted a differential net present value analysis to evaluate the economic potential of the various fuel cell derived technologies.

The baseline case that was used for the comparison consisted of a membrane chlor-alkali cell (CAC) using standard commercial membranes to produce 30 percent caustic soda which is then evaporated to 50 percent commercial grade caustic. For simplicity, it was assumed that the hydrogen by-product produced during the process was burned in the evaporators to concentrate the caustic with no need for any additional fuel. Alternate systems studied that utilized the by-product hydrogen for other purposes incurred a corresponding fuel cost penalty. Conversely, systems that under utilized the hydrogen available were given a hydrogen fuel credit. The CAC plant capacity was set at 200 MT/day and the plant lifetime was fixed at three years.

The systems studied in this analysis consisted of 1) the air depolarized CAC, 2) the baseline CAC coupled to an alkaline fuel cell (AFC), 3) the CAC coupled to the electrochemical concentrator (ECC), 4) the CAC, the ECC and the AFC together, and 5) the CAC and the hydrogen-chlorine fuel cell (HClFC). Input data that was fixed for this analysis included the discount rate, electricity and fuel costs, CAC capital cost, membrane cost, current efficiency, hydrogen utilization and CAC operating current density. The values used for these various parameters are listed in Table 1. Cell operating conditions for the different systems were determined experimentally or obtained from published data.

Key variables used in the sensitivity analyses were the module capital cost and operating current density. All fuel cell derived technologies were related by a module cost that included the price of the electrodes and cell housing. For the ECC, a membrane cost was added. For the analysis, each system was evaluated for its cost savings as a function of the module cost at current densities of 1.0 and 3.5  $\text{kA/m}^2$ . The range of module costs used for the analysis was \$50 to \$2000 per square meters.

Table 1. Input Values for Economic Analysis

Input	Value
Discount Rate	16%
Electricity Cost	\$0.05/kWh
Fuel Cost	\$5.00/MBTU
CAC Capital Cost	\$3,300/ $\text{m}^2$
Membrane Cost	\$550/ $\text{m}^2$
Current Efficiency	95%
Hydrogen Utilization-	
For AFC	100%
For HClFC	5%
CAC Current Density	3.5 $\text{kA/m}^2$

The results of the cost analysis study for the air depolarized CAC system are presented in Figure 11. These results show that at the lower operating current density of  $1.0 \text{ kA/m}^2$ , the air depolarized CAC will not be cost effective versus the standard CAC at any module cost.

The lower current density of operation necessitates that 3.5 times more chlor-alkali cells must be constructed to produce the same amount of products. The relatively high capital investment of the CAC keeps the air depolarized CAC from achieving a positive break even value. The economics improve dramatically at the  $3.5 \text{ kA/m}^2$  current density and show a break even fuel cell module cost of  $\$746/\text{m}^2$ .

The results of the CAC coupled with an AFC are presented in Figure 12. These results indicate a similar module break even cost at both low and high operating current density. The break even costs for the CAC/AFC at  $1.0$  and  $3.5 \text{ kA/m}^2$  are  $\$247$  and  $\$209/\text{m}^2$ , respectively. Insensitivity to the operating current density is because the capital cost varies inversely with the electricity power savings of the AFC. An increase in current density leads to lower capital costs but the voltage penalty suffered by the AFC at the higher current density reduces electric power savings. Both these

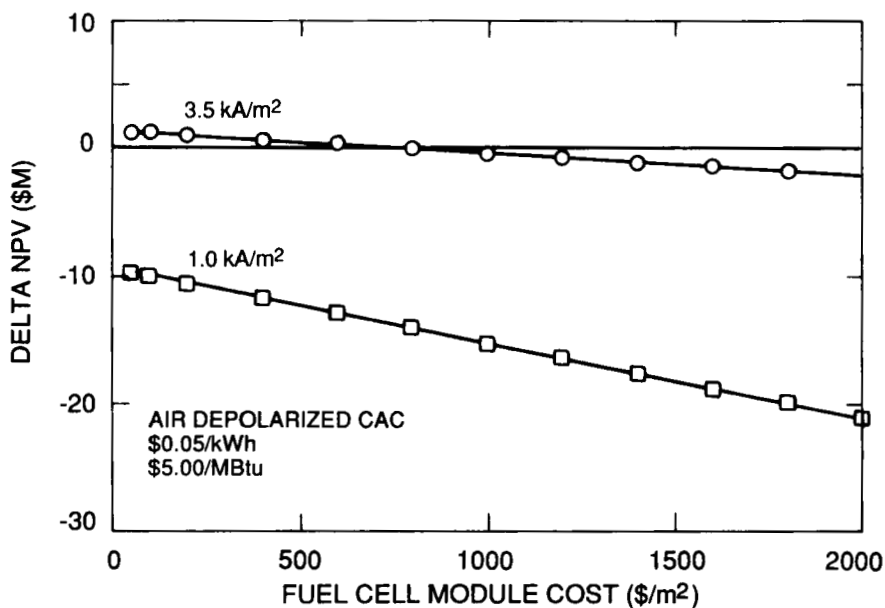


Fig. 11. Differential Net Present Value Analysis of Air Depolarized Chlor-Alkali Cell

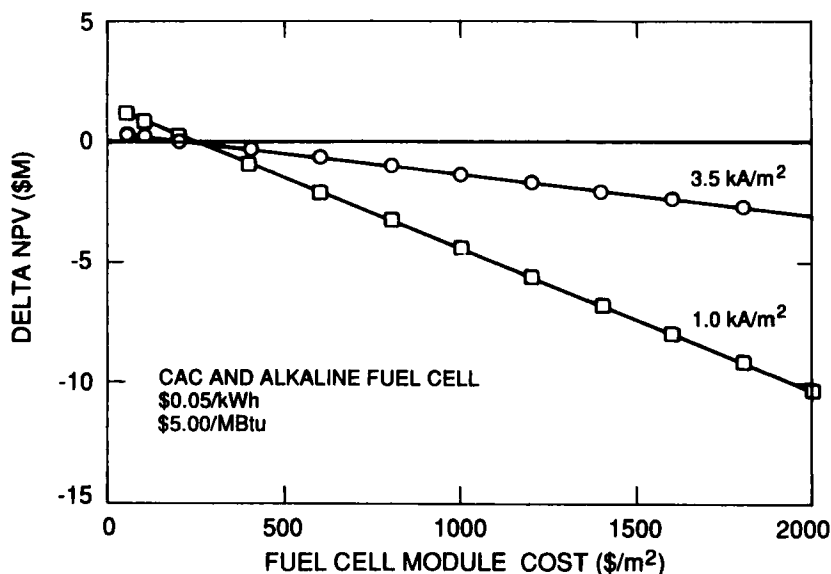


Fig. 12. Differential Net Present Value Analysis of Chlor-Alkali Cell and Alkaline Fuel Cell

break even costs are economically unattractive. This result stems from the fact that the CAC/AFC system utilizes all the hydrogen by-product for producing electricity, but the fuel cost penalty it pays to produce 50 wt% caustic outweighs this electricity cost savings.

The results of the analysis of the CAC and the ECC are presented in Figure 13. The graph indicates a fuel cell module break even cost for the CAC/ECC at 1.0 kA/m² of \$563/m². The CAC/ECC is thus more economically attractive than the previously discussed air depolarized CAC or the CAC/AFC at the low current density. If the operating current density is 3.5 kA/m², the attractiveness of the CAC/ECC is even greater. The fuel cell module break even cost increases substantially to \$2519/m². The favorable results for this system are due in part to the fact that the ECC is concentrating the caustic to 50 wt%. Therefore no fuel cost penalty is being paid as in the case of the AFC. The capital cost is also lower because only 45 percent of the hydrogen is utilized in the ECC as compared to 100 percent in the AFC. The hydrogen utilization is proportional to the capital investment needed. In addition, the unused portion of the hydrogen gives the ECC process a hydrogen fuel credit.

The next system studied combines the previous two systems. The CAC is coupled to a ECC and also a AFC. As mentioned earlier, the ECC uses 45 percent of the hydrogen by-product. In this system, the remaining 55 percent of the hydrogen is then fed into a AFC. The results of the analysis is presented in Figure 14. The economics of the CAC/ECC/AFC is inferior to the CAC/ECC at both operating current

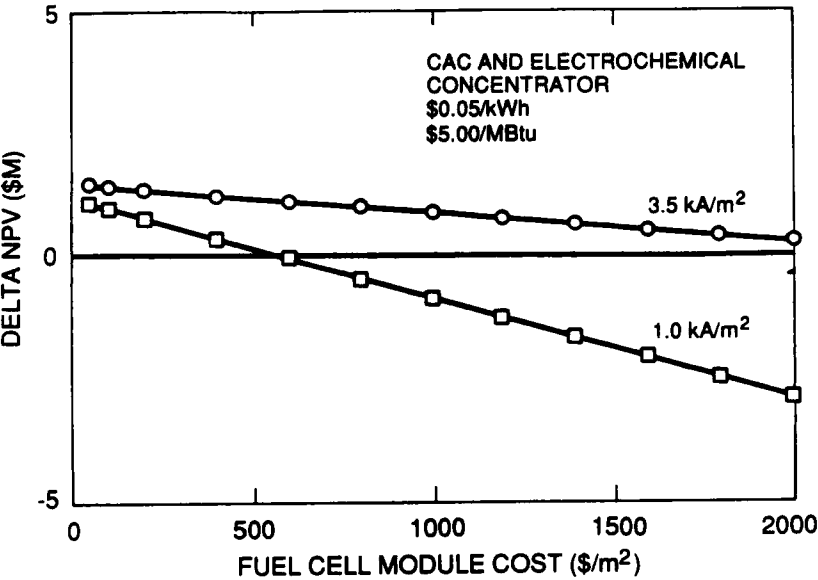


Fig. 13. Differential Net Present Value Analysis of Chlor-Alkali Cell and Electrochemical Concentrator

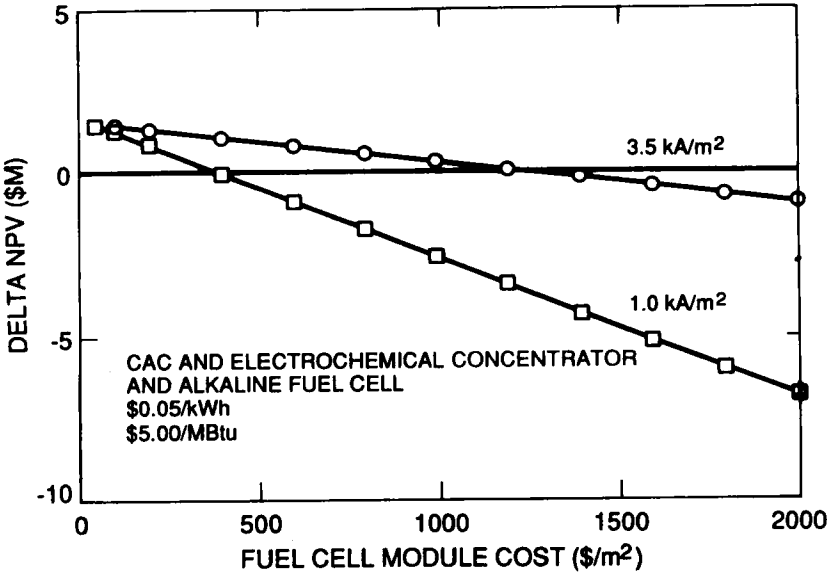


Fig. 14. Differential Net Present Value Analysis of Chlor-Alkali Cell and Electrochemical Concentrator and Alkaline Fuel Cell

densities. The fuel cell module break even cost at 1.0 and 3.5  $\text{kA/m}^2$  is \$389 and \$1248/ $\text{m}^2$ , respectively. These break even costs make this system more attractive than the CAC/AFC case but not as attractive as the CAC/ECC alone.

The last system studied was the CAC coupled to a HClFC. The results of this study are presented in Figure 15. In this system, 5 percent of the hydrogen by-product and chlorine product are utilized to produce HCl to acidify the brine in the chlor-alkali membrane electrolysis cell. This also produces DC power. It is assumed that the remaining hydrogen is enough to concentrate the caustic to 50 wt%. At the lower current density of 1.0  $\text{kA/m}^2$ , the fuel cell module break even cost is a very attractive \$847/ $\text{m}^2$ . The economics of the system improve even more at 3.5  $\text{kA/m}^2$  with a module breakeven cost of \$2684/ $\text{m}^2$ .

## 6. SUMMARY AND CONCLUSIONS

The results of the economic analysis for the different chlor-alkali technologies are summarized in Table 2. The fuel cell module break even cost, at two operating current densities, for each individual case study is presented. In the economic study

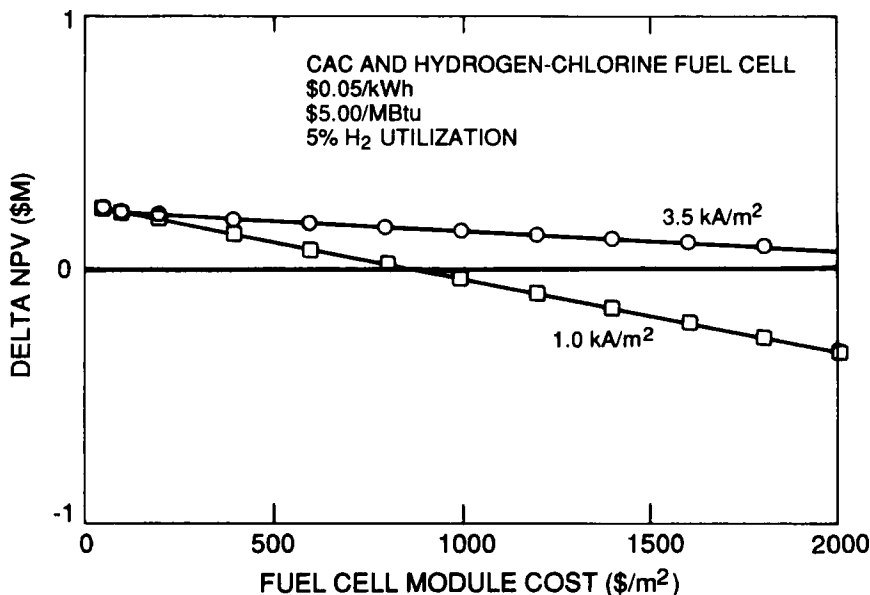


Fig. 15. Differential Net Present Value Analysis of Chlor-Alkali Cell and Hydrogen-Chlorine Fuel Cell

Table 2. Economic Analysis Summary: Fuel Cell Module Break Even Cost (\$/m<sup>2</sup>)

Case Study	Break Even Cost of Additional Technology (\$/m <sup>2</sup> )	
	1.0 kA/m <sup>2</sup>	3.5 kA/m <sup>2</sup>
AD CAC	-1609	746
CAC/AFC	247	209
CAC/ECC	563	2519
CAC/ECC/AFC	389	1248
CAC/HClFC	847	2684

conducted, five different alternatives to the present chlor-alkali process were investigated. All these alternatives were based on fuel cell technologies. The results of the study indicate that the chlor-alkali cell/electrochemical concentrator system and the chlor-alkali cell/hydrogen-chlorine fuel cell system look the most attractive and warrant further study. These two systems offer electricity power cost savings that are substantial enough to offset any increased capital cost that may be incurred.

#### 7. ACKNOWLEDGMENT

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