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Final Report on
**PROCESS ENGINEERING AND ECONOMIC EVALUATIONS
OF DIAPHRAGM AND MEMBRANE
CHLORIDE CELL TECHNOLOGIES**
Contract No. 31-109-38-5474

by

MASTER

Abam Engineers, Inc.

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Prepared for the U. S. DEPARTMENT OF ENERGY
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Final Report on
PROCESS ENGINEERING AND ECONOMIC EVALUATIONS OF
DIAPHRAGM AND MEMBRANE CHLORINE CELL TECHNOLOGIES

Prepared for
The Office for Electrochemical Project Management
Argonne National Laboratory
Under Contract No. 31-109-38-5474

By
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Federal Way, Washington 98003
with assistance from
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December 1980

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SUMMARY

This study explores the chlor-alkali manufacturing technologies of (1), diaphragm cells (2), current technology membrane cells (3), catalytic cathode membrane cells (4), oxygen-cathode membrane cells and to a lesser extent several other related emerging processes. Comparisons have been made on the two bases of 1) conventional industrial economics, and 2) energy consumption.

The current diaphragm cell may have a small economic advantage over the other technologies at the plant size of 544 metric T/D (600 T/D). The three membrane cells all consume less energy, with the oxygen-cathode cell being the lowest. The oxygen-cathode cell appears promising as a low energy chlor-alkali cell where there is no chemical market for hydrogen.

Federal funding of the oxygen-cathode cell has been beneficial to the development of the technology, to electrochemical cell research, and may help maintain the U.S.'s position in the international chlor-alkali technology marketplace.

Tax law changes inducing the installation of additional cells in existing plants would produce the quickest reduction in power consumption by the chlor-alkali industry.

The implementation of these new technologies will have no significant impact upon employment in the chlor-alkali industry.

Alternative technologies such as the solid polymer electrolyte cell, the coupling of diaphragm cells with fuel cells and the dynamic gel diaphragm have a strong potential for reducing chlor-alkali industry power consumption.

Adding up all the recent improvements that have become cost-effective, along with those that are likely to become commercial in the next few years, and the expected reductions in current densities as energy becomes more expensive, the electrical energy required to produce a unit of chlorine by 1990 should be only 50% to 60% of that used in 1970.

In the United States the majority of the market does not demand salt-free caustic. About 75% of the electrolytic caustic is produced in diaphragm cells and only a small part of that is purified. The demand for salt-free caustic is low as salt-free caustic only brings a premium of around \$11.02/metric ton (\$10.00/ST). This study indicates that unless membrane cell costs are greatly reduced or a stronger demand develops for salt-free caustic, the diaphragm cells will remain competitive.

INTRODUCTION

The chlor-alkali industry is the second largest industrial electrolytic consumer of electric power in the United States. The Department of Energy (DOE) has therefore been searching for economical ways of reducing energy consumption in this area (1) (2). The industry has been active in developing new cell concepts and designs that reduce the electrical energy required to produce a unit of chlorine and its co-product caustic soda (3) (4).

Diaphragm cell plants accounted for approximately 75% of the 10 million metric tons of chlorine produced in 1979. During the seventies improvements in these plants have made possible a 20% to 30% reduction in total energy usage. Further improvements by using microporous separators and catalytic (reduced hydrogen overvoltage) cathodes should reduce electrical power requirements another 10% (4).

The commercialization of the ion exchange membrane cell has been a major development of the past few years. Its low salt, high concentration caustic soda product is a major advantage. Forthcoming developments of the cell using either catalytic cathodes or oxygen depolarized cathodes and pressure operation should further reduce the cell energy consumption. The major disadvantages of this cell are the high cost of the cells and the high cost of brine purification. At the present time the membrane cell appears to be closely competitive with the diaphragm cell.

In order to better understand the potential for energy savings in the chlor-alkali industry, the Argonne National Laboratory, under contract with DOE, engaged ABAM Engineers, Inc., to make an economic study of the emerging technologies as compared to diaphragm cell technology. This report gives ABAM's findings.

PURPOSE AND SCOPE

The purpose of the study was to make economic evaluations of developing technologies for reducing energy consumption of chlor-alkali plants. Emphasis was placed on membrane cells because these seem most adaptable to the incorporation of forthcoming new technologies.

The scope of the study covers current and emerging technologies for the production of chlorine and caustic as viewed through the eyes of a manufacturing company. Technology comparisons are made between plant designs which have been optimized economically by marketplace criteria.

The principal comparisons are made between the following four technologies:

- o Conventional diaphragm cell plant (reference case).
- o Membrane cell plant with current commercial technology.
- o Membrane cell plant with catalytic cathodes.
- o Membrane cell plant with oxygen depolarized cathodes.

Limited comparisons are made on the following technologies:

- o Diaphragm cell plant with catalytic cathodes.
- o Hybrid diaphragm cell plant with hydrogen fuel cells.
- o Solid polymer electrolyte membrane cell.
- o High-pressure cell producing liquid chlorine directly.

The study also looks at the characteristics of these technologies with respect to opportunities for the U.S. federal government to facilitate the reduction of energy consumption by the chlor-alkali industry.

CONCEPT AND APPROACH

The conceptual approach toward achieving valid comparisons among the different technologies was to develop a complete envelope of criteria which defined a realistic, commercial plant. Within this envelope several plants were estimated, each utilizing a different major technology. The design and economic guidelines are the same as those used for the design of a competitive commercial plant for a U. S. chlor-alkali producer.

The reference example for technology, economic factors and energy consumption is an optimized "current practice" diaphragm cell plant.

The principal sources of data were the current licensors of chlor-alkali technology in the United States. The data from these and other sources was merged to produce the plant capital and manufacturing cost estimates for each technology studied.

5.0 PROGRAM

The program for implementing the purpose and concept of this study has been structured into four parts.

- o Project Design Criteria and Baseline Diaphragm Plant.
- o Membrane Cell Plant, Two Modified Membrane Plants and Other New Technologies.
- o Capital and Manufacturing Cost Estimates and Energy Audits.
- o Sensitivity Analyses.

5.1 CRITERIA: REFERENCE PLANT AND TECHNOLOGIES

5.1.1 Criteria Envelope

A single set of conditions called a "Criteria Envelope" has been developed so that the different plants will be comparable on a common basis. The envelope is essentially the same as that which would be used by a major industrial firm in considering alternative processes for a new plant to produce chlorine and caustic soda. The criteria envelope includes the factors of plant size, raw material, costs, labor rates, accounting practices, tax rates, sale prices, and operating rate. It includes certain arbitrary criteria solely for the purpose of this comparison such as zero inflation of all economic elements: capital, energy, raw materials, labor and product prices. It also includes the economic comparison criterion that each plant be designed to maximize the discounted cash flow rate of return (DCF).

The maximized DCF criterion as a commonly used, practical measure of an optimum plant design. To determine this optimum, for each plant, the number of cells was varied (with the consequent changes to rectifiers, etc.) and the capital and manufacturing costs determined for each variation. For each, the DCF was calculated until the maximum was found. This case became the optimum plant for this cell. It is used for comparison with the other cell processes, similarly optimized. For the diaphragm cell plant, cell caustic concentrations also influence the maximum DCF. Hence, these were also varied to determine the optimum plant.

A philosophy of design of a "Moderately Well Designed, Operated and Maintained Plant" was chosen. The significance of this choice is that plants can be designed for very low operating costs and high maintenance costs or vice versa. Furthermore, plants can be designed to include many deluxe and expensive features or they can be designed in a very Spartan style. The latter require more highly skilled operators for successful and economic operation. Plant costs can vary as much as +80% to -30% depending on the choice of this criterion.

The criterion of zero inflation was chosen to simplify the economic analysis and also because it is valid for the purpose of comparison between the different processes. The comparison would, however, still be valid in the real-life conditions of inflation. As capital costs and operating costs increase, sales prices will also tend to rise at the same rate.

The 544 metric T/D (600 T/D) plant size was chosen as being about midway between the "optimum design size" diaphragm cell plant of perhaps 910 to 1,360 metric T/D (1,000 to 1,500 T/D) and the less well recognized "optimum size" membrane cell plant of 91 to 272 metric T/D (100 to 300 ST/D).

5.1.1.1 Chlorine Plant Envelope Design Criteria*:

- o 544 net metric tons Cl_2 /day (600 ECU/day).
- o Grass roots plant, not including the purchase of land.
- o Moderately well designed, operated and maintained plant.
- o U.S. Gulf Coast location.
- o Liquid chlorine product.
- o 50% solution, liquid caustic soda product.
- o Solid salt or brine feed.
- o \$12.16/metric ton solid salt cost delivered; \$8.82/metric ton (NaCl) brine cost delivered.
- o 40 mills/KWH power cost.
- o \$0.015/Mcal (\$3.75/MBtu) fuel cost as oil.
- o Boiler efficiency, 85%.
- o \$10.00/hr base labor rate.
- o 150% overhead on labor and supervision.
- o Annual plant maintenance, 5% of capital cost of plant, excluding cell area. Cell renewal and maintenance costs shown as "Cell Renewal" manufacturing costs.
- o Depreciation for tax purposes, 10-year double declining balance for the first 6 years, then straight line for the remaining 4 years.
- o Depreciation for calculation of manufacturing costs: 15-year straight line.
- o 2%/yr taxes and insurance expenses.
- o 10% investment tax credit.
- o Choice of number of cells (balance capital cost vs. operating cost) will be made to maximize discounted cash flow rate of return (DCF).
- o Net sales income (after deducting SG&A and freight allowances), \$358.00/ECU metric. Ten dollar premium added for membrane cell "low salt" caustic.
- o 90% of 365 day/yr operating rate.
- o Costs, expenses and incomes in 1980 dollars.
- o Income tax rate is 46%.
- o Hydrogen not used in boiler is credited at \$0.015/Mcal (\$3.75/MBtu).
- o Platinum catalyst price is \$16.00/g (\$500.00/Troy oz).

*Envelope Criteria Glossary and Comments in Appendix A.

5.1.2 Diaphragm Cell Reference Plant

The diaphragm cell plant has been chosen as a reference plant for this study for two reasons. Firstly, it is the major producer of chlorine and caustic soda in the United States representing approximately 75% of the current production capacity. Secondly, it may be considered a relatively mature technology. A large number of plants have been built. Good data are available for establishing the reference plant design and economics.

The diaphragm cell reference plant incorporates current practice, good technology with respect to energy consumption. These features include minimum spacing, metal anodes, quadruple-effect caustic evaporation, and large size (100,000 to 160,000 amperes) cells.

5.1.2.1 Diaphragm Cell Reference Plant Process Description:

Features: The current diaphragm chlor-alkali cell incorporates anode and cathode compartments separated by an asbestos diaphragm. Feed sodium chloride brine enters the anode compartment in which chloride ion is discharged to chlorine gas on graphite or ruthenium oxide coated titanium anodes. The anode reaction is:

The brine flows by convection through the asbestos diaphragm into the cathode compartment. The (net) cathode reaction is:

The asbestos diaphragm has been formed as a fiber mat on the steel screen cathode by a vacuum depositing process.

Positively charged sodium ions flow through the diaphragm by convection and also under the influence of the attraction of the negatively charged cathode. The sodium ions and the newly formed hydroxyl ions become the sodium hydroxide product.

The catholyte concentration is 10 to 15 wt % and nearly saturated with sodium chloride.

The principal cell operating conditions include the following:

- o Brine feed concentration - 320 g/l NaCl.
- o Anolyte concentration - 220 g/l NaCl. Anolyte acidic due to dissolved Cl_2 . Some operators acidify brine feed to minimize the formation of hypochlorite and chlorate.
- o Salt to caustic ratio in the cathode cell liquor range - 1.0 to 1.5, weight basis.

- o Anode and cathode current density range - 1.50 to 3.10 kA/m² (1 to 2 A/in²).
- o Cell voltage range - 3.0 to 4.0 v
- o Chlorine and caustic current efficiencies - 93% to 97%.
- o Heat generated in the cells by ohmic and other irreversible losses produces cell temperatures in the range of 85°C to 95°C.
- o Chlorine and hydrogen gases leave cells saturated with water at electrolyte compositions and temperatures.
- o Operating pressure - atmospheric.

The cells are generally made of steel and concrete or steel and plastic with steel cathodes and titanium base anodes. Copper bus makes the connections to the anode and cathode.

Maturity: Chlor-alkali manufacture by electrochemical means is an old industry, having started in the late 19th century. The diaphragm cell concept has undergone a slow evolution since its inception in 1886. The major change has been an exponential increase in cell amperage with time from a kiloampere to over 100 kiloamperes. Design of the cells has always been limited by available construction materials. The technology received a considerable boost about a decade ago with the introduction of the ruthenium oxide coated titanium anode. This anode is now used in over 60% of the chlor-alkali cells worldwide. It is cleaner and allows operation at a smaller anode-cathode spacing, which gives significant electrical energy savings by reducing cell voltage.

Problems: Limitations of diaphragm cells include the following:

- o The caustic concentration is limited to about 10% to 15% in concentration.
- o Energy-intensive evaporation is required to concentrate to a shipping concentration of 50 wt % and to precipitate out most of the NaCl.
- o The energy efficiency of the diaphragm cells is near 60% based on the enthalpy of reaction.
- o Asbestos, which is used in making the diaphragms, has in recent years been recognized as a carcinogen.

Potential Improvements: There are several opportunities for improving the performance of diaphragm cells. Some are now available and being installed and some are not yet commercialized:

- o Improved, resin-bonded diaphragms permit closer anode-cathode spacing and a consequent voltage saving. (Available and being installed.)
- o Catalytic coatings on cathodes to reduce hydrogen over-voltage. (First commercial installation in progress.)
- o Microporous diaphragms (4) offer the possibility of the elimination of asbestos, improved current efficiency, and/or higher caustic strength (Full-scale testing in progress).

- o Dynamic gel diaphragms (5) offer the potential of ion exchange functions in a diaphragm cell at much lower cost than the membrane cell. (Laboratory cell work.)
- o The improvement of diaphragm depositing and cell monitoring could save 1% to 5% in current efficiency in many plants.
- o The use of diaphragm cell hydrogen in adjacent fuel cells to produce direct current which would be returned to the diaphragm cell bus. (Research in progress.)

Energy-Related Characteristics: The low concentration of caustic from these cells requires energy-intensive evaporation to increase the concentration to a level suitable for shipping.

5.1.2.2 Diaphragm Cell Reference Chlorine Plant Description:

General: This 544 metric ton (600 T/D) diaphragm cell chlorine plant has been designed to meet the "Plant Envelope Design Criteria." The economically optimum diaphragm cell plant would operate at the highest practical current density. A current density of 2.17 kA/m² (1.4 ASI) was used for this study. Detailed capital and manufacturing cost estimates are given in Tables 5.1 and 5.2. The following assumptions have been made:

- o Neutral feed brine.
- o One percent of Cl₂ used as HCl for brine neutralization.
- o Chlorine liquefaction vent used for HCl production.
- o Raw brine from wells with the following composition:

NaCl	25.0 percent solution basis
Ca ⁺⁺	520 ppm solution basis
Mg ⁺⁺	40 ppm solution basis
SO ₄ ⁼	900 ppm solution basis
- o Polymer-treated asbestos diaphragms.
- o Current density 2.17 kA/m² (1.40 ASI).
- o Cell voltage 3.37 v.
- o Cell liquor 150 gpl NaOH.
- o Transformer-rectifier efficiency 97%.
- o DC bus and connection 3% voltage loss.
- o Current efficiency 95% as chlorine and caustic.
- o Diaphragm life, 1 year.
- o Quadruple-effect cell liquor evaporation.
- o 50% NaOH with 1% salt product.
- o Sulfate removal with CaCl₂.
- o Cooling water temperature maximum 90°F.

Table 5.1

Diaphragm Plant Capital Cost Estimate
 544 metric tons Cl₂/day

	<u>Diaphragm</u>
Cells	\$ 16.9 M
Rectifiers	3.4
Brine and Salt	4.8
Caustic	13.4
Boiler	4.2
Hydrogen	1.8
Chlorine	6.5
Air Supply	0.0
Sulfate Removal	0.6
Caustic and Chlorine Storage	5.2
Hydrochloric Acid	0.5
Cell Renewal	<u>2.0</u>
Process Subtotal	\$ 59.3 M
Utilities and Offsites	<u>23.0</u>
Total Construction Labor and Material	\$ 82.3 M
Construction Overhead	11.87
Engineering	<u>11.87</u>
TOTAL	<u>\$106.0 M</u>

Table 5.2

Manufacturing Cost Estimate
Diaphragm Cell Chlorine Plant
 544 metric tons Cl₂/day, 178,800 metric tons/yr

\$106,000 K Capital Cost

	Factor per ECU (Metric)	Units	Unit Cost \$	Annual Cost \$K	Cost/ECU (Metric) \$
Variable Costs:					
Salt (brine)	1.68	Metric Tons	8.82	2,649	14.82
H ₂ SO ₄ 100%	0.01	Metric Tons	71.65	128	.72
Soda Ash	0.015	Metric Tons	148.81	399	2.23
CaCl ₂	0.007	Metric Tons	165.35	207	1.16
Fuel ²	615	Mcal	.015	1,648	9.22
Cell Power	2884	KWH	0.040	20,624	115.34
Auxiliary Power	292	KWH	0.040	2,089	11.68
Operating Materials (includes cell renewal parts)	3.30	\$	---	591	3.30
Total Variable				28,335	158.47 (143.76/ST)
Fixed Costs:					
Operating Labor Shift: 40 @ 21,000/yr				840	4.69
Operating Labor Day: 25 @ 21,000/yr				525	2.94
Operation Supervisors: 8 @ 31,000/yr				248	1.39
Total Operating Labor & Supervision				1,613	9.02
Operation Overhead: 150% of Total				2,420	13.54
Repair & Maintenance: 5% of Capital (\$89.1 M) (except for cells)				4,371	24.45
Taxes & Insurance: 2% of Capital (\$106.0 M)				2,120	11.86
Depreciation: 15 years (6.66% of Capital)				7,067	39.51
Total Fixed				17,591	98.38 (89.25/ST)
TOTAL MANUFACTURING COSTS				45,926	256.85 (233.01/ST)

Notes:

1. Operating labor includes manpower requirements for maintenance and renewal of cells.
2. Shipping and SG&A costs are not included.

Brine: Brine treatment will follow the standard procedure of using caustic and soda ash to precipitate calcium, magnesium and other metallic ions. Final pH adjustment will be made with HCl, before brine is fed to the cells. The brine will be heated by the hot hydrogen and chlorine.

Cells: The cells used are 130 to 150 kA units. The estimate is a mid-range value for a plant using any one of several cells currently marketed. They are of the latest designs now being offered with dimensional stable anodes, polymer-treated asbestos diaphragms and minimum anode-cathode spacing.

Hydrogen: The hydrogen will be cooled by brine, compressed to 225 kPa (18 psig), and burned in the boiler.

Chlorine: Single train design is used in the chlorine area. Wet, hot chlorine gas from the cell room is cooled with brine in a titanium heat exchanger and further cooled in a similar exchanger using chilled water.

The chilled chlorine then passes through sulfuric acid drying towers for removal of the final water. The dry chlorine is then compressed to 1000 kPa (130 psig) with a centrifugal-type compressor and liquefied by cooling with chilled water and a refrigerant. The non-condensable gas containing approximately 1% of the original chlorine is used as feed for the hydrochloric acid plant.

HCl: Two HCl burners are provided to burn the non-condensable (blow gas) gas with chlorine. Because of the oxygen from the cells and additional oxygen from air dilution of the hydrogen in this gas, the hydrogen consumed will exceed the chlorine, however, the excess is economically insignificant. The burners and cooling system will be oversized to provide for the hydrogen-oxygen heat of combustion. Provision will also be made to prevent flash-back in the blow gas line.

Caustic: The caustic evaporator will be a quadruple-effect, forced circulation unit. It will have a design capability of evaporating three pounds of water per pound of 1135 kPa (150 psig) steam with the condensate returned to the boiler at 170 kPa (10 psig). The 50% NaOH will be cooled and salt reduced to 1%. The salt will be washed with interstage condensate and returned as a slurry to the brine system. Part of the wash water containing most of the Na_2SO_4 will be treated with CaCl_2 and the sulfate removed as CaSO_4 . The filtered brine from the sulfate removal step is then returned to the brine system.

Excess interstage condensate is used for brine, cooling tower and boiler water makeup.

Cooling Water: A cooling tower with its distribution system is used for removing the waste process heat from the chlorine area, HCl plant, the caustic evaporation system and the chilled water system. Makeup water will be interstage condensate and utility water. Chilled water units are used in the chlorine and caustic areas.

Steam: Steam will be produced at 1135 kPa (150 psig) for the evaporator. Makeup will only be needed for water loss as blow down, deaerator vent, steam for blowing tubes and any miscellaneous heating. All (100%) of the makeup water required will be obtained from interstage condensate from the caustic evaporators. Approximately 50% of the fuel required will be hydrogen.

Manpower: The manpower requirements include shift operators for all process areas, extra day operators, cell renewal personnel, shift supervisors and day supervisors. Maintenance manpower is shown as a portion of the total maintenance cost as this is frequently purchased as a contract service.

The diaphragm plant manpower summary is as follows:

Shift operators	40
Day operators	25
Shift supervisors	4
Day supervisors	4

Administrative, staff and services personnel are included in the "Operation Overhead" charge.

Energy: The energy requirements for this typical diaphragm cell plant, operating at 3.37 v/cell, with 0.1 v loss in direct current connections and bus, 95% cell current efficiency, 97% transformer-rectifier efficiency is 2.855 KWH/kg (1.295 KWH/lb) of chlorine at the cell.

One percent of the chlorine is recycled as HCl for brine treating.

The plant motor power requirements are estimated at 0.289 KWH/kg (0.131 KWH/lb) of chlorine.

Based on the above, the energy requirements per metric ton of chlorine available for sale are:

	Reference Diaphragm Plant	
	KWH	Mcal
AC Cell Power	2884	7267
AC Motor Load	292	736
H ₂ Burned in Boiler		883
Purchased Fuel		619
Gross Energy Consumption		9505
H ₂ Credit:		
H ₂ Burned in Boiler		883
H ₂ Balance to Other Uses		-0-
Total H ₂		883
Net Energy Consumption		8622 (31.04 MBTU/ST)

*KWH/Mcal calculated at generating requirements of 2.52 Mcal per KWH.

5.2 EMERGING TECHNOLOGIES

5.2.1 Current Membrane Cell Plant

5.2.1.1 Current Membrane Cell-Process Description:

Features: The membrane chlor-alkali cell is made with anode and cathode compartments separated by a cation-conducting membrane. Ruthenium oxide coated titanium anodes are used exclusively and the anode reaction is the same as in a diaphragm cell. Sodium ions are transported selectively by electrolytic migration to the cathode compartment through a membrane composed of a sulfonated or carboxylated fluorocarbon. No convection occurs through the membrane. The cathode reaction occurs on a steel cathode and is the same as in a diaphragm cell.

Sodium hydroxide at up to 30 wt % concentration can be made economically in a membrane cell. The sodium chloride concentration in the cell liquor is low, on the order of 50 ppm, because the membrane has a strong ability to exclude negative ions and the negative chloride ions have to diffuse against an uphill potential gradient (anode to cathode) in the membrane. Although the membrane tends to exclude negative hydroxyl ions also, the potential gradient for them (cathode to anode) is downhill and some "leak" through. This back migration of hydroxyl ions results in a lowered current efficiency and a loss of sodium hydroxide production. The hydroxyl ions coming through the membrane are neutralized by the acidity of the feed brine. Back migration of hydroxyl ions presently limits the sodium hydroxide concentration in the cell liquor to about 30 wt %. Caustic current efficiency under these conditions is somewhat above 90%. Newer membranes are improving the efficiency. Some suppliers are claiming good efficiency at caustic concentrations approaching 40%.

Membrane cells are assembled in filter-press type construction. Connections for brine and cell liquor inlet and outlet and chlorine and hydrogen outlets are built into the cell frames. Brine and cell liquor are separately removed and then recycled through the anode and cathode compartments respectively for gas disengagement, concentration and temperature control. The cell frames may be made of titanium-clad steel or of a resistant plastic. If metal, the titanium is on the anode side and the steel on the cathode side. The cells may be connected in a monopolar or bipolar mode. There is a tradeoff between a greater cost for copper bus for the monopolar mode versus the additional piping connections required to reduce parasitic conduction losses through the electrolyte between cells in the bipolar series stack mode.

Special brine treatment is required for membrane cells to reduce calcium, magnesium and heavy metal ions to a lower concentration than for diaphragm cells. These ions tend to concentrate on and in the membrane on the anolyte side and form scale that clogs and degrades the membrane.

Maturity: Membrane cells are a new technology. Use of cation-conducting membranes in chlor-alkali cells is a development that has only moved into small commercial plants in the last five years. Membranes continue to evolve at a high rate. Composite membranes have recently been developed which give improved current efficiency and permit higher caustic concentrations without significant increase in resistivity and cell voltage drop.

Problems: Problems associated with membrane cells include the following:

- o Back migration of the hydroxyl ion limits current efficiency and caustic concentration.
- o Voltage drop in the membranes is higher than desirable.
- o Membrane life at high performance could be improved.
- o High purity of brine is required.
- o The total cell cost per cell unit of electrode area is high.

Potential Improvements: Potential improvements would include new membranes which reduce hydroxyl ion back migration, have lower voltage drop, or longer high performance lifetimes. Cell configuration changes will reduce the total cost per unit of cell area.

Energy-Related Characteristics: Back migration of hydroxyl ions limits current efficiency for caustic production and therefore energy efficiency. High voltage drop in the membrane also decreases energy efficiency. Reduced unit cell area costs would permit economical operation at lower current densities, reducing cell voltage and therefore reducing energy consumption.

5.2.1.2 Current Membrane Cell Chlorine Plant Description

General: This 544 metric T/D (600 T/D) chlorine plant using membrane cells with conventional steel cathodes is designed to meet the "Plant Envelope Design Criteria." Detailed capital and manufacturing cost estimates are given in Tables 5.3 and 5.4. The following assumptions were made to correspond with the economically optimized membrane cell plant:

- o Operate on acid brine.
- o One percent of Cl_2 and HCl is used for anolyte dechlorination.
- o Six percent of Cl_2 as HCl is added to acidify brine.
- o Chlorine liquefaction vent gas used for HCl production.
- o Solid salt with following composition:

Ca^{++}	2500 ppm
Mg^{++}	100 ppm
SO_4	6000 ppm
Insolubles	850 ppm
NaCl	balance
- o duPont Nafion membranes.
- o Current density 3.10 kA/m^2 (2.0 ASI).
- o Cell voltage 3.74 v.
- o Brine feed 305 gpl NaCl .
- o Anolyte 220 gpl NaCl .
- o Cell liquor (catholyte) 29% NaOH .
- o Transformer-rectifier efficiency 97%.
- o DC bus and connection 3% voltage loss.
- o Current efficiency 99% as total chlorine, 94% as caustic.
- o Membrane life, 2 years.
- o Boosted flash cell liquor evaporation.
- o Sulfate removal with CaCl_2 .
- o Cooling water temperature 32°C (90°F).
- o Boiler fuel hydrogen with natural gas back-up.

A membrane chlorine cell uses cation-exchange membrane as a separator between the anolyte and catholyte. As this membrane allows Na^+ ions to pass but not an appreciable number of Cl^- ions a sodium hydroxide solution low in salt and of a higher concentration than that from a diaphragm cell is produced. The anode liquor must be dechlorinated and returned to the brine system for resaturation with salt. The cathode cell liquor is pumped to the evaporation system where a part of it is taken off for evaporation to 50% product and the rest is recycled back to the cell and deionized water is added to control the concentration. Cell cooling is needed and this may be done on either the catholyte or anolyte stream. For this plant design the major part of the cooling is done on the catholyte.

Salt Unloading and Storage: Crystalline salt is purchased for this plant rather than brine as it is needed to resaturate the anolyte. Facilities are provided for unloading rail cars and salt storage is available for three weeks of operation.

Table 5.3

Membrane Plant Capital Cost Estimate
 544 metric tons Cl_2 /day

	<u>Membrane</u>
Cells	\$ 32.2 M
Rectifiers	3.3
Brine and Salt	9.2
Caustic	3.0
Boiler	1.5
Hydrogen	1.8
Chlorine	6.7
Air Supply	0.0
Sulfate Removal	0.8
Caustic and Chlorine Storage	5.2
Hydrochloric Acid	1.1
Cell Renewal	2.4
Process Subtotal	\$ 67.2 M
Utilities and Offsites	22.0
Total Construction Labor and Material	\$ 89.2 M
Construction Overhead	11.11
Engineering	11.11
TOTAL	<u>\$111.5 M</u>

Table 5.4

Manufacturing Cost Estimate
Membrane Cell Chlorine Plant
 544 metric tons Cl_2 /day, 178,800 metric tons/yr
 \$111,500 K Capital Cost

	Factor per ECU (Metric)	Units	Unit Cost \$	Annual Cost \$K	Cost/ECU (Metric) \$
Variable Costs:					
Salt (solid)	1.68	Metric Tons	12.12	3,642	20.37
H_2SO_4 (100%)	0.01	Metric Tons	71.65	128	.72
Soda Ash	0.017	Metric Tons	148.81	453	2.54
CaCl_2	0.012	Metric Tons	165.35	355	1.98
Fuel ²	0.00	---	---		
Cell Power	3234	KWH	0.040	23,135	129.39
Auxiliary Power	279	KWH	0.040	1,995	11.16
Operating Materials	11.02	\$		1,971	11.02
(includes membranes and ion exchange resin)					
Total Variable				31,679	177.18 (160.73/\$T)
Fixed Costs:					
Operating Labor Shift: 36 @ 21,000/yr				756	4.23
Operating Labor Day: 22 @ 21,000/yr				462	2.58
Operation Supervisors: 7 @ 31,000/yr				217	1.21
Total Labor & Supervision				1,435	8.02
Operation Overhead: 150% of Total				2,152	12.04
Repair & Maintenance: 5% of Capital (\$79.9 M) (except for cells)				3,775	21.11
Taxes & Insurance: 2% of Capital (\$112.6 M)				2,230	12.47
Depreciation: 15 years (6.66% of Capital)				7,433	41.57
Total Fixed				17,025	95.21 (86.38/\$T)
TOTAL MANUFACTURING COSTS				48,704	272.39 (247.10/\$T)

Notes:

- Operating labor includes manpower requirements for maintenance and renewal of cells.
- Shipping and SG&A costs are not included.

Brine: The spent brine, depleted to approximately 220 gpl NaCl, is circulated through a dechlorination unit back to the brine area for resaturation. About one ton of HCl for each one hundred tons of chlorine produced at the cells must be added to the dechlorination unit. After resaturation a standard brine treatment follows for removal of calcium, magnesium and other metallic ions. A portion of the brine is also treated with calcium chloride for sulfate removal. As very pure brine is needed to extend membrane life the brine is filtered and then deionized using ion-exchange resins. The temperature is then adjusted to fit the desired cell operating conditions. To neutralize the treated brine and to minimize chlorate formation in the cell, HCl is added equivalent to 6% of the chlorine production.

Cells: Commercial membrane cells are available in monopolar and bipolar design. The costs vary depending upon the supplier and design. No particular membrane cell has been picked for this typical plant. The cell capital costs used are believed to be conservative. The relatively higher cost of membrane cells dictates operation at higher current densities than the diaphragm cells. A typical plant would operate at a current density of 3.10 kA/m^2 (2 A/m^2) and with a cell amperage of 5 kA.

The heat produced in the cells is removed with the hydrogen, the chlorine, the circulating anolyte and the circulating catholyte. In this design, a major part of the cooling is provided by the circulating catholyte. Deionized water is added to this stream to make up for the water that is in the caustic solution that goes to the evaporator.

Twenty-nine percent (29%) catholyte strength has been chosen as being somewhat conservative compared to the 33% offered by some cell developers.

Hydrogen: The hydrogen is cooled by a heat exchanger using the plant cooling water supply. The condensate is returned to the catholyte. The cooled hydrogen is compressed to 225 kPa (18 psig) and used for the manufacture of HCl and as boiler fuel. Credit is taken for unused hydrogen at fuel value.

Chlorine: Due to the amount of HCl required for a membrane cell 6% more chlorine must be produced than in a diaphragm plant. The membrane cells operate at a lower temperature so that even with the increased chlorine load the cooling requirements are less. Six percent of the wet cool chlorine is compressed and sent to the acid plant. The chlorine drying and liquefaction facilities are then the same as for the diaphragm plant. As with the diaphragm about 1% of the chlorine is in the vent gases from the liquefaction plant and these also go to the HCl plant.

HCl: Duplicate HCl units, each capable of handling 7% of the chlorine, are provided. The units are cooled by the plant cooling water supply.

Caustic: The cell liquor leaving the membrane cells is 29% caustic. It is pumped into a vacuum flash evaporator where heat from the cells provided by another circulating stream of cell liquor raises the concentration to about 37% caustic. The vapors from this evaporation are boosted with 1135 kPa (150 psig) steam to about 515 kPa (60 psig) and into the heat exchanger of the second effect. Here the 37% caustic is further evaporated to 50%.

Cooling Water: The cooling system for the membrane plant system is similar to the diaphragm plant with a cooling tower used for heat removal.

Steam: The steam will be produced at 1135 kPa (150 psig) in a package boiler capable of burning natural gas or hydrogen. Enough hydrogen is available from the cells to produce all the steam requirements. No purchased fuel will be required except for emergencies. A spare boiler will be installed.

Manpower: The manpower requirements of a membrane cell plant are less than those of a diaphragm plant due to the reduced caustic evaporation equipment and the smaller steam plant. Less manpower is also required for cell renewal.

The membrane plant manpower summary is as follows:

Shift operators	36
Day operators	22
Shift supervisors	4
Day supervisors	3

Energy: The energy requirements for this typical membrane cell plant operating at 3.74 v/cell, with 0.1 v loss in direct current connections and bus, 99% chlorine efficiency, 97% transformer-rectifier efficiency is 3.023 KWH/kg (1.371 KWH/lb) of chlorine at the cells.

In the baseline diaphragm plant, one percent of the chlorine is recycled as HCl while in this typical membrane plant 7% of the chlorine is recycled for brine treating and for cell feed brine acidification.

The plant motor power requirements are estimated at 95% of that for the baseline diaphragm plant or 0.260 KWH/kg (0.118 KWH/lb) of chlorine.

Based on the above, the energy requirements per metric ton of chlorine available for sale from the plants are:

	<u>Typical Membrane Plant</u>	
	<u>KWH</u>	<u>Mcal</u>
AC Cell Power	3234	8150
AC Motor Load	279	703
H ₂ Burned in Boiler		547
Purchased Fuel		-0-
Gross Energy Consumption		9400
H ₂ Credit:		
² H ₂ Burned in Boiler		547
H ₂ Balance to Other Uses		336
Total H ₂		883
Net Energy Consumption		8517 (30.7 MBTU/ST)

*KWH/Mcal calculated at generating requirements of 2.52 Mcal per KWH (10,000 BTU/KWH).

5.2.2 Membrane Cell with Catalytic Cathode Plant

5.2.2.1 Membrane Cell Plant with Catalytic Cathodes-Process Description:

Features: Catalytic cathodes consist of a steel substrate coated with a catalytically active surface layer. Various coatings have been investigated including platinum group metals, cobalt-tungsten-phosphorous alloy, cobalt-zirconium oxide, and Raney nickel. These catalytic coatings can decrease the hydrogen overpotential from 0.3 v at normal current densities on steel cathodes down to 0 to 0.1 v. The catalytic cathodes can be used in either diaphragm or membrane cells, although longer life might be expected in membrane cells, in which the electrolyte is more pure.

Maturity: Catalytic cathodes are a new development spurred by recent rapid escalation of electrical energy costs. The first public disclosure was in 1979.

Problems: The only significant problem is increased cost of cathodes, which includes cost of catalytic materials, manufacturing and shipping costs. Some deterioration of the coatings occurs, particularly when diaphragms are replaced.

Potential Improvements: Potential improvements include longer life, lower cost manufacturing and possibly greater activity to eliminate the last 0.1 v of overpotential.

Energy-Related Characteristics: The saving in overpotential is a relatively constant 0.2 v saving over conventional steel cathodes in the normal range of operating current densities.

5.2.2.2 Membrane Cell with Catalytic Cathode Chlorine Plant Description:

General: This 544 metric T/D (600 T/D) membrane cell with catalytic cathode chlorine plant is designed to meet the "Plant Envelope Design Criteria" as enclosed, plus the following assumptions and changes. This description is for the economically optimized plant for current densities from 1.95 to 3.90 kA/m² (1.25 to 2.50 ASI). Detailed capital and manufacturing cost estimates are given in Tables 5.5 and 5.6. The following assumptions have been made:

- o Operate on acid brine.
- o One percent of Cl₂ as HCl is used for anolyte dechlorination.
- o Six percent of Cl₂ as HCl is added to acidify brine.
- o Chlorine liquefaction vent gas used for HCl production.
- o Solid salt with following composition:

Ca ⁺⁺	2500 ppm
Mg ⁺⁺	100 ppm
SO ₄ ⁼	6000 ppm
Insolubles	850 ppm
NaCl	balance
- o duPont Nafion membranes.
- o Current density 3.10 kA/m² (2.0 ASI).
- o Cell voltage 3.55 volts.
- o Brine feed 300 gpl NaCl.
- o Anolyte 220 gpl NaCl.
- o Cell liquor (catholyte) 29% NaOH.
- o Transformer-rectifier efficiency 97%.
- o DC bus and connection 3% voltage loss.
- o Current efficiency 99% as total chlorine, 94% as caustic.
- o Membrane life 2 years.
- o Boosted flash cell liquor evaporation.
- o Sulfate removal with CaCl₂.
- o Cooling water temperature 32°C (90°F).
- o Boiler fuel hydrogen with natural gas back-up.

A membrane chlorine cell uses a cation-exchange membrane as a separator between the anolyte and catholyte. As this membrane allows Na⁺ ions to pass but not an appreciable number of Cl⁻ ions a sodium hydroxide solution low in salt and of a higher concentration than that from a diaphragm cell is produced. The anode liquor must be dechlorinated and returned to the brine system for

resaturation with salt. The cathode cell liquor is pumped to the evaporation system where a part of it is taken off for evaporation to 50% product and the rest is recycled back to the cell and deionized water is added to control the concentration. Cell cooling is needed and this may be done on either the catholyte or anolyte stream. For this plant design the major part of the cooling is done on the catholyte. The catalyzed cathodes reduce the cell voltage by 0.19 v from the standard steel screen cathodes.

Salt Unloading and Storage: Crystalline salt is purchased for this plant rather than brine as it is needed to resaturate the anolyte. Facilities are provided for unloading rail cars and salt storage is available for three weeks of operation.

Brine: The spent brine, depleted to approximately 220 gpl NaCl, is circulated through a dechlorination unit back to the brine area for resaturation. About one ton of HCl for each 100 tons of chlorine produced at the cells must be added to the dechlorination unit. After resaturation a standard brine treatment follows for removal of calcium, magnesium and other metallic ions. A portion of the brine is also treated with calcium chloride for sulfate removal. As very pure brine is needed to extend membrane life, the brine is filtered and then deionized using ion-exchange resins. The temperature is then adjusted to fit the desired cell operating conditions. To neutralize the treated brine and to minimize chlorate formation in the cell, HCl is added equivalent to 6% of the chlorine production.

Cells: Commercial membrane cells are available in monopolar and bipolar design. The costs vary depending upon the supplier and design. No particular membrane cell has been picked for this typical plant. The cell capital costs used are believed to be conservative. The relatively higher cost of membrane cells dictates operation at higher current densities than the diaphragm cells. A typical plant would operate at a current density of 3.10 kA/m^2 (2 ASI) and with a cell amperage of 5 kA.

The heat produced in the cells is removed with the hydrogen, the chlorine, the circulating anolyte and the circulating catholyte. In this design, a major part of the cooling is provided by the circulating catholyte. Deionized water is added to this stream to make up for the water that is in the caustic solution that goes to the evaporator. Platinum catalyzed cathodes were assumed for this study.

Hydrogen: The hydrogen is cooled by a heat exchanger using the plant cooling water supply. The condensate is returned to the catholyte. The cooled hydrogen is compressed to 225 kPa (18 psig) and used for the manufacture of HCl and as boiler fuel. Credit is taken for unused hydrogen at fuel value.

Table 5.5

Membrane with Catalytic Cathode Plant
Capital Cost Estimate
 544 metric tons Cl₂/day

	<u>Membrane with Catalytic Cathode</u>
Cells	\$ 33.2 M
Rectifiers	3.3
Brine and Salt	9.2
Caustic	3.0
Boiler	1.6
Hydrogen	1.8
Chlorine	6.7
Air Supply	0.0
Sulfate Removal	0.8
Caustic and Chlorine Storage	5.2
Hydrochloric Acid	1.1
Cell Renewal	<u>2.4</u>
Process Subtotal	\$ 68.3 M
Utilities and Offsites	<u>22.0</u>
Total Construction Labor and Material	\$ 90.3 M
Construction Overhead	11.26
Engineering	<u>11.26</u>
TOTAL	<u>\$112.8 M</u>

Table 5.6

Manufacturing Cost Estimate
Membrane Cell with Catalytic Cathode
 544 metric tons Cl_2 /day, 178,800 metric tons/yr

\$112,800 K Capital Cost

	Factor per ECU (Metric)	Units	Unit Cost \$	Annual Cost \$K	Cost/ECU (Metric) \$
Variable Costs:					
Salt (solid)	1.68	Metric Tons	12.12	3,642	20.37
H_2SO_4 (100%)	0.01	Metric Tons	71.65	128	.72
Soda Ash	0.017	Metric Tons	148.81	453	2.54
CaCl_2	0.012	Metric Tons	165.35	355	1.98
Fuel	0.00	---	---		
Cell Power	3074	KWH	0.040	21,988	122.97
Auxiliary Power	279	KWH	0.040	1,995	11.16
Operating Materials	11.02	\$		1,971	11.02
(includes membranes and ion exchange resin)					
Cathode Replacement (\$7.00/ft ²)				194	1.08
Total Variable				30,726	171.84 (155.89/ST)
Fixed Costs:					
Operating Labor Shift: 36 @ 21,000/yr				756	4.23
Operating Labor Day: 22 @ 21,000/yr				462	2.58
Operation Supervisors: 7 @ 31,000/yr				217	1.21
Total Labor & Supervision				1,435	8.02
Operation Overhead: 150% of Total				2,152	12.04
Repair & Maintenance: 5% of Capital (\$80.0 M) (except for cells)				3,816	21.34
Taxes & Insurance: 2% of Capital (\$113.2M)				2,256	12.62
Depreciation: 15 years (6.66% of Capital)				7,520	42.06
Total Fixed				17,179	96.08 (87.16/ST)
TOTAL MANUFACTURING COSTS				47,905	267.92 (243.05/ST)

Notes:

1. Operating labor includes manpower requirements for maintenance and renewal of cells.
2. Shipping and SG&A costs are not included.

Chlorine: Due to the amount of HCl required for a membrane cell 6% more chlorine must be produced than in a diaphragm plant. The membrane cells operate at a lower temperature so that even with the increased chlorine load the cooling requirements are less. Six percent of the wet cool chlorine is compressed and sent to the acid plant. The chlorine drying and liquefaction facilities are then the same as for the diaphragm plant. As with the diaphragm, about 1% of the chlorine is in the vent gases from the liquefaction plant and these also go to the HCl plant.

HCl: Duplicate HCl units, each capable of handling 7% of the chlorine, are provided. The units are cooled by the plant cooling water supply.

Caustic: The cell liquor leaving the membrane cells is 29% caustic. It is pumped into a vacuum flash evaporator where heat from the cells provided by another circulating stream of cell liquor raises the concentration to about 36% caustic. This is 1% less than the 37% from the conventional membrane cell. The voltage saving of the catalytic cathode cell results in less waste heat for evaporating caustic. The vapors from the flash evaporation are boosted with 1135 kPa (150 psig) steam to about 515 kPa (60 psig) and into the heat exchanger of the second effect. Here the 36% caustic is further evaporated to 50%.

Cooling Water: The cooling system for the membrane plant with catalytic cathode system is similar to the diaphragm plant with a cooling tower used for heat removal.

Steam: The steam will be produced at 1135 kPa (150 psig) in a package boiler capable of burning natural gas or hydrogen. Enough hydrogen is available from the cells to produce all the steam requirements. No purchased fuel will be required except for emergencies. A spare boiler will be installed.

Manpower: The manpower requirements of a membrane cell with catalytic cathode plant are less than those of a diaphragm plant due to the reduced caustic evaporation equipment and the smaller steam plant. Less manpower is also required for cell renewal.

The membrane plant with catalytic cathode manpower summary is as follows:

Shift operators	36
Day operators	22
Shift supervisors	4
Day supervisors	3

Energy: The energy requirements for this typical membrane cell plant with catalytic cathode operating at 3.55 v/cell, with 0.1 v loss in direct current connections and bus, 99% chlorine efficiency, 97% transformer-rectifier efficiency is 2.873 KWH/kg (1.303 KWH/lb) of chlorine at the cells.

In the baseline diaphragm plant, 1% of the chlorine is recycled as HCl while in this typical membrane plant with catalytic cathode 7% of the chlorine is recycled for brine treating and for cell feed brine acidification.

The plant motor power requirements are estimated at 95.5% of that for the baseline diaphragm plant or 0.260 KWH/kg (0.118 KWH/lb) of chlorine.

Based on the above, the energy requirements per metric ton of chlorine available for sale from the plant are:

	Membrane Plant with Catalytic Cathode	
	KWH	Mcal
AC Cell Power	3074	7747
AC Motor Load	279	703
H ₂ Burned in Boiler		622
Purchased Fuel		-0-
Gross Energy Consumption		9072
H ₂ Credit		
H ₂ Burned in Boiler		622
H ₂ Balance to Other Uses		261
Total H ₂		883
Net Energy Consumption		8189 (29.5 MBTU/ST)

*KWH/Mcal calculated at generating requirements of 2.52 Mcal per KWH (10,000 BTU/KWH).

5.2.3 Membrane Cell with Oxygen-Cathode Plant

5.2.3.1 Membrane Cell with Oxygen Cathodes-Process Description

Features: Oxygen cathodes are to replace steel cathodes in membrane cells and save an additional 0.8 to 1.0 v. The cathodic reaction is:

Thermodynamically the difference in potential between this electrode and the hydrogen evolving electrode in the same electrolyte is the enthalpy of the reaction at these conditions, or 1.48 v. Because the oxygen-reducing cathode has greater overpotential than a hydrogen cathode, the saving is estimated to be only 0.9 v. This results in an increased cell cooling load of about (1.48-0.90) 0.58 v.

The oxygen cathode is presently made with platinum-doped carbon particles bonded by Teflon particles. This porous cathode sheet is backed by a Teflon paper to exclude electrolyte from the air.

side. Nickel screen is the current collector in contact with the carbon on the electrolyte side. The loading of platinum is about $1/2 \text{ mg/cm}^2$ (approximately $1/2 \text{ g/ft}^2$). Silver has also been used at a higher loading and various oxides are also under investigation.

Maturity: Air cathodes are in the laboratory and early development stage for use in chlor-alkali cells. Air and oxygen electrodes have been used in fuel cells for the space program but fuel cells are yet to be commercialized on a large scale.

Problems: Several problems remain to be solved in order to make the oxygen electrodes commercial. Lower cost catalysts need to be developed. Basic research on catalysts at Case Western Reserve University is aimed at developing such lower cost materials. Long-term, high catalyst activity and electrode life are problems to be solved. Weeping of electrolyte through electrodes is a problem that presently limits the head per electrode to about 40 cm.

Potential Improvements: Potential improvements are lower cost, more active catalysts, longer life catalysts and electrodes and minimization of electrolyte weeping.

Energy-Related Characteristics: The oxygen electrodes can save 0.8 to 1.0 v per cell in the operating current density range of commercial cells. No by-product hydrogen which has energy value is produced. Energy costs are associated with recirculation of air through the cells, CO_2 removal and humidity control.

5.2.3.2 Membrane Cell with Oxygen-Cathode Chlorine Plant Description

General: This 544 metric T/D (600 T/D) chlorine plant using membrane cells with oxygen-cathodes is designed to meet the "Plant Envelope Design Criteria." The economically optimum plant operates at what is presently the maximum current density for these plants, 3.10 kA/m^2 (2.0 ASI). Detailed capital and manufacturing cost estimates are given in Tables 5.7 and 5.8. The following assumptions were also made.

- o 544 metric T/D (600 T/D) Cl_2 capacity O_2 cathode membrane cells are installed.
- o 38 metric T/D (42 T/D) Cl_2 capacity current membrane cells are installed in series to produce hydrogen for HCl plant.
- o Oxygen is obtained from air.
- o Oxygen cells produce no hydrogen.
- o Operate on acid brine.
- o One percent of Cl_2 as HCl is used for anolyte dechlorination.
- o Six percent of Cl_2 as HCl is added to acidify cell feed brine.
- o Cl_2 liquefaction vent gas goes to the HCl plant.

Table 5.7

Membrane with Oxygen Cathode Plant
Capital Cost Estimate
 544 metric tons Cl₂/day

	<u>Membrane with Oxygen Cathode</u>
Cells	\$ 38.0 M
Rectifiers	2.6
Brine and Salt	9.2
Caustic	4.0
Boiler	0.8
Hydrogen	0.3
Chlorine	6.7
Air Supply	2.3
Sulfate Removal	0.8
Caustic and Chlorine Storage	5.2
Hydrochloric Acid	1.1
Cell Renewal	<u>2.8</u>
Process Subtotal	\$ 73.8 M
Utilities and Offsites	<u>23.0</u>
Total Construction Labor and Material	\$ 96.8 M
Construction Overhead	11.93
Engineering	<u>11.93</u>
TOTAL	<u>\$120.7 M</u>

Table 5.8

Manufacturing Cost Estimate
Membrane Cell with Oxygen Cathode Chlorine Plant
 544 metric tons Cl_2 /day, 178,800 metric tons/yr

\$120,700 K Capital Cost

	Factor per ECU (Metric)	Units	Unit Cost \$	Annual Cost \$K	Cost/ECU (Metric) \$
Variable Costs:					
Salt (solid)	1.68	Metric Tons	12.12	3,642	20.37
H_2SO_4 (100%)	0.01	Metric Tons	71.65	128	.72
Soda Ash	0.017	Metric Tons	140.01	453	2.54
CaCl_2	0.012	Metric Tons	165.35	355	1.98
Fuel ¹	547	Mcal	.015	1,456	8.15
Cell Power	2495	KWH	0.040	17,841	99.78
Auxiliary Power	321	KWH	0.040	2,294	12.83
Operating Materials	11.02	\$		1,971	11.02
(includes membranes and ion ₂ exchange resin)					
Cathode Replacement (\$54.36/m ²)				409	2.29
Cathode License Fee	0.88			158	.88
Total Variable				28,707	160.56 (145.65/ST)
Fixed Costs:					
Operating Labor Shift: 36 @ 21,000/yr				756	4.23
Operating Labor Day: 22 @ 21,000/yr				462	2.58
Operation Supervisors: 7 @ 31,000/yr				217	1.21
Total Labor & Supervision				1,435	8.02
Operation Overhead: 150% of Total				2,152	12.04
Repair & Maintenance: 5% of Capital (\$83.1 M) (except for cells)				3,973	22.72
Taxes & Insurance: 2% of Capital (\$119.7 M)				2,414	13.50
Depreciation: 15 years (6.66% of Capital)				8,047	45.01
Total Fixed				18,021	100.79 (91.43/ST)
TOTAL MANUFACTURING COSTS				46,728	261.35 (237.08/ST)

Notes:

1. Operating labor includes manpower requirements for maintenance and renewal of cells.
2. Shipping and SG&A costs are not included.

- o Solid salt with following composition:

Ca ⁺⁺	2500 ppm
Mg ⁼	100 ppm
SO ₄	6000 ppm
Insolubles	850 ppm
NaCl	balance
- o duPont Nafion membranes.
- o O₂ cathode cell voltage 2.8 v.
- o O₂ cathode initial price \$155.00/m² (\$14.40/ft²)*.
- o O₂ cathode life, 1 1/2 yrs.
- o O₂ cathode replacement price \$54.36/m² (\$5.05/ft²).
- o O₂ cathode license fee \$0.88/ECU metric at 40 mill power cost.
- o Membrane cell voltage 3.74 v.
- o Current density 3.10 kA/m² (2.0 ASI) both cells.
- o Brine feed 305 gpl NaCl.
- o Anolyte 220 gpl NaCl.
- o Cell liquor (catholyte) 29% NaOH.
- o Transformer-rectifier efficiency 97%.
- o DC bus and connection 3% voltage loss.
- o Current efficiency 99% as total chlorine, 94% as caustic, both cells.
- o Membrane life, 2 years.
- o Boosted flash cell liquor evaporation.
- o Sulfate removal with CaCl₂.
- o Cooling water temperature 32°C (90°F).
- o Boiler fuel oil and natural gas.

A membrane cell plant using oxygen depolarized cathodes includes most of the same components as a normal membrane cell plant. The primary differences result from the requirement for treated air for the oxygen cathodes and the lack of hydrogen as a cell product.

This plant will have no H₂ for fuel or for sale.

Salt Unloading and Storage: Crystalline salt is purchased for this plant rather than brine as it is needed to resaturate the anolyte. Facilities are provided for unloading rail cars and salt storage is available for three weeks of operation.

*Cathode manufacturing cost estimate is based on the experience of EPRI with alkaline fuel cells (6).

Brine: The spent brine, depleted to approximately 220 gpl NaCl, is circulated through a dechlorination unit back to the brine area for resaturation. About one ton of HCl for each 100 tons of chlorine produced at the cells must be added to the dechlorination unit. After resaturation a standard brine treatment follows for removal of calcium, magnesium and other metallic ions. A portion of the brine is also treated with calcium chloride for sulfate removal. As very pure brine is needed to extend membrane life the brine is filtered and then deionized using ion-exchange resins. The temperature is then adjusted to fit the desired cell operating conditions. To neutralize the treated brine and to minimize chlorate formation in the cell, HCl is added equivalent to 6% of the chlorine production.

Cells: The cell installation includes 544 metric T/D (600 T/D) Cl_2 capacity of O_2 cathode cells. These are similar to conventional membrane cells although since more space is required for the air, the cell assemblies will be longer and the building wider. There will also be two large air headers, one for supply and one return. This will require a slightly higher building.

To provide for the hydrochloric acid required, an additional 38 metric T/D (42 T/D) of current membrane cells are installed in series with the oxygen cathode cells. If byproduct HCl were available at a low price, this investment would be unnecessary. In such a case, the capital investment would be lower and the manufacturing cost, higher.

The heat produced in the cells is removed with the chlorine, the circulating anolyte and the circulating catholyte. In this design, a major part of the cooling is provided by the circulating catholyte. Deionized water and evaporator condensate is added to this stream to make up for the water in the caustic solution that goes to the evaporator.

Air: The oxygen cathode cells require air which has been humidified and is free of CO_2 . The air system includes a CO_2 scrubber and moisture is added to a level such that the water exchange with the cathode is nearly zero. A heat exchanger is also provided to recover the heat from the warm air leaving the cells.

Hydrogen: A small hydrogen system is provided to cool and compress the H_2 gas for the HCl plant.

Chlorine: Due to the amount of HCl required for a membrane cell 6% more chlorine must be produced than in a diaphragm plant. The membrane cells operate at a lower temperature so that even with the increased chlorine load the cooling requirements are less. Six percent of the wet cool chlorine is compressed and sent to the acid plant. The chlorine drying and liquefaction facilities are then the same as for the diaphragm plant. As with the diaphragm about 1% of the chlorine is in the vent gases from the liquefaction plant and these also go to the HCl plant.

Caustic: The cell liquor leaving the membrane cells is 29% caustic. It is pumped into a vacuum flash evaporator where heat from the cells provided by another circulating stream of cell liquor raises the concentration to about 37% caustic. The vapors from this evaporation are boosted with 1135 kPa (150 psig) steam to about 515 kPa (60 psig) and into the heat exchanger of the second effect. Here the 37% caustic is further evaporated to 50%.

Cooling Water: The cooling system for the membrane plant system is similar to the diaphragm plant with a cooling tower used for heat removal.

Steam: The small amount of steam required will be produced at 1135 kPa (150 psig) in a package boiler capable of burning oil or natural gas. A spare boiler will be installed.

The oxygen-cathode cells produce more excess heat (5.2.3.1, p. 27) at the cathode which is available for caustic evaporation. Additionally, because there is no hydrogen gas produced, no water vapor is leaving the cell in this stream. This heat of vaporization is another increase in heat available for caustic evaporation, as compared with the membrane cell.

Manpower: The manpower requirements of a membrane cell plant with oxygen cathodes are the same as those of a normal membrane plant. The added air handling system requires no more manpower.

The membrane plant with oxygen manpower summary is as follows:

Shift operators	36
Day operators	22
Shift supervisors	4
Day supervisors	3

Energy: The energy requirements for this typical membrane cell with oxygen cathode plant operating at 2.8 v/membrane cell with oxygen cathode and 3.74 v per current technology membrane cell, with 0.1 v loss in direct current connections and bus, 99% chlorine efficiency, 97% transformer-rectifier efficiency is 2.330 KWH/kg (1.057 KWH/lb) of chlorine at the cells.

In the baseline diaphragm plant, one percent of the chlorine is recycled as HCl while in this typical membrane plant 7% of the chlorine is recycled for brine treating and for cell feed brine acidification.

The plant motor power requirements are estimated at 90% of that for the baseline diaphragm plant or 0.260 KWH/kg (0.136 KWH/lb) of chlorine.

Based on the above, the energy requirements per metric ton of chlorine available for sale from the plant are:

Typical Membrane Plant with Oxygen Cathodes		
	KWH	Mcal
AC Cell Power	2495	6286
AC Motor Load	321	808
H ₂ Burned in Boiler		-0-
Purchased Fuel		547
Gross Energy Consumption		7641
H ₂ Credit:		
H ₂ Burned in Boiler		-0-
H ₂ Balance to Other Uses		-0-
Total H ₂		-0-
Net Energy Consumption		7641 (27.5 MBTU/ST)

*KWH/Mcal calculated at generating requirements of 2.52 Mcal per KWH (10,000 BTU/KWH).

5.2.4 Related Forthcoming Technologies

Several other possible technological improvements are known to be under consideration in the industry. These are: solid polymer electrolyte cells, high-pressure cells, diaphragm cells with catalytic cathodes, diaphragm cells with microporous diaphragms, diaphragm cells with dynamic gel diaphragms and diaphragm cells in series with membrane hydrogen-air fuel cells. This last program includes the potential of the purification and concentration of the diaphragm cell caustic in the fuel cell. Another possible development is combining other cathodic or anodic processes with chlorine and caustic production respectively in a membrane cell.

5.2.4.1 Diaphragm Cells with Catalytic Cathodes:

Catalytic cathodes can be retrofitted to existing diaphragm cells. A full-scale plant conversion is currently being made by Diamond Shamrock. There is some concern that the porous catalytic metal surface life may be shorter in diaphragm cells because of the mechanical attrition of depositing and replacing diaphragms.

The same saving of 0.19 v is expected in diaphragm cells as in membrane cells.

This modification appears to be an opportunity for a significant reduction in the energy consumption of the U.S. chlor-alkali industry which could be implemented rapidly. The development is essentially complete and the installations can be made in the course of normal cell maintenance. The replacement of all cathodes in existing diaphragm cells would result in a saving of about $\frac{0.2}{3.5} = 5\frac{1}{2}\%$ in 75% of the U.S. production or $(0.055)(0.75)(100) = 4\%$ overall power savings.

5.2.4.2 Diaphragm Cells with Microporous Diaphragm:

There is a replacement for the asbestos diaphragm emerging for the diaphragm cell. This is a membrane manufactured of sheet perfluoro-ethylene with a controlled micropore structure (4). The original purpose of the work was to provide a replacement for the asbestos diaphragm. Development work has produced a membrane which has superior qualities to those of the asbestos diaphragm. The use of this material is said to produce the following benefits:

- o Reduce cell voltage by 0.20 v.
- o Increase current efficiency by 2% to 3%.
- o Increase cell caustic strength.

This development holds good promise for several reasons.

- o Lack of ability to control quality factors in the diaphragm has been a major weakness of the diaphragm cell. This barrier now seems to have been surmounted.
- o This is a development which can be retrofitted to existing chlor-alkali plants and offers the same opportunity as the catalytic cathode in diaphragm cell plants for another early reduction in the power consumption of the U.S. chlor-alkali industry.

5.2.4.3 Diaphragm Cells with Dynamic Gel Diaphragms:

Promising laboratory test work has been reported (5) on a diaphragm which consists of a layer of inorganic cation exchangers on a TPFE felt support. The stable gel diaphragm is maintained dynamically by filtration and by the steep pH gradient existing between the anolyte and the catholyte.

This work foreshadows a means of developing low cost diaphragms which are semi-permeable, as compared to asbestos and the microporous diaphragm. It could be the means of achieving performance like the membrane cell with respect to the rejection of chloride ion within the configuration of the lower cost diaphragm cell.

5.2.4.4 Diaphragm Cell Energy Recovery and Caustic Purification in a Fuel Cell:

Cell liquor from diaphragm cells is 10% to 15% NaOH by weight and nearly saturated with salt. In theory, this liquor could be purified in a hydrogen-air fuel cell with a Nafion membrane. The cell liquor would be fed to the anode compartment in which hydrogen from the chlor-alkali diaphragm cells is oxidized. The hydrogen oxidation reaction is:

Sodium ions pass through the membrane to the cathode compartment in which oxygen is reduced in the following reaction:

The overall reaction is formation of water:

But electrical energy is generated from the hydrogen, and membrane cell grade caustic is produced in the catholyte. This program has the following advantages:

- o The new fuel cells could be retrofitted to existing diaphragm cell plants.
- o The potential of producing a major reduction in the power consumption of the U.S. chlor-alkali industry by modifying existing plants.
- o The reduction of energy required to concentrate the caustic.
- o The upgrading of diaphragm cell caustic to low-salt caustic.

The disadvantages of the program appear to be as follows:

- o The development of hydrogen fuel cell electrodes which are tolerant to diaphragm cell caustic may be a problem.
- o The cost of the fuel cell installation remains to be determined.

5.2.4.5 Packed Membrane Cell:

The present filter-press configuration of the membrane cell limits each cell element to a few square meters. Since each cell element requires a membrane, a cathode, an anode, electrical connections and cathode and anode compartments, a large number of cells (parts) are required for a commercial plant. Predictably, several groups are working to develop a cell which will "pack" or fold a greater area of membrane, cathode and anode into one cell similar to a diaphragm cell. The problems seem to be principally as follows:

- o Bonding the membrane to form tubes or other closed shapes.
- o Provision for membrane maintenance.
- o An appropriate matching cell mechanical design.

These packed membrane cells would cost less than current cells for a plant scale installation. There would seem to be a potential of reducing overall plant costs by at least 10% from success in this work.

5.2.4.6 Solid Polymer Electrolyte Cells:

General Electric and Oronzio De Nora Impianti Elettrochimici have announced the development of a brine electrolyzer based on the GE solid polymer electrolyte technology developed for use in fuel cells in the Gemini vehicle. Substantial reductions in electrolyzer voltage are achieved by bonding highly efficient catalytic cathodes and porous catalytic solid polymer electrolyte anodes to electrolyte ion exchange membranes. While maintaining an equivalent current efficiency to conventional membrane brine electrolyzers, the jointly developed Genor brine electrolyzer realizes cell voltage reductions of 0.5 to 0.8 v at ambient pressure, 80 to 90°C, and 3.25 kA/m² (2.1 ASI).

This development may be also coupled with an oxygen cathode to reduce voltages by an additional 0.8 to 1.0 v, at the same conditions.

This is another technological development which appears to be adaptable to the configuration and accessory hardware of the membrane cell. These mechanical characteristics may facilitate the application development and shorten the time of commercialization.

Because of the potentially large power savings, this development seems worthy of considerable effort.

5.2.4.7 High-Pressure Operation:

Filter-press cell construction allows the possibility of operation of membrane cells considerably above ambient pressure. If, as in water electrolyzers, electrode overpotential is decreased by pressure, this development could result in lower power requirements for the cells as well as eliminating compressing cost for chlorine.

Some Asahi cell plants are operating in the 170-205 kPa (10-15 psig) pressure range and it is reported that the newly announced Diamond membrane cell plant will have the capability of operating at 450 kPa (50 psig).

The obvious extension of this is to design a cell to operate in the 2,000 to 3,500 kPa (300 to 500 psig) range and produce liquid chlorine directly from the cells. The benefits would be as follows:

- o Save chlorine compression and liquefaction costs.
- o Reduce chlorine cooling and drying costs.
- o Reduce hydrogen cooling and compression costs.

- o Reduce power costs.

The detail cell design and capital costs are at the present time undetermined.

5.2.4.8 Other Cathodic or Anodic Processes in Membrane Cells:

The highly specific sodium conducting Nafion membrane opens the possibility of coupling other inorganic or organic electrode processes with either chlorine or sodium hydroxide manufacture. The market demand for chlorine and sodium hydroxide is not generally in balance and it would be desirable to have other alternative products. The Nafion membrane nearly completely isolates the electrolytes in the two-cell compartments except for the passage of sodium ions and some "leakage" of OH^- ions.

5.3 COST ESTIMATES AND ENERGY AUDITS

Capital cost and manufacturing cost estimates have been developed for each of the four major technologies. Energy audits of these technologies have also been performed. These estimates, along with a partial comparison with other technologies and a discussion of the accuracy of these estimates, are discussed in the following sections.

5.3.1 Capital Cost Estimate Comparisons

Capital cost estimates for the four technologies are summarized in Table 5.9.

The capital costs developed for each case should be considered as a moderately conservative estimate in 1980 dollars. The actual cost of a plant would vary depending upon the operating philosophy of the manufacturer. However, the data supplied does provide a valid means of comparing the capital cost, manufacturing cost, and profitability of plants utilizing different chlorine cell technologies.

The diaphragm cell chlorine plant capital cost runs at 6% to 13% lower than the various types of membrane cell plants. The primary cause of the difference is that the cost of membrane cells is about twice the cost of diaphragm cells. Since membrane cells generally require a rock salt feed, which includes storage, handling and dissolvers, and brine de-ionization, the capital cost for the brine system of a membrane plant is again approximately double the capital cost of the diaphragm cell brine system. Membrane cells do have lower capital costs for the boiler and the caustic area. These lower costs are the result of the higher caustic concentration from the membrane cell and the absence of salt in the caustic. However, the cell cost is higher for the newer membrane cell technology. Generally a new technology cost will be reduced as experience is gained in that field. This could result in more competitive position for the various types of membrane cells.

Table 5.9

Chlorine Plant Capital Cost Estimates - 4 cells
544 metric tons Cl₂/day

	<u>Diaphragm</u>	<u>Membrane</u>	<u>Membrane with Catalytic Cathode</u>	<u>Membrane with Oxygen-Cathode</u>
Cells	\$ 16.9 M	\$ 32.2 M	\$ 33.2 M	\$ 38.3 M
Rectifiers	3.4	3.3	3.3	2.6
Brine and Salt	4.8	9.2	9.2	9.2
Caustic	13.4	3.0	3.0	3.0
Boiler	4.2	1.5	1.6	1.5
Hydrogen	1.8	1.8	1.8	0.3
Chlorine	6.5	6.7	6.7	6.7
Air Supply	0.0	0.0	0.0	2.3
Sulfate Removal	0.6	0.8	0.8	0.8
Caustic and Chlorine Storage	5.2	5.2	5.2	5.2
Hydrochloric Acid	0.5	1.1	1.1	1.1
Cell Renewal	<u>2.0</u>	<u>2.4</u>	<u>2.4</u>	<u>2.8</u>
Process Subtotal	\$ 59.3 M	\$ 67.2 M	\$ 68.3 M	\$ 73.8 M
Utilities and Offsites	<u>23.0</u>	<u>22.0</u>	<u>22.0</u>	<u>23.0</u>
Total Construction Labor and Material	\$ 82.3 M	\$ 89.2 M	\$ 90.3 M	\$ 96.8 M
Construction Overhead	11.87	11.11	11.26	11.93
Engineering	<u>11.87</u>	<u>11.11</u>	<u>11.26</u>	<u>11.93</u>
TOTAL	<u>\$106.0 M</u>	<u>\$111.5 M</u>	<u>\$112.8 M</u>	<u>\$120.7 M</u>

The cost of engineering for the membrane cell, and membrane cell with catalytic cathode plants is lower than for the other two cell types. The diaphragm cell plant requires engineering on the caustic evaporation system and the oxygen-cathode plant, for the air supply system, neither of which are required on the other plants. In all other respects except cells, the four plants require essentially the same engineering. For the cell system, most of the engineering is provided by the cell supplier, so that the differences between the plants for purchased engineering in this area is small.

Cell anode royalty costs have been included as a capitalized portion of the cell cost.

5.3.2 Manufacturing Cost Estimates and Comparisons

Manufacturing cost estimates for the four technologies are summarized in Table 5.10. The manufacturing cost is the other major term in determining the profitability of a project. The key variables in the manufacturing cost are the cell power and the operating materials. Because of the high cost of the cells, the highest rate of return is usually obtained when the minimum number of cells are purchased. This results in the cells operating at high current densities, and thus, higher costs for cell power. A current density of 2.17 kA/m^2 (1.4 ASI) for the diaphragm cell as compared to 3.10 kA/m^2 (2.0 ASI) for the current membrane cell plants results in a lower cost for cell power. The higher cost of replacement components for the membrane cell produces a higher cost of operating materials.

The catalytic and oxygen cathode type membrane cells have respectively lower cell power cost because of the voltage reduction over the current membrane cell. This results in an overall lower manufacturing cost and the higher profitability. Both the diaphragm cell and the oxygen-cathode cell plants have to purchase fuel which reduces from the gross savings in cell power costs. As the membrane cell technology matures a lower cell voltage could also allow the manufacturing cost to drop. However, diaphragm cell technology is not standing still and new membrane technology would probably be adopted to produce lower manufacturing cost in the former cell also.

5.3.3 Energy Audit Comparison

The energy audit comparisons has been made on the two bases of "Gross" and "Net Energy Consumption." The comparisons are summarized in Table 5.11.

The gross energy consumptions are commonly used to compare diaphragm and membrane cell plant energy usage. This shows the total energy consumed by the three usages of 1) cell power, 2) motor power, and 3) caustic evaporation. However, in both cases, it is common to use the hydrogen from the cells as a supplementary fuel to produce steam for caustic evaporation. This reduces the requirement for

Table 5.10

Chlorine Plant Manufacturing Cost Estimates - 4 cells
(544 metric tons/day)

	Diaphragm Cell	Membrane Cell	Membrane Cell with Catalytic Cathode	Membrane Cell with Oxygen-Cathode
Total Capital Cost	\$106.0 M	\$111.5 M	\$112.8 M	\$120.7 M
Variable Costs:			<u>Cost per ECU (metric)</u>	
Salt	14.82	20.37	20.37	20.37
H ₂ SO ₄ 100%	.72	.72	.72	.72
Soda Ash	2.23	2.54	2.54	2.54
CaCl ₂	1.16	1.98	1.98	1.98
Fuel ²	9.22	--	--	8.15
Cell Power	115.34	129.39	122.97	99.78
Auxiliary Power	11.68	11.16	11.16	12.83
Operating Materials	3.30	11.02	11.02	11.02
Cathode Replacement	--	--	1.08	2.29
Cathode License Fee	--	--	--	.88
Total Variable	<u>158.47</u>	<u>177.18</u>	<u>171.84</u>	<u>160.56</u>
	(143.76/ST)	(160.73/ST)	(155.98/ST)	(145.65/ST)
Fixed Costs:				
Operating Labor Shift	4.69	4.23	4.23	4.23
Operating Labor Day	2.94	2.58	2.58	2.58
Operation Supervisors	<u>1.39</u>	<u>1.21</u>	<u>1.21</u>	<u>1.21</u>
Total Operating Labor & Supervision	9.02	8.02	8.02	8.02
Operation Overhead	13.54	12.04	12.04	12.04
Repair & Maintenance	24.45	21.11	21.34	22.22
Taxes & Insurance	11.86	12.47	12.62	13.50
Depreciation	<u>39.51</u>	<u>41.57</u>	<u>42.06</u>	<u>45.01</u>
Total Fixed	98.38	95.21	96.08	100.79
	(89.25/ST)	(86.38/ST)	(87.16/ST)	(91.43/ST)
TOTAL MANUFACTURING COSTS	<u>256.85</u>	<u>272.39</u>	<u>267.92</u>	<u>261.35</u>
	(233.01/ST)	(247.10/ST)	(243.05/ST)	(237.08/ST)

Table 5.11
Energy Audit Comparison for
Optimized Plants

	<u>Diaphragm</u>	<u>Current Membrane</u>	<u>Membrane with Catalytic Cathode</u>	<u>Membrane with Oxygen Cathode</u>
AC Cell Power	7267 ¹	8105	7747	6286
AC Motor Power	736	703	703	808
H ₂ Burned in Boiler	883	547	622	-0-
Purchased Fuel	615	-0-	-0-	547
Gross Energy Consumption	9505	9400	9072	7641
H ₂ Credit:				
H ₂ Burned in Boiler	883	547	622	-0-
H ₂ Balance to Other Uses	-0-	336	261	-0-
Net Energy Consumption	8622	8517	8189	7641
	(31.04)	(30.66)	(29.48)	(27.51)

¹All values are Mcal/ECU metric.
 Values in brackets are MBTU/ST.

purchased fuel and furthermore, the energy required to produce the hydrogen has already been charged against the process. Therefore, the "Net Energy Consumption" is the net energy actually withdrawn from the national energy supply to produce this chlorine and caustic for the optimized plant.

As clearly shown by the oxygen cathode the trend of the technology development is to reduce the energy consumption. New diaphragm cell technology is also moving the direction of lower energy consumption. Because of this direction in the technology chlorine plants in the future should not only be cost-effective but also energy efficient.

5.3.4 Effect of Hydrogen Sales

The sale price of hydrogen for chemical processes is about \$0.016/m³ (\$3.00 per thousand cubic feet) (7) as compared to \$0.037/m³ which is equivalent to 0.015/Mcal (\$3.75/MBtu) for fuel. Hence, if a market is available for hydrogen from these plants, all will be sold except that required for the production of HCl. All of the fuel required for steam production will be purchased.

The examples of plant economics, shown in Table 5.12, where hydrogen is sold show increased fuel purchases (except for the O₂ cathode plant) equal to that hydrogen which had been used for fuel. Note that hydrogen current efficiency is essentially 100% in all cases. Each type of cell produces virtually the same net amount of hydrogen.

5.3.5 Accuracy of Data, Estimates and Comparisons

The accuracy of the data and estimates and therefore the comparisons is not the same for the four cell cases studied.

The diaphragm cell plant data came primarily from two technology suppliers and from ABAM's files. The data from each of these sources is based on actual construction cost experience from many diaphragm cell plants. Hence, this data may be considered quite accurate. The error source is the lack of a definitive plant design and probably produces an accuracy factor of +15%.

The conventional membrane cell plant design is based on diaphragm cell plant experience and preliminary designs of the unique membrane cell plant components. However, much work has been done on full-scale cells and some small plants have been built. Furthermore, the unknown labor component of these items is small, hence the current membrane cell plant probably has an accuracy factor of +22%. The only change from the current membrane cell to the catalytic cathode cell in the latter plant is the cathode and slightly increased steam and caustic evaporation capacity, so this estimated accuracy factor should also be +22½%.

Table 5.12

Effects of Hydrogen Sales

	<u>Diaphragm</u>	<u>Membrane</u>	<u>Membrane with Catalytic Cathode</u>	<u>Membrane with Oxygen Cathode</u>
Optimum Current Density (kA/m^2)	2.17	3.10	3.10	3.10
Excess H_2 at Fuel Value:				
Total sales (\$/ECU metric)	358	375	372	369
Purchased fuel cost (\$/ECU metric)	9.22	0.00	0.00	11.40
DCF (%)	17.01	16.50	16.64	16.25
All H_2 Sold to Other Processes:				
Total sales (\$/ECU metric)	396	407	407	369
Purchased fuel cost (\$/ECU metric)	22.20	6.70	8.36	11.40
DCF (%)	19.90	19.42	19.53	16.25

The oxygen-cathode plant has uncertainties and no experience in the estimate components of incremental cell system cost, and oxygen system cost as well as related manufacturing costs. Hence, it has the poorest accuracy factor of $\pm 32\frac{1}{2}\%$. For this reason, more care should be taken in using this data than that for the other three plants.

However, for comparative purposes only and because all estimates were made by the same team, it is felt that the differences between the factors may be used. Therefore, a difference of about $7\frac{1}{2}\%$ is significant between the capital costs of the diaphragm and the first two membrane cells. A difference of $17\frac{1}{2}\%$ between the diaphragm and the O_2 cathode cell and a difference of 10% between the capital costs of the first 2 membrane cells and the O_2 cathode cell.

Manufacturing costs are comparatively closer for the first three types of cells because this data is more accurately available from long runs on a few full-scale cells. These accuracy factors are $\pm 10\%$. For the oxygen cathode cell the manufacturing cost data is based on very small-scale cells and much related experience, therefore, it is given an accuracy factor of $\pm 20\%$.

The above factors, which are all estimates by ABAM, must be recognized when reading the comparisons and calculated results of this study.

5.4 SENSITIVITY ANALYSES

Many variables affect the design and operation of a chlorine plant. Examples are current density, cost of power, and changes in the cost of the various types of cells. How these variables affect such things as cell voltage, capital and manufacturing costs, energy consumption, and discounted cash flow rate of return are discussed below. For most chlorine cells the primary dependent variable is the current density in the electrodes. However, for the diaphragm cell the brine feed rate which is reported as the ratio of salt to caustic soda in the cell liquor is also varied. This influences the cell current efficiency and the caustic concentration. The latter influences evaporating steam consumption and therefore plant fuel costs. A preliminary exploration of the salt to caustic ratio established that the minimum salt to caustic ratio produced the maximum DCF. Hence, the balance of the studies were made on a salt to caustic ratio of 1.11 which appeared to be a practical operating minimum for most of these cells.

5.4.1 Cell Voltage and Current Density

Cell voltage is an important factor in evaluating chlor-alkali cells because it is directly related to power consumption. Power costs account for roughly 40% of a plant's manufacturing costs. Therefore, plant design and optimization results in a compromise between low capital, high manufacturing costs plants and high capital, low manufacturing cost plants.

Equations were developed for cell voltage as a function of current density for each of the four types of cells. These equations are based on cell performance data obtained from suppliers of chlor-alkali cells and evaluations of research being conducted on the new technology cells. The equation used for this study follows:

Diaphragm Cells:

$$\begin{aligned} E &= 2.53 + 0.345 i + 0.24 \log i \\ E &= 2.58 + 0.534 I + 0.24 \log I \end{aligned} \quad (7)$$

Membrane Cells:

$$\begin{aligned} E &= 2.60 + 0.329 i + 0.24 \log i \\ E &= 2.65 + 0.510 I + 0.24 \log I \end{aligned} \quad (8)$$

Membrane Cell with Catalytic Cathode:

$$\begin{aligned} E &= 2.41 + 0.329 i + 0.24 \log i \\ E &= 2.46 + 0.510 I + 0.24 \log I \end{aligned} \quad (9)$$

Membrane Cell with O_2 Depolarized Cathode:

$$\begin{aligned} E &= 1.73 + 0.329 i + 0.12 \log i \\ E &= 1.75 + 0.510 I + 0.12 \log I \end{aligned} \quad (10)$$

where: E = cell voltage (volts)
 i = current density (kA/m^2), $i > 0.155 \text{ kA/m}^2$
 I = current density (A/in^2), $I > 0.1 \text{ ASI}$
 $(1 \text{ A/in}^2 = 1550 \text{ A/m}^2)$

These equations are written in the usual form of $E = f(I)$ for electrochemical reactions. They are based on known cathode and anode over-voltage relationships for the appropriate reactions and the thermodynamic potentials at zero current. They have then been empirically fitted to data received from cell developers (or from researchers in the case of the oxygen-cathode).

For catalytic cathodes, a voltage saving of 0.19 v was assumed as being somewhat conservative with respect to the 0.21 claimed.

For the oxygen-cathode, a voltage saving (with respect to the conventional membrane) of 0.9 v was chosen as in conversations with the researchers at Case Western Reserve University as reflecting the laboratory work and experiences with long-term tests on fuel cells.

Figure 5.1
Cell Voltage vs. Current Density

The curves of voltage vs. current density given in Figure 5.1 are shown with solid and dotted lines. The solid lines show the approximate range of current commercial operation. The dotted lines show potential operation. These latter represent laboratory work and in most cases are operating ranges which are not available or not normally utilized on commercial cells.

The upper limit of current density on the diaphragm cell is about 2.5 kA/m^2 . This seems to be due to the increasing influence of chlorine gas blanketing of the anodes.

The upper limit of current density on the oxygen-cathode cell is about 3 kA/m^2 . This seems to be due to the limit of back diffusion of nitrogen from the air, which is anticipated as the oxygen source for this cell.

5.4.2 Capital Cost and Current Density

Changes in current density directly affect the capital cost of chlorine plants for a fixed production rate. As the current density is increased the cell voltage increases. The increased current density and cell voltage raise the rectifier capital costs. However, as the current density increases the number of cells required to produce a fixed amount of chlorine is reduced. This reduction in capital cost of cells is greater than the extra capital cost required for the rectifiers so that the net effect is a decrease in total capital cost as current density increases. As current density approaches zero, the capital cost of any plant would approach infinity since an infinite number of cells would be required.

For the diaphragm cell plants only, increased current density also reduces the capital costs for the boiler and caustic systems. This is due to the increased cell voltage which increases the cell temperature causing more water to be evaporated from the cell liquor. Since the cell liquor is more concentrated, smaller caustic and boiler systems are required. A graph of total capital cost versus current density is given in Figure 5.2 for each of the four technologies. As discussed above, the total plant capital cost decreases with increased current density. Also, the new technology plants have higher capital costs. This is mainly due to the higher capital costs of the cells. When comparing capital costs for the four types of plants the comparison should be made at the current density at which each plant will be operated.

5.4.3 Manufacturing Costs and Current Density

The manufacturing costs of a chlorine plant change with current density at a fixed production rate. As current density increases the cell voltage increases. AC power requirements and therefore manufacturing costs go up directly with cell voltage. Since total

Figure 5.2

capital costs decrease with increasing current density, taxes and insurance and depreciation for manufacturing cost purposes (which are calculated as a percentage of capital costs) decrease. For the diaphragm case only, where purchased fuel is required to concentrate the caustic, as the current density is increased the required fuel purchased is decreased. This is due to the higher caustic concentration coming off the cells. For all membrane cells as the current density increases and cell voltage increases there will be more heat available for concentrating the caustic. Cell cooling is accomplished by circulating the cell liquor through the heat exchanger in the caustic evaporator. By this method, the heat which must be removed from the cells is used for caustic evaporation. The net effect for all four types of plants is an increase in the manufacturing costs as current density increases.

Plots of manufacturing costs as a function of current density for all four technologies is given in Figure 5.3.

The current membrane plant has higher manufacturing costs than the diaphragm plant because the delivered cost for salt is more than for brine, the cost of replacement components is more, and the cell power requirements are higher. The higher cell power requirements in membrane plants is due to the increased gross production rate of the cells to provide HCl for acidifying the brine. The purchased fuel requirements for diaphragm plants offsets the higher cost of membrane cell replacement costs.

Membrane cell plants with catalytic or oxygen cathodes reduce the manufacturing costs because the cell power is reduced.

Comparisons between the four cell types should be done at the current densities at which the cells would be operated.

5.4.4 Energy Consumption, DCF, Current Density and Capital Cost.

The relationships between energy consumption, discounted cash flow rate of return (DCF), current density, and capital cost of the four types of plants are shown in Figures 5.4 through 5.7. The difference between gross energy and net energy consumption for those plants which produce hydrogen is the fuel value of the hydrogen.

To minimize the energy consumption of any chlorine plant the current density has to be minimized. For low current densities (1.55 to 1.86 kA/m² or 1.0 to 1.2 ASI) the membrane cell plants consume less energy than diaphragm plants. However, the capital cost of such a plant is too high for it to be economical. This is shown by the low DCF.

Figure 5.3
Manufacturing Costs vs. Current Density

Figure 5.4

Energy Consumption and Discounted Cash Flow Rate of Return
vs. Capital Cost and Current Density

Figure 5.5

Energy Consumption and Discounted Cash Flow Rate of Return
vs. Capital Cost and Current Density

- Membrane Cell Plant -

Figure 5.6

Energy Consumption and Discounted Cash Flow Rate of Return
vs. Capital Cost and Current Density

- Membrane Cells with Catalytic Cathodes Plant -

Figure 5.7

Energy Consumption and Discounted Cash Flow Rate of Return
vs. Capital Cost and Current Density

- Membrane Cells with Oxygen Cathode Plant -

DCF is a measure of a plant's profitability and is basically a function of manufacturing and capital costs. High energy consumption (i.e., high manufacturing cost) occurs at low capital investment and vice versa. Therefore, a maximum DCF should occur somewhere between the extremes of high manufacturing cost and high capital investment. For membrane plants and membrane with catalytic cathode plants this maximum occurs at a current density of about 3.25 kA/m^2 (2.1 ASI). For the diaphragm plant and membrane with oxygen-cathode plant the maximum DCF would occur at current densities above their present limits (reference 5.4.1, p. 57). Hence, for practical purposes the maximum DCF is at those limits. For these analyses the DCF for the diaphragm is about 17% while the three types of membrane cell plants are all about one-half percent lower. This is a small difference and approaches the accuracy of the analyses. The value of the maximum DCF's for each type of plant and the current density at which they occur will change somewhat with a company's economic philosophy and with changes in the criteria used for this evaluation (e.g., site location, inflation, market, etc.).

5.4.5 Energy Consumption and Power Cost

The effects of an increasing cost of power is shown graphically in Figure 5.8. The horizontal dashed lines at the left side of each curve indicate the maximum energy consumption of each type of plant. This corresponds to the maximum current density at which the cells can operate. The net energy consumptions on the graph are for plants optimized with respect to DCF at a given power cost. The slopes of the lines for each type of plant show that increased power costs will provide incentive to reduce power consumption. The slopes of the lines for diaphragm, membrane, and membrane with catalytic cathode plants are nearly equal. Thus, the type of plant which uses the least energy does not change as power costs increase for these three plants.

The slope for the line for the oxygen-cathode plant is less than that for the other types of plants. The reasons for this apparently anomalous tendency in the oxygen-cathode plant are due to its significantly greater capital cost and reduced power consumption. Therefore, changes in the cost of power have less impact on the optimum current density. Hence, as power cost rises the optimum current density does not decrease as rapidly as for the other cells. At higher power costs the other cell types tend to overtake the oxygen-cathode cell with respect to energy usage.

This graph appears to indicate that at power costs of \$0.060/KWH, the oxygen-cathode plant would lose most of its energy advantage with respect to the membrane cell with catalytic cathode (see comments on accuracy, p. 43). However, the graph shows only the effect of changing power cost and assumes that other variables would stay constant. However, general inflation and technology will probably also change during the period that power costs rise to \$0.060/KWH.

Figure 5.8

Net Energy Consumption vs. Power Cost

Note: Curves are for economically optimized plants.

An inflationary increase in the capital cost of plants and a similar increase in non-power manufacturing costs will tend to shift all of these lines simultaneously to the right. This will cause the hypothetical intersection of the oxygen-cathode plant and the membrane with catalytic cathode plant to move to a higher power cost.

A relative improvement in the technology of the oxygen-cathode cell compared to the others will tend to move its "line" downward and increase the slope on the graph. Since the oxygen cathode is the newest, and least well developed cell, it may be expected to be improved more rapidly than the others. Therefore, the hypothetical intersection of the "lines" on the graph may be expected to move beyond the \$0.060/KWH value. However, the oxygen-cathode cell will always require air or oxygen facilities and a relatively more expensive cathode, so its "line" on the graph may not be expected to become parallel to that of the membrane cells. At some higher value there will be a power cost at which the energy requirements of economically optimized plants using the two different cells will be equal.

5.4.6 Net Energy Consumption and Cell System Costs

The effects of changes in the cell system costs for the four types of plants are shown in Figure 5.9. The energy consumption figures are for economically optimized plants at each value of cell system cost.

For each type of plant net energy consumption decreases as the cell system cost decreases. The change in energy consumption is due to a shift in the optimum current density. As the cell system cost decreases the economic incentive is to purchase more cells and operate at a lower current density and a lower power cost. The opposite would be true for increased cell system costs.

For diaphragm cell plants the optimum current density, and therefore net energy consumption, changes relatively slowly with changes in the cell system cost because of two factors:

1. The diaphragm cells are presently operating at lower current densities than the membrane cells. Therefore, to reduce the current density by a certain percentage yields less voltage (and power) saving then the same percentage reduction in the current density of a membrane cell.
2. The diaphragm cell plants have relatively higher fixed energy consumptions in AC motor power and net purchased fuel (19% vs. 5% of net total energy, see Table 5.11). This tends to reduce the relative benefit of lower cell costs for diaphragm cell plants.

For these reasons, the slope of the line for the diaphragm cell plant is less than that for the membrane plant.

Figure 5.9

Net Energy Consumption vs. Cell System Cost

- Notes: (1) Curves are for economically optimized plants.
(2) 100 corresponds to current cell system costs including cell area and rectifier area installations.

The conventional membrane cell and membrane with catalytic cathode plants show about the same improvement in energy consumption (slope of lines) with reduced cell system costs. The comparison with the diaphragm cell plant has been given above.

The oxygen-cathode membrane cell plant shows a reduced slope due primarily to the higher cell system cost. The initial reduction of these costs does not seem to produce the same economic incentive to install large numbers of additional cells and thereby significantly reduce current density and power costs.

The implication that additional research on oxygen-cathode cells may be of less benefit than on membrane cells, however, cannot be drawn for two reasons:

1. The oxygen-cathode cell is at an earlier stage of development where improvements are sometimes obtained more easily. Technological improvements will increase the slope of the line.
2. The accuracy of the estimate (see p. 45) for the oxygen-cathode plant is significantly lower than for the other plants. (Estimating inaccuracies may be magnified more on this graph than on the others in this report.)

6.0

RESULTS OF IMPROVED TECHNOLOGY

The production of chlorine and caustic soda by electrolysis of brine is a major consumer of electrical energy using approximately 1.5% of the yearly U.S. generation (5). The rapidly rising cost of energy has given increased incentive to reducing the energy requirements of the industry.

Since the late 60's there have been a number of major improvements in the chlor-alkali electrochemical cell technology. The rise in the cost of fuel has also made it economical in many cases to go to quadruple-effect evaporation which saves 20% of the fuel used for triple-effect evaporation.

In diaphragm cell plants, carbon anodes have been replaced with dimensionally stable metal anodes, the asbestos diaphragm has been stabilized with a chemically resistant polymer, the space between the electrodes reduces, and cells have been designed to operate at lower current densities. These improvements have lowered electrical energy requirements by about 25%. Catalytic (reduced H₂ overvoltage) cathodes are now being offered to the industry and it is expected that microporous diaphragms will soon be available. It is expected these two improvements will further reduce electrical energy by another 10%.

The commercialization of the membrane cell over the past few years is another major advancement. They produce a caustic solution of

higher strength than the diaphragm cell and lower in salt. This reduces greatly the energy needed for caustic liquor evaporation. At the same current densities the voltages required for a single, present day, diaphragm or membrane cell are almost identical. However, due to the higher cost for membranes as compared to diaphragms, the membrane cells are designed to operate at higher current densities and voltages. As a result, the electrical power requirements, per unit of chlorine, when using current technology membrane cells or membrane cells with catalytic cathodes is normally higher than for diaphragm cells. Present day membrane cells also operate at a 3% to 5% lower efficiency. Improvements are being made in this area. The membrane cell appears to be ideally suited to take advantage of the oxygen cathode development. This could lower electrical cell power requirements by as much as 20%.

Adding up all the recent improvements that have become cost-effective, along with those that are likely to become commercial in the next few years, and the expected reductions in current densities as energy becomes more expensive, the electrical energy required to produce a unit of chlorine by 1990 should be only 50% to 60% of that used in 1970.

In the United States, a large percent of the market does not demand salt-free caustic. About 75% of the electrolytic caustic is produced in diaphragm cells and only a small part of that is purified. The demand for salt-free caustic is low as salt-free caustic only brings a premium of around \$11.02/metric ton (\$10.00/ST). This study indicates that unless membrane cell costs are greatly reduced or a stronger demand develops for salt-free caustic, the diaphragm cells will remain competitive.

7.0 ROLES OF THE FEDERAL GOVERNMENT IN ENERGY SAVINGS

7.1 ROLES

The U.S. federal government has several roles available to assist in the reduction of energy usage of the chlor-alkali industry. For the long-term improvements, these seem to lie in the area of supporting selected research. For the short term, the balance between high energy usage and high capital costs can be tilted toward lower energy usage by tax law changes.

7.2 SAVING POWER BY SUPPORTING JOINT FEDERAL-PRIVATE DEVELOPMENTAL RESEARCH

Long-term reductions in the energy consumption of chlor-alkali plants seem to be enhanced by government support of research on a subject such as being done by the DOE funding of research in catalytic oxygen-air cathodes for membrane cells at Case Western Reserve University. With the technology development portion being publically funded, the researchers can maintain communications with others working in related fields and the maximum growth in knowledge and understanding is realized. With the commercial application portion of the research being privately funded and held in confidence, the private industry partner is induced to put their most creative and highly motivated personnel into the development effort. This combination seems to be effective.

7.3 TRADE BALANCE EFFECT

A very important side benefit may be gained as a result of joint federal-private development of new chlor-alkali cell technology.

The technological competition between U.S. and foreign firms in the chlor-alkali field is presently very strenuous. Asahi Chemical of Japan presently has supplied the two largest membrane cell chlorine plants in North America. These are in Canada, but they are negotiating seriously at the present time for one or more major plants in the U.S. They have also won the contract for a large plant in the Netherlands. On the basis of total production capacity installed and on order, they are presently well in the lead.

The DOE support of the development of the oxygen cathode cell with Diamond Shamrock may allow the U.S. to at least stay with the leaders in this promising new technology. There are reported to be vigorous activities in Japan and probably also in several other countries.

The sale of chlor-alkali plant technology has been and continues to be a significant source of foreign exchange for the U.S. Approximately one-third of the foreign plants currently operating use diaphragm cells from Hooker and Diamond Shamrock in the U.S. Normally between 25% and 90% of the cost of these plants appears as purchases in the country supplying the technology.

It appears, therefore, that the present program of joint federal and private development of new technology for the chlor-alkali industry is effective and beneficial for long range reduction of power consumption and foreign trade balance improvement.

7.4 SAVING POWER BY ADJUSTING TAXES

Another method available to the federal government for reducing energy consumption in the chlor-alkali industry is based on the economic fact that the cost of capital competes with the cost of power in the design of these plants. A reduction in the effective cost of capital would shift the optimum plant design to more cells, lower current density, lower voltage and therefore lower power consumption. With the number of different manufacturers and plant locations in this competitive market, the overall result of slightly reduced manufacturing costs would also be expected to produce a reduction in prices.

This reduction in capital costs need only be applied to the elements of the plant which influence energy consumption. It is not the purpose of this study to produce an accurate and practical definition of these elements, but the cells would of course be included.

The tax laws have a large impact on the effective cost of capital. Increasing depreciation rates and investment tax credits are two of the principal opportunities where there seem to be several possible programs for application of tax law changes. Two are mentioned below.

- 7.4.1 A longer term, and lower energy saving, program would provide tax benefits for the energy affecting components of new chlor-alkali plants. This would induce the design and construction of more energy-efficient plants. This could be quite effective on new plants. This program would only reduce national energy consumption as new plants were built.
- 7.4.2 A short-term, and earlier energy saving, program would provide similar tax benefits for the addition of cells and other energy-saving elements to existing plants. The addition of cells to existing plants without increasing production capacity would reduce current density and reduce power consumption. A reduction in national power consumption would commence as soon as an adequate incentive program was implemented.

8.0 CONCLUSIONS AND COMMENTS

8.1 CONCLUSIONS

The conclusions which have been drawn from this study are as follows:

- o The diaphragm cell plant may be somewhat superior economically to the best (catalytic cathode) membrane cell plant.
- o The diaphragm cell plant may consume somewhat more net energy than the current technology membrane cell plant.
- o The oxygen (air) cathode membrane cell plant consumes the least net energy of the four plants studied.
- o The oxygen-cathode membrane cell appears to be close to a competitive technology. It deserves further federal support because of its potential to save energy.
- o The ability of the diaphragm cell plant to utilize pipeline brine rather than requiring solid salt feed is a major economic advantage.
- o The catalytic cathode will become standard on both membrane and diaphragm cells because it is superior to steel cathodes in both economics and energy consumption, if it proves to have adequate service life.
- o The diaphragm cell will probably maintain its economic position with respect to the membrane cells in the short term because the catalytic cathode is available to both. The advent of microporous diaphragms and dynamic gel diaphragms may maintain these close relative positions over an extended period.
- o A desirable development of the membrane cell--which is being very actively pursued--is a design with a "packed" or folded surface. This could produce a "diaphragm cell-like" configuration and greatly reduce the cost of the non-electrolytic components of the cell. This work has the potential of reducing the total plant capital by 10% or more, and reducing power consumption on new plants by about 10%.
- o Improvements (cost reductions) in membrane cell technology would tend to produce greater benefits in energy savings than equal improvements (in proportion to cell cost) in diaphragm cells.
- o New technologies which deserve an economic investigation because of their strong promise for saving energy are as follows:

- Solid Polymer Electrolyte
 - Fuel Cell Coupled to a Diaphragm Cell
 - Dynamic Gel Diaphragm
- o Federal support of development work in the chlor-alkali technology field is beneficial for three reasons:
- It accelerates the development of applied research in the field.
 - It may promote the development of cells which save energy and foreign exchange (for the nation) by utilizing processes from which the economic benefits would not provide an adequate incentive (for a private developer).
 - It tends to improve the U.S. balance of trade in the marketing of technology internationally.
- o The opportunity for the most rapid reduction in energy consumption by the chlor-alkali industry lies in tax law changes which would induce the installation of additional cells in existing plants. This would reduce current density, reduce voltage and thereby reduce power consumption. Benefits of 10%-20% saving by the entire industry could be obtained within 5 years.
- o These changes in cell technology will have an insignificant effect on employment in the chlor-alkali industry.

8.2 COMMENTS ON CONCLUSIONS

The above conclusions are based on plant designs and estimates made according to a single, common envelope criteria. Some would change with plant size (criterion: 544 metric T/D). Some would change with the price of "low-salt caustic" (criterion: \$11.02 per metric ton premium over "Diaphragm Grade.")

Calculated results falling within the margin of error of the estimates are indicated by the use of the term "may be" in the above conclusions.

The economic performance of the diaphragm cell plant improves more with increase in scale than the others. Hence its economic superiority would tend to increase in larger plants and decrease in smaller plants.

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APPENDIX A

ENVELOPE CRITERIA - GLOSSARY AND COMMENTS.

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APPENDIX A

Envelope Criteria - Glossary and Comments

Annual Plant Maintenance:

Five percent has been chosen as a moderately conservative rate for the plants as designed (see "Moderately Well Designed . . ."). Actual rates range from 2 to over 10% depending on plant design and maintenance philosophy.

Costs, Expenses, and Income in 1980 Dollars:

This choice of estimating time base has permitted the use of current dollars and circumvented the need to forecast inflation rates. It is artificial because a plant cannot be designed and built in zero time. However, the report should be more useful for others because the time base is real.

Depreciation for Calculation of Manufacturing Costs:

Manufacturing costs must show a charge of depreciation to be correct. However, accelerated depreciation schedules change each year. To eliminate confusion from these changes, a straight line depreciation rate is used for manufacturing costs.

ECU/day:

"Electrochemical Unit" refers to one short ton of chlorine. This term is an accounting convenience chosen to allow all costs to be referenced to a single product rate-chlorine. It anticipates a (nearly) chemically equivalent production rate of the co-products, caustic soda and hydrogen.

For the oxygen-cathode cell case it is flawed because of the lack of hydrogen production.

For this study, one ECU is measured as one short ton of chlorine available for sale. One ECU metric is measured as one metric ton of chlorine available for sale.

Grass Roots Plant:

This means a plant at a site which was originally a bare "grassy" field. The plant is self-sufficient with respect to utilities, maintenance and administrative facilities.

Moderately Well Designed, Operated and Maintained Plant:

The capital costs have been developed according to ABAM's judgments of the mid-range of requirements and practices of the U.S. chlorine industry.

Salt and Brine:

Salt and brine costs vary widely. These values were obtained from Texas Brine, one of the major suppliers.

SG&A:

Sales, general and administrative expenses. These are selling and corporation expenses incurred away from the plant. Included are such expenses as sales, rail car leasing, personnel, research, planning, corporate officers and staff, and traffic.

90% of 365 day/yr Operating Rate:

This factor represents the historical experience of the U.S. chlorine industry operating at about 90% of design capacity. The on-stream time will normally be 98-99%.

APPENDIX B

MATERIAL AND ENERGY BALANCES AND FLOWSHEETS

- Part 1: Diaphragm Cell
- Part 2: Current Membrane Cell
- Part 3: Membrane Cell with Catalytic Cathode
- Part 4: Membrane Cell with Oxygen Cathode

MATERIAL AND ENERGY BALANCES

Part I: Diaphragm Cell

(Bases 1 kg Cl₂ at cells)

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy					kPa (psig)
									kg	Percent	Stream Enthalpy (kcal/Lg)	KWH	kcal	T°C	T°F	
1	Raw Brine NaCl Ca Mg SO ₄						1.667		6.57	25.0 .0525 .0040 .0900	116			21.1	70	
2	Soda Ash								.0136							
3	Hot Brine					7.929	2.900	0.044	10.873		57			65	149	
4	Wet Cl ₂	1.0		.00012		0.418					256			86.5	187.7	
5	Cl ₂ Product	.99												-34.4	-30	1,000 (130)
6	Cl ₂ to HCl	.01		.00012										-34.4	-30	
7	HCl to Brine				0.0103	0.0229			0.0332		Neg 1			25	77	
8	Cell Liquor		1.128			6.528	1.252	0.044			7.6			96	204.8	
9	NaOH Product		1.128			1.105	0.023	Neg 1	2.256		.7			20	68	
10	Hot H ₂			0.0298		0.4601					28.1			87	188.6	
11	Cool H ₂			0.0298		0.3185					.5			37.8	100	
12	H ₂ to HCl			0.00262		0.0016					2			37.8	100	
13	H ₂ to Boilers			0.0272		0.0169					7.7			37.8	100	
14	Evap. Steam								2.088				1,387	185.6	366	1,135 (150)
15	1st Eff. Cond								2.055				237	115.6	240	170 (10)
16	Sulfate Liquor		0.0002			0.792	0.211	0.044	1.047		55					
17	Salt Slurry		0.001		1.018		1.018		2.037		81					
18	Sulfate Brine		.0002			0.799	.217	0.035	1.051							
19	Sulfate Sludge					0.0066	0.0019	0.0001	0.0172							
20	CaSO ₄									50.0						
21	Brine Sludge					.0070	0.0023		0.0187							
22	CaCl ₂ Sol.					0.0132			0.0206							
23	CaCl ₂									36.0						
24	Int. Stage Cond.					2.094			2.094		137			65.6	150	
25	Cond. to Brine					1.105			1.105		86			60	140	
26	Cond. to Tower								.947					60	140	
27	AC Power Total											3.144	7,922			
28	AC Power Rect.											2.855				
29	AC Motor Load											.289				
30	Cl ₂ CWS								46					32.2	90	
31	Cl ₂ CWR								46					43.3	110	
32	Evap. CWS								148					32.2	90	
33	Evap. CWR								150					43.3	110	
34	Tower Purge								.23					32.2	90	
35	Fuel												1,351			
36	Flue Gas												202			
37	Blow Down								.0418					60	140	
38	HCl Inerts								.023							
39	H ₂								.0197							
40	CO ₂								.0032							
41	H ₂								.0001							
42	HCl CWS								7.8							
43	HCl CWR								7.8							
44	Boiler Makeup								.0413					60	140	
45	Asbestos Waste								.00036							
46	Tower Makeup								.91

PROCESS FLOW DIAGRAM 600 TON PER DAY
DIAPHRAGM CELL CHLORINE PLANT

MATERIAL AND ENERGY BALANCES
Part 2: Membrane Cell

(Bases 1 kg Cl₂ at cells)

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy			T°C	T°F	kPa (psig)
									kg	Percent	Stream Enth (kcal/lb)	KWH	kcal			
1	Salt NaCl Ca ⁺⁺ Mg ⁺⁺ SO ₄ Insolubles								1.561	99.05						
2	Soda Ash									.25						
3	Hot Brine									.01						
4	Met Cl ₂	0.9825			0.0527	10.13	3.50	0.2275	13.910		747			65	149	
5	Cl ₂ Product	.99				0.2390			1.2136		157			80.5	176.9	
6	Cl ₂ to HCl	.08							.93							
7	HCl to Dechlor				.01	.020			.07							
8	Cell Liquor		4.146			10.151			14.297		1,027			85	185	
9	NaOH Product		1.059			1.059			2.118		16					
10	Hot H ₂			.0284		.1215					113			76	168.8	
11	Cool H ₂			.0284		.01763					14			37.8	100	
12	H ₂ to ACl			.0024					.0024							
13	H ₂ to boiler			.0133					.0133				743			
14	Evap. Steam								.9734				646			1135 (150)
15	1st Eff. Cond.								.9424				108			170 (10)
16	Caustic Recycle		3.076			7.531			10.507					85	185	
17	Cell Liquor Recycle		3.076			8.725			11.801		333			37.8	100	
18	Anolyte	.0275				7.860	1.938	.2275	10.053		747			85	185	
19	Cl ₂ from Dechlor.	.0285														
20	HCl to Brine Treatment				.062	.138										
21	Brine Sludge					.024	.009		.045							
22	Int. Stage Cond.								.7675		51			65.6	150	
23	Brine Makeup Water					1.787			1.787							
24	Tower Makeup Water								3.07							
25	Catholyte Makeup Water					1.134								21.1	70	
26	Boiler Makeup H ₂ O					.0195			.0195							
27	Depleted Brine 100 ppm H ₂ O				.0084	7.633	1.807	.2121	9.660					32.2	90	
28	H ₂ CWR								8.9					43.3	110	
29	HCl CWR								8.9					32.2	90	
30	Cl ₂ CWR								35.3					43.3	110	
31	Cl ₂ CWR								35.3					32.2	90	
32	HCl CWR								54.6					43.3	110	
33	HCl CWR								54.6					32.2	90	
34	Tower Purge								0.77					43.3	110	
35	Blow Down					.0195			.0195							
36	Evap. CWR								67.3					43.3	110	
37	Evap. CWR								68.1							
38	AC Power										3.283					
39	AC Motive Power										.260					
40	AC Cell Power										3.023					
41	HCl Inerts N ₂ CO ₂ H ₂								.0039 Neg'l .0001							
42	25% Caustic	.0109				.0267										
43	Sulfate Liquor				.0006	.5542	.1312	.0154								
44	30% CaCl ₂ Sol'n					.021			.0228							
45	Sulfate Sludge					.0125	.0026		.0262							

MATERIAL AND ENERGY BALANCES (cont'd)
Part 2: Membrane Cell

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy			T°C	T°F	kPa (psig)
									kg	Percent	Stream Enth. (kcal/kg)	KWH	kcal			
46	Low Sulfate Brine				.0006	.5647	.1410		.7077				112			
47	Flue Gas															
48	CL Recycle CWS								38.5					32.2	90	
49	CL Recycle CWR								38.5					43.3	110	
50	Net Cl ₂ to HCl	.06							.06							
51	H ₂ Credit			.0127					.0127

PROCESS FLOW DIAGRAM 600 TON PER DAY
MEMBRANE CELL CHLORINE PLANT

MATERIAL AND ENERGY BALANCES
Part 3: Membrane Cell with Catalytic Cathode

(Bases 1 kg Cl₂ at cells)

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy			T°C	T°F	kPa (psig)
									kg	Percent	Stream Enth. (kcal/kg)	KWH	kcal			
1	Salt NaCl Ca++ Mg++ SO ₄ Insolubles								1.561	99.05 .25 .01 .6 .085 .0169						
2	Soda Ash															
3	not Brine				0.0527	10.13	3.50	0.2275	13.910		747			65	149	
4	wet Cl ₂	0.9725				0.2390			1.2136		157			80.5	176.9	
5	Cl ₂ Product	.93							.93							
6	Cl ₂ to HCl	.07							.07							
7	HCl to Dechlor.				.01	.020										
8	Cell Liquor		2.55			6.246			8.796		632			85	185	
9	NaOH Product		1.059			1.059			2.118		16					
10	hot H ₂			.0284		.1215					113			76	168.8	
11	Cool H ₂			.0284		.01763					14			37.8	100	
12	H ₂ to HCl			.0024					.0024							
13	H ₂ to boiler			.0183					.0183				743			
14	Evap. Steam								.9734				647			1135 (150)
15	1st Eff. Cond.								.9424				109			170 (10)
16	Caustic Recycle		1.48			3.625			5.105					85	185	
17	Cell Liquor															
18	Recycle		1.48			4.819			6.299		56			37.8	100	
19	Anolyte	.0275				7.860	1.938	.2275	10.053		747			85	185	
20	Cl ₂ from Dechlor.	.0295														
21	HCl to Brine Treatment				.062	.138										
22	Brine Sludge					.024	.009		.045							
23	Int. Stage Cond.								.7675		51			65.6	150	
24	Brine Makeup water					1.787			1.787							
25	Tower Makeup water								2.80							
26	Catholyte Makeup water					1.194								21.1	70	
27	Boiler Makeup H ₂ O					.0195			.0195							
28	Depleted Brine 100 ppm				.0084	7.633	1.807	.2121	9.660					32.2	90	
29	H ₂ CWS								8.9					43.3	110	
30	H ₂ CWR								8.9					32.2	90	
31	Cl ₂ CWS								44.2					43.3	110	
32	Cl ₂ CWR								44.2					32.2	90	
33	HCl CWS								54.6					43.3	110	
34	HCl CWR								54.6					32.2	90	
35	Tower Purge								.70					43.3	110	
36	Blow Down					.0195			.0195							
37	Evap. CWS								67.3							
38	Evap. CWR								68.1					43.3	110	
39	AC Power											3.133				
40	AC Motive Power											.260				
41	AC Cell Power											2.873				
42	HCl Inerts								.0039							
43	H ₂ CWS								Neg '1							
44	H ₂ CWR								.0001							
45	29% Caustic	.0109				.0267										
46	Sulfate Liquor				.0006	.5542	.1312	.0154								
47	36% CaCl ₂ Sol'n					.021			.0328							

MATERIAL AND ENERGY BALANCES (cont'd)
 Part 3: Membrane Cell with Catalytic Cathode

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy			T°C	T°F	kPa (psig)
									kg	Percent.	Stream Enth. (kcal/kg)	KWH	kcal			
45	Sulfate Sludge					.0105	.0026		.0262							
46	Low Sulfate Brine				.0006	.5647	.1410		.7077							
47	Flue Gas												112			
48	CL Recycle CWS								27.4					32.2	90	
49	CL Recycle CWR								27.4					43.3	90	
50	Net Cl ₂ to HCl	.06							.06							
51	H ₂ Credit			.0077					.0077

PROCESS FLOW DIAGRAM 600 TON PER DAY
MEMBRANE CELL W/ CATALYTIC CATHODE CHLORINE
PLANT

MATERIAL AND ENERGY BALANCES
Part 4: Membrane Cell with Oxygen-Cathode

(Bases 1 kg Cl₂ at cell's)

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy			T°C	T°F	kPa (psig)
									kg	Percent	Stream Enth (kcal/kg)	KWH	kcal			
1	Salt NaCl Ca ⁺⁺ Mg ⁺⁺ SO ₄ Insolubles								1.561	99.05						
2	Soda Ash									.25						
3	Hot Brine				0.0527	10.13	3.50	0.2275	13.910		747			65	149	
4	Wet Cl ₂	0.9725				0.2390			1.2136		157			80.5	176.9	
5	Cl ₂ Product	.93							.53							
6	Hot H ₂			.0023		.0098					9			76	166.8	
7	HCl to Dechlor.				.01	.020										
8	Cell Liquor		8.474			20.746			29.220		1,027			85	185	
9	NaOH Product		1.059			1.059			2.118		16					
10	Evap. Steam								.6813				453			1135 (150)
11	1st Eff. Cond.								.6483				75			170 (10)
12	Caustic Recycle		7.415			18.154			25.569					85	185	
13	Cell Liquor															
14	Recycle		7.415			18.753			26.168		722			37.8	100	
15	Anolyte	.0275				7.360	1.938	.2275	10.053		747			85	185	
16	Cl ₂ from Dechlor.	.0285														
17	HCl to Brine Treatment				.062	.138										
18	Brine Sludge					.024	.009		.045							
19	Int. Stage Cond.								.4344		28			65.6	150	
20	Brine Makeup Water															
21	Tower Makeup Water					1.787			1.787							
22	Catholyte Makeup Water								3.00							
23	Boiler Makeup H ₂ O					.5988			.340					21.1	70	
24	Depleted Brine 100 ppm Fuel				.3084	7.533	1.807	.2121	.0166	9.660			649			1135 (150)
25	Air Proc. Steam								.0166				99			
26	Cl ₂ CWS								.1495							
27	Cl ₂ CWR								35.3					32.2	90	
28	HCl CWS								35.3					43.3	110	
29	HCl CWR								55.4					32.2	90	
30	Tower Purge								55.4					43.3	110	
31	Blow Down					.95			.0166							
32	Evap. CWS					.0166			56.2							
33	Evap. CWR								56.4					43.3	110	
34	AC Power											2.630				
35	AC Motive Power											.300				
36	AC Cell Power											2.330				
37	HCl Inerts															
38	H ₂								.0039							
39	CO ₂								Neg'l							
40	H ₂								Neg'l							
41	25% Caustic		.0109			.0267										
42	Sulfate Liquor				.0006	.5542	.1312	.0154								
43	30% CaCl ₂ Sol'n					.021			.0128							

MATERIAL AND ENERGY BALANCES
Part 4: Membrane Cell with Oxygen-Cathode

Stream No.	Stream	Cl ₂	NaOH	H ₂	HCl	H ₂ O	NaCl	Na ₂ SO ₄	Total		Energy			T°C	T°F	kPa (psig)
									kg	Percent	Stream Enth. (kcal/kg)	KWH	kcal			
45	Sulfate Sludge					.0105	.0026		.0262							
46	Low Sulfate Brine				.0006	.5647	.1410		.7077							
47	Flue Gas												97			
48	CL Recycle CMS								84.8					32.2	90	
49	CL Recycle CWR								84.8					43.3	110	
50	Net Cl ₂ to HCl	.06							.06							
		O ₂	N ₂	A _r	CO ₂											
10	Air to Cell	.6858	2.2323	.0381		.4633								85	185	40*
11	Air from Cell	.4572	2.2323	.0381		.4633								85	185	10*
12	Exhaust Air	.4572	2.2323	.0381		.1659								44	111	
13	Air Feed	.6858	2.2323	.0381	.0014											

*Inches H₂O

PROCESS FLOW DIAGRAM 600 TON/DAY
MEMBRANE CELL W/ OXYGEN CATHODE CHLORINE PLANT

APPENDIX C

ESTIMATION OF ENTHALPY OF REACTION IN CHLOR-ALKALI CELLS

ESTIMATION OF ENTHALPY OF REACTION IN A CHLOR-ALKALI CELL

Heat balances for diaphragm or membrane chlor-alkali cells require accurate values for enthalpy of reaction. Reactants and products are not in their thermodynamic standard states so that calculations are necessary to convert from the standard states to the cell conditions. The general chemical reaction in a cell can be written,

The reaction is considered in the following calculation to occur at a uniform temperature, T , and the hydrogen and chlorine gases are considered to be dry. The overall reaction 1 is the sum of two one-electron half reactions.

The two basic sources of standard-state enthalpy of reaction data were Latimer (1) and the JANAF Tables (2). Latimer provided data to calculate the ΔH of reaction for the unit activity and crystalline standard states of NaCl and NaOH at 25°C . The calculated values of ΔH_{rx} are:

	<u>K Cal/Mol NaOH</u>
NaCl (c), NaOH (aq)	+ 54.313
NaCl (aq), NaOH (aq)	+ 54.383
NaCl (C), NaOH (C)	+ 64.559
NaCl (aq), NaOH (C)	+ 63.629

The reaction is endothermic and requires electrical energy to make it go. It is convenient in cell heat balance calculations to use the ΔH_{rx} in terms of voltage,

$$E_{\Delta H} = \frac{\Delta H_{rx}}{n(23.060)} \quad (2)$$

in which $n = 1$ in reaction 1. The values of $E_{\Delta H}^0$ at $T = 25^\circ\text{C}$ for the Latimer standard states are:

	$E_{\Delta H}^0$ (volts)
NaCl (C), NaOH (aq)	2.355
NaCl (aq), NaOH (aq)	2.315
NaCl (C), NaOH (C)	2.800
NaCl (aq), NaOH (C)	2.759

The JANAF Tables (2) provide data to calculate ΔH_{rx} as a function of temperature for the standard state of NaCl (c) and NaOH (c). The JANAF Tables, however, only give data for water in the ideal gas state and a correction is necessary for heat of vaporization of water; steam table data from Perry (3) were used. Calculated values of ΔH_{rx} and $E_{\Delta H}$ at 25°C and 100°C for NaCl (c) and NaOH (c) are:

	ΔH k cal/mol NaOH	$E_{\Delta H}$ (volts)
25°C	+ 64.667	2.804
100°C	+ 63.980	2.775 (interpolated)

There is a reasonable agreement between the Latimer and JANAF Tables at the common point of 25°C for NaCl (C) and NaOH (C).

Heat of mixing data of NaOH at room temperature from several sources were used to bridge the gap in ΔH between NaOH at unit activity and solid NaOH. The various data are plotted in Fig. 1 for which the standard state is unit activity of NaOH. Data from Lange (4) and Diamond Shamrock (5) are available in the region of 0 to 50% NaOH. At 100% NaOH the curve should connect with the point from Latimer, ΔH NaCl(c),

NaOH (C) - ΔH NaCl(c), NaOH (aq) = 64.559 - 54.313 = 10.246 kcal/mol NaOH. Other points for heat of mixing from Perry (3) and the Chemical Rubber Handbook (6) are also shown. A best-estimate dashed curve was drawn connecting the Diamond Shamrock data with the terminal point for NaOH from Latimer. (This curve is fictitious in that a liquid phase is assumed in the dashed region. Crystallization starts at room temperature at about a 53 weight percent NaOH solution.) An equivalent $\Delta E_{\Delta H}$ scale is given on the right hand side of Fig. 1.

The heat of reaction data are combined with the Fig. 1 heat of solution data to give the curve shown in Fig. 2 for $E_{\Delta H}$ versus NaOH concentration at 25°C. Ranges of concentration of NaOH in diaphragm and membrane cell liquor indicated in Fig. 2 are in a region in which $E_{\Delta H}$ is relatively flat. The directions for corrections for NaCl in the cell liquor and for a higher operating temperature are indicated.

Corrections were made for salt in the cell liquor and higher operating temperature for a 10% NaOH cell liquor. Sufficient specific heat data were available at this caustic concentration, although insufficient data have been found for other concentrations. The reaction thus considered was,

The heat of reaction for equation 3 in a temperature range $65^\circ < T < 105^\circ\text{C}$ is,

$$\Delta H_{rx} = 54.229 - 2.4830 \times 10^{-2} T + 6.4294 \times 10^{-5} T^2 \quad (4)$$

Points at 25°, 80° and 100°C are plotted in Fig. 2.

Figure 1
Heat of Dilution of NaOH at 20 to 25°C vs. NaOH Concentration

Figure 2
Estimated $E_{\Delta H}$ vs NaOH Concentration

Conditions: 25°C, unit activity NaCl feed, no NaCl in caustic cell liquor.

APPENDIX D

DISCOUNTED CASH FLOW RATE OF
RETURN SAMPLE CALCULATION WITH
HP-97 CALCULATOR PROGRAM

DISCOUNTED CASH FLOW RATE OF RETURN

Example Calculation

- D_T = Depreciation for tax purposes (10-year double-declining balance).
- C_C = Capital cost.
- N = Depreciation period (years).
- n = Year.
- AMC = Adjusted manufacturing cost.
- M = Expenditures.
- D_M = Depreciation for manufacturing cost calculations - 15-year straight line.
- T = Income tax.
- R = Income tax rate (46%).
- C = Net cash flow.
- T_C = Tax credit (entire credit used during year one, 10% of capital).
- T_n = Net tax paid.
- S = Sales.
- P = Present value.

Credit: Assumes that the company has sales from ventures other than this chlorine plant. When AMC is greater than sales, 54% of the difference is added to the Net Cash Flow.

- i = Discounted cash flow rate of return.
- $D_T = \left[\left(1 - \frac{2}{N}\right)^{n-1} - \left(1 - \frac{2}{N}\right)^n \right] \cdot C_C$
- $AMC = M + D_T - D_M$
- $T = (S - AMC)R$
- $C = S + D_T - AMC - T_n + T_C + \text{credit}$
- $P = \frac{C}{(1+i)^n}$

DISCOUNTED CASH FLOW RATE OF RETURN

Sample Calculation

<u>Year</u>	<u>Expenditures</u>	<u>Sales</u>	<u>Depreciation</u>	<u>Adjusted Mfg. Costs</u>	<u>Tax</u>	<u>Tax Credit</u>	<u>Net Cash Flow</u>	<u>Present Value</u>
0	106,000	0	0	0	0	0	0	-106,000
1	51,667	64,058	21,200	65,800	0	10,600	30,999	26,492
2	45,926	"	16,960	55,819	3,790	0	21,409	15,637
3	"	"	13,568	52,427	5,350	"	19,849	12,390
4	"	"	10,854	49,714	6,598	"	18,600	9,923
5	"	"	8,684	47,543	7,597	"	17,602	8,025
6	"	"	6,947	45,806	8,396	"	16,803	6,547
7	"	"	"	"	"	"	16,803	5,595
8	"	"	"	"	"	"	16,803	4,782
9	"	"	"	"	"	"	16,803	4,087
10	"	"	"	"	"	"	16,803	3,493
11	"	"	"	38,859	11,591	"	13,607	2,417
12	"	"	"	"	"	"	"	2,066
13	"	"	"	"	"	"	"	1,766
14	"	"	"	"	"	"	"	1,509
15	"	"	"	"	"	"	"	1,290

Net present value = 19

Capital cost = 106,000

DCFRR = 17.01%

Note: All values are in \$K.

FLWSHEET FOR DISCOUNTED
CASH FLOW RATE OF RETURN
CALCULATIONS

001	*LBLA	21 11
002	DSP0	-53 00
003	RCL0	36 00
004	CHS	-22
005	PRTX	-14
006	Z+	56
007	DSP0	-63 00
008	RCL1	36 01
009	PRTX	-14
010	RCL0	36 15
011	PRTX	-14
012	RCL0	36 12
013	DSF3	-63 00
014	PRTX	-14
015	RCL0	36 14
016	PRTX	-14
017	RCLA	36 11
018	DSF4	-63 04
019	PRTX	-14
020	DSF0	-63 00
021	RCL0	36 00
022	RCL0	36 14
023	X	-35
024	ST05	35 05
025	*LBLB	21 12
026	RCL0	36 15
027	ST02	35 02
028	1	01
029	ST+4	35-55 04
030	RCL4	36 04
031	1	01
032	X*Y?	16-32
033	GT00	22 13
034	RCL2	36 02
035	1	01
036	5	03
037	.	-62
038	5	05
039	X	-35
040	1	01
041	2	02
042	.	-24
043	ST02	35 02
044	*LBLC	21 13
045	1	01
046	0	00
047	RCL4	36 04
048	X*Y?	16-34
049	GT00	22 14
050	6	06
051	RCL4	36 04
052	X*Y?	16-34
053	GT00	22 16 15
054	.	-62
055	0	00
056	RCL4	36 04
057	1	01
058	.	-45
059	Y*	31
060	.	-62

061	0	00
062	RCL4	36 04
063	Y*	31
064	.	-45
065	RCL0	36 00
066	.	-35
067	ST06	35 06
068	ST+3	35-55 03
069	GT0E	22 15
070	*LBLD	21 16 15
071	RCL0	36 00
072	RCL3	36 03
073	.	-45
074	4	04
075	.	-24
076	ST06	35 06
077	GT0E	22 15
078	*LBLD	21 14
079	0	00
080	ST06	35 06
081	*LBLD	21 15
082	RCL2	36 02
083	RCL6	36 06
084	.	-55
085	RCL0	36 00
086	1	01
087	5	05
088	.	-24
089	.	-45
090	ST07	35 07
091	RCL1	36 01
092	X*Y?	16-34
093	GT00	22 16 14
094	.	-45
095	.	-62
096	5	05
097	4	04
098	X	-35
099	ST00	35 13
100	GT00	22 16 13
101	*LBLD	21 16 14
102	X*Y?	-41
103	.	-45
104	RCL8	36 12
105	.	-35
106	ST08	35 08
107	0	00
108	ST00	35 13
109	1	01
110	RCL4	36 04
111	X*Y?	16-33
112	ST00	22 16 11
113	RCL8	36 08
114	ST09	35 09
115	GT00	22 16 13
116	*LBLD	21 16 11
117	0	00
118	ST09	35 09
119	RCL5	36 05
120	RCL8	36 08

HP-97 Program for Discounted Cash Flow Rate of Return Calculations

121	.	-45
122	ST05	35 05
123	*LBLD	21 16 13
124	RCL6	36 06
125	RCL1	36 01
126	.	-55
127	RCL7	36 07
128	.	-45
129	RCL9	36 09
130	.	-45
131	RCL0	36 13
132	.	-55
133	RCL5	35 05
134	.	-55
135	RCLA	36 11
136	1	01
137	.	-55
138	RCL4	36 04
139	Y*	31
140	1/X	52
141	X	-35
142	Z+	56
143	0	00
144	ST05	35 05
145	RCL4	36 04
146	1	01
147	5	05
148	X*Y?	16-34
149	GT00	22 12
150	P23	16-51
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