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QUARTERLY REPORT

"Development of an Oxygen Scavenger Unit for
Food Preservation"

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(July 1990 to September 1990)

Contract No. N00014-90-C-0254

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SUMMARY

Aquanautics has received a contract from DARPA (Contract No. N00014-90-C-0254) to study application of its oxygen removal system to food container atmosphere control. This project is broken up into four main tasks: 1) Economic Analysis, 2) Electrochemical Cell Cost Reduction, 3) Process Verification, and 4) Demonstrator Design, Fabrication and Testing. Work on this program began on July 1, 1990 and progress to date on the various subtasks is summarized below.

Task 1.0 - Economic Analysis

- 1) For a scavenger with a 100 % duty cycle, it costs \$ 0.01 to extract 1 standard liter of oxygen using Aquanautics' system.
- 2) For a system with the capacity to remove 5 l/min (same size as that visualized for Natick R & D Center) operational costs total \$ 72 /day.
- 3) Flushing with nitrogen is cheaper when desired oxygen concentration is larger than 2 % and if nitrogen can be delivered on site at bulk prices of \$ 0.04 /lb. Cost for nitrogen flushing increases if desired carbon dioxide concentration is high, since CO₂ would have to be replaced as oxygen is blown out. Also, flushing with nitrogen would increase power load on the refrigeration system.

Task 2.0 - Electrochemical Cell Cost Reduction

- 1) A new electrochemical cell (designated ABC-2500 as each cell has an area of 2500 cm²) was designed and costed. Its fabrication cost for prototype quantities totalled \$ 2735 (target \$ 5000) and for mass production \$ 1286 (target \$ 1200).
- 2) Design concept for ABC-2500 was verified on a 1/10 scale using ABC-250 (250 cm²). Performance with two different carriers show no degradation when compared to older cell designs.
- 3) Prototype of ABC-2500 placed on order and is expected by 10/15/90.

Task 3.0 - Process Verification

- 1) Aquanautics carrier 23 Suzy P was tested with a 15 % CO₂, 5 % O₂ and 80 % N₂ mixture as feed gas to evaluate feasibility of using it in food preservation application.
- 2) Oxygen Production Rate measured in l/min/m² of cell area decreases 50 % when compared to air.
- 3) Electrochemical Power increases by 60 % when compared to loading from air.
- 4) New modified felt design currently being tested shows capability of doubling oxygen production rate thereby compensating for decline with CO₂ rich mixture. It is indicated that pH control could also improve performance.

INTRODUCTION

Aquanautics is under contract with DARPA (Contract No. N00014-90-C-0254) to investigate application of its oxygen removal technology in the area of atmosphere control for food containers. Most foods remain fresher when stored under low oxygen concentrations. When carbon dioxide is added to the atmosphere of a food container, especially in the case of meats, spoilage is further reduced and freshness of appearance maintained. Produce respire consuming oxygen and producing carbon dioxide. Such respiration leads to ripening and finally food loss. Low levels of oxygen retard such respiration and help maintain freshness longer. In the case of meats, preservation requires both freezing and low oxygen content. If storage is effected under carbon dioxide, it is possible to transport and store meat without freezing, maintaining thereby its freshness.

Controlling oxygen content in a food container requires dealing with oxygen ingress into the container. Oxygen enters the container due to two primary reasons:

- 1) Leaks around gaskets in doors and other openings, and
- 2) Periodic opening of doors for access to food.

TransFresh Corporation, which designs and manufactures atmosphere control systems for food containers, estimates that oxygen leakage through gaskets in a typical food container (8' X 8' X 40') totals approximately 3 standard liters per minute when the internal atmosphere contains 5 % oxygen. Oxygen increase due to access door opening could range from 2 % to complete aeration of the container's atmosphere, i.e. 21 %. Based on conversations with Dr. Irwin Taub at the Natick (MA) R D & E Center, it was decided that a typical system for use in a container of standard size (8' X 8' X 8' or 8' X 8' X 16') would have to remove 5 l/min of oxygen. Other important specifications pertinent to design of a demonstrator for the US Army are as follows:

Temperature	=	42 °F,
Oxygen Concentration	=	5 %,
Carbon dioxide Concentration	=	1 to 15 %, and
Balance Gas	=	Nitrogen

This project aims to address both economics and feasibility using Aquanautics' technology for food preservation. Economic analysis was proposed as the first task, and when results of preliminary cost estimates revealed that electrochemical cell costs overwhelmed system cost, that became the priority in another task. In addition process verification and demonstration of the system on a full scale were the last two components of the project.

Progress this quarter (July to September 1990) concentrated on the first three tasks. Economic analysis was completed showing that the Aquanautics system was more economical when compared to the alternative, namely gas purging, when desired oxygen concentration was low. Electrochemical cell design was modified to effect reduction in fabrication costs and a ten-fold reduction from \$ 13,000 /m² to \$ 1285 /m² realized. Initial process verification experiments were also conducted with a view towards identifying performance of Aquanautics' primary carrier candidates in environments containing high CO₂ concentrations. Results of this experiment indicate areas of further improvement that are necessary before a full-scale demonstrator can be built and tested.

This report is structured by task, and activities carried out under the various tasks are reported on in three following sections.

TASK 1.0 ECONOMIC ANALYSIS

1.0 SUMMARY

This section deals primarily with the economics of oxygen removal from a refrigerated food container using the Aquanautics system and compares it with flushing by nitrogen and/or carbon dioxide. The cost of oxygen removal by the Aquanautics system is approximately \$3,000 per shipment of fresh meat for 15 days at a removal rate of 3 l/min of oxygen with a system duty cycle of 17%. For 100% duty cycle the cost of removal of 1 standard liter of oxygen from a food container is about one cent. For food preservation applications identified by the US Army, this translates to a cost of \$ 72 /day for a 5 l/min O₂ removal system. Flushing with nitrogen could be cheaper, if delivery cost of N₂ is of the same order as that of bulk commercial quantities, and desired oxygen content is above 2%. Flushing with N₂ will have a significant penalty if high CO₂ concentrations are desired in the food container atmosphere. Refrigeration costs will also be adversely affected by flushing.

2.0 INTRODUCTION AND BACKGROUND

Oxygen is removed from process industry fluid streams using various means:

- (i) use of chemicals - e.g., for deoxygenation of cooling water and make-up water for boilers,
- (ii) N₂ purging - e.g., in food, beverage and electronic industries, and
- (iii) vacuum - in food and beverage industry.

Aquanautics' oxygen removal technology is appropriate in most deoxygenation applications, but more so in food and beverage industries where flavor loss, non-toxicity, and high CO₂ concentrations are primary requisites.

Chemicals such as sodium sulfite and hydrazine are used for industrial process water but not for edible substances. These chemicals are inexpensive and as 14 ppm sodium sulfite, for example, has to be added.¹ This amounts to 0.014 ¢/gallon of water processed or 0.6 ¢/l of oxygen removed. Additives such as these are plainly unacceptable for food process streams due to potential toxicity.

Deoxygenation of fruit juices, wines and other beverages by vacuum is capital intensive and equipment for this process costs between \$ 100,000 and \$ 150,000 for a typical orange juice plant (1.5 l/min O₂ removal).²

¹T. Chakraborty, Exxon, Private Communication, 1990.

²D. McMurchy, Myers and Co., Private Communication, 1990.

For food processing and preservation, the only viable competitor to Aquanautics' oxygen scavenging system is purging with N₂ either generated and compressed on-site or delivered in its cryogenic form. The inherent disadvantage of both N₂ purging and vacuum deoxygenation is that they also remove valuable gases like CO₂ from a shipping or storage container or volatile flavor components present in all beverages and fruit juices.

CO₂ is a desirable component in food container atmospheres, especially as a means of keeping meat fresh. For the DARPA project, the desirable CO₂ concentration is assumed to be 15% based on a recommendation from Dr. Irwin Taub of the US Army Food Laboratories in Natick MA. Mr. Larry Bell of TransFresh (a manufacturer of refrigerated and modified atmosphere containers for food transportation) has suggested that a shipping container with fresh meat might be flushed with CO₂ at the port of exit and would have to be maintained at between 20% and 40% to compensate for CO₂ leakage during transit.

For shipment of fresh meat, N₂ purging to maintain low O₂ concentration is not a viable option because N₂ purging would actively vent CO₂ and increase refrigeration costs. For wine or fruit juice deoxygenation, N₂ purging will strip volatile flavor components that are desirable in a final product. Notwithstanding the above limitations of N₂ purging, this analysis provides a comparison of operating costs between it and Aquanautics' system.

3.0 COST ESTIMATION PROCEDURE

Two manifestations of Aquanautics' Oxygen removal system were considered for this analysis. These technologies are briefly described below.

- i) The conventional cobalt-based carrier removes oxygen from a gaseous feed stock by formation of a stable oxygenated complex. Oxygen is vented by oxidizing this carrier in the anode of an electrochemical cell and effecting phase separation in an unloader. The carrier is regenerated by reduction in the cell cathode. This system is inherently efficient requiring less than 1 V of cell potential and a theoretical minimum of 2 electrons for each oxygen molecule removed.
- ii) A newly discovered family of iron-based compounds removes oxygen from a gaseous feed stock by oxidation of the metal ion. This carrier is regenerated by subsequent reduction of the metal ion at the cathode of an electrochemical cell and returned to the loader for further oxygen removal. Oxygen is generated at the electrochemical cell anode by electrolysis of water. This system uses compounds that the FDA recognizes as GRAS (Generally Regarded as Safe) for food applications. These compounds are more power-hungry than cobalt-based carriers requiring more than 2 V and a theoretical minimum of 4 electrons for every oxygen molecule removed.

Table 3.1 summarizes calculation of the cost of removing one standard liter of oxygen from a food container using a cobalt-based carrier. Table 3.2 summarizes economics for a similar system, this time using the new iron compounds as oxygen scavengers. The final cost estimates do not include a profit margin.

Table 3.1. Cost Details for Oxygen Removal using Cobalt-based Carriers.

	UNITS	CAPACITY			REMARKS
		(std lpm)			
		1	3	10	
INPUT ASSUMPTIONS					
OXYGEN CONCENTRATION	%	5	5	5	
DUTY CYCLE	%	100	100	100	
OPERATING COSTS					
CARRIER					
COST	(\$/MOLE)	\$15	\$15	\$15	
LIFE	(MIN)	60000	60000	60000	
VOLUME	(L/LPM)	40	40	40	
CONCENTRATION	(MOLAR)	0.4	0.4	0.4	
SEPARATOR					
COST	(\$/M ²)	\$20	\$20	\$20	
LIFE	(MIN)	480000	480000	480000	
POWER CONSUMPTION					
CELL	(W/LPM)	200	200	200	
PUMP	(W/LPM)	23	23	23	
BLOWER	(W/LPM)	2.5	2.5	2.5	
COST	(\$/W-MIN)	1.67E-06	1.67E-06	1.67E-06	
LABOR/MAINTENANCE					
LEVEL OF EFFORT	MH/CY/LPM	8	4	1.6	MH/CY/ LPM =
COST	\$/MH	25	25	25	Manhour /cycle/ lpm
CAPITAL COST					
ELECTROCHEMICAL CELL					
O ₂ PRODUC. DENSITY	(LPM/M ²)	0.5	0.5	0.5	
COST	(\$/M ²)	\$1600	\$1600	\$1600	
RECTIFIER					
VOLTAGE		12	24	48	
CURRENT		17	25	42	
COST	(\$/KVA)	\$1000	\$450	\$260	
OTHER EQUIPMENT					
BLOWER	(\$/LPM)	\$27	\$9	\$3	
LOADER	(\$/LPM)	\$4,000	\$4,000	\$4,000	Hoechst- Celanese
UNLOADER	(\$/LPM)	\$130	\$130	\$130	
PLUMBING	(\$/LPM)	\$75	\$75	\$75	
INSTRUMENTS	(\$/LPM)	\$500	\$167	\$50	
PACKAGING	(\$/LPM)	\$300	\$167	\$100	
CAPITAL AMORTIZATION					
PLANT LIFE	(YEARS)	5	5	5	
COST OF CAPITAL	(% P.A.)	15%	15%	15%	
OUTPUT					
OPERATING COSTS					
CARRIER	(\$/L)	\$0.00400	\$0.00400	\$0.00400	
SEPARATOR	(\$/L)	\$0.00008	\$0.00008	\$0.00008	
POWER	(\$/L)	\$0.00038	\$0.00038	\$0.00038	
LABOR	(\$/L)	\$0.00333	\$0.00167	\$0.00067	
TOTAL	(\$/L)	\$0.00779	\$0.00613	\$0.00513	
SPECIFIC CAPITAL COST					
ELECTROCHEMICAL CELL	(\$/MIN/L)	\$3,200	\$3,200	\$3,200	
RECTIFIER	(\$/MIN/L)	\$200	\$90	\$52	
OTHER EQUIP.	(\$/MIN/L)	\$5,032	\$4,548	\$4,358	
TOTAL	(\$/MIN/L)	\$8,432	\$7,838	\$7,610	
TOTAL CAPITAL COST		\$8,432	\$23,514	\$76,103	
AMORTIZED CAPITAL COST	(\$/L)	\$0.005	\$0.004	\$0.004	
TOTAL PRODUCT COST	(\$/L)	\$0.012	\$0.010	\$0.009	

Table 3.2. Cost Details for Oxygen Removal using New Iron-based Carriers.

	UNITS	CAPACITY			REMARKS
		(std lpm)			
		0.5	1.5	5	
INPUT ASSUMPTIONS					
OXYGEN CONCENTRATION	%	5	5	5	
DUTY CYCLE	%	100	100	100	
OPERATING COSTS					
CARRIER					
COST	(\$/MOLE)	\$0.22	\$0.22	\$0.22	
LIFE	(MIN)	17280	17280	17280	
VOLUME	(L/LPM)	20	20	20	
CONCENTRATION	(MOLAR)	0.20	0.20	0.20	
SEPARATOR					
COST	(\$/M^2)	\$600	\$600	\$600	
LIFE	(MIN)	1576800	1576800	1576800	
POWER CONSUMPTION					
CELL	(W/LPM)	850	850	850	
PUMP	(W/LPM)	0	0	0	
BLOWER	(W/LPM)	150	150	150	
COST	(\$/W-MIN)	1.67E-06	1.67E-06	1.67E-06	
LABOR/MAINTENANCE					
LEVEL OF EFFORT	MH/CY/LPM	8	4	1.6	MH/CY/ LPM =
COST	\$/MH	25	25	25	Manhour /cycle/ lpm
CAPITAL COST					
ELECTROCHEMICAL CELL					
O2 PRODUC. DENSITY	(LPM/M**2)	1.74	1.74	1.74	
COST	(\$/M^2)	\$2200	\$2200	\$2200	
RECTIFIER					
VOLTAGE		24	48	48	
CURRENT		18	27	89	
COST	(\$/KVA)	\$360	\$260	\$260	
OTHER EQUIPMENT					
BLOWER	(\$/LPM)	\$300	\$130	\$55	
LOADER	(\$/LPM)	\$4,000	\$4,000	\$4,000	Hoechst-
UNLOADER	(\$/LPM)	\$0	\$0	\$0	Celanese
PLUMBING	(\$/LPM)	\$0	\$0	\$0	with gas
INSTRUMENTS	(\$/LPM)	\$500	\$167	\$50	evolving
PACKAGING	(\$/LPM)	\$300	\$167	\$100	anode
CAPITAL AMORTIZATION					
PLANT LIFE	(YEARS)	5	5	5	
COST OF CAPITAL	(% P.A.)	15%	15%	15%	
OUTPUT					
OPERATING COSTS					
CARRIER	(\$/L)	\$0.00005	\$0.00005	\$0.00005	
SEPARATOR	(\$/L)	\$0.00022	\$0.00022	\$0.00022	
POWER	(\$/L)	\$0.00167	\$0.00167	\$0.00167	
LABOR	(\$/L)	\$0.01157	\$0.00579	\$0.00231	
TOTAL	(\$/L)	\$0.01351	\$0.00772	\$0.00425	
SPECIFIC CAPITAL COST					
ELECTROCHEMICAL CELL	(\$MIN/L)	\$1,264	\$1,264	\$1,264	
RECTIFIER	(\$MIN/L)	\$306	\$221	\$221	
OTHER EQUIP.	(\$MIN/L)	\$5,100	\$4,464	\$4,205	
TOTAL	(\$MIN/L)	\$6,670	\$5,949	\$5,690	
TOTAL CAPITAL COST		\$3,335	\$8,924	\$28,452	
AMORTIZED CAPITAL COST	(\$/L)	\$0.00361	\$0.00322	\$0.00308	
TOTAL PRODUCT COST	(\$/L)	\$0.0171	\$0.0109	\$0.0073	

The assumptions underlying input parameters identified in Tables 3.1 and 3.2 are described below.

- (1) Oxygen Concentration: This refers to the desired oxygen concentration in the food container.
- (2) Duty Cycle: This refers to the portion of time that the Aquanautics system will be in use.
- (3) Carrier Cost: This is based on projected production cost of carrier in tonnage quantities as obtained from Synthetech for cobalt-based carrier. Since the new iron-based compounds are commercially available, market costs in large quantities were employed for this purpose.
- (4) Carrier Life: This refers to the period of time that the carrier can remove oxygen in an energy-efficient and effective manner. The carrier would have to be replaced at the end of its lifetime.
- (5) Carrier Volume: This is the volume of carrier required by a system of unit capacity (units of standard liter per minute oxygen removed are commonly used here). Since Aquanautics' system is modular and scales up linearly, it is assumed that this parameter will remain constant as long as cell loader volume remain the same for unit capacity. This is a close approximation only, since as plant capacity gets larger, volume of carrier engaged in plumbing will not increase proportionately. However, holding volume of plumbing is small when compared to that of other components. Volume of carrier is calculated using Equation 3.1.

$$V = 5 + \frac{20}{x} + \frac{15}{y} \quad (3.1)$$

where, x is desired oxygen concentration in fractions of an atmosphere,

y is oxygen production density in the cell (l/min/m²), and
the constants are empirically determined factors used to calculate holding volumes in various components.

- (6) Concentration of Carrier: Carriers are aqueous solutions where the concentration of compounds is dictated by performance and solubility. This parameter affects carrier cost since every unit volume of carrier will have to contain an amount of carrier compound specified by its desired concentration.
- (7) Separator: This refers to separator membranes used in the electrochemical cell. This cost has been separated from that of the cell because it is process-specific. All other components of the electrochemical cell can be used for both processes described earlier. For traditional cobalt-based carriers, microporous polypropylene sheet (Celgard™ from Hoechst-Celanese) is used. This is a cheap material and is expected to last about one year. For iron-based carriers a cation-exchange membrane (Nafion™ from DuPont) is used. These are more expensive than microporous membranes, but last longer.
- (8) Power Consumption: This relates to the power required for various components of the system. Power consumption for the electrochemical cell is 200 W/lpm with cobalt

carriers and about 850 W/lpm for iron compounds. Carrier pump power consumption is calculated on the basis of carrier flow of 10 l/min/m² of electrode area and 2 psi total pressure drop. Power Cost: is assumed to be 10 ¢/kW-hr. This is not strictly applicable to storage during shipment of fresh meat. Shipboard systems would restrict overall system power consumption and economic assumptions would have to be modified to account for the cost of delivering power from the ship's power plant. In the case of iron-based compounds, carrier pump power is neglected because, it is assumed that a commercial system would exploit a tank cell design. This design calls for integration of loading functions into the cell cathode whereby, gaseous feed stock is sparged through carrier resident in the cathode while it simultaneously undergoes electrochemical reduction.

- (9) Labor/Maintenance: This refers to man-hours spent to maintain a system over one life cycle of the carrier. These numbers are assumed and reflect the fact that labor cost does not increase proportionally with system size.
- (10) Cost of Labor: Mr. Larry Bell of TransFresh reports a labor rate of \$ 25 /man-hour for port labor in maintaining systems on board shipping containers.
- (11) Cell Oxygen Production Density: This is the electrochemical performance of carrier and is taken as 0.5 lpm/m² of cell area for cobalt carriers and 1.74 l/min/m² for iron carriers.
- (12) Cell Cost: Cost of procuring electrochemical cells was projected on production basis.
- (13) Rectifier: Battery chargers are assumed to suffice, and their prices are taken from the catalogue of McMaster-Carr Supply Co., pp. 1520.
- (14) Blower: The cost of blowers is obtained from McMaster-Carr Supply Co., pp. 105 of the catalogue.
- (15) Loader: Loader cost is the most critical component of the system capital cost. Loader cost was estimated using empirical observations in the laboratory.

It has been observed that two Hoechst-Celanese cartridges of 1.5 m² surface area each can absorb up to 250 ml/min of oxygen from air. Permeability of such a cartridge can therefore be calculated as per Equation 3.2.

$$k = \frac{0.25 \text{ l/min}}{3 \text{ m}^2 \times 0.2 \text{ atm}} = 0.4 \text{ l/min/m}^2/\text{atm.} \quad (3.2)$$

For feed stock containing 2 % oxygen, the absorption rate will be 0.008 lpm/m². Since the cost of membrane cartridges is around \$ 80 /m², a loader for the system will cost \$ 10,000 /l/min at 2% oxygen concentration.

- (16) Unloader: Unloader cost is estimated to be \$130 /l/min of oxygen. This cost is estimated based on an empirically determined unloader volume of 6 l/l/min.
- (17) Instruments: The cost of instrumentation and control system is estimated to be \$ 500. Instrumentation associated with such a system is likely to consist primarily of an oxygen sensor which will be used to control or activate a system depending on

oxygen level in the container. Control of cell potential and current will also be undertaken by the control system in conjunction with the power supply.

- (18) **Packaging:** This item reflects cost to package all components on a skid-mount that can then be assembled on the food container.
- (19) **Capital Amortization:** Plant life is assumed to be 5 years and the cost to borrow money is assumed to be 15% per annum.

Table 3.3 and Figure 3.1 summarize cost contributions of various components of the system (normalized to cents/standard liter of oxygen removed).

Table 3.3. Cost contributions of various system components.

Component	Cobalt-based Carrier	Iron-based Carrier
Loader	0.20 ¢	0.20 ¢
Cell	0.17 ¢	0.07 ¢
Carrier	0.40 ¢	0.01 ¢
Power	0.04 ¢	0.17 ¢
Labor	0.07 ¢	0.23 ¢
Others	0.02 ¢	0.05 ¢
Total	0.90 ¢	0.73 ¢

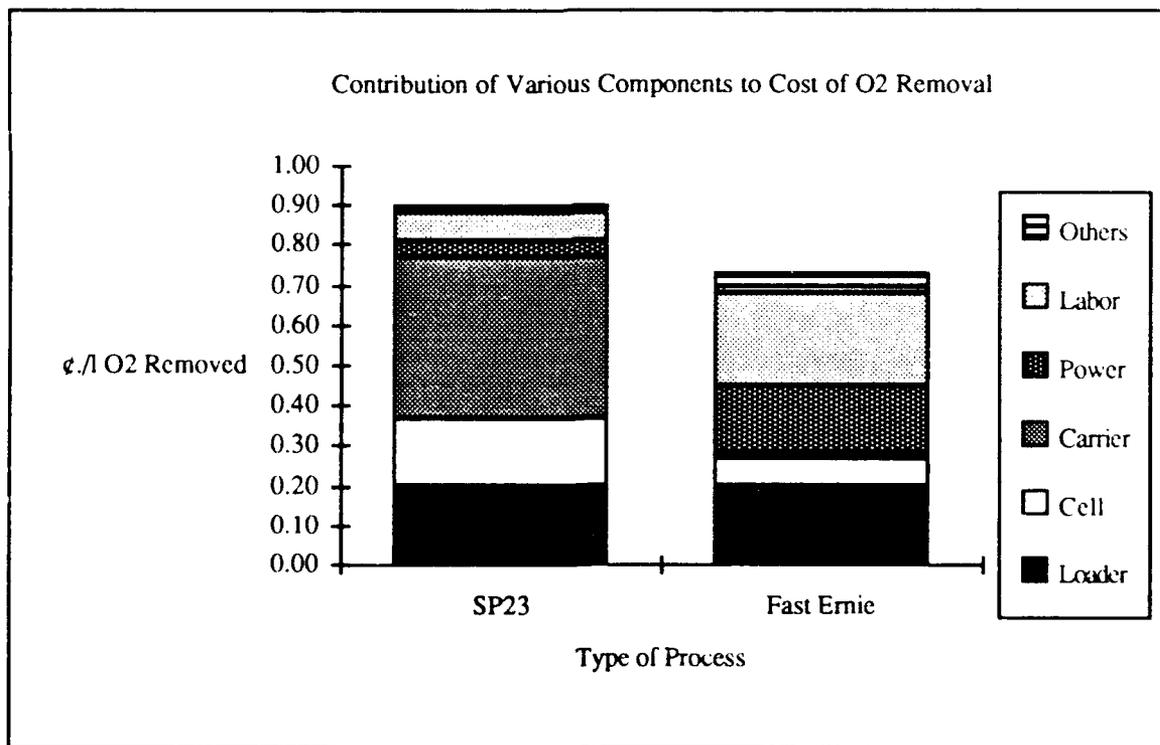


Figure 3.1. Graphical depiction of cost breakdown by component for candidate systems.

This data is depicted graphically in the bar chart in Figure 3.1. Costs of carrier, loader and cell are predominant for the cobalt-based carrier system whereas labor, power and loader costs are major factors for iron compounds. Future gains in economics are to be obtained by addressing these components. Overall, systems based on iron compounds are likely to

be less costly to operate than system based on cobalt. However, in situations where power is not readily available, like on ships or in remote locations, the higher power consumption implicit in iron-based carriers make them less desirable.

4.0 COMPARATIVE COST: FLUSHING WITH GASES

Low oxygen concentration can be maintained in a container by flushing with desirable gases such as nitrogen, carbon dioxide or a mixture of the two. The rate at which such gases need to be used in flushing depends on the following parameters.

- i) Rate of oxygen ingress into containers due to leaks,
- ii) Purity of the nitrogen or carbon dioxide used for flushing, and
- iii) Desired composition of atmosphere inside container.

If the concentration of oxygen impurity in the flushing gas is negligible, rate at which flushing would have to be carried out will be directly proportional to oxygen ingress rate and inversely proportional to the desired oxygen concentration. If 'p' is desired partial pressure of oxygen in the container it will take $1/p$ liters of the flushing gas to remove one liter of oxygen and maintain the desired oxygen concentration. For example, if there is one liter of oxygen ingress into a container which is maintained at 5% ($p=0.05$) oxygen, quantity of N_2 or CO_2 required to dilute this atmosphere will be $1/0.05$ or 20 liters. It is also to be noted that either pure N_2 or CO_2 or a mixture thereof could be used as the flushing gas, depending on the desired N_2/CO_2 ratio. Since CO_2 is approximately 5 times more expensive than N_2 , CO_2 should be chosen only when it is necessary for food preservation. As mentioned earlier, high concentrations of CO_2 (up to 40 %) are desired for preservation of meat freshness. Figure 4.1 compares cost of gas flushing to that of a system incorporating Aquanautics' technology.

For transportation of meat or use of a container for storage at remote places carrying excess gas on-board will lead to extra transportation cost. In this competitive analysis, cost to carry extra nitrogen and carbon dioxide were not considered, and hence the advantage shown accruing to Aquanautics' system is conservative. In reality it is likely that storage of nitrogen for flushing and extra carbon dioxide for meat preservation would make flushing a more costly proposition. As far as the Aquanautics system is concerned, profit was not taken into consideration.

In Figure 4.1, the curve labeled SP23 refers to the most commonly used cobalt-based carrier, while Fast Ernie is a code name assigned to the most commonly used iron-based compound. CO_2 was assumed to cost 20 ¢/lb and N_2 cost was taken as 30 ¢/100 ft³ or 3.8 ¢/lb. These figures were obtained from telephone quotes of bulk price from gas suppliers. When only N_2 need be used, the break-even point for an Aquanautics system falls at a point where desired oxygen concentration in the container is 2 %. The break-even concentration is higher when carbon dioxide is necessary. For pure CO_2 flushing this break-even occurs at 10 % while for a 84-16 mixture of N_2 and CO_2 break-even is at 4 %. Cost to remove one liter of oxygen using Aquanautics system reaches an asymptote above oxygen concentrations of 1 %. This asymptotic cost is less than 1 ¢/l of oxygen removed.

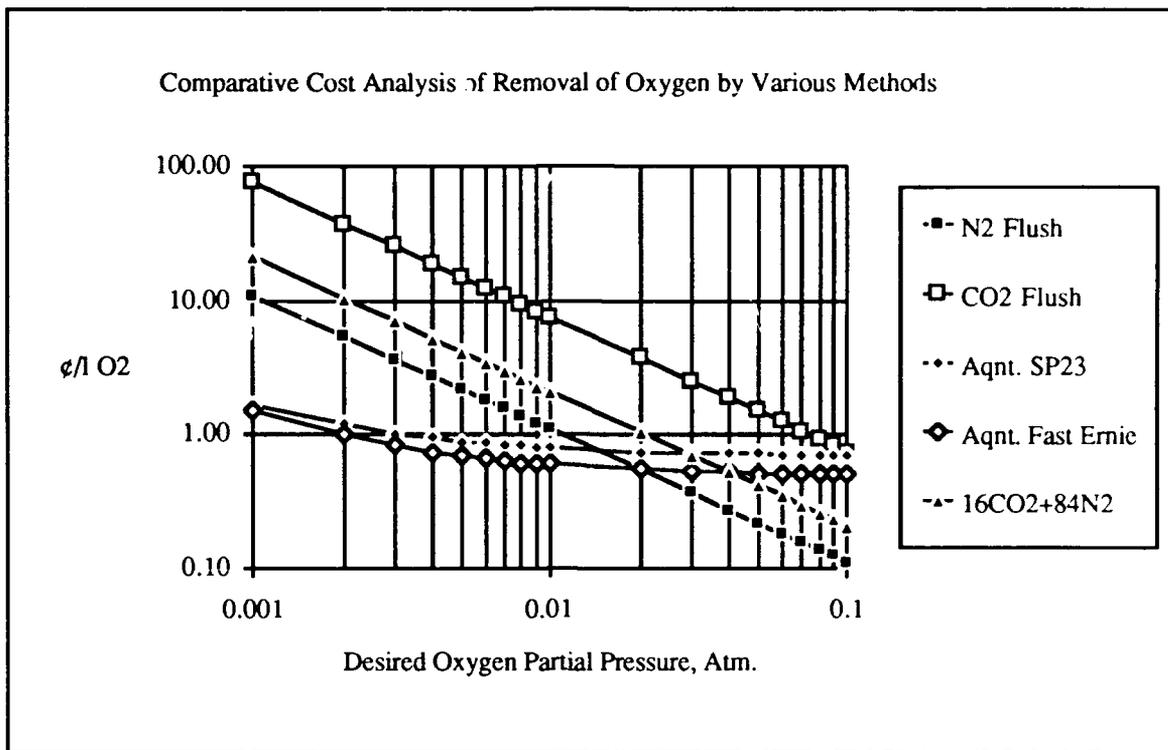


Figure 4.1. Comparison of Aquanautics cost to remove oxygen with gas flushing.

TASK 2.0 ELECTROCHEMICAL CELL COST REDUCTION

1.0 INTRODUCTION

In estimating cost of various components for an Aquanautics system to remove oxygen from a controlled atmosphere food container, it was determined that cell cost formed an inordinately high portion of the overall system cost. Establishing economic viability of an oxygen scavenging system based on Aquanautics' technology, therefore, required development of a low-cost electrochemical cell. Task 2.0 of the DARPA Phase VI program was therefore dedicated to modifying the design of Aquanautics' proprietary ABC (Aquanautics Bipolar Cell) to make it easier to assemble and cheaper to fabricate.

2.0 BACKGROUND

The ABC-250³ cell was developed for use in undersea applications like the Autonomous Underwater Vehicle (AUV) and Underwater Power Source (UPS). Its design therefore reflected constraints peculiar to undersea applications. The major concern in such devices is compactness, and hence the ABC-250 was designed with package size as the primary consideration. In spite of this, cost of acquiring one square meter of cell was reduced from \$ 90,000 for an off-the-shelf commercial design to \$ 13,000. This seven-fold reduction was, however, not sufficient to justify economics of on-land applications of Aquanautics' CCOS technology.

A few additional considerations that enter the design process for an electrochemical cell are as follows:

- 1) Ability to incorporate High Surface Area (HSA) electrodes like graphite felts,
- 2) Ability to operate in a bipolar mode without loss in efficiency due to shunting,
- 3) Ease of stacking,
- 4) Ease of assembly,
- 4) Ability to withstand corrosive environments, and
- 5) High reliability and leakproof operation.

The concerns enumerated above were addressed and successfully resolved in the ABC-250 design, and subsequent tests proved that a five cell stack of ABC-250 operated in both monopolar and bipolar modes without experimentally distinguishable difference in performance.⁴ Improvements in volume utilization enabled greater than two-fold increase in packaging efficiency (measured as cell separator area packaged in a unit volume of cell). Table 2.1 summarizes improvements achieved with the ABC-250 over commercially available cells.

³Final Report, October 1987 - September 1988, Artificial Gill Program, Contract No. N00014-87-C-0335, submitted to DARPA, pp. 15-17.

⁴Quarterly Report, October 1988 - December 1988, Long Endurance Underwater Power System, Contract No. N00014-87-C-0335, submitted to DARPA, pp. 56-60.

Table 2.1. Comparison of Cell Characteristics.

Characteristic	ABC-250	Commercial
Compactness, m ² separator area/m ³ cell volume	25.0	9.0
Shunt Resistance X Electrode Area, Ω - m ² (3 M KCl)	7.5	0.3 - 0.8
Ratio of utilized electrode area to total area	0.47	0.16
Power loss due to pumping with graphite felt (normalized)	1.08	1.0

Figure 2.1 is a comparison of the electrode frame profiles for both the ABC-250 and commercial cells that depicts how the above improvements were obtained. Higher shunt resistance which is vital to improved bipolar-mode performance was obtained by careful design of electrolyte channels which conduct electrolyte flow from the manifolds to the electrode chamber. The design of these channels exacts a nominal penalty in terms of pumping power expended in circulating electrolyte, although pumping losses are more than compensated for by superior cell performance.

3.0 CELL COST PARAMETERS

Figure 3.1 depicts cross-section of an assembled ABC-250 stack containing one cell. The various components of such a cell are depicted in this drawing.

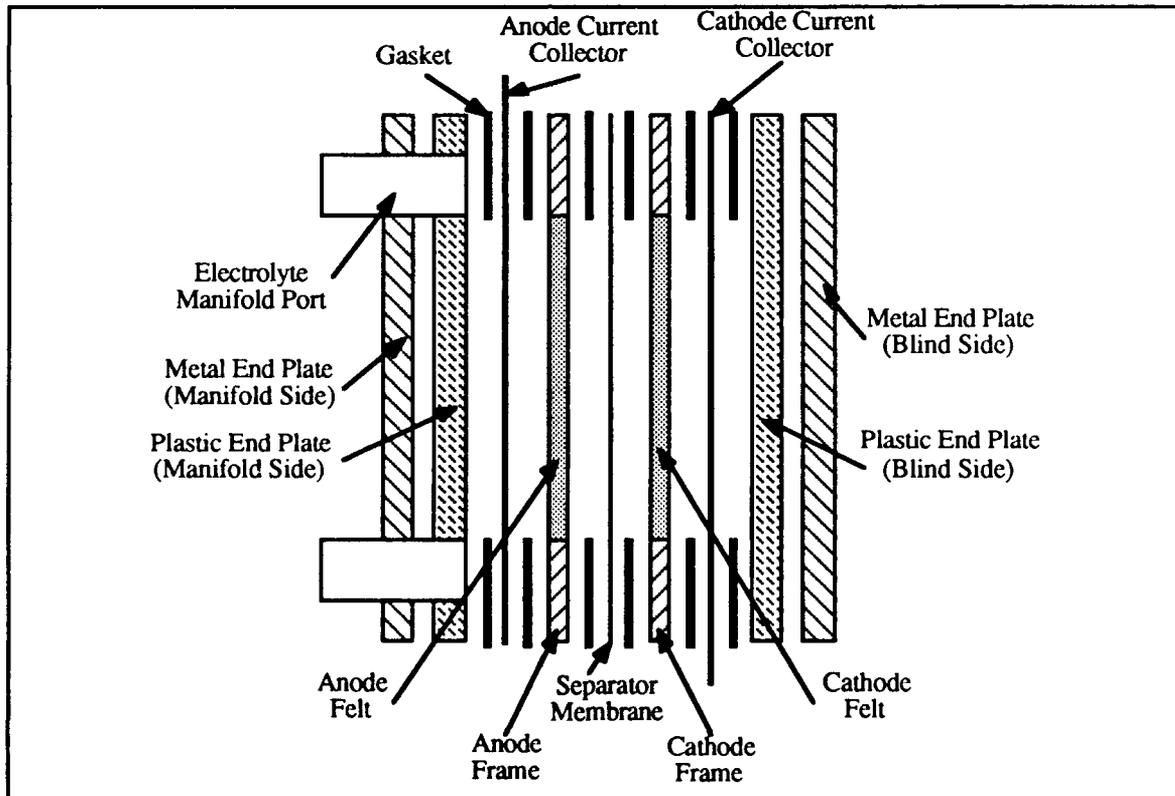


Figure 3.1. Cross-section of ABC-250 depicting its various components.

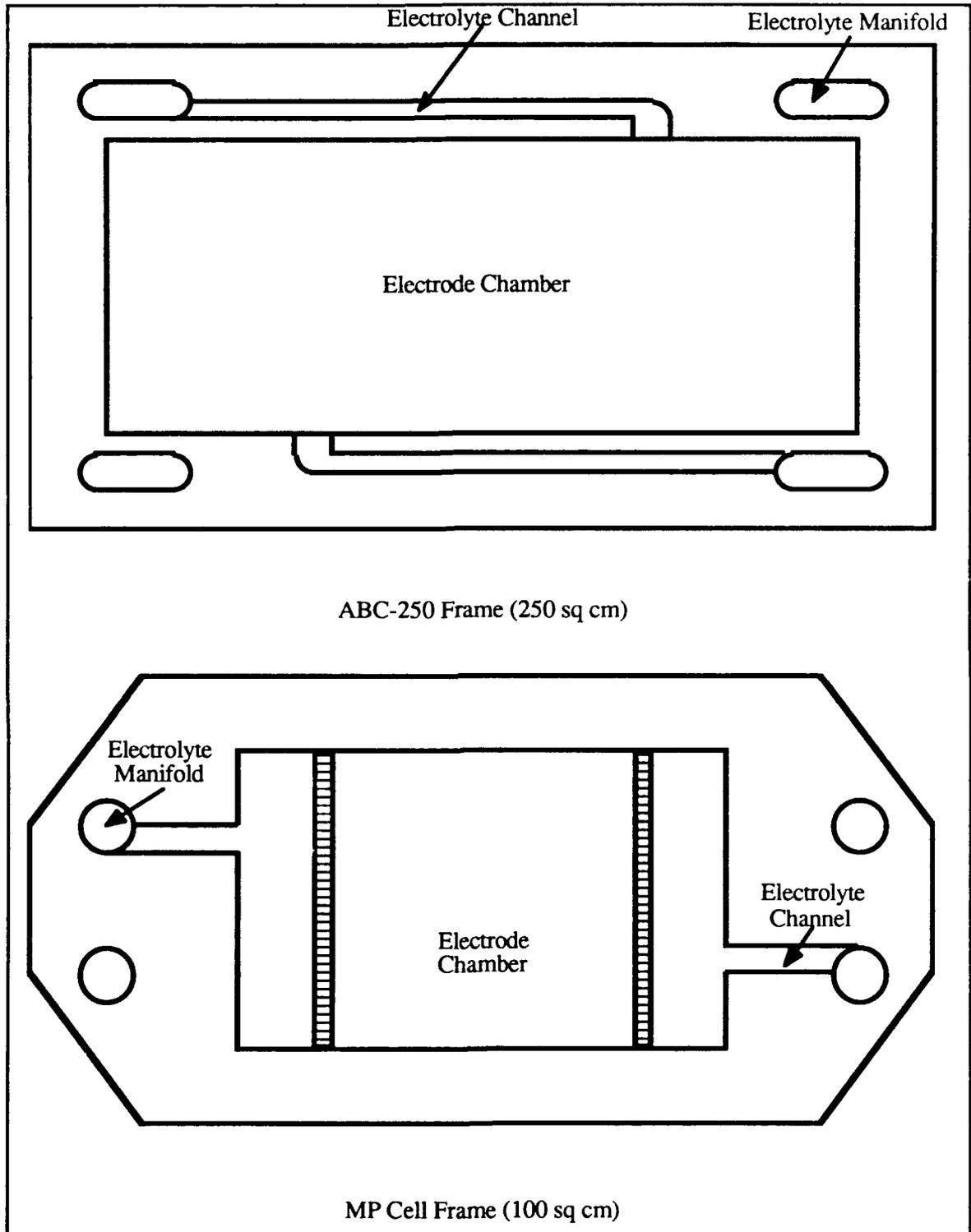


Figure 2.1. Comparison of ABC-250 cell frame with that of commercial Multi-Purpose (MP) cell.

Table 3.1 lists prices associated with manufacture of one m² of ABC-250 cells using the current design. In analyzing cost components of the current ABC-250 design on a unit separator area basis as shown in Table 3.1, it is obvious that the primary reason for its high cost is the large number of components that have to be manufactured. It is apparent that for every square meter of cell area, 40 anode and cathode frames have to be fabricated and assuming five stacks of eight cells each, a total of 45 current collectors have to be machined. The other major contributor to cell cost, namely felt and separator preparation is also a function of the number of felts and separators that have to be cut and prepared.

Table 3.1. Cost Components in Manufacture of ABC-250.

Parts Description	Cost/m ²
End Plates (Plastic and Stainless Steel including plumbing)	\$ 1,600
Electrode Frames (Anode and Cathode)	\$ 3,000
Current Collectors	\$ 2,800
Gaskets	\$ 400
Bolts, Nuts, Plumbing supplies and Miscellaneous	\$ 150
Felt and Separator Preparation	\$ 5,050
Total Cost	\$ 13,000

Moreover, frames designed for the ABC-250 have an enclosed electrolyte channel. To accomplish this, each frame is machined in two mirror image halves and channels milled on the surface of each half. The two halves are then glued together after matching the position of bolt holes, manifolds and channels. The cost of machining two halves, building a fixture to glue the two halves together and the actual process of gluing a frame contribute to its high cost. This design has also proven unreliable, because gluing techniques used currently do not adequately prevent leaks through the joint.

4.0 DESIGN MODIFICATIONS TO REDUCE COSTS

4.1 Frame Design

The major component of frame fabrication cost was deduced to be its two-part construction. To reduce its fabrication cost a simple open-channel design was considered, wherein the electrolyte channel would be machined on the surface of a one-piece frame. It was decided that a gasket surface could be used to form the fourth wall of the channel as shown by the cross-sectional view depicted in Figure 4.1. This design automatically reduced fabrication cost of the frame and also made it leak-proof because of the elimination of a glue joint. Cost of machining each frame was therefore cut by more than half. This also permitted use of opaque materials like PVC which is cheaper than the Lexan™ previously employed. Lexan's transparency permitted quality control on glue joints in the previous two-part frame.

4.2 Size of Individual Cell

The unit size of an ABC-250 cell (250 cm²) was chosen with undersea applications in mind. It was an optimal size for packaging in underwater vehicles being considered at the time of its design. Because of its size, a total of 40 individual cells have to be constructed

to make up one m² of total cell area. A second tool in cost reduction therefore involved building larger unit cells that would reduce the number of parts that would have to be fabricated to provide one m². The size chosen for on-land applications of CCOS technology was 2500 cm².

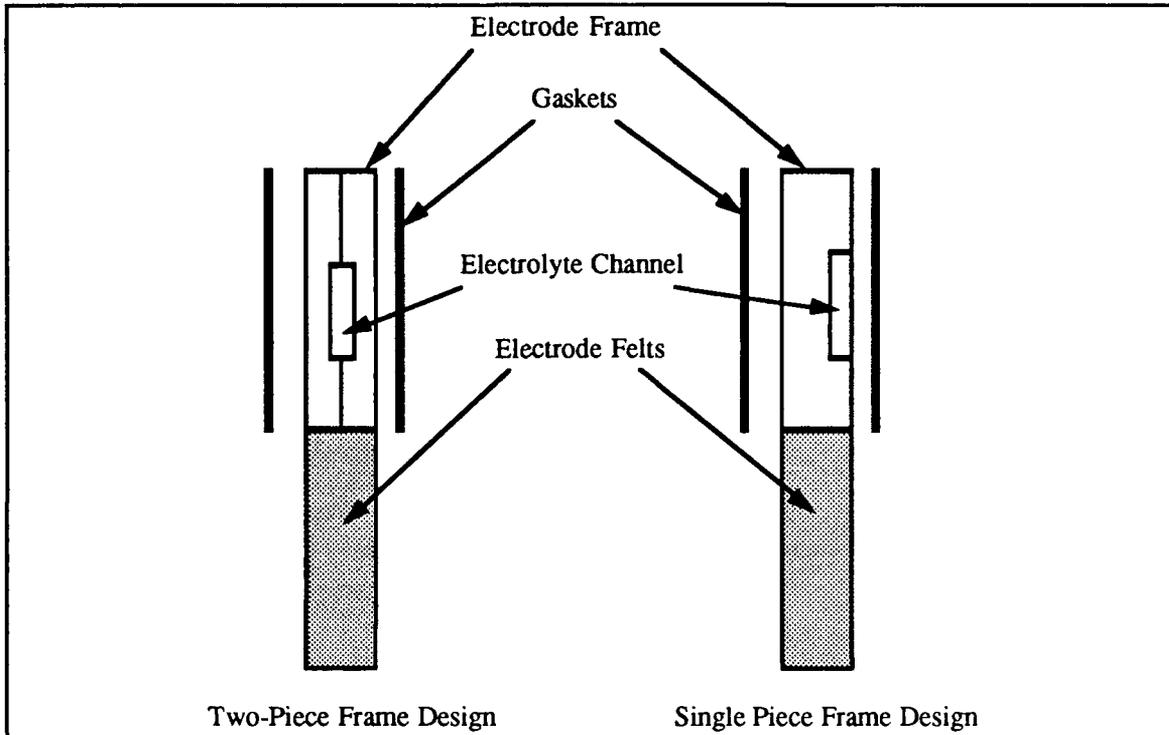


Figure 4.1. Difference between old and new frame designs.

Table 4.1 illustrates the reduction in number of parts that would have to be fabricated for every m² of cell area. It is pertinent to note here that since an optimal stack size for an ABC-250 cell is eight, one m² of cell area is obtained by assembling five stacks of eight cells each. For the 2500 cm² cell, referred to as ABC-2500, one stack of four cells should suffice.

Table 4.1. Reduction in Parts Count Obtained from Increasing Unit Cell Size.

Part Description	ABC-250	ABC-2500
Metal End Plates	10	2
Plastic End Plates	10	2
Electrode Frames (Anode and Cathode)	80	8
Current Collectors	45	5
Gaskets	170	18
Felts	80	8
Separator Membranes	40	4

Cost of materials for the various components is expected to increase in direct proportion to the increase in size and hence savings are not expected in materials cost. However, fabrication costs which form the largest component of ABC-250 cells do not increase in

proportion to component size. This is due to the fact that machining costs are predominantly attributable to setup of machine tool and mounting the component on machine. Fewer components involve fewer setups and hence lead to lower costs on a cell area basis. Therefore, cost of machining an ABC-2500 cell frame, which is roughly ten times the size of an ABC-250, frame will not increase ten-fold. It is this non-linearity that Aquanautics seeks to exploit in order to drive machining costs down.

4.3 Machining Operations

Compactness requirements during design of the ABC-250 dictated that bolts used to assemble a stack of cells be placed as close to the electrode compartment as possible. As a result bolt holes had to be drilled or punched in all components including frames, current collectors, gaskets and membranes. This multiplied machining operations that had to be performed on each component resulting in large fabrication costs. In the ABC-2500, since compactness is not as important, the bolts can be moved outside the cell components as shown in Figure 4.2. This means that bolt holes need not be drilled into frames, gaskets, current collectors and membranes simplifying their fabrication significantly.

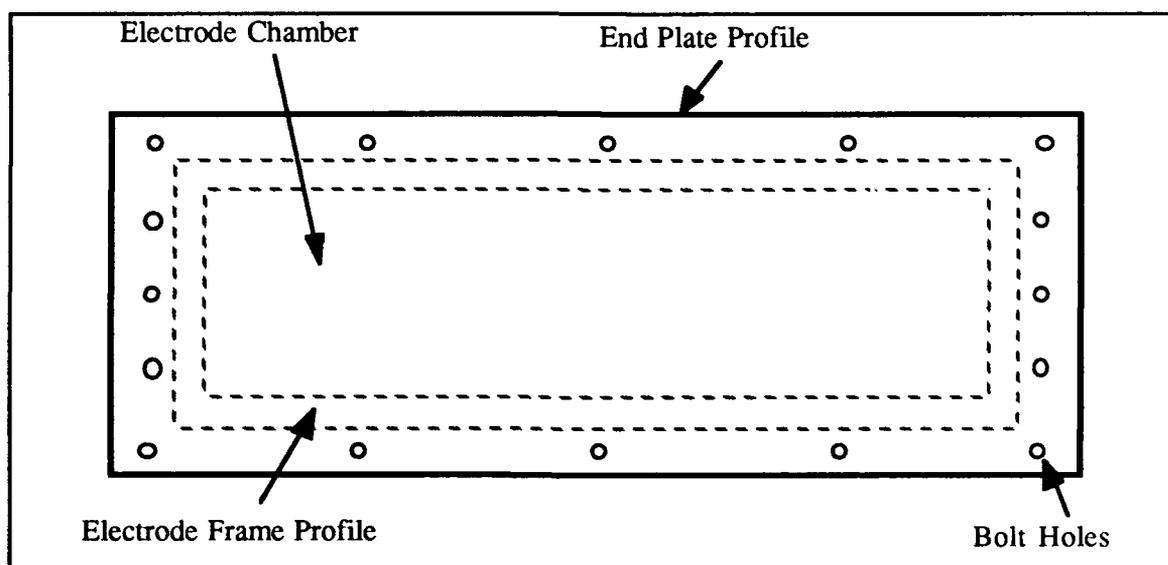


Figure 4.2. Depiction of new bolt hole emplacement.

4.4 One-Piece End Plates

This represents the first of two techniques to further reduce cell fabrication costs by reducing the number of components. Current ABC-250 cells employ two end plates at each end of a stack. This is illustrated in Figure 3.1. The metal end plate, made of either stainless steel or anodized aluminum, is used to provide stiffness while clamping the various cell components together. A plastic end plate assembled inside the metal plate provides electrical insulation for cell components from the conductive metal. The plastic end plates also serve as manifolds, where pipes and plumbing carrying electrolyte are attached to the cell.

Aquanautics' investigation was aimed at determining possible materials that would serve both purposes. The concept of ribbed plastic such as those used in walkways on construction manifolds proved promising. The ribs would provide stiffness required to

properly seal gaskets and the plastic/fiberglass backing plate would be used to press against internal cell components.

4.5 Molding Self-Gasketing Frames

Every ABC-250 cell uses four gaskets as shown in Figure 3.1. While the cost of fabricating gaskets is not as large as that of frames and current collectors, they contribute to increasing cell assembly costs. To reduce this cost component, Aquanautics investigated the use of softer materials for electrode frames. This innovation was intended to serve two purposes:

- 1) The frames could be molded and attached to current collectors by chemical bonding. Molding, especially for large production runs offers cost savings over machining. Attachment of frames to a current collector on either side could eliminate two gaskets and provide a better seal against leaks. Cell assembly becomes easier because the number of cell parts is reduced.
- 2) Use of a soft elastomer (shore A hardness of 80 to 90) to make the frames could eliminate the need for gaskets altogether. Whereas gaskets are currently used to effect a seal between frame and cell membrane, (see Figure 3.1) soft frame materials would be self-gasketing. Further reduction in the number of cell parts as well as assembly costs would result.

5.0 DESIGNING AND COSTING AN ABC-2500 CELL

Based on the design changes enumerated in the preceding section, drawings of 2500 cm² cell were made and fabrication shops selected for costing. Costing was done in two stages. The first stage design incorporated features described under subsections 4.1 through 4.3. This design, therefore, involved using two-piece end plates and machined frames with gaskets for sealing. To obtain a second stage cost estimate, concepts of one-piece ribbed plastic end plates and molded frames described in subsections 4.4 and 4.5 respectively were introduced.

5.1 Stage # 1

Stage # 1 of the cell cost estimation was started after the first three design modifications described in Section 4.0 had been implemented. Electrode frame design had been modified to implement a single-piece structure, individual cell size had been increased from 250 cm² to 2500 cm², and the number of machining operations had been reduced by moving bolts external to frame, gasket, membrane and current collector profiles.

Drawings of the ABC-2500 design were submitted to four potential subcontractors for fabrication cost estimates. Table 5.1 identifies names of these subcontractors and the parts for which quotes were required from each. Fabrication cost estimates were calculated on the basis of two ranges of quantities - a prototype run of 1.5 m² involving six cells and a production run of 125 m² involving 500 cells. Table 5.1 also indicates cost estimates for each component on a per m² basis.

Copies of price quotations from these subcontractors are included in Appendix A.

Table 5.1. Fabrication Costs for Various Components of ABC-2500 Cell (1 m² cell area).

Part Name	Potential Subcontractor	Prototype Cost	Production Cost
Metal End Plate - Blind	Diamond Tool and Die, Inc.	\$ 175.67	\$ 65.23
Plastic End Plate - Blind	Diamond Tool and Die, Inc.	\$ 112.69	\$ 28.29
Gasket	Gasket Specialties, Inc.	\$ 135.20	\$ 106.60
Current Collector	Graysix Company	\$ 140.00	\$ 17.50
Electrode Frame - An & Cat	Diamond Tool and Die, Inc.	\$ 871.44	\$ 205.04
Separator Membrane	Gasket Specialties, Inc.	\$ 10.00	\$ 1.80
Metal End Plate - Manifold	Diamond Tool and Die, Inc.	\$ 175.67	\$ 65.23
Plastic End Plate - Manifold	Diamond Tool and Die, Inc.	\$ 136.80	\$ 32.25
Anodizing End Plates	Francis Plating of Oakland	\$ 80.00	\$ 68.00
Electrode Felts - An & Cat	Gasket Specialties, Inc.	\$ 20.00	\$ 2.00

Materials cost for each of these components was estimated by requesting quotes from suppliers that had been used by Aquanautics during the ABC-250 design process. Table 5.2 summarizes materials costs by part and identifies suppliers from whom quotes were obtained. Once again, costs were worked out on the basis of both prototype quantities and production quantities as in Table 5.1. It may be noted here that cost estimates from both Gasket Specialties, Inc. and Diamond Tool and Die, Inc. included cost of materials. In other words, estimates for fabrication provided by them and listed in Table 5.1 represent cost of procuring the finished part including materials and fabrication labor. Therefore, materials costs for parts fabricated by those subcontractors are indicated as being \$ 0.00 in Table 5.2.

Table 5.2. Materials Costs for Various Components of ABC-2500 Cell (1 m² cell area).

Part Name	Material and Supplier	Prototype Cost	Production Cost
Metal End Plate - Blind	Aluminum - Jorgensen Steel	\$ 0.00	\$ 0.00
Plastic End Plate - Blind	PVC - McMaster-Carr	\$ 0.00	\$ 0.00
Gasket	EPDM - Gasket Specialties	\$ 0.00	\$ 0.00
Current Collector	Titanium - Titanium Sales	\$ 341.13	\$ 275.23
Electrode Frame - An & Cat	PVC - McMaster-Carr	\$ 0.00	\$ 0.00
Separator Membrane	3401 - Hoechst-Celanese	\$ 46.00	\$ 46.00
Metal End Plate - Manifold	Aluminum - Jorgensen Steel	\$ 0.00	\$ 0.00
Plastic End Plate - Manifold	PVC - McMaster-Carr	\$ 0.00	\$ 0.00
Electrode Felt - An & Cat	Graphite - Nat'l Elec Carbon	\$ 456.17	\$ 338.10
Fasteners and Miscellaneous	Steel and PVC - McMaster	\$ 34.09	\$ 34.09

Table 5.3 summarizes the cost of fabricating one square meter of ABC-2500 by component for both prototype and production quantities. This table can be compared directly to Table 3.1 which lists costs of an ABC 250 and this comparison will illustrate areas in which cost savings were effected.

Table 5.3. Summary of Costs by Cell Component (1 m² cell area).

Parts Description	Prototype Cost	Production Cost
End Plates (Plastic and Aluminum including plumbing)	\$ 708.82	\$ 287.00
Electrode Frames (Anode and Cathode)	\$ 871.44	\$ 205.04
Current Collectors	\$ 481.13	\$ 292.73
Gaskets	\$ 135.20	\$ 106.60
Bolts, Nuts, Plumbing supplies and Miscellaneous	\$ 6.09	\$ 6.09
Felt and Separator Preparation	\$ 532.17	\$ 387.90
Total Cost	\$ 2734.85	\$ 1285.36

5.2 Stage # 2

Stage # 2 of cell cost estimation includes the last two design modifications described in Section 4.0. These are design of a single-piece end plate made of ribbed plastic, and implementation of molded frames. Work on these is proceeding. Two molding shops have been contacted to acquire cost estimates for molding frames and bonding them to current collectors. They are Rubber Engineering and Development Corporation (REDCO) of Carson City NV and Gasket Specialties, Inc. of Emeryville CA. They are currently determining cost estimates on the same basis as other parts in Stage # 1.

Suitable suppliers for ribbed plastic material envisioned for single-piece end plates have not yet been identified. Work on identifying such suppliers and obtaining samples for testing is proceeding.

6.0 TESTING OF OPEN-CHANNEL FRAME DESIGN CONCEPT

6.1 Objective and Background

The most important design change effected in developing the ABC-2500 was using a single-piece frame design, where an open-channel machined on one face of the frame was sealed using a gasket. Figure 4.1 depicts the difference between single and two component frame designs.

It is obvious from Figure 4.1 that in the old two-piece frame design, an enclosed channel was provided by gluing two plates together. Improper gluing sometimes resulted in electrolyte leakage through the seam. On the other hand, the channels worked quite well in that there was no blockage or impediment to electrolyte flow. While designing an open-channel or one-piece frame shown on the right hand side of Figure 4.1, it was felt that leakage through frame seams would be avoided. On the other hand there was concern that the soft gasket would extrude into the electrolyte channel and block flow.

In order to test efficacy of the single-piece frame design, two frames were made for an ABC-250 cell. The rationale behind this was to evaluate performance of frame design on a small scale rather than spend resources fabricating the larger ABC-2500. Moreover, gaskets, end plates, current collectors and fasteners for the ABC-250 were already available and this permitted quick and cheap evaluation of the new frame design.

Accordingly, two ABC-250 frames using the open-channel design concept were fabricated and an ABC-250 cell assembled using them. It was decided to evaluate performance of this cell using two carrier solutions that are widely used at Aquanautics, namely compound # 64 (33 Suzy P) and compound # 72 (23 Suzy P). This allowed comparison between data acquired with the new frames and the vast data base that exists for these compounds.

6.2 Experimental Setup

Figure 6.1 depicts apparatus used for evaluation of the new frame design.

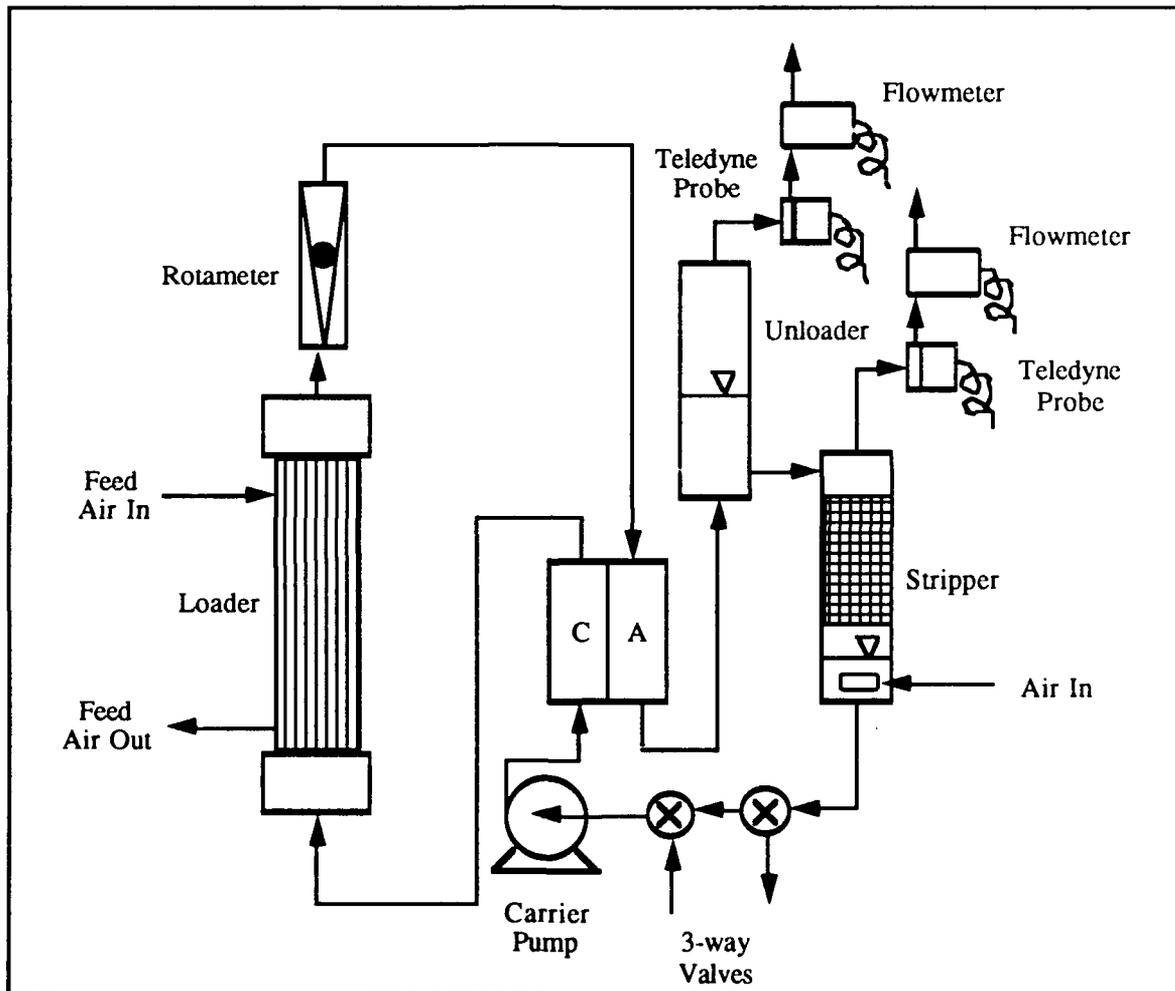


Figure 6.1. Schematic Depiction of Experimental Setup.

Loading of carrier was effected by use of a hollow fiber shell and tube exchanger (model # 50201040) from Hoechst-Celanese. This cartridge provides 2.3 m^2 of surface area for loading. A gear pump from Tuthill Pump Company of California was used to circulate carrier. Two three-way valves were used to introduce and drain carrier from the setup. In this experiment, the unloader was augmented by a stripper. The unloader was a simple phase separator, where carrier mixed with oxygen from the cell anode was fed into the bottom of a reservoir. The mixture flowed upwards into the reservoir causing buoyancy to separate oxygen bubbles from the carrier solution. Carrier from the bottom of the unloader

was then fed into a stripper. The stripper was intended to remove dissolved oxygen from the carrier and consisted of a packed tower. Carrier from the unloader was poured down a packed column consisting of plastic pall rings. Air was introduced from the bottom of the column by sparging it through a pool of carrier that collected at the base of the stripper. The output gas streams from both unloader and stripper were analyzed for oxygen content by Teledyne oxygen probes that were connected to signal conditioners. Flowmeters from Sierra Instruments (Side-Trak model) and Omega Engineering (model # FMA-502-V) were used to measure flow rates of output gas streams from the unloader and stripper respectively.

The electrochemical cell was assembled using Ultracarbon felt as the anode and VDG felt as the cathode. Titanium sheets were used as current collectors and Celgard 3501 microporous hydrophilic polypropylene from Hoechst-Celanese employed as the separator membrane. One ABC-250 cell with a separator area of 250 cm² was employed in this experiment.

In initial experiments using compound # 64 (referred to hereby as 33 Suzy P) the stripper and its associated instrumentation was not used. Additionally, two Microswitch (model # 142PC01D) differential pressure transducers were used to measure pressure drop across both anode and cathode compartments of the electrochemical cell. This was intended to reveal if the new design imposed additional flow restrictions in the carrier loop when compared to the old two-piece frame design.

Data from the various instruments were acquired using a Scientific Solutions, Inc. data acquisition and control board mounted on an IBM-PC compatible. Data was recorded on disk and analyzed using an Excel spreadsheet.

6.3 Experimental Procedure and Results for 33 Suzy P

Carrier was made up to a concentration of 0.4 M with 1.5 M KCl used as the supporting electrolyte and 0.008 M DAMF as the catalyst. The carrier pH was adjusted to around 7.2. It was then introduced into the experimental rig using the system of three-way valves shown in Figure 6.1. Two experiments were conducted with 33 Suzy P. The first one consisted of measuring performance of the cell at different carrier flow rates. After this was finished, a long term run with 33 Suzy P was recorded for comparison with previously established benchmarks for the carrier.

6.3.1 Results of Carrier Flow Rate Study

Carrier flow rate was set using the rotameter and data was recorded at 90 second intervals. Data was recorded for each value of carrier flow rate until five consecutive data points indicated that a steady state had been attained. The results were analyzed by averaging the data from these five steady state points representing approximately 7.5 minutes of data. The carrier flow rate was varied in steps of 3 l/min/m² (75 ml/min) from a low value of 3 l/min/m² (75 ml/min) to a high of 24 l/min/m² (600 ml/min). Important cell parameters were plotted as a function of carrier flow rate and these results are presented here. All data was taken with the cell operating at a constant potential of 0.5 V.

Figure 6.2 represents the variation in pressure drop through both electrode chambers as a function of carrier flow rate. It is apparent that the denser Ultracarbon felt used as an anode causes a greater pressure drop than the VDG felt cathode. Anode pressure drop is on an average 80 % higher than cathode pressure drop. The graph in Figure 6.2 also shows that

pressure drop is a linear function of flow rate and results of linear regression analysis are also presented.

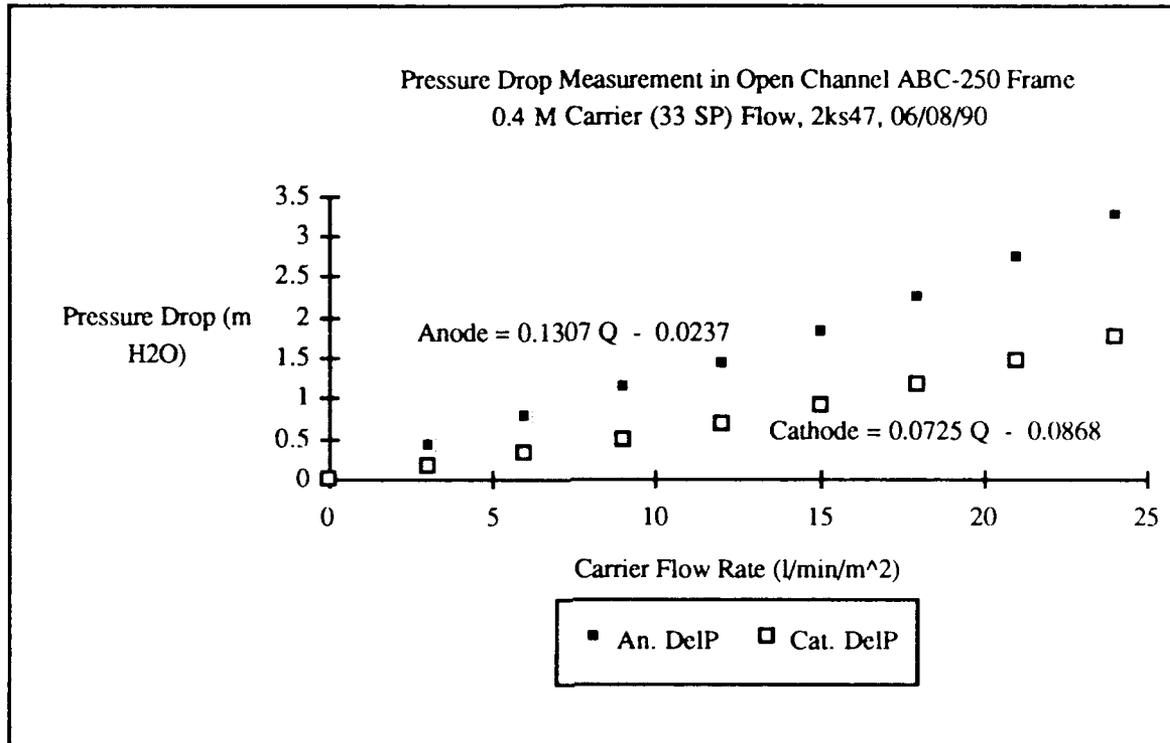


Figure 6.2. Variation of Electrode Pressure Drop with Carrier Flow Rate.

Figure 6.3 depicts variation of oxygen production rate with flow rate of carrier. It shows that oxygen production initially increases with carrier flow rate and then levels off between 9 and 15 l/min/m². At higher flow rates, oxygen production rate seems to decrease. This may be an artifact due to decreased unloading efficiency at higher carrier flow rates. Gas-liquid separation at the unloader is usually hindered by higher flow velocities giving rise to entrapment of bubbles in carrier. These entrapped bubbles are returned to the cell cathode where freshly reduced carrier reabsorbs the oxygen. The dramatic increase in oxygen production rate between 3 l/min/m² and 6 l/min/m² is attributable to increased effectiveness of gas removal. At the lower flow rate, oxygen generated in the anode is not swept away because of low flow velocities. This oxygen then blankets the felt electrode increasing cell resistance and slowing down the process. As carrier flow rate is increased, it becomes more effective in sweeping away oxygen gas that is generated, from the felt matrix.

Figure 6.4 depicts variation of electrochemical power and theoretical pumping power as a function of carrier flow rate. Pumping power is calculated at the pump head and does not include pump inefficiencies. The trend in electrochemical power mirrors that of oxygen production. The power is higher at low flow rates due to the increase in cell resistance caused by gas blanketing of the anode. Minimum electrochemical power is seen at 6 l/min/m². At higher flow rates, electrochemical power increases due to inefficient unloading. As a consequence of this inefficiency more oxygen is returned to the cell cathode causing expenditure of power without commensurate extraction of oxygen. Another phenomenon that contributes to this inefficiency is the increase in the amount of dissolved oxygen that is returned to the cell cathode at higher carrier flow rates.

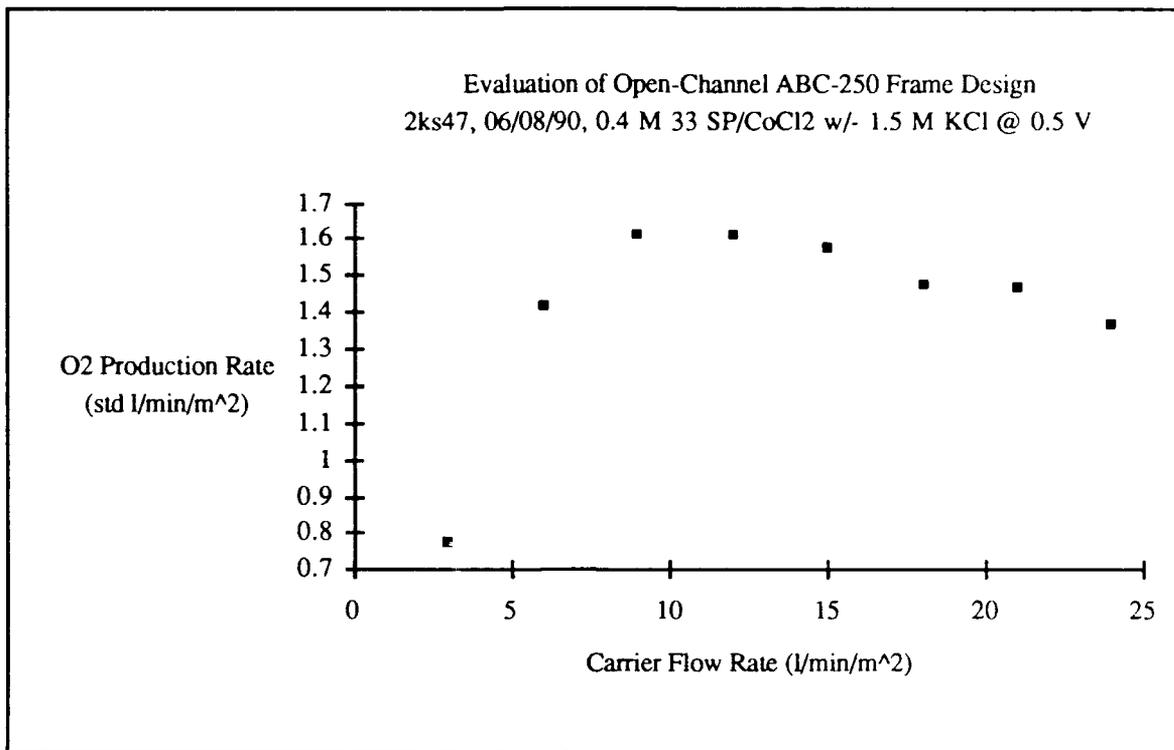


Figure 6.3. Variation of Oxygen Production with Carrier Flow Rate.

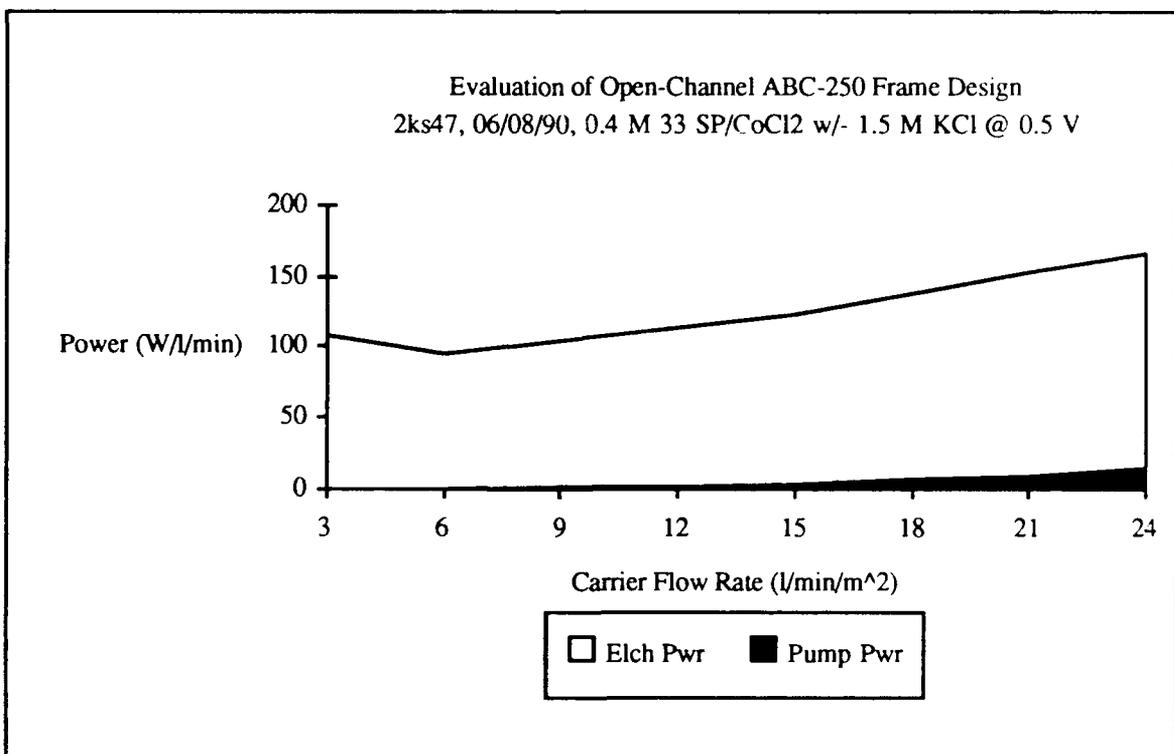


Figure 6.4. Variation of System Power with Carrier Flow Rate.

6.3.2 Results of Long Term Run

In the long term run, data was taken with carrier flow rate adjusted to a constant value of 12 l/min/m² (300 ml/min) and cell potential set at a constant value of 0.5 V. All operating parameters were tracked as a function of time. This included pressure drop across both cell electrodes. The pressure drop did not increase indicating that the frames performed flawlessly where hydrodynamics was concerned.

Figure 6.5 depicts oxygen production rate as a function of time for 33 Suzy P. A peak production rate of 1.6 l/min/m² (40 standard ml/min) was noticed for a day after the experiment started. Although this represents a value below the peak performance of 2.4 l/min/m² that had been recorded with 33 Suzy P in October 1988,⁵ the performance compared well with that recorded using the same batch of carrier in a smaller cell. Batch-to-batch variations of this order are not unprecedented and as a result, it can be said that use of an open-channel frame did not impair cell performance in any measurable way. Oxygen production declined steadily after a period of two and a half days (60 hours) until it reached unmeasurably small values approximately one week into the experiment.

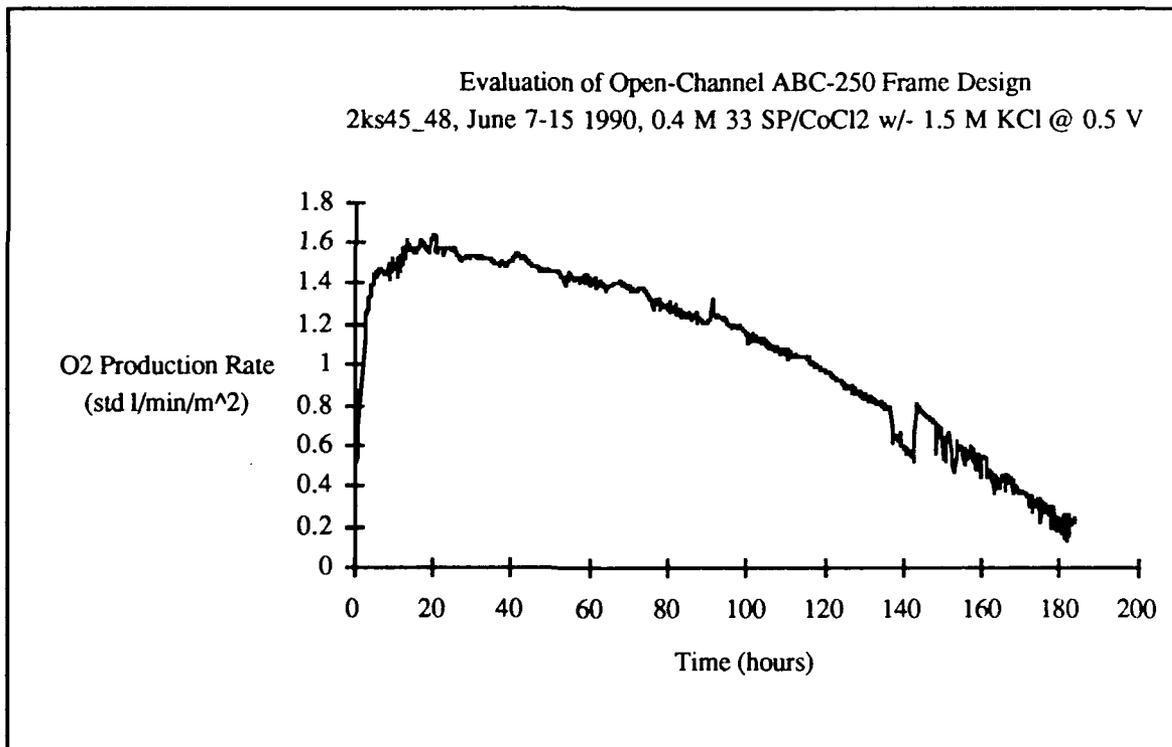


Figure 6.5. Oxygen Production from 33 Suzy P.

Figure 6.6 depicts electrochemical power expended in the cell with new open-channel frames. The power is seen to remain constant at a level between 100 and 125 W/l/min for a period of four days. After that it is seen to gradually increase to 200 W/l/min at day # 6

⁵Quarterly Report, October 1988 - December 1988, Long Endurance Underwater Power System, Contract No. N00014-87-C-0335, submitted to DARPA, pp. 49-52.

after which a dramatic increase is seen. This data compares well with previous observations that have been recorded with this carrier. Electrochemical power values as low as 70 W/l/min have been recorded previously with the cell producing 2 l/min/m². But, since power values recorded in this experiment were the same as or lower in some instances than comparable observations made with the same batch of carrier in smaller cells, the cell design was not deemed to adversely affect electrochemical performance.

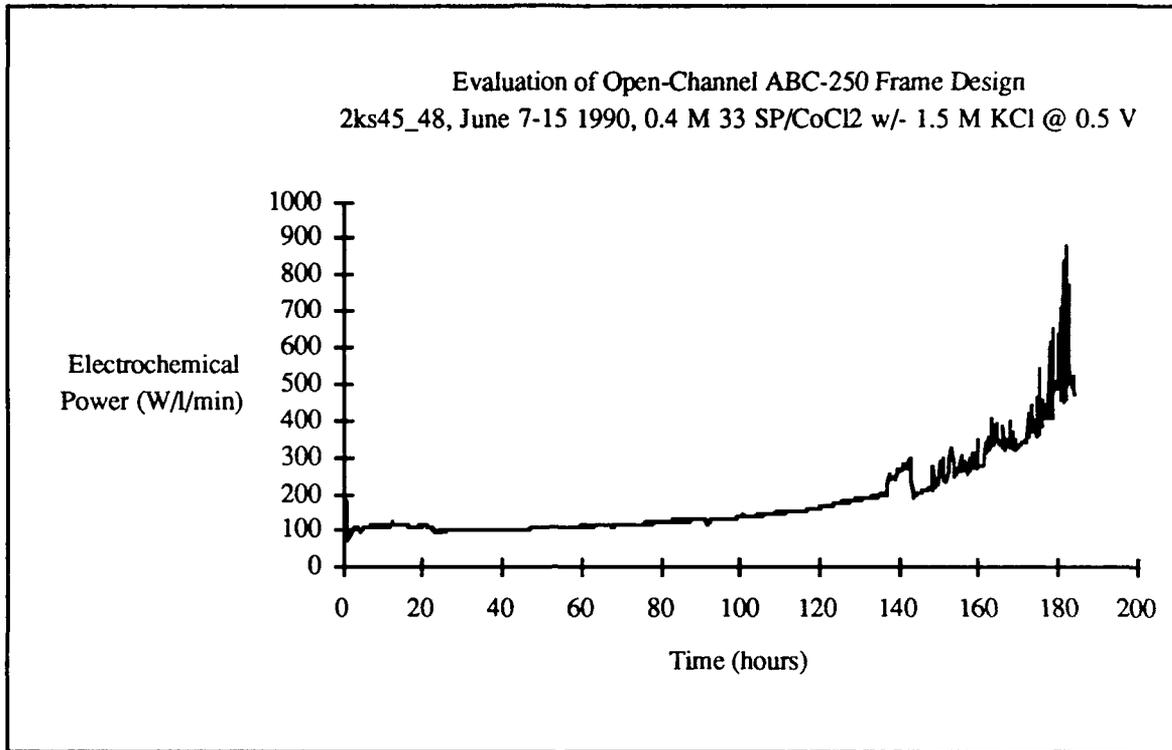


Figure 6.6. Electrochemical Power for 33 Suzy P.

Figure 6.7 depicts variation of electron count as a function of time for 33 Suzy P. The electron count is seen to be constant at about 3 for a period of about 60 hours after which it is seen to increase gradually to a value of 4.5 on day # 6. This behavior is similar to that noted previously with this carrier and also with experiments conducted in smaller cells with the same batch of carrier. The electron count is used as an indication of carrier lifetime, whereby longevity of a carrier is calculated as the time taken for the electron count to exceed 4. According to this criterion, 33 Suzy P lasted 80 hours which is in line with previously reported lifetimes of 3 days.

6.4 Experimental Procedure and Results for 23 Suzy P

Compound # 72 (commonly referred to as 23 Suzy P) is the leading candidate for an oxygen scavenging system such as that being contemplated for the DARPA project. Its chief virtue is longer life than any other carrier tested to date at Aquanautics. Lifetimes, reported as time for electron count to exceed a value of 4, of up to six weeks have been measured with 23 Suzy P when unloading is done by air sparging. Pure oxygen unloading has, however, only yielded a lifetime of four weeks.

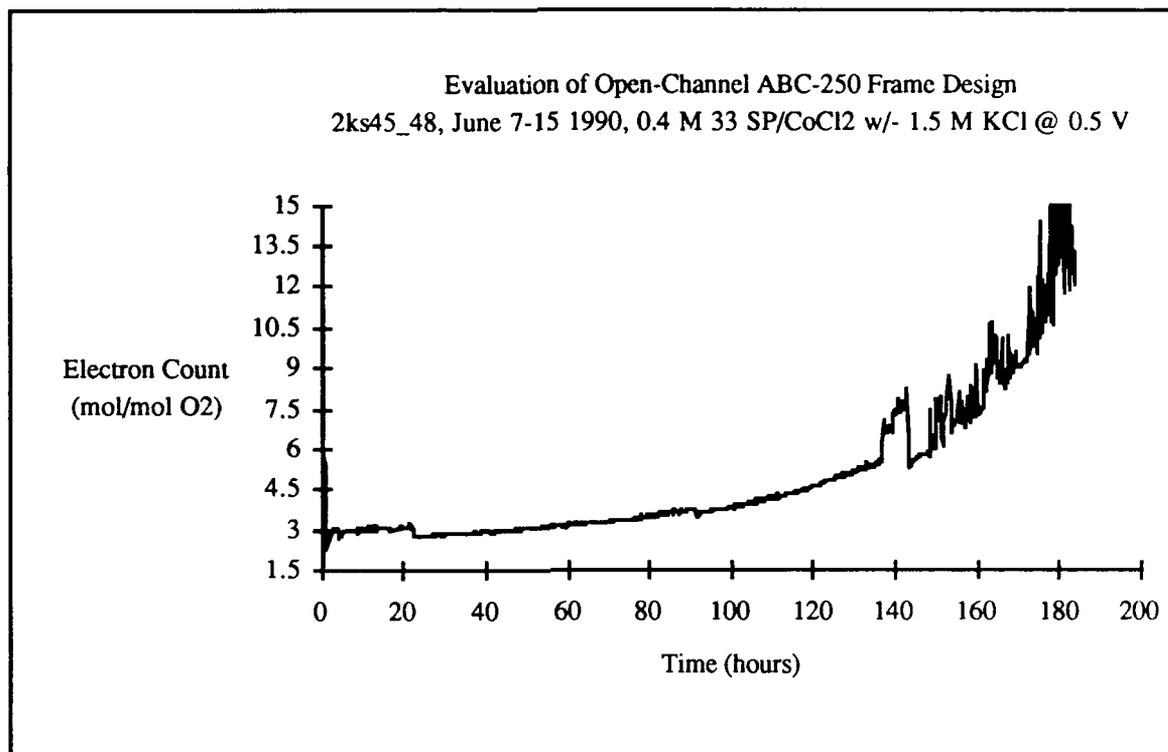


Figure 6.7. Electron Count for 33 Suzy P.

Since this carrier is slated for use in the DARPA project, it was necessary to measure cell performance over the long term using the open-channel frame design. Consequently the cell used in the previous experiment with 33 Suzy P was rinsed with 2 M HCl and prepared for use with 23 Suzy P. The experimental apparatus was modified to include a stripper after the unloader as depicted in Figure 6.1. Air was sparged through the stripper and oxygen removed from carrier at this point was measured by monitoring oxygen content and flow rate of the stripper effluent. The rationale for a stripper was to investigate the cause of lower lifetime under pure oxygen unloading. By incorporating both pure oxygen unloading and air-sparged unloading in series in the same experimental rig, it was expected that reasons for diminished lifetime under pure oxygen unloading would be identified.

Carrier was made up to a concentration of 0.4 M with 1.5 M KCl as the supporting electrolyte. No catalyst was added since prior experimentation had proven that performance of 23 Suzy P was not effectively catalyzed by compounds known for that purpose at Aquanautics. The carrier pH was adjusted to 7.6 prior to its introduction, via the three-way valve system, into the rig. Cell potential was held constant at approximately 0.9 V for the duration of the experiment. Carrier flow rate was held constant at 6 l/min/m² (150 ml/min) for the duration of this experiment.

Figure 6.8 shows oxygen production from the cell measured at the unloader and stripper. Pure oxygen represents measurements made at the unloader, while total oxygen is obtained by adding in oxygen separation effected at the stripper. Peak oxygen production rates of 1 l/min/m² (25 standard ml/min) were noticed in the beginning. This value started to decline after two days of operation and continued to do so until oxygen production was not measurable after about six weeks. The intermittent spikes in oxygen production after about three weeks were due to periodic shut down of the power supply. It was hoped that

periodically interrupting power supply to the cell would help clear the felt electrode of entrapped oxygen bubbles and any impurity that may have coated its surface. It is apparent that when power supply to the cell is resumed after the shut down, there is a temporary increase in performance. More detailed experiments are planned to investigate the possibility of using this technique with two banks of cells and to identify any benefits this may accrue to carrier lifetime.

One important observation that can be gleaned from Figure 6.8 is that additional oxygen removed at the stripper is commensurate with dissolved oxygen concentrations that are expected based on independent measurements of oxygen solubility in carrier solutions. This indicates close to 100 % separation efficiency at the unloader, i.e. all gaseous oxygen is being removed. Therefore only dissolved oxygen is reaching the stripper.

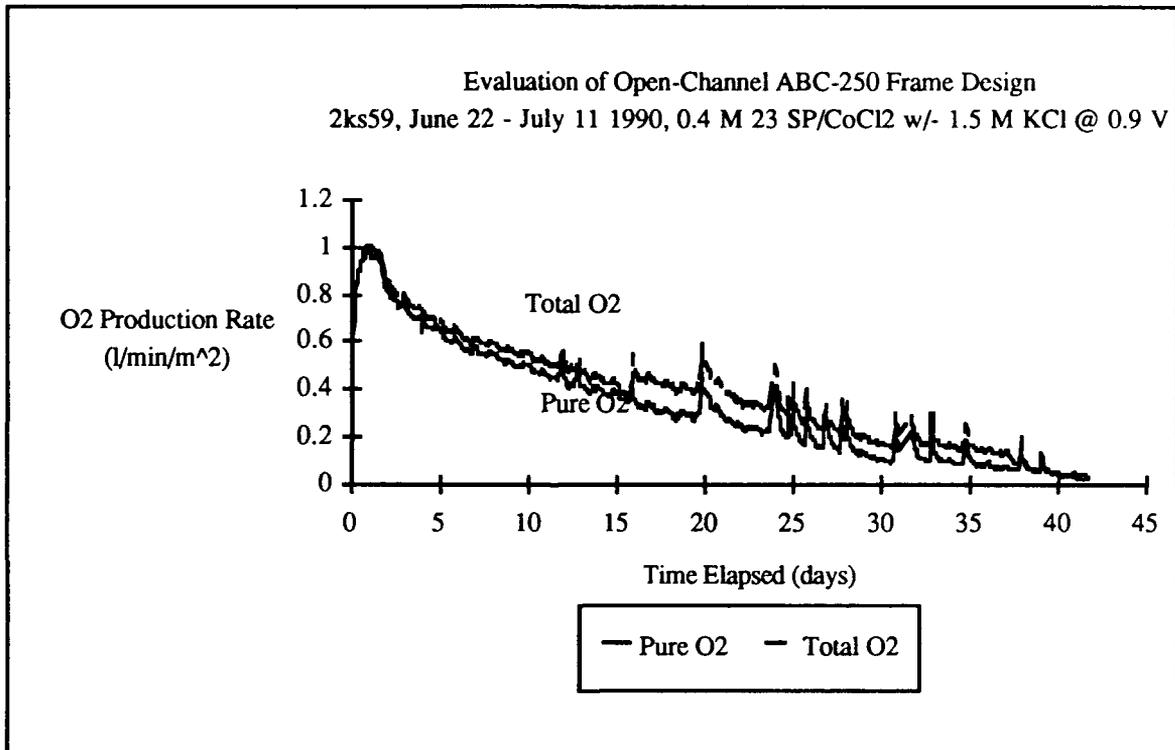


Figure 6.8. Oxygen Production Rate with 23 Suzy P.

Figure 6.9 depicts electrochemical power expended at the cell. Power is calculated on the basis of both pure oxygen from the unloader and total oxygen that includes the stripper. Obviously power calculated on the basis of pure oxygen is higher than that calculated on the basis of total oxygen. The two curves diverge dramatically after about three weeks. This implies that as carrier performance degrades, dissolved oxygen removed at the stripper forms a proportionally larger fraction of the oxygen evolved at the cell anode. This divergence is so pronounced that at the end of five weeks, power calculated on the basis of pure oxygen is twice that calculated from total oxygen implying that pure oxygen and dissolved oxygen are present in equal proportions.

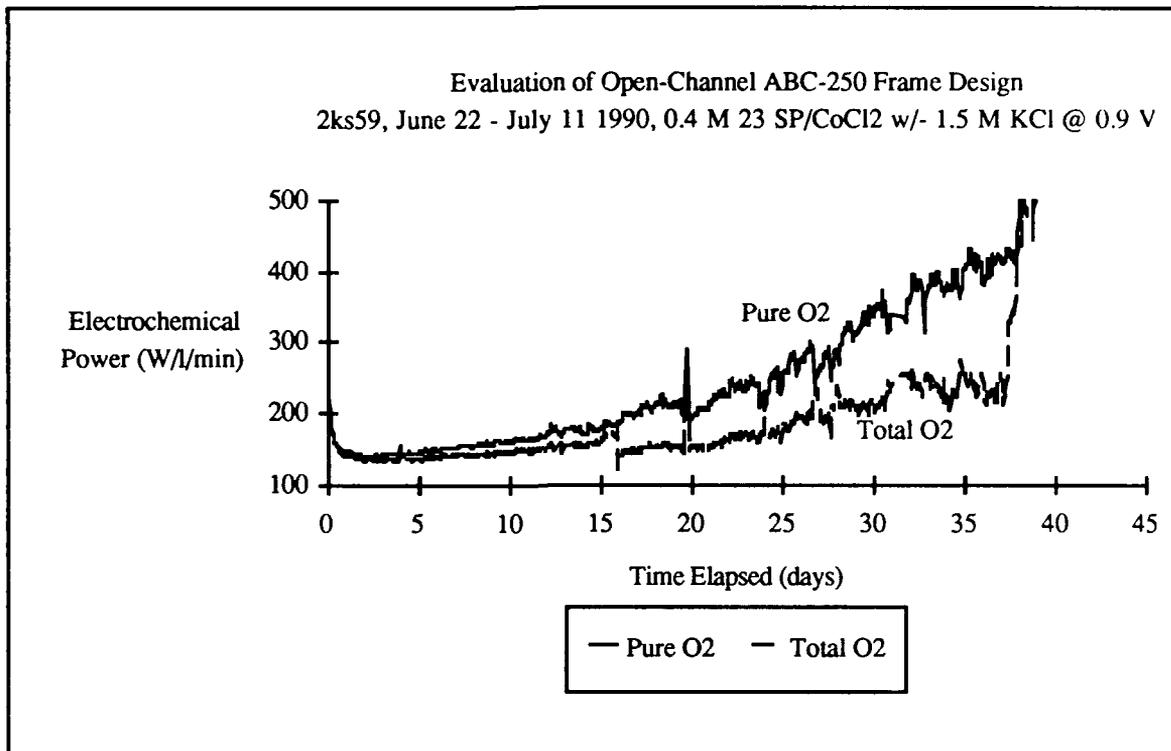


Figure 6.9. Electrochemical Power for 23 Suzy P.

Figure 6.10 depicts electron count as a function of time. As in Figure 6.9, electron count is calculated on the basis of both pure and total oxygen. Electron counts calculated from total oxygen are naturally lower than those computed from pure oxygen. This curve makes plain why lower lifetimes (lifetime is arbitrarily defined as time taken for electron count to exceed 4) are noted with pure oxygen unloading when compared to air sparging. The reason is that in the latter dissolved oxygen is also removed and gets factored into the calculation of electron count, thereby depressing it artificially. Figure 6.10 reveals that electron count for pure oxygen exceeds 4 after about four weeks, while electron count for total oxygen exceeds 4 after 38 days. Both these observations match experimental results for 23 Suzy P in smaller cells.

6.5 Conclusions from Testing of Open-channel Frame

Experiments conducted with two of the most frequently used carriers at Aquanautics indicate that the open-channel frame design works as well or better than the conventional two-piece frame that incorporates an enclosed channel. The following salient points summarize conclusions that can be drawn from the results of tests described in preceding sections.

- 1) Pressure drop in the carrier loop for both electrodes match data previously obtained from experiments conducted with two-piece frame designs. The overall pressure drop in the new open-channel frame design remained constant over the one week lifetime of 33 Suzy P indicating that the gaskets were not being extruded into the channel.

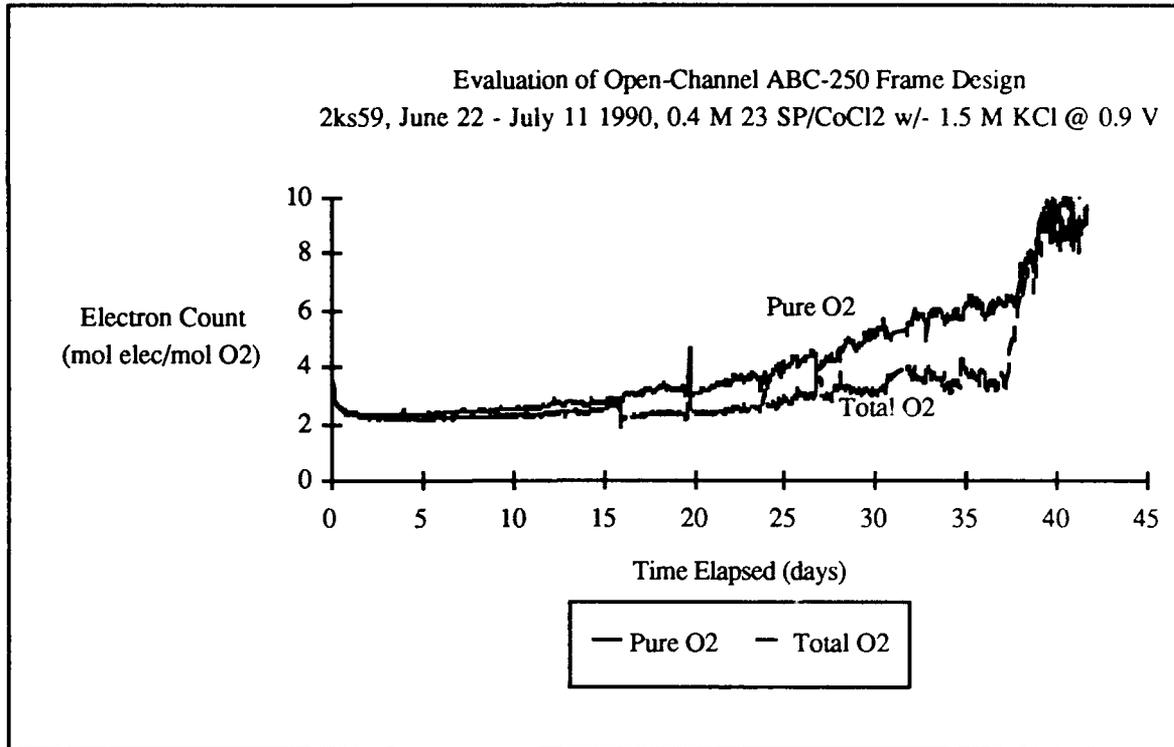


Figure 6.10. Electron Count for 23 Suzy P.

- 2) Oxygen production peaks at a carrier flow rate of about 12 l/min/m² and decreases at higher flows. This may be due to separation inefficiencies at the unloader, but the overall trend is similar to that observed with 33 Suzy P previously in two-piece frame designs.
- 3) Long term behavior of 33 Suzy P was similar to that established in previous testing within limits imposed by batch-to-batch variations in carrier performance. Peak oxygen output of 1.6 l/min/m² was measured although the carrier seemed to last a little longer than expected.
- 4) Performance of the cell with 23 Suzy P matched previous observations very well. Pure oxygen unloading resulted in a lifetime measured at 4 weeks while the carrier lasted about 38 days when air sparging was the method of unloading. A peak of 1 l/min/m² was measured, albeit for a short duration.

Based on these salient points, it can be conclusively said that an open-channel or single-piece frame design does not adversely affect cell performance. On the contrary, elimination of a potential leak path has enabled use of an assembled stack for a period in excess of four months. The only maintenance that has been found essential is rinsing with 2 M hydrochloric acid in between tests, i.e. prior to introduction of a new batch of carrier. It can therefore be concluded that open-channel frames are ideal for a 2500 cm² area cell design.

7.0 FUTURE WORK

Based on the significantly reduced fabrication cost of the new cell design and the successful testing of an open-channel frame - a concept central to the cost savings effected in cell fabrication - fabrication of a prototype ABC-2500 cell has been ordered. This prototype will be constructed with metal end plates and machined frames, a concept identified as Stage # 1 in a Section 5.0. Work on this subtask will continue next quarter and will consist primarily of testing the prototype cell. Prototyping of a molded frame design (Stage # 2) will depend on resources available after the first prototype has been tested, and will proceed only after consultation with the project manager.

TASK 3.0 PROCESS VERIFICATION

1.0 INTRODUCTION

Food preservation requires a fixed mix of carbon dioxide and oxygen for optimal longevity. This necessitates use of stored carbon dioxide and removal of oxygen to maintain composition of a container's atmosphere. Dr. Irwin Taub of US Army Natick R. D. & E. Center has indicated that an optimal mix of gases would include 15 % carbon dioxide and 5 % oxygen. All prior experience with Aquanautics' carriers has been with oxygen generation from air as feed stock. The effects of carbon dioxide have not been studied extensively. Therefore, as part of process verification an experiment was performed to evaluate the effect of carbon dioxide on carrier performance.

A custom mixture of gases containing 15 % CO₂, 5 % O₂ and balance nitrogen was ordered for this purpose and fed to the loader instead of air as is normally the case.

2.0 EXPERIMENTAL SETUP

Figure 2.1 depicts the arrangement of experimental apparatus used here.

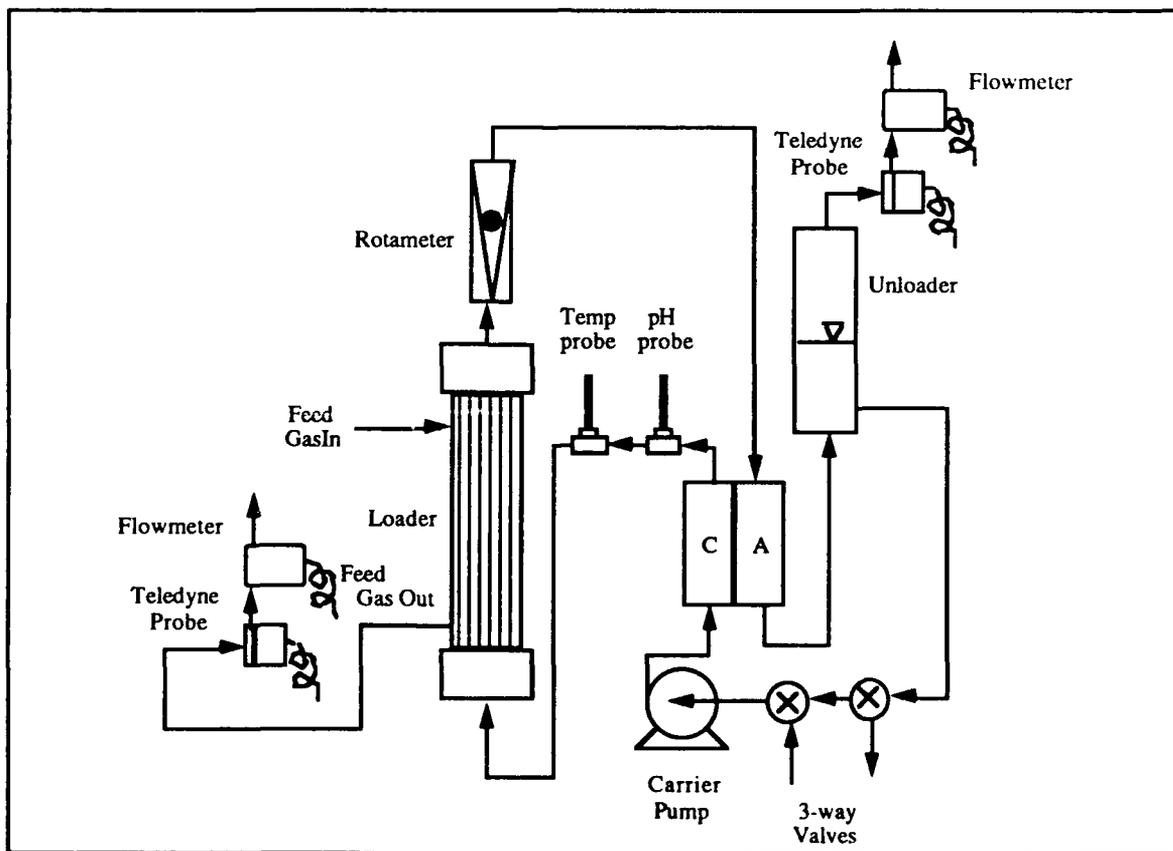


Figure 2.1. Schematic Depiction of Experimental Apparatus

Carrier loading was effected by use of a Hoechst-Celanese hollow fiber shell and tube contactor (model # 50201040). The carbon dioxide-rich mixture was fed to the shell side of the loader and its oxygen content and flow rate were measured at the loader outlet using a Teledyne probe and flowmeter (Omega Engineering, Inc. model # FMA-502-V) respectively. Carrier was circulated using a gear pump from Tuthill Pump Company of California. A three-way valve system was used to introduce carrier into the experimental apparatus. Carrier pH was measured by an inline probe from Omega Engineering, Inc. which was assembled along with its associated temperature probe in the carrier circuit using "tee" fittings. Oxygen output purity and flow rate were also measured at the unloader exit using a Teledyne probe and a Side-Trak model flowmeter from Sierra Instruments respectively.

The electrochemical cell was assembled with an Ultracarbon felt anode, VDG felt cathode, Titanium current collectors and Celgard 3501 microporous polypropylene as the separator. One ABC-250 cell with a separator area of 250 cm² was used for this experiment.

3.0 EXPERIMENTAL PROCEDURE

The electrochemical cell assembled for experiments described under the section dealing with subtask 2.0 (Electrochemical Cell Cost Reduction) was used in this test. After long term evaluation of the open channel frame had been completed, the cell was rinsed with 2 M HCl and then water. After all residual impurities and sediment had been removed in this manner, the cell was stored overnight under a 1 M solution of KCl.

Carrier solution consisting of 0.4 M 23 Suzy P (compound # 72) was made up along with 1.5 M KCl as the supporting electrolyte. No catalyst was used. This carrier was introduced into the experimental rig using the carrier pump and the three-way valve system shown in Figure 2.1. Initially, air was used as feed stock, and the cell operated at a constant potential of 0.9 V. Data from all the instruments was recorded at one hour intervals and stored on disk for future analysis.

After the carrier had been broken in for five days with air as feed stock, the carbon dioxide-oxygen mixture was fed to the loader for a day. Air feed was restored then to evaluate if the high carbon dioxide concentration had caused permanent damage to carrier. This pattern was repeated twice, and on day # 14 of this experiment, it was noticed that the carrier pH had decreased to 5. At this stage carrier was removed from the rig, its pH readjusted to 7 by addition of KOH, and then reintroduced into the rig. Alternate air and CO₂ mixture feed was resumed for a period of 12 days at the end of which carrier pH had declined to 5 again. In situ pH adjustment was effected and the experiment terminated after two more days of data acquisition with air as feed stock.

4.0 RESULTS AND DISCUSSION

4.1 Oxygen Production Rate

Figure 4.1 depicts the oxygen production rate monitored throughout the experiment. In this figure, two curves are plotted, one showing oxygen production measured at the unloader and the other showing oxygen uptake at the loader. The difference between these

two measures of system performance can be attributed to errors in flowmeter calibration. It is instructive to note, nonetheless, that oxygen removal rate measured at the unloader and loader track one another quite accurately reflecting the absence of net oxygen consumption or production anywhere within the system. The higher oxygen production rate value is that calculated from measurements at the unloader.

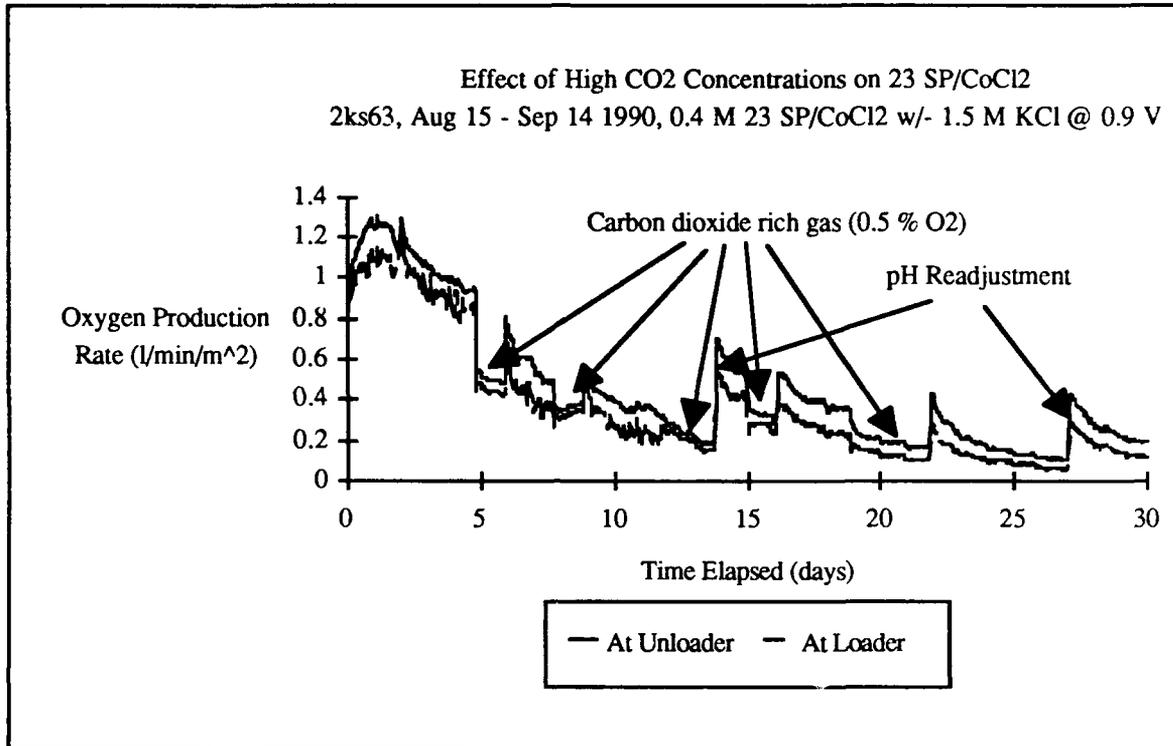


Figure 4.1. Oxygen Production Rate.

It can also be seen that oxygen production rate decreases when the carbon dioxide-rich gas mixture is fed to the loader. The decrease in system performance when the CO₂-O₂ mixture was used ranged from 40 to 60 % when compared to performance in air. This decline in performance was however shown to be temporary and reversible. This is evidenced by the fact that when the CO₂-O₂ mixture was replaced by air feed, carrier performance recovered to a level commensurate with an extrapolation of previous air feed data. This trend was apparent at all stages in the carrier's lifetime.

Figure 4.2 compares oxygen production rate measured in this experiment with that measured over the lifetime of 23 Suzy P in another experiment where only air was used as the feed stock. This comparison illuminates the following salient points.

- 1) Initial performance of the batch of carrier used in this experiment was 25 % better than that used for the control experiment where air was fed to the loader continuously.
- 2) Once allowance is made for this better initial performance, oxygen production rates in both experiments tracked one another quite well until, carbon dioxide-rich mixture was introduced. It is illustrative to note that 23 Suzy P goes through a characteristic behavior pattern when run at constant cell potential. Performance improves as the carrier breaks in and reaches a maximum two days into its lifetime.

After reaching this peak, performance declines steadily until at the end of four weeks (six weeks if air-sparged unloading is employed), oxygen output is too small to be detected accurately.

- 3) Once carbon dioxide was presented to the carrier the rate of decline in performance became steeper than in the control where only air was used as feedstock. Thus although reintroducing air to the loader allowed almost complete recovery of performance, the background rate at which performance in air declines became faster. The background rate of performance decline can be visualized by extrapolating air-performance data across those time intervals where the CO₂-O₂ mixture was used.
- 4) The dramatic decline in performance is arrested and reversed by adjusting carrier pH back to neutrality. However data taken after pH-adjustment shows that performance decreases at a faster rate once carbon dioxide is reintroduced into the carrier.

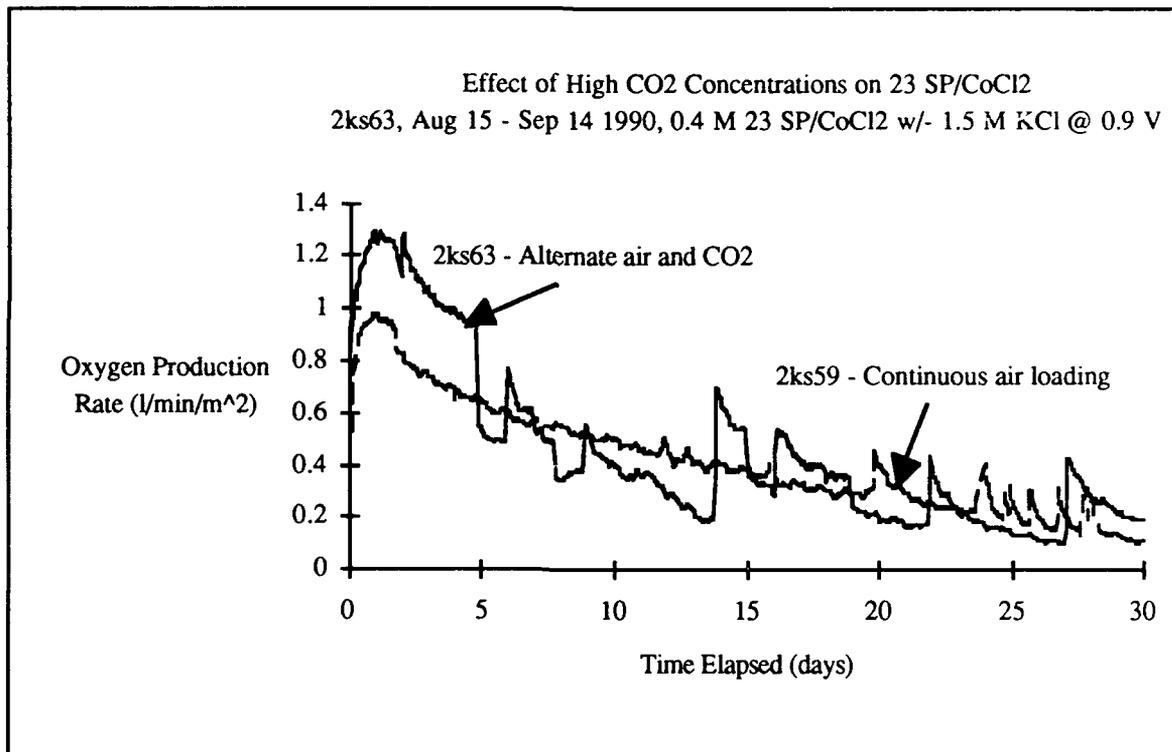


Figure 4.2. Comparison of Oxygen Production Rates.

4.2 Electrochemical Power

Figure 4.3 depicts electrochemical power monitored as a function of time. This figure illustrates clearly, the penalties associated with having high carbon dioxide concentrations in the feed stock. After the initial break-in period, power reached a constant value of approximately 200 W/l/min before the CO₂-O₂ mixture was introduced. Electrochemical power increased by approximately 50 % upon introduction of this mixture. Moreover, when air was reintroduced at the loader, deterioration of carrier performance proceeded at a faster rate. This conforms to the accelerated deterioration in oxygen production rate observed simultaneously. In the control experiment where only air was used,

electrochemical power remained constant for the first two weeks of operation before exceeding 200 W/l/min (see subsection 6.4 in the report on Task 2.0). In this experiment, however, when air performance is extrapolated, increase in power was more dramatic and the 200 W/l/min threshold was exceeded in one week. Power was seen to increase by between 50 and 70 % over the air-feed baseline upon introduction of the CO₂-O₂ mixture.

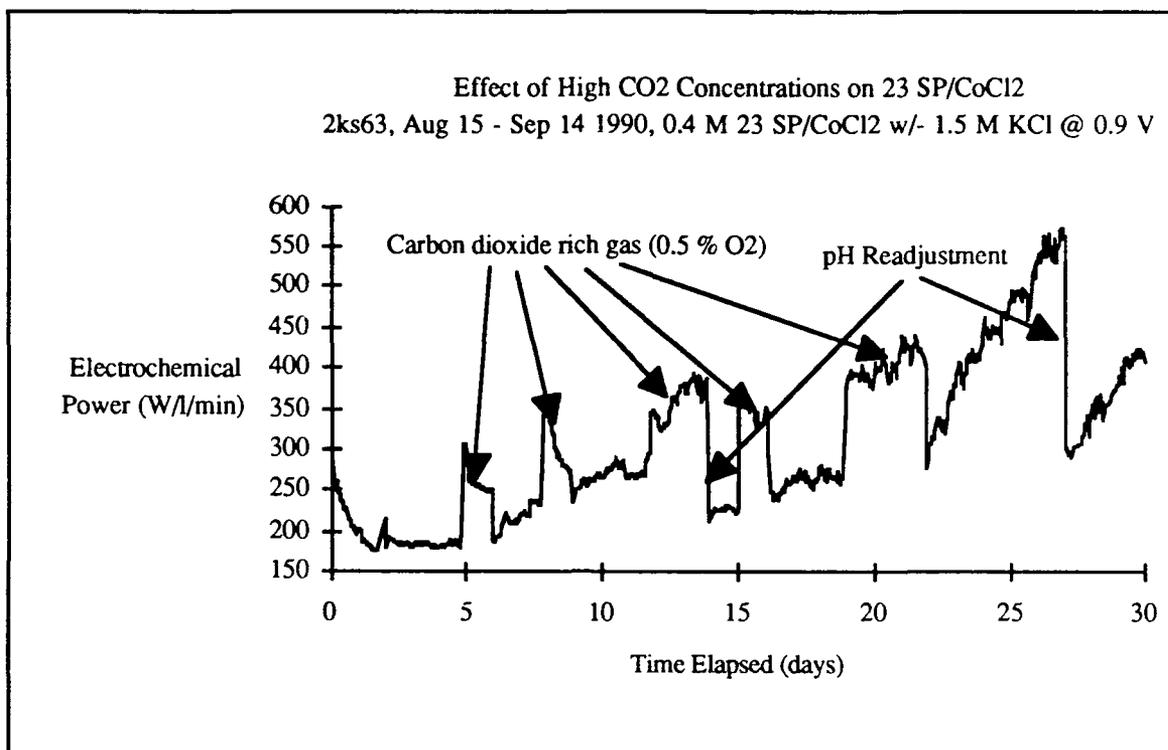


Figure 4.3. Electrochemical Power.

The following reasons can be attributed to this increase in power.

- 1) Introduction of a high carbon dioxide concentration causes carrier pH to decrease. While the carrier binds and releases oxygen even at low pH, it does so more inefficiently. At pH 5, the ligand is known to protonate whereby it loses its ability to bind oxygen. The equilibrium constant for oxygen binding decreases thereby presenting higher concentration of unbound carrier species to the cell anode. These unbound carrier molecules consume electrochemical power in a parasitic fashion as they are oxidized and reduced without releasing any oxygen.
- 2) The low oxygen concentration (5 % or 0.05 atmospheres) may cause less complete carrier oxygenation leading to the same wasteful power consumption described above. This problem is also exacerbated by the low pH typical of carrier fed with carbon dioxide.
- 3) Carbon dioxide dissolves in carrier and forms carbonate which is known to bind to the oxidized carrier molecule. This makes its reduction potential more negative, thereby making it harder to regenerate or restore the oxygen-binding capability of the carrier.

The effect of pH on carrier performance is clearly illustrated by the fact that when it was adjusted back to neutrality on two occasions, dramatic decreases in power were obtained. This offers one solution to combating the adverse effect of pH decrease when carrier is used with high carbon dioxide concentrations, namely using a pH controller to inject KOH into the carrier in such a way as to maintain carrier pH at a constant value of 7 throughout its lifetime. The effect of carbonate presence is also clearly illustrated by the fact that power decreased whenever the CO₂-O₂ mixture was replaced by air-feed.

4.3 Electron Count

Figure 4.4 depicts electron count calculated over the carrier lifetime. Electron count follows a pattern similar to that of the electrochemical power. Since power increase is caused by an increase in the concentration of deoxygenated carrier species leaving the loader, this is reflected in the electron count. The electron count measures system efficiency by calculating the number of electrons expended in releasing one oxygen molecule. Inefficiencies caused by presence of deoxygenated carrier species are reflected in cell current that is used to repetitively oxidize and reduce these unbound species without participating in oxygen removal.

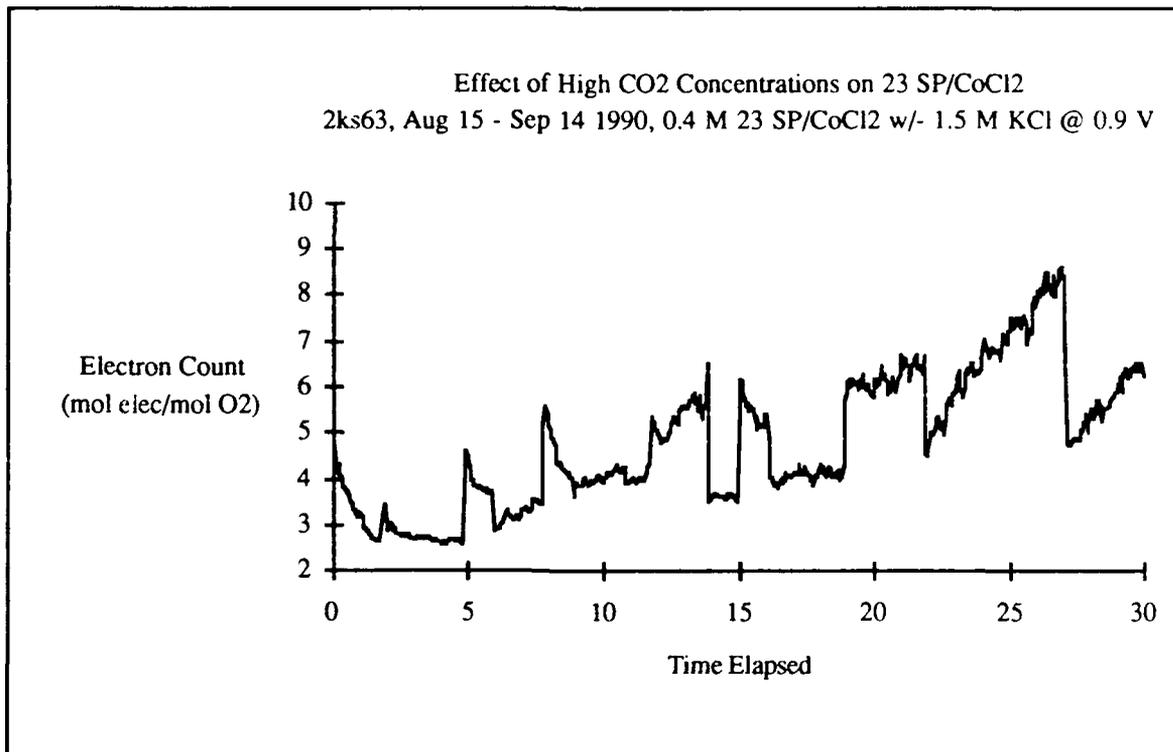


Figure 4.4. Electron Count.

5.0 CONCLUSIONS AND FUTURE WORK

The following conclusions are apparent from the experiment conducted with high carbon-dioxide concentrations in the feed stock.

- 1) Performance (oxygen production rate) degradation of approximately 40 to 60 % when compared to air-feed systems is to be expected when using carriers for oxygen extraction from food containers.
- 2) Electrochemical power can be expected to increase by between 50 and 70 % when the loader feed stock is atmosphere from a food container as opposed to air.
- 3) Constant monitoring and control over carrier pH is essential to maintaining an acceptable level of performance.
- 4) Since addition of KOH for pH control will result in a buildup of salt in the carrier solution, prior addition of KCl may be avoided to prevent possible precipitation of salt at a later stage.

Future work is expected to concentrate on three areas of interest.

- 1) Further experiments are planned with 23 Suzy P wherein the cell is run with a constant feed containing 15 % carbon dioxide and 5 % oxygen. These experiments should be run at constant current so as to monitor performance of the cell when it is removing a fixed quantity of oxygen. This will yield more definite scale-up information allowing design of a small-scale extractor as well as the demonstration unit.
- 2) In addition to traditional cobalt-based carriers like 23 Suzy P, Aquanautics has been experimenting with Iron-based compounds that undergo metal-centered oxidation when brought in contact with oxygen. These carriers can then be regenerated at the cathode of an electrochemical cell. Cobalt-based carriers, on the contrary do not undergo metal-centered oxidation in the presence of oxygen, but bind it in a stable complex. The iron-based compounds have the advantage of being classified as GRAS (Generally Regarded as Safe) for food applications by the FDA (Food and Drug Administration). They are also expected to be inert to presence of carbon dioxide and their longevity may be better than that of 23 Suzy P. Their primary disadvantage lies in higher electrochemical power consumption, which has been measured at being between 500 and 600 W/l/min.
- 3) Electrode research is being carried out at Aquanautics with the goal of increasing oxygen production rates. This research is directed at modifying the graphite felts currently in use in order to endow them with greater surface area increasing thereby the number of potential reaction sites. Current status indicates that a two-fold increase in oxygen production rate is attainable cutting in half cell costs for a demonstration unit.

After these research items have been investigated thoroughly, a small scale system shall be designed and assembled to verify the concept of the oxygen extraction system. This test shall employ a small refrigerator to simulate a refrigerated food container.

APPENDIX A COPIES OF CELL FABRICATION QUOTES

A QUOTATION FROM



GRAYSIX COMPANY

2427 Fourth Street • Berkeley, California 94710-2488 • Phone (415) 845-5936

TO: Aquanautics Corp.
980 Atlantic Avenue, Suite 101
Alameda, CA. 94501

DATE: 7/11/90

QUOTATION NO. 3036

ATTN: Krishnan (Jinny) Shrinivasan

REF:

WE ARE PLEASED TO QUOTE AS FOLLOWS:

<u>P/N</u>	<u>Description</u>	<u>Qty./Price ea.</u>	
		<u>4</u>	<u>250</u>
ABC2-00-04	Current Collector	\$30.00	\$ 3.75

Material supplied cut to size by Aquanautics.

PRICES DO NOT INCLUDE SALES OR USE TAXES UNLESS SPECIFIED.

DELIVERY: 2 weeks - Proto.
3 weeks - Production run
SUBJECT TO ACCEPTANCE:

TERMS: Net 30 days

F.O.B. Our shop Berkeley

THANK YOU FOR THE OPPORTUNITY TO QUOTE.

GRAYSIX COMPANY

Matthew D. Gray
BY: Matthew D. Gray

SPECIALIZING IN PRECISION SHEET METAL FOR THE ELECTRONICS INDUSTRY



GASKET SPECIALTIES INC. WORK SHEET

<input type="checkbox"/> ORDER	DATE ORDERED	INITIALS
<input type="checkbox"/> QUOTE	DATE QUOTED	INITIALS
<input type="checkbox"/> OTHER		

CUSTOMER Aquanautics

DATE 7-6-70

PHONE 521-4331

P.O. NUMBER _____

BUYER Jinny

QTY.	SIZE, DESCRIPTION, MATERIAL, THICKNESS	CODE	UNIT PRICE
10	Dwg# ABC2-00-03 1/16" EPDM		7.80
1000	Pitts		6.15
1	N/R Setup		120.00
10	Dwg# ABC2-00-06 "Cutting Only" (Hydrophilic Polypropylene film) 18"		2.50
1000	Pitts		.45
1	N/R Setup		75.00
10	Felt "Cutting Only" (1/2" felt 10x40 sheets)		2.50
500			.25
1	N/R Setup		25.00

DATE & TIME WANTED _____ AVAILABILITY _____ TERMS _____

SHIP VIA _____ F.O.B. _____

REC'D BY _____ PRICING BY _____ DATE _____

DIAMOND TOOL & DIE, INC.
 508 29TH AVE.
 OAKLAND, CA. 94601

Phone 415-534-7050
 FAX 415-534-0454

RFQ NO.

DATE 07/09/90

CUSTOMER: AQUANAUTICS
 980 ATLANTIC AVENUE
 ALAMEDA, CA 94501
 ATTN: JINNY SHRINIVASAN

TERMS 1Z10 NET 30
 DELIVERY TO BE ARRANGED
 F.O.B OAKLAND, CA
 Quote good for 30 days.

QUANTITIES/UNIT PRICE	1	40	0	0	0
03477 ABC2-00-10 of	\$263.50	\$97.85	\$0.00	\$0.00	\$0.00

LABOR AND MATERIAL

QUANTITIES/UNIT PRICE	1	40	0	0	0
03478 ABC2-00-02	\$169.03	\$42.43	\$0.00	\$0.00	\$0.00

LABOR AND MATERIAL

QUANTITIES/UNIT PRICE	4	500	0	0	0
03479 ABC2-00-05	\$108.93	\$25.63	\$0.00	\$0.00	\$0.00

LABOR AND MATERIAL

QUANTITIES/UNIT PRICE	1	40	0	0	0
03480 ABC2-00-09	\$205.20	\$48.37	\$0.00	\$0.00	\$0.00

LABOR AND MATERIAL

QUANTITIES/UNIT PRICE	1	40	0	0	0
03481 ABC2-00-10	\$263.50	\$97.85	\$0.00	\$0.00	\$0.00

LABOR AND MATERIAL

Thank you for this opportunity to quote.
 May we be of further service to you in the future.

*Note: prices based on
 all or none quantities*

Quoted By: Don Holt