

UNIVERSITY OF HAWAI'I

FINAL TECHNICAL REPORT Reporting Period: 20 May 2005 through 19 August 2006

Defense Advanced Research Projects Agency. Grant No. HR0011-05-1-0039

Subsea Power Generation Systems Utilizing Seafloor Methane

Submitted to:

Defense Advanced Research Projects Agency. 3701 N. Fairfax Drive Arlington, VA 22203-1714

Submitted by:



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ABSTRACT

The Hawai'i Natural Energy Institute of the University of Hawai'i, under funding from DARPA, initiated an R&D project to advance the design, testing, and deployment of technologies and systems that produce electrical power from methane and associated compounds in the seafloor sediment in situ. The goals of this effort are to identify viable systems for a range of possible mission profiles and available methane resource; and to demonstrate feasibility of concept of these systems through experimentation and performance characterizations of key technologies. During the present project period, the principal objectives were to conduct a technology review, and initiate system design and performance analyses. Technology risk mitigation laboratory studies also were initiated. This Final Report summarizes results of technical activities undertaken during the period extending from 05/20/05 through 08/19/06. The results of this study were generally positive, although uncertainties remain that need to be addressed via additional experiments and analyses. No fundamental issues were uncovered that would preclude net power production of the order of 100 W from seafloor methane using existing technologies. It appears possible to develop and deploy a first prototype for field testing within a 5 year time horizon, given appropriate resources. It is recommended that this prototype be tested first in relatively shallow waters and utilize free gas seeps as a fuel resource. Lessons learned from this testing would be applied to refine the prototype for operation at greater depths. The system is expected to utilize a low-temperature fuel cell and a hybrid oxygen supply system comprising stored H₂O₂ solutions and membrane contactors to extract DO from sea water.

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EXECUTIVE SUMMARY

A study was conducted to evaluate the technical feasibility of generating electrical power in the deep ocean from seafloor methane and to initiate the design of a first prototype system for field deployment. Although uncertainties remain that warrant additional investigation, information collected to date suggest that it should be possible to produce net power of the order of 100 W employing existing technologies. The lifetime of such a system remains unclear; however, values of 1-5 years do not appear to be unreasonable, and this probably can be extended through careful design, component redundancy, and future R&D.

The recommended configuration for the seafloor power system would thermochemically reform methane fuel gas from seeps or hydrates to H_2 , which would be converted to electricity in a low temperature fuel cell. Although the long-reaching goal is for the system to be self-sufficient, i.e., to run entirely on ambient fuel and oxidizer resources, our study has concluded that some stored oxidizer brought from the surface will be required, since the current level of technology to extract dissolved O_2 from sea water is not adequate to provide the concentrations needed to reform methane. DO extraction does appear to be a viable option to supply the fuel cell cathode.

Seafloor methane and DO resources were assessed. It was concluded that the energy density of sediment porewater methane and methane dissolved in sea water was too low to sustain operation of a nominal 100 W system. Gas seeps on the seafloor were ranked as the best option to fuel this system, followed by hydrate outcroppings. This restricts the range of potential operating sites. Although the DO resource is extensive, ambient concentrations limit the maximum partial pressures of O₂ that can be recovered in a mass exchanger to about 8 kPa. Based on our resource assessment, we propose two candidate sites to deploy a prototype for field testing. The first is a shallow site in the Santa Barbara Channel where there are strong and persistent hydrocarbon gas seeps that have been extensively characterized. The second site is in deep water in the Gulf of Mexico (GOM) where hydrate outcroppings (and gas seeps) have been observed. Coordinates and oceanographic conditions for both sites are included in this report. Our preferred strategy is to field test a first prototype at the shallow site off California which would allow diver access and facilitate deployment, on-the-fly modifications and repairs, recovery, and data collection. Lessons learned from this initial testing could then be applied to develop a refined and robust system that would be tested at the deep, relatively inaccessible site in the GOM, where the level of risk is higher and the logistics are much more complicated. This staged approach should enhance the probability of a successful proof-of-concept demonstration.

Models of the methane reforming process, PEM and alkaline fuel cells, and direct mass exchangers and membrane contactors to extract DO were developed and associated laboratory experiments were performed to pursue assessments of candidate technologies and the design of an integrated system. A final conceptual design has not yet been identified, pending validation of the membrane contactor model; estimated parasitic pumping losses; and fuel cell performance at elevated pressure and low O_2 mole fraction in methane carrier gas. Preliminary case studies, that couple the reforming, membrane contactor, and AFC models, however, have produced encouraging results that suggest that net power production may be possible with a system operating at seafloor pressures and utilizing DO extraction to supply the fuel cell and stored oxidizer for the reformer. Our experiments have confirmed that aqueous solutions of H_2O_2 can be used successfully to reform methane and are a good choice for the stored oxidizer.

The obvious next step will be to fully test and characterize the major components (i.e., reformer; fuel cell; membrane contactor) individually, first on the benchtop, then in pressure chambers at simulated underwater conditions, and finally offshore. Data obtained will be applied to calibrate and refine our models and for system integration.

In summary, no critical hurdles or fundamental deficiencies in principle or concept were uncovered that would definitively preclude net power production from seafloor methane using existing technologies. It appears possible to develop and deploy a first prototype for field testing within a 5 year time horizon, given appropriate resources. It is recommended that this prototype be tested first in relatively shallow waters and utilize free gas seeps as a fuel resource. The system is expected to utilize a low-temperature fuel cell and a hybrid oxygen supply system comprising stored H_2O_2 solutions and membrane contactors to extract DO from sea water.

I PROJECT DESCRIPTION

The goals of this investigation were: (1)to assess technical feasibility of the concept of generating electrical power, heat, or fuel in the deep ocean from the vast pool of seafloor methane; and (2) if this assessment is positive, then pursue development of best candidate systems concluding with the production of a final design of a prototype.

General technical feasibility (Goal No. 1 above) was examined during the present period of performance that extended from 20 May 2005 through 19 August 2006, by conducting a review of the resource (to quantify reasonable ranges for the extractable supply of fuel and oxidizer, identify contaminants, and characterize relevant ambient conditions) and applicable technologies against the background of levels of performance required to service potential military and commercial applications. Conceptual design studies of candidate systems were conducted and laboratory experiments were initiated to secure data needed to reduce uncertainty related to the primary high risk issues. These primary risk areas are anticipated to center around fuel and oxidizer production and gas quality.

If it could be substantiated that the concept offers adequate benefits to offset technical risks, then a targeted RD&D program comprising four subsequent 12 month Options would be pursued that progressively narrow the field of potential designs until only one best candidate for demonstration remains. A final design of a prototype will be prepared and priced. Fabrication, testing, and field deployment of the prototype may be possible contingent on funding.

The following tasks were undertaken during the initial period of performance:

- TASK 1. Conduct a comprehensive review of data in the technical literature to establish ranges of methane quality and volume, available oxygen, and other relevant conditions (e.g., temperature and currents) that could impact system performance, in target seafloor regions. Methane sources that will be considered include hydrates in the sediment, seafloor seeps of free gas, methane in sediment pores and pore water, and, possibly, methane dissolved in the water column adjacent to strong methane sources.
- TASK 2. Determine criteria for component selection (e.g., no or limited maintenance, desired life, ambient operating conditions, etc.). Identify potential end uses (i.e., define and categorize mission profiles of relevance to the interests of DARPA and national security that would enjoy significant benefits from the development of the proposed concept).
- TASK 3. Review literature on candidate oxygen extraction systems to identify attainable values of performance and power consumption and suitability for application in deep subsea power systems; or consider alternative supply strategies.
- TASK 4. Based on attainable ranges of fuel and oxidizer flow rates and quality, and other criteria, review potential pre-processing techniques and candidate fuel cell types. While we anticipate that a fuel cell module will constitute the primary energy conversion device, other means to utilize the seafloor methane resource will also be considered.

- TASK 5. Develop a system model to integrate subsystems and to conduct parametric studies to optimize configurations and quantify range of efficiencies, power output, etc. Apply these results to prepare conceptual designs of candidate systems that have a high probability of successful implementation under the different methane and oxidizer availability scenarios at power levels adequate to meet the requirements of end uses identified in Task 2.
- TASK 6. Conduct preliminary cost analysis of candidate systems identified in TASK 5.
- TASK 7. Initiate bench top laboratory experiments to identify viable techniques for fuel clean up and conversion of prototypical seep gas or gas generated from sediment hydrates under deep ocean conditions and to estimate performance limits and energy budgets of these techniques.
- TASK 8. Based on the resource evaluations (Task 1), technology reviews (Tasks 2 and 3), and the results of the system integration and modeling studies (Tasks 5 and 6) and preliminary risk mitigation experiments (Task 7), identify principal risks and benefits; evaluate technical feasibility; determine performance and cost metrics; estimate performance and cost targets; and develop an RD&D plan for subsequent phases that include critical paths and milestones.

II TECHNICAL ACCOMPLISHMENTS

The original scope of work evolved over the period of performance of this project. In particular, Tasks 5, 6 and 8 were scaled back, since it has not been possible to date to identify clearly a viable oxygen supply system, while Tasks 3 and 7 were expanded significantly to address, via additional experiments, a number of critical technical issues that emerged during the course of this study. As discussed below, current or near-time-horizon technologies to extract ambient oxygen dissolved in sea water do not appear to be capable of providing sufficiently high concentrations of O_2 to sustain operation of a methane reformer; some form of stored oxidizer probably will be required. Although strategies have been proposed to address this problem, further investigation is necessary to demonstrate whether any of these strategies are actually feasible. At the current level of uncertainty about the oxygen supply, proceeding with the conceptual design of a complete, integrated system, and the optimization and costing of this system, probably would not produce meaningful results.

An accounting is provided below of the accomplishments of this study in four general areas of consequence to the development of a nominal 100W seafloor power system: 1) resource evaluation; 2) identification of candidate sites for prototype deployment; 3) component and system requirements; and 4) assessment of technologies for fuel gas conditioning, oxygen supply, and power generation. Results obtained since the third Quarterly Report are also included in this Section. Technical details have been provided in the previous three Quarterly Reports and are included in this Final Report, for convenience and completeness, as Appendices A, B, and C.

II.1 Methane and oxygen resource evaluation

Ambient fuel and oxidizer resources were evaluated and ranked on the basis of their ability to sustain operation of a seafloor power system that can produce of the order of 100W for an extended period of time (years). Implicit to this assessment was whether technologies currently exist to process the available ambient resources to produce the volumes, concentrations, and levels of purity required by the candidate power generation units (in this case, fuel cells) and the energy penalties associated with this processing. Clearly, energy parasitics of the fuel and oxidizer processing must not exceed the gross power generated. The costs of the technologies were a secondary consideration.

II.1.1 Methane resource

II.1.1.1 resource viability

Four major sources of methane exist near the seafloor. At depths typically below about 500 m, vast quantities of methane hydrate are found worldwide, dispersed in the sediment on the continental margins. Although most of this hydrate lies beneath the seafloor, surface hydrate mounds have been observed to occur at many locales. Methane gas seeps, usually from thermogenic sources, have been detected over a range of depths. Methane dissolved in sea water or sediment porewater can be found throughout the oceans and in estuarine environments.

Table 2.1.1, reproduced from the proposal for this project, provides estimates of net power production for two sets of methane and oxygen supply rates at different values of overall system efficiency (defined as net power divided by the higher heating value of the methane fuel). The O_2 capture efficiency determines the amount of oxygen that can be extracted assuming that 100 l/s of sea water with 100 µmol/l dissolved O_2 is processed by an artificial gill or similar device. Methane supply rates are the stoichiometric values corresponding to the O_2 supply rate.

Sea water	DO	O ₂ Capture	O ₂ Supply	CH ₄	Assumed	Estimated
Collection	Concentration	Efficiency	Rate [g/s]	Supply	System	Net Power
Rate [l/s]	[µmol/l]			Rate [g/s]	Efficiency	[W]
100	100	10%	0.032	0.008	10%	45
100	100	10%	0.032	0.008	20%	89
100	100	20%	0.064	0.016	10%	89
100	100	20%	0.064	0.016	20%	178

 Table 2.1.1
 Net Power for O₂-Limited System

Based on the information provided in this Table, the minimum methane supply rate needed to attain the target power is approximately 0.016 g/s, which is equal to 10^{-3} mol/s or about 24 standard cm³/s.

During the first three quarters of this investigation, an extensive survey of the technical literature on the four major sources of seafloor methane was undertaken as detailed in Appendices A, B, and C. Additional information on hydrates and pore water methane was provided by NRL. Their report is included as Appendix D. Table 2.1.2 summarizes the major conclusion about the candidate methane resources.

Resource	Primary Advantages	Primary Disadvantages	Ranking
Methane gas vents	Large fluxes of gas phase	Not widely available;	Best choice
	CH ₄ ; no energy required to	temporal stability of gas	for proof-of-
	produce gas; found in	vents unknown; gas may	concept
	shallow and deep water	contain high levels of	
		contaminants	
Hydrates	Large amounts of methane	Gas recovery requires	Second
	in hydrates in many areas	energy; recovery	choice
	of the deep ocean;	technologies not verified;	
	relatively clean gas	generally available only at	
		depths $> 500 \text{ m}$	
Pore water methane	Widely available	Concentrations and natural	Unacceptable
		fluxes only capable of	
		sustaining milli- or micro-	
		watts of power; difficult to	
		recover methane	
Dissolved methane in	Widely available	Concentrations too low to	Unacceptable
sea water	throughout the ocean	produce any significant power;	
		unneur to recover methane	

Table 2.1.2 Comparison of seafloor methane resources

Sediment pore water methane and methane dissolved in sea water are available throughout the oceans; however, concentrations typically are extremely low. NRL analyzed heat flow and pore water chemistry data from methane-rich regions for this study (Appendix D) and estimated an average natural flux of CH₄ upward through the sediment of approximately 0.1 mol/m²/year (approximately 3×10^{-9} mol/m²/s). At this level, all the pore water methane over a region of about 3×10^{5} m³ (30 hectares) would need to be collected to produce the target power. Over most of the ocean, the amount of methane dissolved in sea water rarely exceeds a few nanomolar (Nihous & Masutani, 2006), which is six orders of magnitude smaller than in sediment pore water. Near strong seafloor methane sources, concentrations have been observed to reach micromolar levels over a limited region. Even at these unusually high levels, the minimum methane supply rate of 10^{-3} mol/s would require processing 10^2 - 10^3 l/s of sea water at 100% CH₄ collection efficiency. At typical nanomolar levels, this would increase to thousands of cubic meters of sea water per second—which clearly is not a feasible option to sustain a 100 W power generation unit.

Unlike pore water methane and methane dissolved in the water column, seafloor vents of free methane gas and methane hydrates represent highly concentrated sources of fuel. As discussed in the three Quarterly Reports included as Appendices, seafloor vents appear to provide the best opportunity for the deployment of a first proof-of-concept, subsea power generation system. In the long-term, methane hydrates—particularly surface outcroppings and deposits just beneath the seafloor—will also be viable candidates for exploitation, since they are more widely available than vents, albeit at depths below 500 m. Recovery of methane gas from the solid hydrates is the primary technical disadvantage of this resource. Recovery will impose an energy penalty on the system and techniques that have been proposed to accomplish need to be verified.

To summarize, our evaluation of the four major sources of seafloor methane has led us to dismiss methane dissolved in sediment pore water or sea water as a viable fuel resource for the present application. CH_4 gas vents are the clear first choice to test and demonstrate a proof-of-concept nominal 100W seafloor power generation facility. Methane hydrates also appear to be viable, contingent upon confirmation of appropriate gas recovery techniques. One major consequence of these conclusions is to limit the range of potential operating sites to vicinities near methane vents and rich hydrate beds. This may not be as restrictive as it seems, since anecdotal information in the literature suggests that seafloor vents and outcroppings are encountered in many areas of strategic and commercial interest.

II.1.1.2 contaminant species in fuel

The two candidate methane sources, seeps and hydrates, will provide gas mixtures comprising primarily CH_4 , alkanes and heavier hydrocarbons, some CO_2 , and other trace contaminants. Since conventional PEM or alkaline fuel cells are targeted to be employed as the power generating unit, the raw fuel gas will need to be converted to H_2 via a reforming step. Catalytic thermochemical reforming (probably followed by water-shift) is believed to present a manageable level of risk when adapted to the relatively unique conditions of the present application (e.g., high pressure, limited available oxidizer; hands-off service); hence, it currently is the method of choice. The sensitivity of both the fuel cell module and the reformer to various

catalyst poisons are well-documented. It is therefore essential, particularly in light of the anticipated inability to perform maintenance/repair service, that contaminant species of consequence in the raw gas entering the reformer and the reformed gas entering the fuel cell exist at acceptably low levels so as not to degrade performance or lifetimes of these components.

A survey of the literature on the composition of gas collected from seafloor methane seeps and produced by the decomposition of marine hydrates was initiated by the UH personnel at the start of this project. NRL also undertook a parallel review and their report on this subject is included as Appendix E. Table 2.1.3, reproduced from the first Quarterly Report, outlines profiles of contaminants in gases collected from various sources and sites. Although these analyses were not comprehensive, the evidence suggests that H_2S is the species of greatest concern. Table 2.1.4, extracted from the NRL report, provides supplemental information on H_2S levels.

Based on the literature reviews, a baseline of 1000 ppmV H₂S was adopted and laboratory gas mixtures with this level of contaminant loading were employed to investigate the performance of potential gas purification processes. Data on gases released from the strong vents offshore Coal Oil Point in the Santa Barbara Channel that have been extensively documented support a baseline of 1000 ppmV H₂S. In the case of methane gas released from hydrates, several examples have been reported where H₂S was detected in significant excess of 1000 ppmV. Milkov et al. (2005) analyzed hydrates from the Cascadia Margin and determined an average sulfide concentration of 0.27% (i.e., 2700 ppmV). It has been observed that there can be large variations in H₂S over the same general area. Kastner et al. (1998) reported sulfide concentrations as high as 18.5% (185,000 ppmV) in hydrates from one location on the Cascadia Margin; however, Milkov (2005) states that this is an unusual exception and their review of the available data for sites throughout the world concludes that contaminants generally are present in released hydrate gas at very low trace levels. He suggests a conservative, representative concentration of sulfide of about 1000 ppmV, which agrees with our baseline value. In consideration of the possibility of excessively high sulfide content at a given locale, predeployment surveys should be conducted to screen out sites with unacceptable gas quality.

II.1.2 Oxygen resource

This investigation was undertaken assuming that, to the extent that is practicable, oxygen dissolved in sea water would be employed to react with the seafloor methane (via partial oxidation in the reformer and full oxidation of the product H_2 in a fuel cell) to produce electrical power. The dissolved oxygen (DO) resource was evaluated to identify ambient concentrations at different depths and locations. This information is critical to assess the capabilities of technologies, such as artificial gills, to extract and concentrate the O_2 so that it can be used in the reformer and fuel cells.

Oxygen from the atmosphere diffuses into sea water through the air-water interface. Biological processes, such as respiration and photosynthesis, modulate the dissolved oxygen pool, along with various aqueous chemical reactions. As shown in Figure 2.1 which was included in the research proposal, dissolved O_2 levels typically decline with increasing depth. Certain transport

	Gas Composition										
					NonMethane			Sample	Seafloor		
Ref.					Hydrocarbons	a1	Gas	Depth	Depth		No. of
No.	CH ₄	N ₂	O ₂	CO ₂	Total	H ₂ S ¹	Source	(m)	(m)	Location ²	Samples
1	79.4	13.8	4.5	>0.1	2.2		seep	1	20	а	4
1	76.7	14.4	6.0	>0.1	-		seep	1	20	а	6
1	79.5	12.6	5.0	>0.1	2.8		seep	1	20	а	2
1	90.8	4.9	1.8	0.2	2.4		seep	10	20	а	2
1	84.4	8.1	3.0	0.1	-		seep	10	20	а	2
1	86.4	7.5	2.8	>0.1	3.2		seep	10	20	а	2
1	84.2	2.5	0.3	10.6	2.3		seep	20	20	а	1
1	81.9	1.4	0.2	13.4	-		seep	20	20	а	4
1	84.0	1.5	0.3	11.2	3.0		seep	20	20	а	4
2	98.0				0.1	ND	seep	123	123	b	
2	98.1				0.004	ND	seep	43	43	с	
2	93.2				0.003	ND	seep	83	83	d	
3 ³	87.5	0.8	0.1	1.3	10.2	0.002	seep	57	67	e	168
4	99.1	0	0	0.83	0.043	0.02	hydrate	~3160	3160	f	
5						0.27	hydrate			g	
						0.04 to					
6						0.15	hydrate			h	
¹ ND=not	detected by odo	r									
² a= Shan	e Seep (Coal Oil	Point C	A)								
b=Coqui	ille Bank (Cape]	Blanca O	R)								
c=Bluff	Seep (Eel River	CA)									
d=Hecta	Bank Seep (Flo	rence OR	5)								
f=K 7R	e-seep rents (Coar OII Point CA)										
$\sigma = Casca$	a=Cascadia Margin										
h=Blake	h=Blake Ridge - East Coast										
³ NonMet	³ NonMethane Hydrocarbons included 5.1% C ₂ H ₆ , 3.1% C ₃ H ₈ , 0.9% n-C ₄ H ₁₀ , 0.4% iso-C ₄ H ₁₀ , 0.2% n-C ₅ H ₁₂ , 0.2% iso-C ₅ H ₁₂ , 0.3% C ₆ H ₁₄ ,										
Reference	Deference Kay (Column 1): No. 1 = Clark et al. (2002): No. 2 = Colling et al. (2005): No. 2 = Clark et al. (2000): No. 4 = Charles et al. (2004): No. 5 = $M^{(1)}_{112}$, $M^{(2)}_{122}$, M										
		0.1 - Clair	<i>cei ui.</i> (2	.005 <i>)</i> , 110. 2	$2 = \text{Conter } ei \ ai. (2005)$	1, 100.5 - Clai	к <i>еі Ш</i> . (2000), Г	10. 4 – Charlou e	<i>i ui.</i> (2004), 110. 5	- willkov <i>ei ül</i> . (200 <i>3</i>), 110.
o = Pau	6 = Pauli et al. (1996)										

 Table 2.1.3
 Summary of gas compositions of seep gas and dissociated hydrates reported in the literature

Region	% H ₂ S	Reference
Northern California	odor	Brooks et al., 1991
Hydrate Ridge Cascadia Margin	<3	Bohrmann et al., 1998
Blake Ridge	0.04-0.15	Paull et al., 1996
Hydrate Ridge, Cascadia Margin	18	Kastner et al., 1998
Cascadia Margin	0.27	Milkov et al. 2005
Green Canyon, Gulf of Mexico	0.51	Milkov et al. 2005
Congo Angola Basin	0.05	Milkov et al. 2005
Southern Summit, Oregon	0.06-1.20	Milkov et al. 2005
Black Sea	0.25	Milkov et al. 2005
Caspian Sea	0.05	Milkov et al. 2005

 Table 2.1.4
 Hydrogen sulfide in hydrate gases from different regions



Dissolved Oxygen (micromol/kg)

Figure 2.2.1 O₂ variability: comparison of dissolved oxygen profile in the Northern Pacific and the anoxic Carioca Basin. HOT data extracted from http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html.

phenomena, such as upwellings which push low- O_2 water to the surface, and basin circulation can affect the local oxygen content.

The National Oceanographic Data Center of NOAA (NODC) provides an extensive database on monthly and yearly averaged DO concentrations at various depths throughout most of the world's oceans. These data were coded and we are able to determine dissolved oxygen concentrations at a given depth at locations on a 1 degree latitude x 1 degree longitude grid (approximately 60 x 60 nautical miles). This level of accuracy and resolution appears to be acceptable for the purpose of evaluating oxygen extraction techniques during the conceptual design phase. As in the case of the methane resource, it is presumed that better site-specific DO information will be collected by oceanographic surveys, in order to produce reliable preliminary and final designs.

Since the start of this project, we have been concerned about the possibility that O_2 is depleted locally in regions adjacent to strong seafloor methane sources. Anecdotal reports suggest that this behavior does occur. Since the performance of the present system is oxygen-limited, any reduction of DO levels is a major issue. To date, we have not been able conclusively to resolve this question. A review of the available data has revealed no consistent correlation between depleted concentrations of O_2 and elevated levels of methane; however the database is not comprehensive and the spatial resolution generally is too coarse to identify phenomena occurring at a relative fine scale (i.e., meters or tens of meters). Additional field surveys that map DO, dissolved hydrocarbons, and currents near vents and hydrate accumulations are needed to address this concern during preliminary and final design.

II.1.2.1 contaminant species in oxidizer

DO must be extracted from the sea water solvent and fed as a gas in order to accomplish the methane reforming. While it may be possible to supply oxygen to the fuel cell cathode with liquid carriers such as sea water or PFCs (perfluorocarbons),this needs to be verified (see Section II.4); the conventional approach again is to feed O_2 as a gas. Specific contaminants that can compromise operation and lifetimes of the reformer and fuel cell and their levels will depend on how DO is processed and supplied to these components. For example, membrane separation to provide gas phase O_2 may or may not selectively filter out other dissolved gases, such as N_2 , CO_2 , etc. Transfer of the DO into another liquid carrier such as PFC may not exclude other dissolved chemical or biological contaminants in sea water which could negatively impact the fuel cell cathode. As mentioned previously, since the O_2 supply system has not yet been identified, the issue of contaminant species in the oxidizer is deferred until more information on the selected systems is available.

II.1.3 Resource evaluation summary

The primary results of the investigation of ambient fuel and oxidizer resources to determine their suitability to sustain operation of a seafloor power system are:

• The minimum methane supply rate needed to attain a target net power of the order of 100 W is approximately 10⁻³ mol/s.

- Methane dissolved in sediment pore water or sea water is not a viable fuel resource for the present application.
- CH₄ gas vents are the first choice to test and demonstrate a proof-of-concept seafloor power system.
- Methane hydrates, like vents, represent a highly concentrated sources of fuel and appear to be a viable option; however, techniques to recover methane gas from hydrates need to be verified.
- Confining the fuel source to vents and hydrates restricts the range of potential operating sites.
- The primary contaminant of concern in vent gas and hydrate gas is H₂S; levels in excess of 1% H₂S by volume have been detected, but a typical concentration which will be employed to test gas clean-up systems is 1000 ppmV.
- Data from the National Oceanographic Data Center of NOAA have been coded to determine DO concentrations at a given depth at locations on a 1 degree latitude x 1 degree longitude grid; the level of accuracy is believed to be acceptable to proceed with a conceptual design study.
- We have not been able conclusively to rule out the possibility that O₂ is depleted locally in regions adjacent to strong seafloor methane sources; this is an important concern since the present system is oxygen-limited.
- Contaminants of concern in the oxidizer supply will depend on the procedures employed to extract DO from sea water and deliver it to the reformer and fuel cell; these procedures have not been finalized so the assessment of oxidizer contaminants has been deferred.
- Additional site-specific data on the ambient methane and oxygen resource will need to be collected during the preliminary and final design phases.

II.2 Candidate sites for prototype deployment

The ultimate goal of the present RD&D program is to deploy and field test a first prototype seafloor power system that utilizes seafloor methane and dissolved oxygen in sea water to generate of the order of 100W net. Toward this end, candidate sites for this proof-of-concept demonstration were evaluated. Site selection is an essential step in advancing the design process, since it establishes many of the critical design parameters, such as fuel quality, ambient DO levels, depth of operation, operating pressures and temperatures, currents, accessibility, etc. It was decided to provide options for both vents and hydrates. Based on our survey of the methane resource, four sites in two geographical areas within the U.S. EEZ were identified. The first area is off Coal Oil Point in the Santa Barbara Channel, shown in Figure 2.2.1 reproduced from Leifer *et al.* (2000). Very active and relatively shallow (<100 m depth) natural gas bubble seeps have been surveyed there. The 1° latitude-by-1° longitude square closest to the Coal Oil Point seeps that was used to determine dissolved O₂ concentrations is shown in Figure 2.2.2.

Three other sites overlying seafloor hydrate mounds in the Gulf of Mexico (GOM) also merit consideration. These include the Atwater Valley mounds shown in Figure 2.2.3 and surveyed by NRL. The sites encompass the three mounds and corresponding gas bubble seeps discussed in Leifer & MacDonald (2003). Figure 2.2.4 provides the coordinates of the three sites.



Figure 2.2.1 Map of natural gas seep field off Coal Oil Point, Santa Barbara Channel.



Figure 2.2.2 1° latitude by 1° longitude square from WOA01 database (NODC) closest to Coal Point seeps.



Figure 2.2.3 Map of Atwater Valley gas hydrate mounds in the Gulf of Mexico.



Figure 2.2.4 Map showing 3 bubble seeps above seafloor hydrate deposits (▲) in the Gulf of Mexico and the Atwater Valley mounds (●); corresponding 1° latitude by 1° longitude square from WOA01 database (NODC) are outlined in red.

Corresponding environmental data are presented in the form of depth-varying profiles. A thick black line always identifies the Santa Barbara Channel site and terminates at 600 m depth (the seafloor is reached before the next WOA01 depth level of 700 m). A thin blue line represents the easternmost site in the Gulf of Mexico (centered at longitude 89.5°W). Thin green and red lines correspond to the two sites in the Gulf of Mexico respectively centered at longitude 91.5°W and longitude 92.5°W; due to the proximity of these two sites, the data are essentially the same.

Annual mean temperature is shown in Figure 2.2.5. Figure 2.2.6 presents the annual mean salinity.

The following equations are used to derive several of the environmental parameters:

$$\sigma_{t}(z) = \rho\{0, T(z), \overline{s}(z)\} - 1000$$

$$p(z) = p_{atm} + g \int_{0}^{z} \rho\{p(z'), \overline{T}(z'), \overline{s}(z')\} dz'$$

$$f_{O_{2}}(z) = [DO] \frac{X_{O_{2};dry}\{p_{atm} - p_{sat}(\overline{T})\}}{C_{0}^{*}(\overline{T}, \overline{s}) \exp\{-v_{liq,O_{2}}(p - p_{atm})\}}$$

Due to the nonlinearity of some physical relationships, these parameters strictly are not annual means. Instead, they are estimates obtained with the annual means of temperature, salinity and DO. The topmost equation is a practical definition of potential density (σ_t) where pressure effects on density are excluded. σ_t is sufficient to understand the relative stability of water masses. The second equation, implicit in the pressure *p* allows the simultaneous determination of pressure and density ρ . The last equation relates DO to oxygen fugacity; low oxygen fugacities (of the order of less than one bar) can be interpreted as oxygen partial pressures. In those equations, the functional dependence of density on temperature, salinity and pressure is the formula proposed by Fofonoff (1985). The solubility C_0^* of oxygen in equilibrium with a saturated humid atmosphere of standard composition ($X_{O2;dry} = 0.2095$) is given in García & Gordon (1992).

Figures 2.2.7 and 2.2.8 show σ_t and ρ , respectively. As expected, Figure 2.2.9 exhibits a hydrostatic pressure *p* that is quasi-linear with depth.

DO profiles are provided in Figure 2.2.10. An oxygen minimum is notable in the GOM, while DO levels plummet with depth in the Santa Barbara Channel; this latter feature is typical along coastlines where upwelling and oxygen utilization are substantial. For the purpose of possible oxygen extraction from sea water, however, the true measure of useful oxygen content is oxygen fugacity, shown in Figure 2.1.11. It is observed that the relatively higher DO near-surface values in Santa Barbara merely reflect colder sea water temperatures in Northern California. The slightly lower near-surface oxygen fugacities for the GOM represent the effect of higher vapor pressures with higher temperatures.



Figure 2.2.5 Annual mean temperature profiles from WOA01 database for the selected 1° latitude by 1° longitude squares.



Salinity (ppt)

Figure 2.2.6 Annual mean salinity profiles from WOA01 database for the selected 1° latitude by 1° longitude squares.



Sigma-t (kg/m³)

Figure 2.2.7 σ_t estimates for the selected 1° latitude by 1° longitude squares



Density (kg/m³)

Figure 2.2.8 Density estimates for the selected 1° latitude by 1° longitude squares.



Pressure (bar)

Figure 2.2.9 Pressure estimates for the selected 1° latitude by 1° longitude squares.



Dissolved Oxygen (ml/l)

Figure 2.2.10 Annual mean DO profiles for the selected 1° latitude by 1° longitude squares.



Oxygen Fugacity (kPa)

Figure 2.2.11 Oxygen fugacity estimates for the selected 1° latitude by 1° longitude squares.

Data on currents at the candidate sites, if they exist, have not been located to date. While this information is not essential during the conceptual design phase, it will be needed eventually to develop a deployment plan and to address anchoring and structural issues. Current information would also be useful with respect to sea water collection for DO extraction, since ambient currents could be used to offset the parasitic power losses of pumps employed to push DO-laden sea water through gas separation membranes.

The information provided above, in addition to the profiles of fuel gas composition described in Section II.1.1, is believed to constitute an adequate data set to undertake a conceptual-level design study for two scenarios utilizing gas vents or hydrate outcroppings at the candidate sites.

The three seep sites in the GOM lie between 500 m and 1000 m depth and the hydrate mounds in Atwater Valley are found between 1000 m and 1500 m. As indicated in Figures 2.2.10 and 2.2.11, ambient DO concentrations and fugacities at these deep sites are about half the values encountered around the shallow gas vents in the Santa Barbara Channel. Since the power generation system is expected to be oxygen-limited, the reduced DO content presents a significant disadvantage for the deep sites. Moreover, as discussed below, other factors, including accessibility and servicing, and reformer performance, favor a shallow site for a proof-of-concept experiment. It would be reasonable, therefore, to recommend a shallow gas vent for first prototype deployment to enhance the probability of successful execution of this complicated

endeavor. Trials in deeper sites could then be attempted, applying the knowledge and expertise gained from the shallow deployment.

II.2.1 Candidate sites summary

The primary results of the survey of candidate sites for the deployment of a prototype subsea power generation system utilizing seafloor methane are:

- Based primarily on our survey of the methane resource, four sites in two geographical areas within the U.S. EEZ were identified. The first area is off Coal Oil Point in the Santa Barbara Channel. The other three sites overlie seafloor hydrate mounds in the Gulf of Mexico.
- The methane source in the Santa Barbara Channel is free gas vents at relatively shallow depths typically less than 100 m. These vents have been studied extensively, so an excellent database exists on gas composition, contaminants, flow rates, and spatial and temporal properties.
- The GOM sites include deep gas seeps and hydrate mounds. The seeps occur at depths between 500 m and 1000 m; hydrate mounds located in Atwater Valley are located between 1000 m and 1500 m.
- Ambient conditions, including temperature, pressure, density, salinity, DO concentrations and fugacities, have been secured for the candidate sites. This information is believed to be sufficient to conduct a conceptual design study of the power generation system.
- Data on currents at the sites have not been located; while these data are not essential during the conceptual design phase, they will be needed later to develop deployment plans and to address various structural and anchoring issues.
- DO levels and fugacities at the deep sites are approximately half the values at the shallow vents; this is a significant disadvantage for the present oxygen-limited system. Other factors also favor a shallow locale for first prototype deployment and testing.
- It is recommended that the first prototype be sited on a gas vent in the Santa Barbara Channel or similar shallow location to enhance the probability of success. Knowledge and expertise gained from this trial could then be applied to deeper deployments and to systems utilizing hydrate sources, which have greater inherent technical risks.

II.3 Component and system requirements

The primary requirement for the power system under development is that it be capable of generating net power of the order of 100 W. This establishes general thresholds of performance for individual components, taking into consideration the feasible range of capabilities of current technologies. While net power output is the principal parameter, the design of the system is also determined by several other operating requirements, including intended end-uses, desired lifetimes, accessibility and maintenance schedules, and cost. With the exception of costs, which are not immediately relevant for technical proof-of-concept, these requirements related to the mission profile of the seafloor power generation system are discussed below.

II.3.1 Mission profiles

Selection of individual components and the design of the integrated system will be based on satisfying specific mission profiles under constraints imposed by resource availability and ambient operating conditions. Following discussions with DoD program personnel and other potential end users (e.g., AUV/UUV developers; ocean scientists pursuing long-term seafloor monitoring) and a survey of the literature, we have attempted to define an appropriate profile for the nominal 100 W (net) subsea power system.

II.3.1.1 lifetime

This project is part of a larger program to develop means to sustain activities of importance to national security and defense, including surveillance and environmental monitoring, in the littoral zone, beyond limits currently imposed by a number of factors, but primarily the lifetime of conventional energy sources such as marine batteries. The subsea power generating systems using seafloor methane, which are the focus of the present effort, were conceived for application in the deep ocean as well as the shallow littoral region.

The lifetime of conventional energy storage devices for subsea applications, such as marine batteries, typically does not exceed 6 months to a year, depending on ambient conditions, power draw, etc. Furthermore, certain instruments and devices consume too much power to be reliably operated by batteries. Table 2.3.1 from Kurasaki (2004) provides examples of peak and duty cycle power consumption of some typical oceanographic instruments.

Instrument	Peak Power Requirement, W	Duty Cycle Power
	_	Budget, W
Air-Sea Flux	1-2	
Gyroscope	10	0.06
Seismograph	1.5	
Acoustic Doppler Current	0-100	0.07
Profiler		

 Table 2.3.1 Power requirements of some seafloor instrumentation.

Assuming that conventional fuel cell technology will be applied in the system under design and that minimal or no servicing will be possible for deeply deployed devices, we tentatively propose that the target lifetime be 3 to 5 years. This would provide a substantial performance benefit over batteries that would probably justify development. While it is not possible at this point to anticipate all possible failure modes since specific components have not been selected, the two most vulnerable components appear to be the fuel cell module and reformer catalysts. Fouling could also occur in the fuel gas purification and DO extraction systems, and various ancillary equipment (e.g., pumps) could fail. It will be essential carefully to evaluate individual component lifetimes during the preliminary design phase and to optimize operational procedures for longevity as well as incorporate, as necessary, redundant (back-up) equipment into the system.

At this point, there is a definite limitation on the lifetime of the candidate fuel cell modules. Operating histories of conventional fuel cells have been reported fairly extensively in the literature. The range of reported lifetimes are: PEMFC ~ 3,000 hours; Alkaline FC ~ 5,000 hours; SOFC > 10,000 hours. These values generally correspond to well-maintained units operating with conventional design limits. With the exception of SOFC, which currently is not being considered as a prime candidate for this application, these lifetimes fall short of one year (8760 hours). Factors that affect fuel cell longevity are discussed in Section II.4.1. One obvious, but non-trivial, means to extend the lifetime of the fuel cell module is to incorporate back-up stacks that can be switched into service when the online fuel cell fails. By this means and/or by operating with a modest duty cycle (say, 20%) it appears possible to attain the proposed 3-5 year lifetime. (Note, however, that on-off operation can compromise fuel cell lifetimes, particularly for PEMFC.)

II.3.1.2 maintenance schedule

Systems utilizing seafloor methane seeps deployed in the shallow littoral zone or at diveraccessible depths (typically < 1,200 feet of sea water--fsw) can be serviced. Except in very cold water, hydrates are found below these depths and power systems supplied with methane from hydrates will need to be designed to operate over their targeted lifetimes with no maintenance. Although ROVs (remotely operated vehicles) could perform some simple repair or recovery operations, the cost is expected to be prohibitively high. The following preliminary maintenance schedule should be employed for component selection purposes:

- Below 1,200 fsw depth: no servicing or repair over the mission lifetime.
- Above or at 1,200 fsw depth: annual servicing or repair possible at < 300 fsw (military diver scuba limit); longer maintenance intervals with increasing depth.

II.3.1.3 applications

Two primary products have been identified for the subsea power generation systems:

ELECTRICITY GENERATION. The objective is to produce electricity for recharging AUVs (autonomous underwater vehicles) or UUVs (unmanned underwater vehicles), or for underwater instruments or monitoring devices, particularly those with electrical requirements that exceed the capabilities of batteries or microbial fuel cells.

FUEL (AND OXIDIZER) PRODUCTION. The objective is to produce and store fuel (e.g., H_2 , pure CH₄, methanol) and, possibly, oxidizer to refuel AUVs or UUVs. Electricity is generated only at levels needed by system equipment such as pumps.

From a thermal systems perspective, the second application (Fuel Production) constitutes a subset of the first application: in this case, the fuel cell module is transferred from being part of the electrical power generation system to the end-use. The primary functions that need to be performed by the electrical power generation system, i.e., DO extraction, fuel gas purification and reforming to hydrogen, are the same as for Fuel Production. The main point of departure is that relatively high concentration O_2 gas might need to be produced and stored for AUV/UUV

use. Employing liquid carriers to deliver oxidizer to the (on-board) fuel cell cathode, which is being investigated for electricity generation, does not appear to be an option in the second application. In consideration of these points, it is recommended that the design effort focus on electricity generation, since the results should provide much of the information needed to respond to a fuel production application. Moreover, while several prototype fuel-cell-powered AUVs recently have been tested (Sawa *et al.*, 2005; <u>http://www.jamstec.go.jp/jamstec-e/rov/auv_ex1.html</u>), the overwhelming majority of military, commercial, and scientific AUV/UUVs employ conventional battery designs. Besides being validated technology, battery-powered underwater vehicles enjoy certain technical advantages (Davies & Moore, 2006) and appear to represent the primary user base for a seafloor power station for years to come.

Low-power systems, such as microbial fuel cells that are under development under funding by DARPA ATO, may be suitable for many instrument power applications. The advantage of the subject nominal 100 W system relates to active monitoring and surveillance devices and recharging AUV/UUVs to extend mission range and duration and to reduce exposure associated with surfacing. The feasibility of employing the subject power system to perform this function was examined and is discussed in below.

AUV/UUV Battery Charging Application

Battery technologies employed in current AUVs are listed in Table 2.3.2.

Technology	Energy Density	Voltage/Cell	
	W-h/dm ³	V	
Lead-acid	10-20	2.8	
NiCd/NiMH	10-30	1.2	
Silver-Zinc	30 - 50	1.45	
Lithium Ion	40 - 70	4.0	

Table 2.3.2 Properties of battery cell technologies used in AUVs (Storkersen & Hasvold 2004).

Batteries packs are composed of combinations of individual cells connected in series and in parallel to achieve the necessary voltage and current. The estimated recharging capability of a 100 W fuel cell is presented in Table 2.3.3. It is assumed that the fuel cell can be operated at any combination of voltage and current and that power transmission (i.e., recharging) efficiency is approximately 100%. Actual transmission efficiency may be as low as 70% - 80%, which will increase recharging time commensurately. Appropriate circuits need to be designed to provide the necessary electrical characteristics. A number of recent publications describe circuits that are being tested for *in situ* AUV battery recharging (Kojiya *et al.*, 2004; Kawasaki *et al.*, 2004; Han *et al.*, 2006). Given the power requirements of some of the larger AUVs, an on-site energy storage system comprising batteries or capacitors may be needed to supplement the fuel cell in order to reduce the excessively long recharging times. The fuel cell output would be stored by these devices during the periods between charging events.

			<i>a</i>	Charging	Recharge
AUV	Energy	Voltage	Capacity	Current	Time
	kWh	V	Ah	А	Н
Duke Robotics	0.5	29.6	16	3.4	4.7
Remus 100	1.0	14	71	7.1	10.0
HUGIN 1	3.6	32	113	3.1	36.2
HUGIN 3000	4.0	8	500	12.5	40
HUGIN 1000	15	50	300	2.0	150.0

Table 2.3.3	ALIV hattery	recharging pro	nerties of a	100 W fue	cell system
1 abic 2.3.3	AU V Dattery	recharging pro	perfices of a	100 w 1uc	i con system

The recharging times do not appear to be prohibitively excessive in comparison to values reported in the literature; however, in these conventional situations where available power is not an issue, recharging protocols are optimized for acceptable thermal management. This typically results in relatively long recharging times.

AUV/UUV recharging appears feasible even with a system based on a relatively low power fuel cell, provided that energy storage is included and appropriate electronics can be designed to provide the necessary voltage-current characteristics over time and to minimize transmission losses.

II.3.2 System requirements summary

System requirements were developed for the nominal 100 W (net) subsea power generation system to guide the selection and integration of components:

- The design net power output is of the order of 100 W.
- A target lifetime of 3-5 years would appear to provide adequate benefits over conventional batteries to justify development.
- Although it is not possible at this point to anticipate all possible failure scenarios since specific components have not been selected, the two most vulnerable components appear to be the fuel cell module and reformer catalysts. Other areas of concern include fouling of the fuel gas purification and DO extraction subsystems and failures of various ancillary equipment such as pumps.
- Operating histories for PEMFC and AFC reported in the literature suggest that lifetimes of these devices are less than 1 year; attaining the target lifetime of 3-5 years may require redundant components and/or reduced duty cycle operation.
- Component lifetimes need to be critically assessed once they have been tentatively identified on the basis of performance.
- System lifetimes also depend on the ability to perform repairs or maintenance. Limited access will impose more stringent requirements on components. We propose the following maintenance schedule: no servicing or repair over the mission lifetime below 1,200 fsw depth; annual servicing or repair will be possible at < 300 fsw (military diver scuba limit); longer maintenance intervals with increasing depth up to 1,200 fsw.
- The two primary products for the subsea power generation system are: 1) electricity production for instrument power or AUV/UUV battery recharging; 2) production and

storage of fuel (e.g., H₂, pure CH₄, methanol) and, possibly, oxidizer to recharge fuel cell or combustion-driven AUVs or UUVs.

• The system to produce fuel for AUVs constitutes a subset of the one required to generate electrical power. It is recommended, therefore, that the present design effort focus on electricity generation, since those results should provide much of the information needed to respond to a fuel production application

II.4 Technology assessments

A range of options were considered to convert the chemical energy of methane to electrical power. At larger scales, Otto, Brayton, and Rankine cycles (i.e., internal combustion, gas turbine, and vapor power cycles, respectively) conventionally are applied for this purpose. In the present application, however, the extremely low target power and limited accessibility for maintenance make these options considerably less competitive or impracticable. To put things in perspective, 100 W = 0.13 horsepower. The smallest gasoline-powered internal combustion engines used for model (radio controlled) aircraft with displacements of a few cm³ typically produce around 1 hp. Furthermore, Otto, Brayton, and Rankine cycles require a host of rotating or reciprocating components that are subject to wear and failure. Fuel cells, on the other hand, are well-suited to generate power in the range of interest (i.e., of the order of 100 W). The cells themselves have no moving components, although pumps and fans may be required to supply fuel and oxidizer to the anode and cathode, and to circulate liquid electrolytes or remove condensates. Electricity is produced directly by the fuel cell, without a generator that is required in conventional combustion power systems. Ignoring cost issues, the primary drawbacks of fuel cells are their vulnerability to catalyst poisons in the reactant streams and limited validated lifetimes. Table 2.4.1 compares the power systems that were evaluated for this application.

Although the associated disadvantages do not entirely preclude consideration of the three conventional combustion cycles, the fact that existing fuel cells can readily generate the desired levels of power without significant scale-down, as well as their relative (mechanical) simplicity, favor the selection of a fuel cell for the present application. It should be noted, however, that developments in the area of micro electrical mechanical systems (MEMS) warrant monitoring for future opportunities utilizing these technologies. In particular, there recently have been significant advances in the area of micro- and meso-scale generators (approximately 50 W output; rotational speeds of 10^5 rpm) based on closed Brayton cycle devices (Collier *et al.*, 2004). These concepts are still under development, but at some point may provide a viable alternative to fuel cells for seafloor power generation at the sub-kilowatt level.

The selection of a fuel cell as the power module defines the other components of the systems which can be divided into three categories: 1) fuel supply, 2) oxidizer supply; 3) ancillary equipment. The chief function of the fuel supply is to provide H_2 to the fuel cell with an acceptable level of contaminants at an adequate rate to sustain system net power production of the order of 100 W. Specific contaminant species and their concentration limits depend on the type of fuel cell. For example, the performance of PEMFC is degraded by CO while AFC is sensitive to CO_2 . The fuel supply will comprise equipment to collect and clean the raw seafloor methane gas, and a reformer to convert the raw gas to H_2 . Additional treatment of the reformed gas may be required to eliminate CO or CO_2 .

System	Major Components	Advantages	Disadvantages
Otto cycle	Fuel and oxidizer	Validated technology;	Poorly suited for low
	supply; IC engine; generator	systems exist that run on methane (CNG); relatively insensitive to contaminants; long	power application; moving parts vulnerable to failure; requires electrical generator
		appropriate maintenance	
Brayton cycle	Fuel and oxidizer supply; compressor; combustion gas turbine; heat exchangers; generator	Validated technology; can run on methane; relatively insensitive to contaminants; long lifetimes possible with appropriate maintenance	Components may not be available at the required scale; moving parts vulnerable to failure; thermal management; requires electrical generator
Rankine cycle	Fuel and oxidizer supply; combustor; evaporator & condenser; pumps to circulate working fluid; vapor turbine; generator	Validated technology; relatively insensitive to contaminants; can run on methane long lifetimes possible with appropriate maintenance	Components may not be available at the required scale; moving parts vulnerable to failure; requires electrical generator
Fuel cell	Fuel and oxidizer supply; reformer; fuel cell; pumps etc. for liquid electrolytes	Well-suited to produce target levels of power; minimal moving parts to wear or fail; directly generates electricity; relatively low temp. operation of certain fuel cells reduces thermal management problems	Vulnerable to catalyst poisons; requires reformer to convert methane to hydrogen; limited lifetimes

Table 2.4.1 Comparison of power generation options

The chief function of the oxidizer supply is to provide O_2 (or other oxidizers) to the fuel cell and the reformer with an acceptable level of purity at an adequate rate to sustain system net power production of the order of 100 W. The oxidizer supply will comprise equipment to extract dissolved oxygen from sea water and deliver it to the reformer as a gas, and to the fuel cell cathode either as a gas or at elevated concentrations in a liquid carrier. If it is not possible to extract DO from the ambient sea water and produce acceptably high levels of oxygen for the reformer and fuel cell, or if the power penalty to extract and concentrate DO is excessive, then the oxidizer supply may need to include a quantity of high density, stored oxidizer (e.g., liquid H₂O₂).

Ancillary equipment include all other components that are not critical to the operation of the fuel supply, oxidizer supply, or fuel cell subsystems, such as circuits to condition the power output of

the fuel cell for the AUV recharging application, pumps to recirculate produced water in the fuel cell to the reformer or to discharge the excess, system instrumentation and controls, heat exchangers for thermal recovery, the platform and mooring, etc. Ancillary equipment are not a major concern in a conceptual level feasibility analysis, so they were not examined extensively.

As described in the excerpts from the three Quarterly reports in Appendices A, B, and C, a fairly extensive suite of analyses and experiments were conducted to: 1) identify viable candidate technologies for the three major components: the fuel and oxidizer supplies and the fuel cell module; 2) characterize the performance of these technologies under the assumed operating conditions; and 3) develop models of the three components and integrate these models to perform a first-order systems analysis to estimate net power production. The principal results of are summarized below. Additional details are reported in the Appendices.

II.4.1 Fuel cells for seafloor power generation

Factors that must be considered in identifying and assessing candidate fuel cells for this specialized application include: 1) lifetime and maintenance; 2) performance at elevated pressure; 3) performance at low oxygen levels; 4) operating temperature; and 5) vulnerability to impurities in the fuel and oxidizer streams. Lifetime, maintenance schedules, and catalyst poisons were discussed in the previous sections. Most fuel cells have been developed to operate at pressures over a limited range around one standard atmosphere (absolute). Ambient pressure in the ocean, however, increases roughly linearly with depth at a rate of approximately one standard atmosphere every 10 meters. Given the distribution of the seafloor methane resource, the subsea power generation system would need to operate under conditions where ambient pressure is of the order of $10 - 10^2$ bar. While it may be possible to operate the system at lower pressures than ambient by enclosing components in pressure hulls, this comes with the risk of leakage and power penalties associated with the discharge of waste gases and liquids into the surrounding water column (i.e., pumping and compression losses).

As discussed in previous Quarterly Reports and in Section II.4.3 below, extraction of DO represents a major technological challenge. In the absence of a supply of stored oxidizer, decreasing levels of dissolved oxygen with depth may limit the maximum concentration of O_2 that can be supplied to the fuel cell cathode. Fuel cells that are unable to perform acceptably at low cathode oxygen levels need to be excluded from the candidate pool. The limited availability of O_2 also has implications with regard to operating temperature, insofar as the scarcity of this resource demands that thermal losses to the environment be minimized, since these losses must ultimately be sustained by oxidation of seafloor methane. Although insulation and heat recovery schemes are expected to be employed, as a general rule of thumb, lower operating temperature of the system components reduces the driving potential for thermal leakage to the relatively cold ambient sea water.

While many configurations exist, the five major types of commercial fuel cells are molten carbonate, solid oxide, phosphoric acid, PEM, and alkaline. PEM and alkaline fuel cells can operate at the lowest temperatures of this group, which offers advantages with respect to thermal management at the anticipated scale of operation. Moreover, the power output of PEMFC and AFC modules is appropriate for this application. For these reasons, they have been the focus of

our investigation. The following section presents a short overview and comparison of PEMFC and AFC.

II.4.1.1 comparison of Alkaline and PEM fuel cell technology

Fuel cells employing alkaline electrolytes were the first to receive R&D attention and to be demonstrated. The Bacon cell, in a 5 kW configuration, powered a tractor in 1955. The 1.4 kW systems that provided power and potable water for the Apollo space missions to the moon in the late 1960s were based on the Bacon cell. Technological refinements resulted in a lighter and higher performance cell stack developed for the space shuttle in the early 1970s. Three of these 12 kW units are the primary power supply for the space shuttle orbiter still in use today with little change in technical detail.

The early interest in alkaline electrolyte fuel cells arose from the recognition that the rate of oxygen reduction on cathode catalysts, the limiting factor in cell performance, was much higher in alkaline than in acid electrolytes. For space applications where pure hydrogen and oxygen were used as reactants, alkaline electrolyte served well but sensitivity to carbonation by CO₂, even at the trace levels present in ambient air, thwarted attempts to commercialize alkaline fuel cells for terrestrial use. Since the 1970s, fuel cell power plants using phosphoric acid or membranes containing sulfonic acid ionomer (Nafion®) have been the focus of development.

Space shuttle power plants were optimized for efficiency, running at low current density and high voltage in order to minimize consumption of hydrogen and oxygen. Size was not a primary concern since the weight of the power plants represented a small fraction of the weight of stored H_2 . Also, cost did not drive the design so high loadings of noble metal were used in the electrodes. The design of earth-bound acid electrolyte power plants, on the other hand, must consider cost, power, and size. The characteristics of existing fuel cell designs therefore tend to be optimized for a particular end-use, and may not represent the actual potential of that type of fuel cell for use in different applications.

Appleby & Yeager (1985) provide a useful starting point to compare AFC and PEMFC. They examined the performance of the orbiter AFC and PEM cells employing Nafion® 117, the 7 mil (0.007 inch = 0.18 mm) thick perfluorosulfonic acid membrane available at that time. The orbiter cells were fabricated using high loadings of Pt alloy powder catalysts on the anode and cathode (10 mg/cm² PtPd and 20 mg/cm² AuPt). The PEM cell had been developed for use (but never used) in the Gemini earth orbital missions and employed electrodes with high loadings of Pt black powder (4 mg/cm² on anode and cathode).

Figure 2.4.1 presents performance curves for selected alkaline and membrane fuel cells using pure H_2 and O_2 reactants. Data for the orbiter AFC stack was reported by Appleby & Yeager (1985) and Poast *et al.* (2003). Performance of that device has not changed much over the past 20 years. The AFC stack runs between 82° to 89°C at 4 bar absolute pressure of H_2 and O_2 . Three curves are shown for the Gemini membrane cell for operation at 82°C and 1 and 2 bar absolute, and at 104°C and 7 bar absolute. Also included in the figure is performance data for an automotive PEM cell (HNEI, 2005). This cell uses only 0.4 mg/cm² platinum supported on



Figure 2.4.1 Comparison of the performance of AFC and PEMFC utilizing pure H₂ and O₂.

carbon in the electrodes with a 2 mil thick membrane. At low current density (100 to 300 mA/cm^2), the new automotive PEM cell performs comparably to the Gemini cell, that has ten times the noble metal catalyst loading, but runs about 50 mV lower than the Orbiter AFC. At high current densities approaching1 A/cm², the automotive cell exceeds the performance of the Gemini cell and appears to be on the same level as the Orbiter cell. This behavior is believed to result from a number of improvements made to earlier PEMFC designs: at low current density, the use of liquid ionomer in the catalyst layer increases contact of the catalyst with the membrane; at high current density, the thinner membrane reduces resistance losses while the thinner catalyst layer reduces reactant diffusion polarization.

Each of the three Orbiter stack units is 38 cm wide, 35 cm high and 101 cm long, and comprise 32 cells. The cells contain 35-45% KOH as electrolyte trapped in a microporous separator previously made of asbestos but more recently of inert ceramic. The electrodes have active areas of 465 cm². The stacks are assembled in bipolar configuration with separator plates of gold-plated magnesium in which channels are machined for delivery of the reactant gases. Because the electrolyte concentration varies as a function of water produced by the cell reaction, the anode is backed by porous sintered nickel plate with holes machined for passage of hydrogen to the catalyst. As the electrolyte volume increases, it is absorbed in the pores of the nickel plate. At intervals in the cell stack, plates are included to circulate dielectric (SC40) coolant. The three AFC stacks, connected in parallel, deliver 18 kW nominal power at 27.5V (0.86 V/cell at 470 mA/cm²). The total system weight is 120 kg, which yields a specific power density of 150 W/kg.

Specific power density is a useful standard to assess the performance of alkaline and membrane fuel cell power plants developed for the same application (e.g., space exploration, such as in the case of fuel cells for the Space Shuttle and Gemini missions), but area power density (W/cm²) may be a better metric to compare the relative potential for development for different applications. Table 2.4.2 was prepared from the Orbiter AFC and automotive PEMFC data plotted in Figure 2.4.1 and presents area power densities (APD) of these cells at current densities of 0.3, 0.5, and 1.0 A/cm². At low current density. This suggest that a power plant optimized for efficiency (higher voltage) would use alkaline cell technology whereas a power plant optimized for high power density (at the expense of efficiency) would employ PEM cell technology. For the subsea power generation system where fuel, and particularly, oxidizer consumption rates (i.e., efficiency) are important considerations, AFC may offer a slight advantage over PEMFC, although values in Table 2.4.2 suggest that this may not be significant.

Current	Alkaline	Alkaline	Membrane	Membrane
Density				
A/cm ²	V	W/cm ²	V	W/cm ²
0.3	0.92	0.28	0.84	0.25
0.5	0.86	0.43	0.80	0.40
1.0			0.72	0.72

 Table 2.4.1
 Comparison of alkaline and membrane fuel cell performance

The suitability of alkaline or PEM cell technology for a particular mission application typically is determined by a number of factors in addition to power density, such as cost, size (neither of which are of critical importance in the case of the subject subsea power system), and durability. Both PEM and alkaline cell performance decreases with time. The life limiting factor in the Orbiter alkaline stack is corrosion of the cell's fiberglass/epoxy frame by the aqueous potassium hydroxide electrolyte (Poast *et al.*, 2003). Corrosion around the edge seals leads to electrolyte shunt currents and cross over. Recent improvement in the edge seals has extended AFC life from 2500 hours to 5000 hours. Over that period, average cell voltage was observed to decrease by about 40 mV at 200 mA/cm². A portion of this loss is due to re-crystallization of the noble metal black catalysts.

In current PEM stacks developed for automotive use, similar degradation of performance occurs over the same time period. The extent and rate of this deterioration depends strongly on the work cycle. Frequent stops and starts cause high voltage excursions at the cathode that can aggressively corrode the anode catalysts and supports. Failure of the proton exchange membrane due to chemical attack by hydrogen peroxide formed in the cell can be the life-limiting factor. Reported lifetimes of the present generation of PEM fuel cells for typical duty cycles are comparable to those of alkaline cells. It has been suggested—but not verified—that PEMFC lifetimes can significantly exceed AFC lifetimes under steady and continuous operation.

Impurities in the fuel and oxidizer supplied to the fuel cell will compromise the operation of both AFC and PEMFC. H_2S and other sulfur compounds that exist in the methane gas from seafloor seeps or released from hydrates will poison catalysts in the reformer and fuel cells. Since the reformer will be first to contact the fuel gas, these compounds must be removed upstream of this component. The reformed gas entering the fuel cell should therefore be free of any significant levels of sulfur species but may contain CO and CO₂. PEM cells are extremely sensitive to CO poisoning of their platinum catalysts. Alkaline cells are also vulnerable to CO but carbonation of the KOH electrolyte by CO₂ in either the fuel or oxidizer streams is usually cited as the most serious impurity-induced problem. Recent work has demonstrated that the performance of an AFC will start to deteriorate once a critical fraction, about 40%, of the electrolyte has been carbonated (Sambhy *et al.*, 2005). The rate of carbonation scales with the concentration of CO₂ in the fuel and oxidizer and the flow rate of these streams through the cell. The time required to reach the critical fraction will depend on reactant purity as well as how the fuel cell is operated (i.e., at high or low current density). At CO₂ levels found in air (about 370 ppmV) this may be of the order of hundreds, or even thousands, of hours.

Regarding performance at elevated pressure and low oxygen levels, the latter issue has been reviewed and discussed in each of the three previous Quarterly Reports. The limited data available suggest that it should be feasible to operate PEM and alkaline fuel cells at extracted O_2 levels corresponding to the oxygen minimum in the ocean. Under these conditions, current densities would be of the order of tens of mA/cm², requiring relatively large stack planform areas to produce the desired nominal 100 W net power. Experiments need to be conducted to confirm the behavior of AFC and PEMFC at very low O_2 concentrations and preliminary results are presented in the following Section. Employing liquids with high oxygen solubility to extract dissolved O_2 from sea water and deliver it to the fuel cell cathode has been proposed as a means

to circumvent fundamental limitations in the oxidizer supply. This approach may be feasible only for use with AFC where water production occurs at the anode and which employs a liquid electrolyte that wets the cathode. PEMFC, on the other hand, is very sensitive to cathode flooding; produced water at the cathode needs to be continuously removed so that the limiting current is not seriously degraded. It is unclear whether a PEMFC could function at all with a liquid O₂ delivery system.

As in the case of low oxygen levels, there is limited data on current PEMFC and AFC performance at pressures in excess of about 10 bar (high pressure PEM electrolysis, however, has been extensively investigated). A review of the literature suggests that there is nothing to preclude operating either PEMFC or AFC at deep ocean pressures. For given concentrations of H_2 and O_2 , respectively, in fuel and oxidizer gas mixtures, increasing the pressure of the gas streams increases the density of these reactants and is anticipated to result in higher current densities (see, e.g., Gelfi *et al.*, 2003). This effect can be detected in the Gemini PEMFC data in Figure 2.4.1. It should be noted that, the dew point of produced water vapor increases with pressure. At a given cell operating temperature, condensation may occur or increase as the partial pressure of H_2O vapor is increased. This may affect water management. It is not clear whether either alkaline or membrane cells enjoy an advantage over the other with respect to high pressure operation. This topic warrants further experimental investigation.

Finally, water and thermal management of PEMFC are critical functions that need to be performed adequately at the risk of degradation or failure. The membrane electrolyte must be hydrated, otherwise reactant gas crossover will increase, leading to local hot spots and membrane decomposition. Too much water, however, will flood the cathode and impede transport of oxygen to this electrode, with a resultant drop in output power. Flooding can be exacerbated at elevated operating pressure, since condensation proceeds until the partial pressure of produced steam is reduced below the saturation pressure corresponding to the gas temperature. If mole fractions of reactants are not adjusted and the steam partial pressure increases with operating pressure, then the amount of condensed water will increase accordingly; temperatures may also rise to some extent due to the released latent heat. Parasitic losses and capital costs associated with the water management subsystem can be significant, although progress has been reported in passive management techniques using microporous plates. Temperatures in the PEMFC must also be carefully controlled, since performance drops substantially with decreasing temperature and the membrane can be compromised at elevated temperatures; furthermore the relationship between temperature and humidity (water management) must be considered to coordinate water and thermal management. Water management is much less of an issue for AFCs, although it is important to maintain temperatures in these cells within a reasonable window. Overall, AFCs have an advantage over PEMFCs with respect to thermal and water management.

Table 2.4.2, reproduced from

http://www.eere.energy.gov/hydrogenandfuelcells/fuelcells/pdfs/fc_comparison_chart.pdf, compares features of the five major types of fuel cells. Considering the five factors identified at the beginning of Section II.4.1, it is obvious that all of these cells have significant drawbacks. AFC or PEMFC may be the best choices at the target scale of output power if low-temperature operation (to reduce the potential for heat losses) is a critical selection factor. Phosphoric acid cells, which are relatively robust and, consequently, long-lived, may need to be considered if fuel and oxidizer impurities cannot be reduced to acceptable levels.
Fuel Cell Type	Common Electrolyte	Operating Temperature	System Output	Efficiency	Applications	Advantages	Disadvantages
Polymer Electrolyte Membrane (PEM)*	Solid organic polymer poly- perfluorosulfonic acid	50 - 100°C 122 - 212°F	<1kW - 250kW	50-60% electric	 Back-up power Portable power Small distributed generation Transportation 	 Solid electrolyte reduces corrosion & electrolyte management problems Low temperature Quick start-up 	 Requires expensive catalysts High sensitivity to fuel impurities Low temperature waste heat
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100°C 194 - 212°F	10kW – 100kW	60-70% electric	• Military • Space	• Cathode reaction faster in alkaline electrolyte so high performance	• Expensive removal of CO_2 from fuel and air streams required
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	150 - 200°C 302 - 392°F	50kW – 1MW (250kW module typical)	80 to 85% overall with combined heat and power (CHP (36-42% electric)	• Distributed generation	 High efficiency Increased tolerance to impurities in hydrogen Suitable for CHP 	 Requires platinum catalysts Low current and power Large size/weight
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 - 700°C 1112 - 1292°F	<1kW – 1MW (250kW module typical)	85% overall with CHP (60% electric)	 Electric utility Large distributed generation 	 High efficiency Fuel flexibility Can use a variety of catalysts Suitable for CHP 	 High temperature speeds corrosion and breakdown of cell components Complex electrolyte management Slow start-up
Solid Oxide (SOFC)	Solid zirconium oxide to which a small amount of yttira is added	650 - 1000°C 1202 - 1832°F	5kW – 3MW	85% overall with CHP (60% electric)	 Auxiliary power Electric utility Large distributed generation 	 High efficiency Fuel flexibility Can use a variety of catalysts Solid electrolyte reduces electrolyte management problems Suitable for CHP 	 High temperature enhances corrosion and breakdown of cell components Slow start-up

Table 2.4.2 Comparison of fuel cell technologies (reproduced fromhttp://www.eere.energy.gov/hydrogenandfuelcells/fuelcells/pdfs/fc_comparison_chart.pdf)

*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 100W and operating at 60 - 90°C.

II.4.1.2 supplementary fuel cell experiments

During the final quarter of this project, preliminary laboratory experiments were performed with alkaline fuel cells to investigate performance at low O_2 levels and to explore whether AFCs can operate using liquid carriers. These experiments were not part of the original scope of work and represent additional effort provided to DARPA at no additional cost.

Single cell alkaline fuel cells from Astris Energi Inc. (LABCELL LC50-1) were tested. The manufacturer claims that these cells will produce nominal 3.75 W when operated with pure H_2 and air. The cells have an active area of 50 cm². Specifications are available on the manufacturer's website (http://www.astris.ca/PR/pdf/Astris-LC50.pdf).

A schematic diagram of the reactant and electrolyte flow systems is provided in Figure 2.4.2 and photographs of one of the cells and the test system are shown in Figures 2.4.3 and 2.4.4. Experiments initially were conducted to establish baseline performance at the manufacturer's recommended operating conditions. These tests were performed with laboratory grade H₂ and air at flow rates of 50 mL/min and 250 mL/min, respectively. Gas flow rates were set using Aalborg GFC-series mass flow controllers. Heat exchangers upstream of the fuel cell raised the temperatures of the H₂ and air to 75°C. Triple distilled and deionized water was mixed with reagent grade potassium hydroxide (KOH) to obtain a 6 M solution. A reservoir of this liquid electrolyte was maintained at 75°C and circulated through the fuel cell with a digital peristaltic pump. The electrolyte was changed frequently, to minimize problems associated with carbonation, since the reservoir was open to room air.



Figure 2.4.2 Schematic diagram of AFC reactant and electrolyte flow systems.



Figure 2.4.3 Photograph of the single alkaline fuel cell.



Figure 2.4.4 Photograph of the test setup.

Electrical characteristics of the fuel cells were determined by connecting the electrodes to a bank of calibrated precision resistors. A National Instruments data acquisition system was used to measure the potential across the electrodes. Cell current was estimated by Ohms Law by dividing this measured voltage by the known value of the load resistor. Fuel cells were first allowed to stabilize at zero current to establish the open circuit potential. The load resistor bank was then connected between the electrodes, allowing current to flow. Measurements were performed as different resistors were switched into the circuit in descending order (of resistance). Cell potential was allowed to stabilize before advancing to the next resistor. This process was repeated until the limiting current of the fuel cell was reached.

Figure 2.4.5 presents measured voltage-current characteristics of three LC-50 alkaline fuel cells designated as Nos. 134, 136, and 137. Variations between individual cells appear to be negligible. Comparison of these results with performance information provided in data sheets available on the manufacturer's website, however, reveals significant discrepancies. Our measured limiting current density was approximately five times smaller than values claimed by the manufacturer (i.e., 20 mA/cm² versus 100 mA/cm²). Various causes for this difference have been investigated and the manufacturer was consulted but, to date, no satisfactory explanation has been identified. This will continue to be explored.



Figure 2.4.5 Voltage-current characteristics of three small alkaline fuel cells supplied with laboratory grade air and hydrogen at 75°C and circulating 6M KOH electrolyte.

The cells also exhibited large voltage drops over the polarization curve. At maximum power, the cells are rated at 100 mA/cm² at a potential range of 0.57 - 0.77 V. The observed experimental potential was 0.5 - 0.6 V at 20 mA/cm². Cell resistance was calculated from the experimental data and was found to be 10 times greater than a value estimated from information provided by

the manufacturer. The IR-free potential curve is plotted along with the measured potential for cell No. 134 in Figure 2.4.6. The IR drop (i.e., difference between the two curves) at maximum current density was 0.35 V. Possible contributions to IR drop in fuel cells are resistances of the electrolyte and electrodes. The electrolyte in the present tests was circulated continuously and replaced regularly to maintain proper KOH concentration and minimize carbonation effects. High cell resistances appear to be due to the resistance of the electrode and electrode contacts. These performance issues were considered when the cells were tested with other oxygen sources.





Low Oxygen Content

One of the primary concerns of this investigation is whether it will be possible to supply sufficiently high concentrations of O_2 extracted from sea water to the fuel cell cathode. In previous Quarterly Reports, simulations of O_2 mass transfer modules and fuel cells were conducted assuming an attainable (based on ambient levels of the dissolved O_2 resource and Henry's Law) oxygen partial pressure of 8 kPa in a mixture of gases supplying the cathode. Since partial pressure is fixed, the corresponding oxygen mole fraction in the mixture decreases directly with (total) operating pressure: 8% at 1 bar, 0.8% at 10 bar, and 0.08% at 100 bar. AFC model results presented in the Third Quarterly Status Report (Appendix C) predict a precipitous drop in performance with decreasing O_2 mole fraction; however, these results have not been experimentally verified. As discussed in Section II.4.1.1, current density in fuel cells has been observed to increase at elevated operating pressure, provided that the mole fractions of the fuel and oxidizer species remain the same. Kinetic theory predicts that the collision frequency of gas

molecules with a solid surface (impingement rate) is proportional to the number of molecules per unit volume, n, of that species in a mixture of gases (Vincente & Kruger, 1965):

$$Z = n (kT/2\pi m)^{1/2}$$

where k, T, and m are, respectively, the Boltzmann constant, temperature, and the molecular mass. Assuming that the rates of reaction on the electrodes scale with this collision frequency, performance would then be expected to depend on O_2 partial pressure (which is a measure of concentration), rather than mole fraction.

In any event, in the absence of a stored supply of oxidizer, the fuel cell cathode will need to operate at O_2 levels below those employed in conventional applications (i.e., levels between pure O_2 and standard air). In order to determine changes in fuel cell performance under these low oxygen conditions and obtain data for comparison with the fuel cell models that we have developed, experiments were initiated using the LC-50 alkaline fuel cells. Mixtures of $0.8\% - 4.0\% O_2$ in nitrogen were fed to the cathode. Other test conditions were the same as those described above for the experiments shown in Figures 2.4.5 and 2.4.6. The results are presented in Figure 2.4.7. Limiting current was observed to decrease by approximately 50% as O_2 concentration was reduced from about 21% to 1.6% by volume. A large IR drop in cell potential can again be seen in these data. No results are shown for the 0.8% O_2 case, since the fuel cell was found to be effectively inoperable at this condition.



Figure 2.4.7 Voltage-current curves for LC-50 alkaline fuel cell at different cathode oxygen levels; operating conditions the same as in Figure 2.4.5.

Although these tests confirm the anticipated degradation in fuel cell performance at low oxygen levels, the quantitative information on limiting current should be interpreted with caution, given the previously noted differences between measured voltage-current characteristics and the manufacturer's rating, as well as the unusually high IR values. The results do suggest that AFCs can operate at O_2 partial pressures as low as about 1 kPa.

Since all the experiments were conducted at the same total pressure (i.e., pressure of the mixture of N_2 and O_2), both O_2 concentration (number of molecules or moles/unit volume of gas) and mixture fraction changed. It is not possible, therefore, to determine whether the observed behavior of the fuel cell was due to concentration, mole fraction, or a combination of the two. Additional tests, outside the scope of work, have been designed to address this issue by varying one of the two quantities while holding the other constant. For example, streams of pure N_2 and O_2 issuing from the mass flow controllers at the same pressure could be mixed upstream of the cathode in proportions that yield a target concentration of oxygen. The pressure of the gas streams could then be changed and the proportions of N_2 and O_2 adjusted to maintain the target O_2 concentration. This would allow us to vary O_2 mole fraction while keeping its concentration constant. Unfortunately, there was insufficient time to initiate these tests, which should be undertaken if this project is continued.

Liquid Oxygen Carriers

The final series of supplemental experiments explored the feasibility of using a liquid to deliver oxygen to the fuel cell cathode. Various artificial gills have been proposed in the past to provide oxygen for underwater human respiration or AUV propulsion. Those devices were reviewed in the first Quarterly Report (see Appendix A) and typically employ a liquid with high O₂ solubility to extract dissolved oxygen from sea water and release it into a recirculating carrier gas. In the present application, the extracted oxygen could be supplied to the cathode by this carrier gas or directly by the high-O₂-solubility liquid. Alternatively, O₂ could be transferred directly from the sea water to the carrier gas, eliminating the need for the intermediate liquid. As discussed in past Quarterly Reports and in Section II.4.3. below, various disadvantages have been identified with each of these options and it is unclear at this point whether any of them can be applied successfully to produce net power over an acceptably long period in the present application.

With regard to the operation of the fuel cell module, if we assume that some type of oxygen extraction from sea water will be pursued, then O_2 will be supplied to the cathode either in a gas mixture or dissolved in a liquid carrier. Gas mixtures are used in conventional fuel cells. Issues specific to this application which need to be understood are: performance at low oxygen mole fraction and high operating pressure; non-conventional carrier gases such as methane (which is available from the seafloor source and can therefore be replenished, unlike N_2); and the effects of impurities that may carryover from the sea water with the dissolved O_2 . The previous section discussed some experiments that were initiated to study the behavior of AFCs at low oxygen levels. The system employed in those experiments can also be used to test fuel cell performance with dilute mixtures of oxygen in methane (to minimize the risk of ignition) supplying the cathode. These tests will be undertaken if this project is continued.

Liquid carriers to supply oxygen to the cathode have been proposed previously but we have not been able to locate information in the peer-reviewed literature that confirms the feasibility of this approach. One U.S. patent (Brokman & Goldstein, 1993) claims that oxygen diffusion through a perfluorocarbon (PFC) layer will have minimal effect on cathode potential. Oxygen-rich organic fluid coatings on the cathode structure of metal/air batteries and hydrogen-oxygen fuel cells were examined. Flourinated hydrocarbons, such as perflourodecalin, with high oxygen affinities were used as a hydrophobic layer to deter water evaporation from the liquid electrolyte and to deliver O_2 to the catalyst. Electrodes consisted of nickel foam, nickel fibers, or nickel coated fibers completely impregnated with perflourodecalin. Air scrubbed of CO₂ was delivered to the electrode with and without the PFC liquid layer. Table 2.4.3 taken from the patent shows very little difference in overpotential with liquid phase impregnation.

Air Electrode Polarization Results						
Overpotential (incl. IR drop) mV						
Current Density	Air Supplied	Air Supplied				
(mA/cm^2)	Via Gas Phase	Via Oil Phase				
50	108	110				
100	150	160				
200	234	250				

Table 2.4.3 Overpotential of an air electrode with a conventional hydrophobic layer and one impregnated with perflourodecalin (Brokman & Goldstein 1993).

The Astris Energi alkaline fuel cells were tested to explore the feasibility of utilizing liquid carriers to supply O_2 to the cathode. A schematic diagram of the set-up employed in these experiments is shown in Figure 2.4.8. Oxygenated distilled water was pumped through the fuel cell as a precursor to experiments using the PFC, perfluorooctylbromide (PFOB). The transport properties of water are well known over a wide range of conditions (unlike PFOB) and the data can therefore be more easily compared with results of the models we have developed. In addition, the concentration of oxygen dissolved in water can be monitored with a commercially-available oxygen probe and meter (Orion 842).

Pure oxygen was sparged into distilled water in the oxygenation chamber. The DO level was maintained between 27 and 30 mg/L, which is approximately the value found in water in equilibrium with a pure oxygen atmosphere. The oxygenated water was pumped through a heat exchanger to increase its temperature to 75°C before it entered the cathode compartment of the alkaline fuel cell. Water flow rate was varied between 50 to 300 mL/min. Hydrogen and electrolyte flow rates and temperatures were the same as in the tests presented in Figures 2.4.5 – 2.4.7. Results are shown in Figure 2.4.8. Limiting current in the cells was approximately 0.88 mA/cm². Potential at open circuit for the cells was highest at a flow rate of 50 mL/min but this difference disappeared as maximum current was reached. This suggests that the increased flow rate did not improve oxygen diffusion into the gas diffusion layer. The limiting current attained in these test are very similar to that predicted by our alkaline fuel cell model for the case where water is used as an oxygen carrier.







Figure 2.4.8 Voltage-current characteristics of alkaline fuel cells. Cathode supplied with O_2 using 75°C oxygenated distilled water; DO concentration = 30 mg/L.

Following the oxygenated water experiments, tests were conducted using PFOB. PFOB is an inert fluid that is employed regularly in medical procedures as a source of O₂ to cells and organs (Weers, 1993). It is not anticipated to attack any of the wetted materials in the AFC nor contaminate the aqueous electrolyte. Since PFOB is hydrophobic, it is expected to deter water evaporation from the electrolyte. 100 mL of PFOB was twice frozen at 6°C to remove all dissolved gases from the liquid. The PFOB was then allowed to equilibrate with an overlying headspace of pure oxygen gas in a closed vessel, heated to 55°C, and pumped through the fuel cell at a rate of 200 mL/min. Materials used in the PFOB flow loop limited the maximum temperature to 55°C, which was lower than the 75°C used in the gas and oxygenated water tests.

The observed cell potential as a function of current density is compared with the oxygenated water and gas data in Figure 2.4.9. PFOB increased the limiting current density of the cell from 0.88 mA/cm^2 observed with oxygenated water to 1.68 mA/cm^2 . While this was a significant improvement, our previous analysis predicted that limiting current would scale with O₂ solubility, which is18 times greater in PFOB than in water. Possible explanations for the smaller-than-expected increase include the lower temperature and that the PFOB was not saturated with O₂, as was the case in the water tests. Since a means to measure DO levels in the PFOB was not available, it could not be determined how much oxygen had dissolved. Furthermore, the analysis also indicates that limiting current density depends on the diffusivity of O₂ through the liquid carrier, which is not known for PFOB. If oxygen transport through PFOB is slower than through water, then this will significantly reduce gains in current as gas testing because the diffusion rate of oxygen through the liquid was much slower than through the gas, even though the partial pressure of oxygen in the liquid was higher than in the gas.



Figure 2.4.9 Alkaline fuel cell performance for different oxygen carriers; carrier temperature = 75° C except where noted.

II.4.1.3 fuel cell models

Computer models have been developed to predict the performance of the PEMFC and AFC as a function of operating conditions. These models can be linked to models of the fuel and oxidizer supply subsystems by the appropriate energy and mass balance relationships to conduct parametric studies of the subsea power generation device. Details of the PEMFC and AFC models and some trial calculations are included in Appendices B and C.

The PEMFC model considers the two-dimensional device shown in Figure 2.4.10. The two dimensions are along the flow channels (x) and across the membrane electrode assembly (z). It is assumed that the system is isobaric and that the porosity of the gas diffusion layers is constant. Transport phenomena through catalyst layers are not included in the model. In the anode flow channel at x = 0, mixtures of hydrogen, water, and perhaps inert gases, are supplied at temperature T(0). In the cathode flow channel at x = 0, mixtures of oxygen, water, and perhaps inert gases, are supplied at temperature T(0). The temperature field is assumed to depend only on x. Heat transfer along the x direction is considered negligible. The determination of fuel cell characteristics proceeds from x = 0 along the flow channel. The model calculates temperatures, reactant and product fluxes, and current densities along the flow channel as well as cell potential.

The AFC model considers the one-dimensional device shown in Figure 2.4.11. The model architecture is derived from Vargas & Bejan (2004). Its implementation necessitated several important corrections to Vargas & Bejan's work and an extension to mixed reactants. The latter



Figure 2.4.10 Diagram of two-dimensional PEM fuel cell.



Figure 2.4.11 Diagram of one-dimensional alkaline fuel cell.

development required the consideration of Stefan-Maxwell diffusion within the gas diffusion layers (in addition to Knudsen diffusion).

The AFC is divided into seven control volumes comprising the flow channel, gas diffusion layer and reaction layer in both the anode and the cathode, and the electrolyte. Seven time-dependent ordinary differential equations were formulated for the temperatures in each control volume, assumed to be uniform. The user specifies the composition, temperature, and pressure of the fuel and oxidizer supply streams entering the electrode flow channels, as well as various heat and mass transfer coefficients and thermodynamic properties. The model calculates steady state polarization (i.e., voltage-current) and temperature.

Experiments are required to calibrate and verify the model results. In particular, operation at elevated pressure and low O_2 mole fractions need to be examined. Furthermore, if development of the O_2 supply system indicates that liquid carriers are a viable option, then the fuel cell models (probably the AFC model, since liquid carriers may not be compatible with PEMFC) must be modified to account for this mode of oxygen delivery to the cathode.

II.4.1.4 fuel cells for seafloor power generation summary

Fuel cells appear to be the best choice among conventional power generation devices to convert the chemical energy of methane to electricity on the seafloor, at the present target level of power production (nominal 100 W net). Over the past 15 months, analyses and experiments have been conducted to identify viable candidate fuel cells. The primary results of this effort are:

- No ideal candidate fuel cell exists for this application; all "commercially available" fuel cells suffer from various disadvantages that significantly compromise their ability to meet the performance requirements for seafloor power generation. Work-arounds to minimize these disadvantages may be possible to adapt conventional fuel cells to this unconventional end use and secure adequate performance. Development of a fuel cell optimized for this application is not believed to be practicable, since it would probably require (much) more than the 5 years allotted to field deploy a prototype, substantial R&D funding, and may depend on major technology breakthroughs.
- Heat losses to the relatively cold environment must be minimized, since these losses ultimately are sustained by methane oxidation—which wastes the limited O₂ resource. Lower operating temperature reduces the driving potential for thermal leakage and was therefore applied as one of the conditions to rank different types of fuel cells.
- With regard to thermal leakage, PEM and alkaline fuel cells are preferable since they operate at the lowest temperatures, typically well below 100°C; phosphoric acid fuel cells operate at temperatures nearly 100°C higher, while molten carbonate and solid oxide fuel cells require temperatures in excess of 600°C.
- The low operating temperatures of PEMFC and AFC necessitate high noble metal catalyst loadings to promote redox reactions on the electrodes. While the associated cost may not be a serious drawback for specialized defense applications, these catalysts are vulnerable to poisoning by certain impurities found in the raw fuel gas (H₂S) or produced during the reforming of methane (CO). This vulnerability to poisoning is a major

disadvantage of PEMFC and AFC. The higher temperature fuel cells (phosphoric acid, molten carbonate, and solid oxide) are generally more robust.

- PEMFC membranes must be hydrated and should not be allowed to overheat. Water and thermal management in the PEMFC may be difficult to implement properly and could seriously compromise performance and longevity.
- The KOH electrolyte employed in the AFC is subject to carbonation by CO₂, which is found both in the raw fuel gas and is produced during reforming. Carbonation of the electrolyte is usually cited as a primary factor that degrades performance over time and limits the lifetime of AFCs. CO₂ must be removed from the H₂ and O₂ feedstreams prior to entering the fuel cell. Some of the CO₂ in the fuel gas will condense out, since the AFC operates below the dew point of the reformate and CO₂ is highly soluble in water.
- Reported lifetimes of AFCs and PEMFCs are comparable and of the order of 5000 hours (7 months continuous operation). PEMFC lifetime depends on duty cycle: frequent stops and starts cause high voltage excursions at the cathode that can aggressively corrode the anode catalysts and supports. Failure of the proton exchange membrane due to chemical attack by hydrogen peroxide formed in the cell can be the life-limiting factor. It has been contended that PEMFC lifetimes can increase by an order of magnitude if the fuel cell is run continuously and steadily under optimal conditions; however, evidence confirming this has not been found in the archival literature. AFC lifetime may be limited by corrosion due to the KOH electrolyte that leads to shunt currents and crossover. AFC performance is also degraded over time as a result of carbonation of the electrolyte and re-crystallization of the noble metal black catalysts.
- There is minimal probability that a single fuel cell module will operate successfully over the target 5-10 year period using current AFC and PEMFC technology, especially since the modules will not be easily accessible for periodic maintenance. It may be possible, however, to reach this goal by providing a sufficient degree of redundancy in the system design; i.e., including back-up fuel cell modules that can be switched into service after a predetermined period of operation or upon failure of the module in service.
- In spite of their shortcomings, we propose that AFC and PEMFC represent the best candidates for the subsea power application and that the design strategy should be to continue to focus on these types of fuel cells unless information emerges that clearly precludes their use. If AFC and PEMFC are found to be unacceptable, then high temperature fuel cells can be considered, with phosphoric acid being the first alternative, followed by SOFC.
- Appropriate means must be applied to reduce the level of certain gas impurities (e.g., H₂S, CO, and CO₂) in the fuel and oxidizer streams to acceptable values prior to entering the fuel cell. These values will be determined by reference to the rather extensive body of literature on FC fuel purity standards and experiments that will be performed at elevated operating pressures.
- Limitations in the oxygen supply may require that the selected fuel cell be operated at O_2 partial pressures of ≤ 8 kPa and possibly with oxygen delivered to the cathode either by methane carrier gas or a liquid perfluorocarbon.
- Liquid O₂ carriers do not appear to be feasible for use with PEMFC due to problems with water management. Liquid carriers might be an option for AFC, which produces water on the anode, and a patent exists that supports this concept. Tests were initiated using a

small (50 cm²) nominal 3.75W AFC purchased from Astris Energi to explore operation at low oxygen partial pressure and with unconventional O_2 carriers.

- Experiments were conducted at a gas mixture pressure of slightly over 1 bar (absolute), for various mole fractions of O₂ in N₂ supplied to the cathode. Preliminary results suggest that the tested AFC can be operated at oxygen partial pressures as low as about 1 kPa. Limiting current was observed to decline by about 50% as the mole fraction of O₂ was reduced by an order of magnitude, from 21% to 1.6%. While these results are encouraging, they must be interpreted with caution, since the performance claimed by the manufacturer could not be reproduced and the cells appeared to have unusually high IR characteristics. Further testing should be pursued.
- To date, the experiments were unable to distinguish between the effects of mole fraction and partial pressure. It should be possible to extract oxygen from sea water at a partial pressure of 8 kPa at all of the candidate sites identified in Section II.2. Our AFC model predicts that performance will drop precipitously with depth as extracted O₂ mole fraction declines (even though its partial pressure remains constant). Kinetic theory arguments, however, suggest that partial pressure, rather than mole fraction, is the relevant parameter. Experiments must be conducted in which oxygen mole fraction and partial pressure are varied independently, in order to determine how each of these factors influences fuel cell performance.
- The AFC was tested using oxygenated distilled water and perfluorooctylbromide to deliver O₂ to the cathode. Results indicate that operation is possible with liquid carriers, at least over short time periods. The degree of degradation in performance observed with oxygenated water was very similar to predictions of our alkaline fuel cell model. The limiting current was significantly higher for PFOB than oxygenated water, but not to the extent anticipated. Reasons for this discrepancy are being explored.
- Experiments have been devised, but have not yet been initiated, to investigate using methane carrier gas to deliver oxygen to the cathode. Methane is being considered since it is expected that the carrier gas will be lost over time by diffusion into sea water during the extraction of dissolved O₂. A supply of the carrier gas is needed to make up this loss. Methane, unlike N₂, is readily available from the seafloor source.
- Additional long-term tests need to be performed fully to characterize the operation of the selected type of fuel cell (AFC or PEMFC) at elevated pressure and with O₂ levels that can be provided by the oxygen supply system that remains to be identified. These experiments will yield data to calibrate the fuel cell models we have developed that will be integrated with the models of the fuel and oxidizer supply subsystems to perform parametric simulations of the system.

II.4.2 Fuel supply system

Presuming that PEMFC or AFC will be applied to produce electricity, the fuel supply system will need to collect the seafloor methane, convert it to hydrogen, and remove H₂S, CO, and CO₂ (if AFC is employed), as well as any other contaminants that could poison catalysts or corrode components. During the present conceptual design phase, efforts focused on identifying currently available technologies that can be adapted to seafloor operating conditions to reform and purify the fuel gas. Experiments and modeling studies were conducted to characterize performance and to evaluate material (notably, O₂) and energy requirements of the reformer and

gas clean-up components. This information is needed for system integration and model development.

Characteristics of the raw fuel gas from seeps and hydrates were presented in Section II.1.1.2. These profiles were employed as the baseline for the experiments and thermochemical simulations. The following sections summarize the major results of our studies of the reformer and gas purification components. Additional information can be found in the Quarterly Reports reproduced as Appendices A, B, and C.

II.4.2.1 thermochemical reforming of methane

Catalytic thermochemical reforming (usually followed by water-shift) of CH_4 to H_2 is a mature technology that is used extensively in industry. It is believed to present a manageable level of risk when adapted to the unique conditions of the present application (e.g., high pressure, limited available oxidizer; hands-off service) and, hence, it has been selected as our method of choice.

During this conceptual design phase, effort focused on three topics: 1) confirming the feasibility of reforming at high pressure; 2) estimating O_2 requirements; and 3) establishing ranges of operating conditions (e.g., temperature) needed for system integration and optimization.

In thermochemical reforming, hydrogen is produced from methane by partial oxidization via the following overall reaction:

$$CH_4 + nO_2 \rightarrow 2H_2 + CO + (n - 0.5) O_2; n > 0.5.$$

Additional H₂ can be generated by converting the CO in the syngas mixture to CO₂ using steam:

$$\text{CO} + \text{mH}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 + (\text{m-1}) \text{H}_2\text{O}; \text{m} > 1.$$

Catalysts are employed to lower the activation energy and reduce the operating temperature.

When properly implemented, the produced gas concentrations approach equilibrium values. In the present investigation, equilibrium calculations for methane reforming were performed using the software package FACTSageTM 5.1. Calculations were conducted on a unit mole CH₄ basis. Various ratios of O_2 to C (n, above) and H₂O to C (m, above) were explored. Ranges of these ratios were selected based on our prior reforming experience with other hydrocarbon fuels. Nominal values of n and m were 0.55 and 1.24, respectively.

Figure 2.4.12 summarizes the calculated equilibrium gas composition at pressures ranging from 1-100 atmospheres and reforming temperatures between 500°C and 1000°C. It can be seen that methane conversion to H₂ is favored at low pressure and high temperature. H₂ approaches a maximum value at temperatures above 700°C (975 K) for the range of conditions investigated. Also shown in the figure for comparison are product gas data from CH₄ reforming experiments conducted using 20 g of Ni catalyst at 800°C, 1 atmosphere, oxygen/carbon ratio n = 0.55, and

steam/carbon ratio m = 1.24. There is reasonably good agreement between the data and the calculated equilibrium values.



Figure 2.4.12 Predicted equilibrium mole fractions of the products of catalytic, autothermal, methane reforming as functions of temperature and pressure for oxygen/carbon ratio n = 0.55 and steam/carbon ratio m = 1.24. Experimental product gas data obtained using 20 g of Ni catalyst at 800°C, 1 atm., and the same values of n and m as the calculations.

Reforming Experiments

Experiments were conducted to investigate catalytic thermochemical reforming at elevated pressure and using unconventional oxidizers; and to obtain data for model development and system optimization. The reformer is a lab-scale, fixed-bed, catalytic reactor that has been used in previous investigations of LNG reforming. Initial tests were performed at approximately 1 atm (absolute) employing the original low pressure system with a 1.93 cm i.d. x 45.7 cm long, 316 stainless steel reformer tube. The system was subsequently modified to operate at high pressure.

The reactor temperature is maintained by an electric tube furnace with a heating length of 30.5 cm. A nickel-based steam reforming catalyst, GW-91 EW from Süd-Chemie, is crushed to produce a particle size in the range of 1.4 - 4.75 mm. Between 15 g and 20 g of catalyst is

placed in a 20 cm section at the middle of the reformer tube. Temperatures in the reactor are measured both immediately before and after the catalyst bed. Different systems are employed to deliver reactants in the low and high pressure tests. Reactant flows are controlled and recorded along with relevant operating temperatures and pressures using a LabView[®]-based data acquisition system.

Reformate issuing from the reactor is directed to a condenser where most of the water vapor is removed. A slip stream of the gas flows through a coalescing filter to extract remaining aerosol and vapor prior to analysis. The dry effluent gas is analyzed with a Shimadzu 14A gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a CarboxenTM 1000 column (45/60, SUPELCO). Helium with 8% hydrogen serves as carrier gas. The stable gas species – H₂, N₂, CO, CH₄, CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ – were quantified. In each analysis the temperature is held at 45°C for 1 minute, increased for 9 minutes to 225°C, held at 225°C for 2 minutes, and then decreased for 10 minutes back to 45°C. The GC system is equipped with a six-port sampling valve which automatically injects a dried reformate sample from the reactor every 22 minutes.

Bottled air and methane (Grade 5.0) were employed in the tests conducted at 1 atm pressure. Relative proportions of these gases were set with electronic mass flow controllers. The air and methane were mixed prior to the addition of steam upstream of the reactor using a vaporizer where water was heated to 100° C. Two test conditions were examined; steam-to-carbon (S/C) ratio and oxygen-to-carbon (O/C) ratio were: 1) O/C = 0.555, S/C = 1.24; and 2) O/C = 0.122S/C = 1.66. Reforming temperature was 800°C in both tests. The first set of conditions was selected to represent a high methane conversion scenario with limited probability of coke formation based on autothermal reforming conditions (no external heating) and a 20% heat loss. The second set was selected to simulate a scenario where unused hydrogen from the fuel cell could be recycled to provide supplemental heat for the reforming process. The measured average H₂ and CH₄ concentrations of the product gas stream for the first set of test conditions are included as data points in Figure 2.4.12 and suggest that the process has reached equilibrium. The gas composition was stable over the test duration of 6 hours and no catalyst deactivation was observed. The experimental results for the second set of conditions did not agree as closely with equilibrium predictions, indicating that methane conversion was limited by reaction kinetics due to a lower oxygen-to-carbon ratio than the first test condition.

To conduct reforming experiments at elevated pressure, and to explore using hydrogen peroxide as an oxidizer, the system had to be modified. The reactor tube was replaced with a section of schedule XXS 3/4" stainless steel pipe that had suitable geometry and material properties to withstand both high temperature (~900°C) and high pressure (~80 atm). The reactor length increased from 45.7 cm to 61 cm and its i.d. was reduced by over 40%, from 1.93 cm to 1.1 cm. High pressure mass flow controllers were used to meter high purity methane, oxygen and nitrogen from gas cylinders. Liquid reactants (water or aqueous solutions of H₂O₂) were supplied to the reactor from a high pressure reservoir. Argon from a gas cylinder flows through a mass flow controller into the head space of the reservoir, pushing the liquid out through an injector at the desired flow rate. Resistance element heat tracing was applied to the transfer lines between the reservoir and the reactor to preheat the liquid and produce a vapor prior to entering the reactor. Pressure in the reactor is set and controlled with a back pressure regulator. Reformate gas is sampled for GC analysis downstream of this regulator. A schematic diagram and photograph of the high pressure reforming system are provided in Figures 2.4.13 and 2.4.14, respectively.



Figure 2.4.13 Schematic diagram of high pressure methane reforming test facility.



Figure 2.4.14 Photograph of the laboratory-scale reforming test bed designed to operate at pressures up to 80 atm.

II.4.2.2 supplementary reforming experiments

During the final quarter of this project, experiments were performed to investigate reforming of methane over a range of operating pressures representative of the ocean floor at depths down to ~ 600 m (future tests will extend this to the full 800 m depth equivalent pressure limit of the reactor). A primary goal was to determine if equilibrium models adequately describe the high pressure reforming process. A second set of experiments was undertaken to explore the use of hydrogen peroxide as an alternative (high-density) O₂ carrier for seafloor applications.

Methane Reforming at Elevated Pressure

Table 2.4.4 summarizes the conditions examined in the high pressure reforming tests. Reactor pressure was the primary variable investigated, ranging from 7 to 58 atm. Increasing pressure resulted in gas hourly space velocity (GHSV) decreasing from nearly 6000 to 700 hr⁻¹. GHSV is defined as the reactant volumetric flow rate divided by the catalyst volume. Equilibrium concentrations of CH₄, H₂, H₂O, CO and CO₂ in the product gas were calculated using FACTSageTM 5.1 for the reactant mixtures and reforming conditions shown in the Table. Figure 2.4.15 compares the predicted concentrations with the experimental data. Very good agreement is observed, suggesting that equilibrium models describe well the high pressure reforming of methane as implemented in our tests.

Experimental values plotted in Figure 2.4.15 are averages of at least four measurements of gas composition. From the error bars displayed on the graph, it is clear that experimental conditions were very stable, in terms of both reactor pressure and gas composition. H₂ concentration in the gas decreased from \sim 75% to 68% as pressure increased from 7 to 58 atm. Gas phase CO concentration also declined from 10% to 7%. CO₂ concentration is relatively unaffected by pressure; values were between 12.5% to 14.5%. Note that the concentration of unreacted methane increased from 1 to 9.5%. Reduced methane conversion also results in reduced gas yield. Results given in Table 2.4.5 show a decline in gas yield, over the range of test pressures, from 4.8 to 3.3 liter gas per liter of CH₄ entering the reformer.

The good agreement between experimental results and equilibrium calculations indicate that, for the operating conditions examined, the methane reforming proceeds with minimal interferences. There was some concern since elevated pressure is known to induce carbon formation and coking of the catalyst, but none was observed. Longer term tests should be performed for verification. In general, these experiments confirm the viability of catalytic thermochemical reforming of methane to H_2 at pressures typical of depths where hydrothermal vents or methane hydrates exist on the seafloor.

	No.	Feed rate, ml/min			Ratio		Pressure	Temperature	GHSV	
Test No.	of Samples	CH_4	O ₂	H ₂ O _(?)	N ₂	S/C	O2/C	(atm)	°C	(hr^{-1})
1	4	500	80	1.8	500	4.5	0.16	7	800	5888
2	4	500	80	1.8	500	4.5	0.16	28	800	1472
3	4	500	80	1.8	500	4.5	0.16	46	800	896
4	4	500	80	1.8	500	4.5	0.16	58	800	711

 Table 2.4.4
 High pressure reforming test conditions.



Figure 2.4.15 Comparison of equilibrium reformate concentrations and data as a function of pressure at $O_2/C = 0.16$; S/C = 4.5; $T_{Reactor} = 800^{\circ}C$ and employing 15 g of G91-EW Ni-based catalyst. (Equil=chemical equilibrium calculation, Exp=experimental result)

Pressure	Inert Free Gas Yield			
(atm)	mole/mole CH ₄			
6.8	4.8 ± 0.3			
28.4	3.8 ± 0.1			
45.6	3.8 ± 0.3			
58.2	3.3 ± 0.3			

 Table 2.4.5
 Variation of inert-free gas yield as a function of reactor operating pressure.

The use of H₂O₂ as an oxygen carrier for reforming

A major limitation for operating a reformer on the seafloor is having oxygen available at sufficiently high concentrations. O_2 is employed to oxidize a portion of the fuel to generate heat required to sustain the endothermic reforming reactions. The experiments described above utilized O_2 from a high pressure gas cylinder. Additional experiments, outside the original scope of work, were performed to evaluate the use of a second oxidizer, hydrogen peroxide (H₂O₂), that is liquid at ambient conditions but can be decomposed, either catalytically or thermally, to water and oxygen according to the following reaction:

$2H_2O_2 \rightarrow 2~H_2O+O_2$

This reaction is exothermic, releasing 106 J/mole H_2O_2 when the final products are in the gas phase. Hydrogen peroxide can thus provide O_2 , H_2O_2 and heat, all of which could be utilized to operate a reformer and fuel cell on the seafloor. Moreover, since it is a liquid, the amount of oxygen available per unit volume is large, which is desirable from the perspective of minimizing the size of tanks used to bring down oxidizer from the surface and to store it. Pure H_2O_2 has a molarity of about 42 mol/liter at 1 atm pressure and 25°C (this will increase at the higher ambient pressures and lower temperatures the seafloor). Since decomposition of a mole of hydrogen peroxide yields 0.5 mole of O_2 , the oxidizer density is about 21 mol O_2 /liter H_2O_2 . In comparison, pure O_2 gas stored at, say, 80 atm and 5°C, contains only 3.5 mol O_2 /liter.

As described above, liquid reactants are metered into the reformer from a high pressure tank. Prior to conducting the H_2O_2 tests, the tank and transfer lines were passivated with dilute nitric acid, since hydrogen peroxide spontaneously decomposes on contact with many metals. Based on a 0.5 lpm CH₄ flow rate to the reformer and the decomposition reaction shown above, a mixture of 9% H_2O_2 in deionized water at a flow rate of 1.8 ml/min was calculated to provide the desired oxygen-to-carbon (0.15) and steam-to-carbon (4.4) ratios. These values match the reactant ratios that were used in the methane reforming experiments described above that employed bottled O_2 as an oxidizer.

To calibrate the H_2O_2 delivery system, a mixture of 9% H_2O_2 and 91% deionized water was placed in the liquid reactant reservoir and metered into the empty reformer at a rate of 1.8 ml/min. The reactor was maintained at a temperature of 800°C using the tube furnace and the pressure was set at 8.8 atm. CO_2 was introduced into the reformer at a flow rate of 1.0 lpm to simulate the reactant gas flow expected during experiments and to act as a sweep gas that could easily be separated from the O_2 by GC. After analyzing several samples of the outlet gas, the flow of the H_2O_2/H_2O mixture was stopped and replaced with a flow of O_2 from a gas cylinder.

The flow was varied from 31 to 107 ml/min to provide a series of O_2 concentrations to the GC. The resulting calibration curve is shown in Figure 2.4.16 with the corresponding regression equation. Using this equation, the GC area counts from the earlier analysis of gas from the 9% H_2O_2 and 91% deionized water liquid flow were converted to O_2 concentrations as shown in Table 2.4.6. Nine samples were analyzed with an average O_2 concentration of 6.2% and a standard deviation of 1.9% (absolute).

Results of the reforming experiments using 9% H_2O_2 and 91% deionized water as a reactant are shown in Table 2.4.7. Reformate composition predicted by chemical equilibrium is presented for comparison. As with the earlier experiments using O_2 from gas cylinders, agreement between experiment and equilibrium is quite good, with differences being <2% (absolute) for all species.

These results provide preliminary validation of the use of H_2O_2 as a liquid oxygen carrier for reforming applications. Additional verification testing should be conducted over a range of pressures and oxygen-to-carbon ratios. Using higher concentration H_2O_2 solutions should also be investigated.



Figure 2.4.14 O₂ calibration curve for GC based on concentrations mixed with mass flow controllers.

	an empty rerorm	
Sample No.	Area Counts	% O2
2	46,816	6.0
3	29,700	3.2
4	40,000	4.9
5	51,000	6.7
6	44,929	5.7
7	44,030	5.5
8	72,268	10.1
9	55,960	7.5
Average	48,088	6.2
Standard Dev.	11,655	1.9

Table 2.4.6Variability of concentration of O_2 produced from thermally decomposing H_2O_2 in
an empty reformer at 800°C, 8.8 atm.

Table 2.4.7Comparison of gas composition from catalytic methane reforming experiments
using a mixture of 9% H₂O₂/91% H₂O at 8 atm, 800 °C with composition
predicted by chemical equilibrium at the same conditions.

Species	Equilibrium	Experimental
H_2	75.70	77.75
CH ₄	0.71	1.03
CO	10.88	10.04
CO_2	12.71	11.18

II.4.2.3 reformer oxygen and energy requirements

Analyses were conducted to estimate the oxygen and energy requirements of the methane reformer system. This information is needed to design the O_2 supply system and for system modeling and integration.

<u>Oxygen</u>

The amount of oxygen required to reform methane was estimated based on the target power output from the fuel cell module, i.e., approximately 100 W. A methane flow of 151 ml CH₄ per minute contains 100 W of power based on its heat of combustion (complete oxidation) at standard temperature and pressure. If an overall system efficiency of 10% is assumed, the methane flow rate to produce 100 W of power would increase ten fold to 1.51 slpm. The amount of O₂ needed for (partial oxidation) reforming can be shown to be about 30% of stoichiometric O₂, i.e., 30% of what would be consumed to oxidize methane to CO₂ and H₂O. Since two moles of O₂ are needed to oxidize a mole of CH₄, the estimated oxygen requirement for methane reforming is $0.30 \times 2 \times 1.51$ slpm ~0.9 slpm or about 0.02 g/s = 0.00061 mol/s = 0.037 mol/min = 19,360 mol/year. Whereas it may be possible to supply oxygen directly to the fuel cell module with a liquid carrier, such as PFOB, the reformer requires gas-phase O₂, either in pure form or in a mixture of gases. Gas mixtures with low values of O₂ mole fraction are not suitable for reforming. Furthermore, if O₂ is supplied in a gas mixture of reactive and diluent species, then the composition of the mixture will affect the reforming process and needs to be controlled. This

has significant implications with regard to the design of the dissolved oxygen extraction system which has been considering a range of carrier gas species.

Exploratory experiments suggest that hydrogen peroxide solutions can be used in place of oxygen gas to reform methane and provide O_2 , steam, and heat. An annual oxygen consumption of 19,360 mole can be supplied by slightly less than a cubic meter of pure liquid H_2O_2 ; a five year supply could be stored in a 2 m diameter x 1.5 m tall tank.

<u>Energy</u>

An assessment of energy requirements for fuel reforming was conducted during the third quarter of this project. Reforming was modeled as a series of five sequential process steps comprising (1) raising reactants to the selected reforming temperature and pressure (which includes phase change of liquid water to vapor); (2) reaction at the selected reforming temperature and pressure with products predicted by chemical equilibrium; (3) cooling of reformate to the selected water gas shift reaction temperature and pressure; (4) water gas shift reaction at the selected temperature and pressure with products predicted by equilibrium; and (5) cooling of water gas shift products to fuel cell inlet temperature and pressure.

The energy budgets of these steps were evaluated for selected values of reforming temperature, water gas shift temperature, and system pressure. Product compositions of reactions assumed that chemical equilibrium was achieved, which appears reasonable based on our experimental results. With the objective of maximizing H₂ yield, and under the constraint of a neutral or negative (heat releasing) system energy balance, steam-to-carbon (S/C) and O_2 -to-carbon (O_2/C) ratios were varied to identify optimal reactant inputs. System performance indicators at reforming temperatures of 800° C and 1000° C, a range of system pressures from 1 to 80 atm (bar), and a heat loss of 18% are shown in Figure 2.4.15. Efficiencies presented in the figure are defined as the enthalpy of H₂ in the reformate divided by the enthalpy of the methane supplied to the reformer. Note that H₂ yield is favored at low pressure and that as pressure increases, both S/C and O_2/C ratios increase but result in declining H₂ production per mole methane. Increasing reformer operating temperature to 1000° C (the two bar groupings on the right of the figure) results in improved H₂ yield with lower S/C and O_2/C ratio than at 800°C. This indicates that increasing reformer temperature is more effective than increasing steam as an excess reactant to increase H₂ yield. This is borne out by the energy balances for three cases shown in Figures 2.4.16-2.4.18. These results summarize the energy requirements of the five process steps. At each condition, the cumulative enthalpy is negative (i.e., heat release) as required. This excess would equate to an 18% heat loss from each of the five process steps.



Figure 2.4.15 Predicted conversion efficiency (enthalpy of H_2 in reformate/enthalpy of CH_4 in fuel feed), O_2 to carbon ratio, steam to carbon ratio, and H_2 production per mole of methane for various reforming temperatures and pressures and optimized S/C and O_2/C ratios. A heat loss of 18% is included in the calculation.



Figure 2.4.16 Energy balance for methane reforming at 1 atm., 800° C, S/C = 1.1, and $O_2/C = 0.6$. Numbered bars on abscissa are defined as: (1) enthalpy required to raise reactants from 4° C to reformer temperature (including heat of vaporization of liquid water), (2) enthalpy of reforming reaction with products predicted by chemical equilibrium, (3) enthalpy rejected to cool reformate to the selected water gas shift reaction temperature and pressure, (4) enthalpy of reaction for the water gas shift at the selected temperature and pressure with products predicted by equilibrium, and (5) enthalpy rejected to cool water gas shift products to fuel cell inlet temperature and pressure.



Figure 2.4.17 Energy balance for methane reforming at 80 atm., 800° C, S/C = 3.5, and $O_2/C = 0.9$. Numbered bars represent same quantities as in Figure 3.6.4.



Figure 2.4.18 Energy balance for methane reforming at 80 atm., 1000° C, S/C = 2.4, and $O_2/C = 0.8$. Numbered bars represent same quantities as in Figure 3.6.4.

II.4.2.4 fuel gas contaminant removal

Tables 2.1.3 and 2.1.4, and the data discussed in Appendix E, indicate that sources of seafloor methane may be contaminated with a variety of substances that could compromise operation of the reformer and fuel cell. Among these contaminants, H_2S poses the greatest threat to the reformer and also to the fuel cell catalysts if the seafloor methane mixture is employed as a carrier gas to deliver extracted O_2 to the cathode. CO_2 also is a concern if an AFC is selected.

Since the type of fuel cell remains to be selected, attention focused on hydrogen sulfide. A sulfur removal test bed was designed to operate at ambient temperature and pressures < 80 atm, and with liquid or dry sorbents. Figure 2.4.19 presents a photograph of the completed system; a schematic diagram is shown in Figure 2.4.20.



Figure 2.4.19 Photograph of the sulfur removal sorbent test bed to investigate removal of H₂S from methane gas mixtures at ambient temperature and pressures up to 80 atm.



Figure 2.4.20 Schematic diagram of the sulfur removal sorbent test bed.

The primary component of the sulfur removal test bed is the sorbent column. This column can be loaded with solid or liquid sorbents for testing and evaluation. It is constructed from Schedule 80 nom. 1 inch (25 mm) stainless steel pipe which is 45.7 cm in length and has an inner diameter of 2.43 cm. All components including the sorbent column have been treated with a Sulfinert[®] coating which prevents sulfur compounds from being adsorbed on working surfaces of the system. The system is capable of operating at pressures up to 80 atm.

Methane doped with 1043 ppmV hydrogen sulfide (H₂S) and nitrogen was supplied to the system from gas bottles and metered using electronic mass flow controllers. Flow rates were controlled and recorded along with system temperature and pressure using a LabView[®]-based data acquisition system. Nitrogen was used primarily to leak test the system before an experiment and to purge the system after completion of a test.

An activated alumina sorbent (Dynocel 628, Porocel Corp. NJ) was employed in the sulfur removal experiment. Properties of this sorbent are listed in Table 2.4.8. In each test, nominally 20 g of sorbent was placed in the column forming a bed ~5.5 cm deep. Initial tests were performed at room temperature and pressures of 14 atm and 28 atm.

Chemical	Al2O3+Promoter	99.60%
	Na2O	0.36%
	SiO2	0.02%
Physical	Total pore volume	0.47ml/g
	Surface area	300m2/g
	Bulk density	785kg/m3
	Size	2mm (1/16")

Table 2.4.8Properties of the solid sorbent (Dynocel 628)

Performance was evaluated by measuring the concentration of H_2S exiting the sulfur removal sorbent test bed. A Shimadzu 2041 gas chromatograph shown in Figure 2.4.21 was employed to analyze the gas mixture. This instrument is equipped with a sulfur chemiluminescent detector (SCD) and capillary column (Rtx-1, 60m-0.53mm-7.00µm, Restek Corporation). Helium (He) serves as carrier gas and a six-port sampling valve is used to make automatic injections into the GC. The column temperature was run isothermally at 100°C for the duration of the analysis. During the experimental runs, the GC system repeatedly sampled the effluent gas with a cycle time of 1.1 minutes. The sulfur detection limit was approximately 500 ppb. Test conditions for the two experiments are provided in Table 2.4.9.



Figure 2.4.21 Shimadzu gas chromatograph used in the H₂S removal experiments.

	Test 1	Test 2
Inflow of CH_4 + 1043 ppm H_2S (Ipm @ STP)	1	1
Temperature (°C)	27	27
Pressure (atm)	14	28
Sorbent mass (g)	20	20
Sorbent volume (cc)	25.6	25.6
GHSV at reactor conditions (hr ⁻¹)	185	92

Summary of H₂S removal test conditions

Table 2.4.9

Results of the sulfur removal sorbent test bed experiments are summarized as breakthrough curves shown in Figure 2.4.22. In both tests, H_2S concentration in the gas exiting the bed remains below the detection limit of the instrument (500 ppb) for more than 75 minutes. As breakthrough occurs, the H_2S detected in the outlet gas exponentially increases from sub-ppm levels to >15 ppm. Beyond this range the detector soon becomes saturated. Increasing pressure serves to increase the time until breakthrough occurs and is likely due to improved penetration of the gas into the pore volume of the sorbent and the increased residence time of the gas in the sorbent bed as indicated by the reduced GHSV. Additional testing should be performed to explore the effects of bed geometry, pressure, temperature, and other sorbent characteristics on system performance.



Figure 2.4.22 Breakthrough curve for Dynocel 628 as a function of pressure at 27°C. Feed gas is methane with 1043 ppm H_2S

Based on results of the two tests conducted to date, sulfur loading capacities for Dynocel 628 were calculated. These values were in turn used to compute bed volume requirements for a

seafloor installation at a methane flow rate of 1 mmol/s and system lifetimes of three (minimum) and five (maximum) years. Results are given in Table 2.4.10. Sulfur loading rates determined using the test bed ranged from 5.8 to 6.7 mg S per g of sorbent. At these sulfur capacities, a seafloor installation designed for a three year life at a pressure of 28 atm would require a sorbent volume of 0.6 m³ or 470 kg of sorbent. A five year life would increase the required sorbent volume and the worst case scenario is for a seafloor installation operating at 14 atm, which would require 1.2 m³ of sorbent volume or 920 kg. These numbers are clearly preliminary and modifications to reactor geometry, sorbent selection, and operating pressure can be expected to improve system performance, thereby reducing sorbent volume requirements.

-	Test 1	Test 2
Sulfur Sorbent Test Bed Results		
Inflow of $CH_4 + H_2S$ (lpm @ STP)	1	1
H2S concentration (ppm)	1043	1043
Test Temperature (°C)	27	27
Test Pressure (atm)	14	28
Sorbent mass (g)	20	20
Sorbent volume (cc)	25.6	25.6
GHSV at reactor conditions (hr ⁻¹)	185	92
Time of break through, H2S>500 ppb (min)	77.2	90.4
Sulfur flow rate (mmol/s)	0.00078	0.00078
Methane flow rate (mmol/s)	0.743	0.743
Total Sulfur Removed (mmol)	3.59	4.21
Total Methane Purified (mmol)	3442.5	4031.1
Sulfur loading (mg S/g sorbent)	5.8	6.7
Sulfur loading (mmol S/g sorbent)	0.18	0.21
Seafloor Installation Requirements		
Required methane flow rate (mmol/s)	1	1
Sorbent needed for 3 year life @ 1 mmol CH4/s (kg)	550	469
Sorbent needed for 5 year life @ 1 mmol CH4/s (kg)	916	782
Sorbent needed for 3 year life @ 1 mmol CH4/s (m ³)	0.70	0.60
Sorbent needed for 5 year life @ 1 mmol CH4/s (m ³)	1.2	1.0

Table 2.4.10Summary of sulfur loading capacities for Dynocel 628 and sorbent volume
requirements for a seafloor installation.

II.4.2.5 fuel supply system summary

Experiments and analyses have been conducted to identify currently available technologies that could be adapted to seafloor operating conditions to reform and purify the fuel gas, and to characterize performance and to evaluate material (notably, O₂) and energy requirements of these components. The primary results of this effort are:

- Catalytic thermochemical reforming, followed by water-shift, of CH₄ to H₂ appears to be a viable option for small subsea power stations employing fuel cells as the energy conversion device.
- Methane reforming tests conducted at operating pressures up to 58 atm. were successful; no significant problems were encountered. Based on our survey of the literature, these experiments may represent the first systematic investigation of high pressure methane reforming.
- Reformate composition data over a range of pressures agree well with equilibrium values calculated using the FACTSageTM 5.1 software package. This suggests that equilibrium models can be employed to estimate performance of the reforming process for system integration and optimization.
- Concentrations of H₂ and CO were observed to decrease with increasing operating pressure; CO₂ concentration was relatively unaffected by pressure, but the amount of unreacted methane increased significantly. Reduced methane conversion also results in reduced gas yield. Over the range of expected pressures, none of these effects is expected substantially to compromise system performance.
- While elevated pressure is known to induce carbon formation and coking of the reformer catalyst, none was observed in our experiments conducted to date. Longer term tests should be performed for verification.
- The amount of O_2 needed for reforming can be shown to be about 30% of stoichiometric O_2 , i.e., 30% of what would be consumed completely to oxidize methane to CO_2 and H_2O . For a nominal 100 W system operating at 10% overall efficiency, this corresponds to approximately 2 x 10⁴ mol O_2 /year. The reformer requires gas-phase O_2 , either in pure form or in a mixture of gases. Gas mixtures with low values of O_2 mole fraction are not suitable for reforming. Furthermore, if O_2 is supplied in a gas mixture of reactive and diluent species, then the composition of the mixture will affect the reforming process and needs to be controlled.
- Equilibrium calculations indicate that the cumulative enthalpy of all steps of the reforming process is negative (i.e., there is a net heat release). This excess would equate to an 18% heat loss from each of the five process steps which include: raising reactants to the selected reforming temperature and pressure; reaction at the selected reforming temperature and pressure; cooling of reformate to the selected temperature and pressure; and cooling of water gas shift reaction at the selected temperature and pressure. The energy to drive the reformer comes from oxidation of a portion of the methane fuel gas; the energy content of the reformate is less than that of the original reactants.
- While, in concept, thermochemical reforming appears to be a good candidate for the present application, engineering studies will need to be pursued to develop simple and robust methods to meter reactants appropriately and to control operating conditions including temperatures and pressures.
- To account for the possibility that extraction of dissolved oxygen from sea water will not be able to provide the high concentrations of gas phase O₂ required for reforming or will impose too high an energy penalty on the system, experiments were conducted to explore the use of liquid hydrogen peroxide as a stored oxidizer.

- H₂O₂ decomposes to provide O₂, H₂O, and heat. Pure H₂O₂ has an oxidizer density of about 21 mol O₂/liter H₂O₂. This compares favorably to pure O₂ gas stored at, say, 80 atm and 5°C, which contains only 3.5 mol O₂/liter.
- Tests were performed at 8-9 atm. and 800°C in which H₂O₂ was used successfully in place of O₂ gas to reform methane to H₂. To our knowledge, these experiments represent the first investigation of hydrogen peroxide reforming of CH₄. Reformate composition predicted by chemical equilibrium agreed within < 2% (absolute) for all species. Additional verification testing should be conducted over a range of pressures and oxygento-carbon ratios. Using higher concentration H₂O₂ solutions should also be studied.
- High pressure contaminant removal experiments were initiated. A review of the literature identified H₂S and, possibly, CO₂, as the species found mixed with seafloor methane that pose the greatest threat to the operation of the reformer and fuel cells. H₂S deactivates catalysts and CO₂ can result in carbonation of the AFC electrolyte. Since it has not been determined if AFC will be employed, the present investigation focused on H₂S. Breakout curves were obtained for a commercially-available activated alumina sorbent at two values of pressure (14 and 28 atm.). The bottled gas mixture entering the sorbent bed comprised methane doped with 1043 ppmV H₂S. This value of H₂S concentration was selected based on literature on seafloor methane seeps and released gases from hydrates.
- As configured, our test facility was able easily to reduce H_2S levels to from 1043 ppmV to below 500 ppbV at a mixture flow rate of 1 slpm and temperature = 27°C.
- Increasing pressure serves to increase the time until breakthrough occurs and is likely due to improved penetration of the gas into the pore volume of the sorbent and the increased residence time of the gas in the sorbent bed as indicated by the reduced GHSV (gas hourly space velocity). Additional testing needs to be performed to explore the effects of bed geometry, pressure, temperature, and other sorbent characteristics on system performance.
- Based on these initial, non-optimized results, sorbent bed capacities were estimated for a nominal 100 W system. Approximately 0.6 m³ of sorbent is required for 3 years of continuous operation; 1.2 m³ is required over a 5 year lifetime. Modifications to reactor geometry, sorbent selection, and operating pressure can be expected to improve system performance, thereby reducing sorbent volume requirements from these preliminary estimates.

II.4.3 Oxygen supply system

At the time that this project was conceived, it was anticipated that the oxygen supply system might present a major technical hurdle, particularly if a large portion of the required O_2 was to be extracted from ambient sea water. This concern has been borne out over the course of our investigation. Although, the fuel supply and fuel cell subsystems are problematic, options do appear to exist and candidate devices have been identified. The strategy for the oxygen supply system, on the other hand, has not been finalized.

The oxygen supply system must provide about 0.002 mol O_2 /s (3 slpm) in order to produce ~100 W net power at a system efficiency of 10%. As discussed in Section II.4.2.3, approximately 30% of the oxygen is consumed by the reformer and the other 70% in the fuel cell. The reformer

requires gas phase O_2 at relatively high concentrations while, depending on the type of fuel cell, it may be possible to deliver oxygen to the cathode with a liquid carrier and at lower concentrations.

There are two approaches to supply O_2 : 1) extraction of DO from the ambient sea water; and 2) stored oxidizer brought down from the surface at the time of deployment. Extraction of DO for underwater human respiration or for use by submersible vehicles has been pursued for some time (see Appendix A) and a few patents have been granted for related technologies (e.g., Bonaventure et al., 1986). To our best knowledge, however, no commercially-available devices for subsea applications currently exist (although various prototypes reportedly have been fabricated). Ambient levels of DO limit the attainable concentration of O₂. Sea water near the surface is at equilibrium with air, which sets a limit on O₂ partial pressure of about 18 - 20 kPa (the partial pressure of O_2 in the air in contact with the ocean surface). DO concentrations decline with depth. As discussed in Section II.4.1.2, an O₂ partial pressure of 8 kPa in an extracted gas mixture appears feasible at the candidate seafloor sites for prototype deployment. This level of O₂ may not, however, be sufficient for reforming and will also degrade fuel cell performance as discussed previously. Stored oxidizer could be required to provide a portion or all of the oxygen consumed by the system. To minimize the size of storage devices, liquid oxidizers such as H₂O₂ are favored over gases due to their higher oxygen content per unit volume.

Over the past 15 months, a broad range of options were explored to supply oxidizer to the subsea power generation system. Options investigated to recover DO from ambient sea water included direct contact mass exchange such as bubble columns and sea water spray systems, as well as various configurations of membrane gas extraction. Both experiments and analyses were conducted and their results have been described in detail in the Quarterly Reports included in this report as Appendices A, B, and C.

The use of high-oxygen solubility liquids, specifically perfluorocarbons such as PFOB, to deliver O_2 to the fuel cell cathode also was studied (see Section II.4.1.2). The rationale for using these substances is that higher concentrations of oxygen will accumulate in them, as compared to a carrier gas such as N_2 or CH₄, when placed in contact with sea water containing DO. Under certain scenarios, this higher concentration may be exploited to enhance the rate of O_2 delivery to the fuel cell cathode with an accompanying improvement in limiting current.

Finally, experiments were initiated to explore the use of liquid H_2O_2 as a stored oxidizer. To date, work has focused on determining whether it is a suitable oxidizer for methane reforming.

II.4.3.1 direct contact DO extraction

Direct contact heat and mass exchangers are often used in industrial processes where fluid purity is not an issue, since these devices usually have lower transport resistances and are relatively simple to implement. During this project, we conducted studies of dissolved oxygen extraction by bubbling carrier gas through sea water and by spraying sea water into carrier gas. In the former case, a confined bubble plume of O_2 -depleted carrier gas would rise through the sea water, scrubbing up dissolved oxygen as shown in Figure 2.4.23. The bubbles would be


Figure 2.4.23 Sketch of the concept to extract O₂ using gas bubbles.

collected after ascending an adequate distance and the O_2 -replished gas would then be directed into the reformer and fuel cell to supply these components with oxygen. Calculations indicated that the rise height of the bubble plume may need to be large (> 10 m) in order to extract sufficient oxygen. This would complicate the design and operation of such a system.

Direct contact mass transfer can also be accomplished by spraying the sea water into the carrier gas. Figure 2.4.24 shows a sketch of this concept. Compact exchangers are possible using this approach, since residence time is not linked to bubble rise height. Some power would be consumed to generate the liquid spray, except in scenarios where the reformer and fuel cell are operated at pressures below ambient. In this case, the spray could be driven by the pressure difference. Operating at reduced pressure inside a containment hull offers some advantages including higher reformer efficiencies. Disadvantages include the energy penalty of discharging waste products, particularly gases, into the sea water to maintain the reduced pressure.



Figure 2.4.24 Sketch of spray exchanger to extract dissolved O₂ from sea water.

Results of the laboratory experiments and analyses of the bubble and spray DO extraction methods are provided in Appendices B and C. While these types of direct contact mass exchangers appear to have some potential for application in a seafloor power generation system, implementation may be complicated (e.g., providing adequate rise height for a bubble plume; reducing parasitic power consumption to acceptable levels) and performance appears to be marginal at best. In consideration of these deficiencies, membrane mass exchangers were explored as a possible alternative.

II.4.3.2 membrane mass exchangers

Most concepts proposed to extract DO from sea water have been based on membrane contactors. As an example, Nagase *et al.* (2003) investigated artificial gill modules that employ bundles of hollow fibers made of a micro-porous membrane material. Membrane contactors eliminate sea water carryover (which can compromise lifetimes and performance of the reformer and fuel cell) and can be configured to provide high interfacial area and volumetric flows to promote the rate of mass transfer. Transport resistance of the membrane can be kept low by appropriate selection of materials and thicknesses. For micro-porous materials, membrane transport resistance is negligible. Furthermore, unlike the direct contact exchangers we explored, membrane contactors can be applied to liquid carriers such as PFCs as well as gas carriers

Laboratory experiments of membrane DO extraction have been initiated; however, the majority of effort has been invested into modeling studies (see, e.g., Appendices B and C). Appendix C introduces the membrane contactor model. During the final period of this project this model was extended and calibrated using operating information for a commercial device. The performance of an AFC supplied by a membrane contactor also was investigated.

Membrane Contactor Model and Fuel Cell Performance

In the calculations reported in Appendix C, it was confirmed that a source of sweep gas would be necessary to maintain the continuous extraction of DO from sea water in a membrane contactor module; N_2 played the role of this hypothetical sweep gas. Yet, unless a stored supply of N_2 was brought down from the surface, only methane would be available from seafloor seeps or dissociating hydrate beds. Accordingly, the main thrust of the modeling and design activities during the final period has been to extend the previous analyses of an alkaline fuel cell and of an oxygen-extracting membrane contactor to accommodate gas streams involving three species. In all cases, the additional gas of interest is CH₄. At the anode of the fuel cell, this allows the inclusion of methane leftover from the reforming process. At the cathode, the presence of methane would arise from using available seep gas to sweep oxygen from sea water in the mass exchanger modules.

In the membrane contactor algorithm, the value of the outlet gas-phase oxygen flow rate $N_{GO2}(0)$ is iterated as before until a target stoichiometric ratio $N_{GO2}(0)/N_{GO2}(A)$ (where (A) designates conditions at the inlet to the contactor) is obtained. This calculational loop, however, is imbedded in another one involving nitrogen composition $X_{N2}(0)$, where X is the gas-phase mole fraction; here, the target is a 'neutral' N₂ flow rate such that $N_{GN2}(0) = N_{GN2}(A)$. N₂ is present in

the sweep gas since it desorbs from sea water along with O₂. Additional parameters are methane solubility $\alpha_{CH4} \approx 1.4 \times 10^{-5}$ mol/m³-Pa and the shell-side methane mass transfer coefficient $k_{shell;CH4} \approx 0.90 \ k_{shell;O2}$. Figures 2.4.25 and 2.4.26 summarize results obtained for the 'standard' module considered previously when total pressure is either 1 bar or 10 bar. Sea water flows outside of the hollow fibers (shell side) and carrier sweep gas flows inside the hollow fibers (lumen side).

It can be seen that at near-atmospheric pressures (1 bar), the gas mixture includes about 80% nitrogen; at pressures typical of 100 m water depths (10 bars), however, gas composition is shifted largely to methane with mole fractions of the order of 90%. This effect of pressure is reflected in a dramatic increase in the amount of make-up methane that must be supplied upstream of the mass exchanger, from 14 μ mol/s (per standard module) to 883 μ mol/s. In terms of *in situ* gas volume flow rates, though, the ratio is one order of magnitude smaller. At higher pressures, the enhanced capacity for the sweep gas to dissolve into sea water is evident as methane saturation in the outlet sea water stream goes from 10% at 1 bar to more than 60% at 10 bar.

Next, the gas compositions determined at the mass exchanger outlet were used as input for the cathodic feed stream of the AFC model described in Section II.4.1.3. A set of calculations was performed as gas compositions at the fuel cell anode were set to reflect possible outputs from a reforming module. Table 2.4.11 lists the cases that were examined: 'A' corresponds to a (reforming) oxygen-to-carbon ratio of 0.645 and a steam-to-carbon ratio of 0.914, and 'B' to an oxygen-to-carbon ratio of 0.122 and a steam-to-carbon ratio of 1.66. The first number in the case label is the reforming temperature in °C, and the second is the pressure in atmospheres. It was further assumed that any carbon monoxide is oxidized to CO_2 , and residual steam condensed out between the reformer and the fuel cell. Figures 2.4.27 to 2.4.30 show the polarization and power curves predicted by our models for a 225 cm² AFC. In these cases, the cathode was fed by approximately 100 standard contactor modules.

Case Label	Hydrogen Mole Freation	Carbon Dioxide	Methane Mole Erection
			Mole Flaction
Reference	0.90	0.10	0.0
A800_1	0.535	0.26	0.205
A1200_1	0.883	0.117	0.0
B800_1	0.598	0.147	0.255
B1200_1	0.948	0.052	0.0
A800_10	0.288	0.293	0.419
A1200_10	0.873	0.12	0.007
B800_10	0.366	0.122	0.512
B1200 10	0.93	0.055	0.015

Table 2.4.11Anode inlet composition.

Standard Module (1 Bar, 10°C)



Figure 2.4.25 Membrane contactor extraction of DO model results at 1 bar and 10°C. Carrier gas comprises CH₄, N₂, and O₂.



Figure 2.4.26 Membrane contactor extraction of DO model results at 10 bar and 10°C. Carrier gas comprises CH₄, N₂, and O₂.





Figure 2.4.27 Polarization curves predicted by AFC model. Cathode O₂ levels determined using membrane contactor model at 1 bar and 10°C; anode fuel gas composition from equilibrium calculations.





Figure 2.4.28 Power curves predicted by AFC model. Cathode O₂ levels determined using membrane contactor model at 1 bar and 10°C; anode fuel gas composition from equilibrium calculations.





Figure 2.4.29 Polarization curves predicted by AFC model. Cathode O₂ levels determined using membrane contactor model at 10 bar and 10°C; anode fuel gas composition from equilibrium calculations.





Figure 2.4.30 Power curves predicted by AFC model. Cathode O₂ levels determined using membrane contactor model at 10 bar and 10°C; anode fuel gas composition from equilibrium calculations.

The effect of anodic gas composition is observed to be quite modest, barring the possible presence of catalyst poisons. It appears that for the conditions studied, fuel cell behavior is limited by oxygen supply at the cathode. The modeled AFC unit produces gross power of about 50 W at 1 bar and only 6 W at 10 bar. This order of magnitude decrease is the result of a commensurate reduction in the limiting current, even though cell potential slightly increases at higher pressure (as in the Nernst formula). Note that, as discussed in Section II.4.1.2, fuel cell response to diminished O₂ mole fraction at elevated sweep gas mixture pressure (but constant partial pressure) needs to be confirmed. Taking the modeled results at face value with an O₂ stoichiometric ratio of 2, two fuel cell units could produce a gross power of 100 W with an overall oxygen input of 620 μ mol/s at a total pressure of 1 bar. Similarly, 16 fuel cell units could produce a gross power of 100 W with an overall oxygen input of 460 μ mol/s at a total pressure of 10 bar.

The above simulations provide valuable insight into the sensitivity of system performance to the oxygen supply; however, the validity of the results of an uncalibrated model of a hypothetical membrane contactor is a concern. Moreover, it is difficult to estimate accurately associated parasitic power losses of a hypothetical device. This is important in the evaluation of marginal systems such as the present where such losses could approach or exceed gross power output. During the second half of this project, we have been searching for a commercial membrane contactor that could be applied to the seafloor power system and used to ground truth our model. Recently, a device was identified that warrants consideration. Specifications for the Liqui-Cel 10 x 28 Extra Flow are shown in Figures 2.4.31 and 2.4.32 taken from their website product literature (www.liqui-cel.com). This contactor is used to remove dissolved gases to purify processing water, beverages, etc. Its active area of 130 m² coincidentally corresponds to 100 of the 'standard' modules considered by the model. This effectively eliminates the unresolved issue of stacking mass exchanger modules. The operation of this hardware with sea water was assumed to be possible, although the size of the membrane pores (0.05 μ m radius) may require some preliminary filtering.

The computer algorithm developed so far was calibrated to model the Liqui-Cel 10 x 28 Extra Flow. At atmospheric pressure and 20°C, 3.5 ft³/min of pure N₂ was used to degas 160 gpm of water assumed to be at equilibrium with air. The target oxygen extraction ratio (X40 fiber) was 83.2%. Results are shown in Figure 2.4.33. To obtain an accurate calibration, the oxygen mass exchange coefficient had to be estimated. A value of $k_{shell;O2} = 1.56 \times 10^{-4}$ m/s (156 µm/s) was obtained, i.e., nearly 60% better than the straw-man value adopted for the standard module.

Subsequently, three-gas calculations for the Liqui-Cel 10 x 28 Extra Flow could be performed under the same conditions as specified earlier (cf., Figures 2.4.25 and 2.4.26). Figures 2.4.34 and 2.4.35 show the results. An important consideration in the present application, however, is the need to limit power losses. The nominal water flow rate of 160 gpm (about 10 l/s) for this unit was found to require a minimum of 220 W of shell-side pumping power according to the characteristic curve in Figure 2.4.32. It was assumed that lumen-side power losses were small enough to be neglected at this stage of analysis since overall gas flow rates did not reach excessive values. This power requirement would exceed the power generation capabilities of the fuel cell units considered so far when they operate with oxygen-poor cathodic feedstreams.

10x28 EXTRA-FLOW PRODUCT DATA SHEET



Liqui-Cel[®]



n		Ext	ro Elou				
	Extra-Flow with Center Baffle						
Liquid Flow Guidelines		X50: 10 – 48 m ³ /hr (44 – 210 gpm) X40: 10 – 57 m ³ /hr (44 – 250 gpm)					
Membrane Type		X50 Fiber			X40 Fiber		
	Recomm CO2 rem	ended for oval from v	water		Recommer gas transfe	nded for all other er applications	
Porosity		~40%			~25%		
OD / ID		300 / 220 micron			300 / 200 micron		
Membrane/Potting Material		Polypropylene / Epoxy					
Typical Membrane Surface Area		1400 ft ² (130m ²)					
Maximum Shellside Working Temperature/Pressure of Fiber* [Using 50 mm vacuum on Lumenside. Add 1.05 kg/cm ² (15 psid) when vacuum is not used 1		X50 Fiber 4 kg/cm² or 7.2 bar 1 kg/cm² or 2.0 bar		25°C, 9.5 50°C, 7.4 70°C, 2.1	(40 Fiber kg/cm ² or 9.3 bar kg/cm ² or 7.2 bar kg/cm ² or 2.0 bar		
8	(12) (15	2ºF, 105 p i8ºF, 30 ps	sig) iig)		(77º (122 (158	F, 135 psig) ⁰F, 105 psig) ⁰F, 30 psig)	
ximate)							
Shellside Lumenside		26.1 liters (6.9 gal.) 10.6 liters (2.8 gal.)			23.4 liters (6.2 gal.) 9.0 liters (2.4 gal.)		
nd Char	acteristi	cs					
316L SS Vessel/CF3M SS End Caps Mechanical finish or <25RA with Electropolish		er Reinforced Plastic (FRP) h PVDF for all wetted faces and FRP flanges					
3 inch class 150 raised face flange per ANSI B16.5 80A at 10K flat face flange per JIS B2238 3 inch sanitary flange							
1 inch class 150 raised face flange per ANSI B16.5 50A at 10K flat face flange per JIS B2238 1.5 inch sanitary flange							
10.6 Kg/cm ² (10.3 bar or 150 psi) Shellside (Liquid Only) 9.1 Kg/cm ² (9.0 bar or 130 psi) Lumenside 316 LSS 6.3 Kg/cm ² (6.2 bar or 90 psi) Lumenside FRP NOTE: Refer to Cartridge Characteristics for maximum operating conditions.							
Material					Applications		
EPDM (ANSI / NSF 61, FDA CFR title 2			?1 Compliant) [†]		General Purpose		
St	Stainless Steel Housing			FRP Housing			
ANSI / JI 111 kg. (137 kg. (10 kg. (168 kg. (S (244 lbs.) (302 lbs.) (23 lbs.) (370 lbs.)	Sanitar 81 kg. 107 kg. 10 kg. 138 kg.	y (177 ll: (235 ll (23 lbs (303 ll:	os.) bs.) s.) os.)	33 kg. 57 kg. 10 kg. 44 kg.	(73 lbs.) (125 lbs.) (23 lbs.) (98 lbs.)	
	Area ing Fiber* r ² nd Char. 316L SS V Mechanica Electropol	Normal Normal Recomm CO2 rem 300 Area 300 Ing 50°C, 7. Fiber* 50°C, 7. 70°C, 2. 7 rot used.] (12: (15: (12: wimate) 26.1 10.6 10.6 Mechanical finish or Electropolish • 3 inch class 150 • 80A at 10K flat ff • 3 inch class 150 • 80A at 10K flat ff • 1 inch class 150 • 50A at 10K flat ff • 1 inch class 150 • 50A at 10K flat ff • 1 inch class 150 • 50A at 10K flat ff • 1 inch class 150 • 50A at 10K flat ff • 1 inch class 150 • 50A at 10K flat ff • 1.5 inch sanitary fl • 1.6 Kg/cm² (10) • 9.1 Kg/cm² (2.0) • 1.6 Kg/cm² (10	X50 Fiber Recommended for CO2 removal from V ~40% 300 / 220 mid Area ing X50 Fiber Fiber* 50°C, 7.4 kg/cm² o 70°C, 2.1 kg/cm² o r0°C, 2.1 kg/cm² o (122°F, 105 p (158°F, 30 ps ximate) 26.1 liters (6.9 10.6 liters (2.8 nd Characteristics 316L SS Vessel/CF3M SS End Mechanical finish or <25RA	X50 Fiber Recommended for CO2 removal from water ~40% 300 / 220 micron Polypro Area 140 ing Fiber* 50°C, 7.4 kg/cm² or 7.2 ba 70°C, 2.1 kg/cm² or 2.0 ba 1158°F, 30 psig) (122°F, 105 psig) (158°F, 30 psig) (158°F, 30 psig) ximate) 26.1 liters (6.9 gal.) 10.6 liters (2.8 gal.) 10.6 kg/cm² (10.3 bar or 150 psi) 3 inch class 150 raised face flange 1 inch class 150 raised face flange 1 1.5 inch sanitary flange 1 1.6 kg/cm² (10.3 bar or 150 psi) 9.1 kg/cm² (0.0 bar or 130 psi) Lun NOTE: Refer to Cartridge Characteristi operating conditions. A CFR title 21 Compliant) [*] Stainless Steel Housing <t< td=""><td>X50 Fiber Recommended for CO2 removal from water ~40% 300 / 220 micron Polypropyler Area 1400 ft² (* ing X50 Fiber Fiber* 50°C, 7.4 kg/cm² or 7.2 bar 70°C, 2.1 kg/cm² or 2.0 bar r² (122°F, 105 psig) (158°F, 30 psig) ximate) 26.1 liters (6.9 gal.) 10.6 liters (2.8 gal.) nd Characteristics stall 316L SS Vessel/CF3M SS End Caps Mechanical finish or <25RA</td> Fiber Inch class 150 raised face flange per JIS B223 sur 3 inch class 150 raised face flange per JIS B223 3 inch class 150 raised face flange per JIS B223 3 inch class 150 raised face flange per JIS B223 1.5 inch sanitary flange 1 1ich class 150 raised face flange per JIS B223 1.5 inch sanitary flange 1 10.6 Kg/cm² (9.0 bar or 130 psi) Lumensic NOTE: Refer to Catrridge Characteristics for operating conditions. NOTE: Refer to Catrridge Characteristics for operating conditions. 107 kg. (231 bs.) ASI (JUS Sanitary 111 kg. (244 lbs.) 107 kg. (233 lbs.) 108 kg. (370 lbs.) 107 kg. (233 lbs.) 108 kg. (370 lbs.) 108 kg. (3</t<>	X50 Fiber Recommended for CO2 removal from water ~40% 300 / 220 micron Polypropyler Area 1400 ft ² (* ing X50 Fiber Fiber* 50°C, 7.4 kg/cm² or 7.2 bar 70°C, 2.1 kg/cm² or 2.0 bar r² (122°F, 105 psig) (158°F, 30 psig) ximate) 26.1 liters (6.9 gal.) 10.6 liters (2.8 gal.) nd Characteristics stall 316L SS Vessel/CF3M SS End Caps Mechanical finish or <25RA	X50 Fiber X Recommended for CO2 removal from water Recommer gas transfer \sim 40% 300 / 220 micron 300 Polypropylene / Epoxy 300 300 Area 1400 ft ² (130m ²) 300 Fiber* 50°C, 7.4 kg/cm ² or 7.2 bar 70°C, 2.1 kg/cm ² or 2.0 bar 25°C, 7.4 70°C, 2.1 kg/cm ² or 2.0 bar r² 1(122°F, 105 psig) (77° (158°F, 30 psig) (122 ximate) 26.1 liters (6.9 gal.) 23.4 l 10.6 liters (2.8 gal.) 9.0 lit stimate) 26.1 liters (6.9 gal.) 9.0 lit nd Characteristics Stend Caps Fiber Reinford stimate) 26.1 liters (2.8 gal.) 9.0 lit nd Characteristics Stend Caps Fiber Reinford stimate) 23.4 l 9.0 lit 10.6 Kg/cm ² (0.0 bar or 150 psi) Shellside (Liquid 9.0 lit 1 10.6 liters (2.8 gal.) 9.0 lit 1 10.6 kg/cm ² (0.0 bar or 150 psi) Shellside (Liquid 9.1 kg/cm ² (0.0 bar or 150 psi) Shellside (Liquid 1 1.5 inch sanitary flange 1.5 inch sanitary flange <td< td=""></td<>	

NOTE: All dimensions are nominal values



Liqui-Cel[®] Membrane Contactors

10x28 EXTRA-FLOW PRODUCT DATA SHEET







Cartridge Specifications						
Characteristics	Test Conditions	Specifications				
Performance 02 Removal	Shellside water flow: 160 gpm, 20°C (68°F)	X40 : 83.2% minimum				
	Lumenside N ₂ Flow: 3.5 ft ³ /min, 1.0 atm at 20°C	X50 : 81.3% minimum				
Pressure Drop	Shellside water flow: 160 gpm, 20°C (68°F)	X40: 6.0 psi maximum				
		X50: 7.9 psi maximum				

Curves represent nominal values using water.

Test condition O_2 Removal: N_2 -vacuum combo mode, Vacuum: 50 mm Hg N2 sweep: 0.25 SCFM. 20° C.

Test condition CO₂ Removal: Air vacuum combo mode, vacuum: 75 mm Hg, air sweep 1 scfm. 25° C.

Characteristics may change under different operating conditions.

¹All wetted components of the Liqui-Cel[®] High Purity Extra Flow Membrane Contactor, when used in accordance with recommendations given in our product literature for treatment of processing water, alcoholic and non-alcoholic beverages, and aqueous, acid and non-acid food products at and below ambient temperatures, are in compliance with all relevant FDA regulations as specified in Title 21 of the Code of Federal Regulations.

This product is to be used only by persons familiar with its use. It must be maintained within the stated limitations. All sales are subject to Seller's terms and conditions. Purchaser assumes all responsibility for the suitability and fitness for use as well as for the protection of the environment and for health and safety involving this product. Seller reserves the right to modify this document without prior notice. Check with your representative to verify the latest update. To the best of our knowledge the information contained herein is accurate. However, neither Seller nor any of its affiliates assumes any liability whatsoever for the accuracy or completeness of the information contained herein. Final determination of the suitability of any material and whether there is any infringement of patents, trademarks, or copyrights is the sole responsibility of the user. Users of any subtance should satisfy themselves by independent investigation that the material can be used safely. We may have desorbed certain hazards, but we cannot guarantee that these are the only hazards that exist.

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Figure 2.4.32 Liqui-cel membrane contactor product information (continued).

Liqui-Cel 10 x 28 Extra Flow Calibration Run (1 atm, 20°C, 160 gpm, N₂)



Figure 2.4.33 Results of model calibration using Liqui-cel membrane contactor product data. Operation at 1 atm. and 20°C; sea water flow rate = 160 gpm; N_2 sweep gas.

Liqui-Cel 10 x 28 Extra Flow (1 Bar, 10°C, 50 gpm)



Figure 2.4.34 Simulated DO extraction at shallow seafloor conditions. Model calibrated for Liqui-cel membrane contactor. Operation at 1 bar and 10° C; sea water flow rate = 50 gpm; sweep gas comprises mixture of CH₄, N₂, and O₂.



Figure 2.4.35 Simulated DO extraction at deeper seafloor conditions. Model calibrated for Liqui-cel membrane contactor. Operation at 10 bar and 10°C; sea water flow rate = 50 gpm; sweep gas comprises mixture of CH_4 , N_2 , and O_2 .

Reducing the sea water flow rate to 50 gpm (3.15 l/s) for a listed pressure drop of 1 psi (nearly 7 kPa) yielded an order-of-magnitude reduction in the shell-side pumping power (i.e., isentropic pumping power \approx volumetric flow rate x pressure increase = 0.00315 m³/s x 6894 Pa = 21.7 W; dividing this value by a pump efficiency of 60% yields about 36 W). At the same time, calculated oxygen flow rates $N_{GO2}(0)$ were large enough at 10 bar (609.1 µmol/s > 456 µmol/s) or close enough to fuel-cell needs at 1 bar (495.2 µmol/s instead of 620 µmol/s) to suggest that a single Liqui-Cel 10 x 28 Extra Flow (and a power loss of about 20 - 36 W) might be sufficient for a system producing gross power of about 100 W. Alternatively, it may be reasonable to assume that two or more of these contactor/fuel cell modules may need to be placed in service with the additional units being dedicated to providing for parasitic power consumption.

As mentioned previously, our original membrane contactor model was modified to accommodate a three species sweep gas consisting primarily of methane, since, unlike N_2 , a supply of CH₄ is available on the seafloor to make-up for losses due to dissolution into sea water in the contactor. At elevated pressures of the order of 10 bars, a substantial amount of methane has to be supplied to sustain sweep gas requirements (e.g., 0.04 mol/s). It can be seen in Figure 2.4.35 that methane saturation in the outlet sea water stream approaches 90% while there is practically no dissolved methane in the inlet sea water stream (1.6 ppm, based on equilibrium with air at the ocean surface). Yet, ambient methane concentrations in the vicinity of active seafloor seeps or decomposing hydrate seafloor deposits are likely to be substantially higher than the very low value corresponding to atmospheric equilibrium. Figure 2.4.36 shows that, all things being otherwise equal, large methane concentrations in the sea water inlet stream may dramatically reduce make-up methane requirements; Figure 2.4.37 indicates that DO extraction also would diminish, albeit to a relatively modest extent.

Finally, the availability of pumps capable of producing large liquid flow rates at low heads was cursorily examined. The power consumption of about 20 - 36 W required by the Liqui-Cel 10 x 28 Extra Flow operating with 50 gpm of sea water would have to be suitably matched. To date, no off-the-shelf pump hardware was found that could provide the necessary flow rate without requiring excessive power. Axial flow propeller units available from Flygt, Figure 2.4.38, may have potential for use in the present application, but probably need to be optimized. Figure 2.4.39 provides some of the characteristics of these pumps. The operating point for our application (50 gpm at 0.7 m of head) clearly lies outside the pump curves shown in the figure. Yet, the effect of propeller size reduction in the existing commercial units, say from 30 inches to 16 inches suggests that a further reduction, down to perhaps 4 to 6 inches, could yield a good match with the Liqui-Cel 10 x 28 Extra Flow requirements. It may also be possible to exploit ambient currents to provide a portion of the flow head and thus reduce pump power consumption. These issues will need to be pursued in the preliminary design phase.

II.4.3.3 stored oxidizer

Calculations presented in the preceding section assumed that only the fuel cell would be supplied with O_2 by membrane contactors that extract DO from ambient sea water. The methane reformer would need a different oxidizer source, since the minimum oxygen concentration it requires



Liqui-Cel 10 x 28 Extra Flow (10 Bars, 10°C, 50 gpm)

Figure 2.4.36 Required methane to make-up for dissolution into sea water in the membrane contactor as a function of methane fugacity of sea water entering the contactor. Operation at 10 bar and 10° C; sea water flow rate = 50 gpm.



Liqui-Cel 10 x 28 Extra Flow (10 Bars, 10°C, 50 gpm)

Figure 2.4.37 O_2 levels in sweep gas at outlet of the membrane contactor as a function of methane fugacity of sea water entering the contactor. Operation at 10 bar and 10°C; sea water flow rate = 50 gpm.



Horizontal propeller pumps For high flow and ultra-low head



Figure 2.4.38 Flygt axial flow propellor pump brochure.



Figure 2.4.39 Flygt axial flow propeller pump product information.

probably is higher than what can be attained by DO extraction at the depths of interest. Since our exploratory experiments (see Section II.4.2.2) support the proposal that H_2O_2 solutions can be used to reform CH_4 , one strategy for a first prototype is to pursue development of a hybrid oxygen supply system consisting of both DO extraction devices and stored hydrogen peroxide.

As discussed in Section II.4.2.3, less than one cubic meter of pure liquid H_2O_2 will provide enough oxygen to sustain continuous reformer operation for a year. Although hydrogen peroxide is available commercially at concentrations up to 98% by weight in bulk quantities, concentrations above 70% wt. are classified as propellants and pose a detonation hazard. It might be prudent, therefore, to consider storing H_2O_2 at lower concentrations, say, between 50% wt. and 70% wt. (which corresponds to H_2O_2 mole fractions of 0.346 and 0.553, respectively). The water component of these solutions would also be utilized as steam in the reforming process.

For the purpose of discussion, let us assume that hydrogen peroxide will be stored as an aqueous solution with a mole fraction of 0.50 (about 65% wt.), so approximately 10 cubic meters will be needed to supply the reformer for 5 years. The density of this solution is about 1280 kg/m³, which is 25% larger than the density of ambient sea water (that ranges between 1025 and 1030 kg/m³) at the candidate sites (see Figure 2.2.8). Other physical properties of hydrogen peroxide solutions that may be useful to design storage and delivery components can be found at the website http://www.h2o2.com/intro/properties/physical.html.

H₂O₂ solutions are reportedly very stable. Losses of less than 1% per year are typical when stored properly at room temperature. At the lower temperatures representative of the seafloor, losses are expected to decline further. Although the spontaneous decomposition hazard is often cited, this problem apparently can be avoided by following well-established practices. Specifically, certain materials should be avoided and all wetted parts must be thoroughly cleaned and passivated.

II.4.3.4 oxygen supply system summary

The oxygen supply system represents a major technical challenge. A strategy to provide the necessary oxidizer for methane reforming and fuel cell operation remains to be determined. Production of net power depends on the selection of appropriate components. Experiments and analyses have been conducted to explore a number of options. The primary results of these investigations include:

- Extraction of DO from ambient sea water, using existing technologies or those that can reasonably be anticipated to be available for use within a 5 year time horizon, does not appear to be sufficient to meet all the oxidizer requirements for seafloor power generation utilizing methane as a fuel. Specifically, attainable concentrations of extracted DO are less than what is needed to thermochemically reform methane to the H₂ utilized by the fuel cell.
- A possible strategy to address this problem is to employ a hybrid system comprising DO extraction to supply the ~70% of total O₂ partitioned to the fuel cell, and stored oxidizer brought down from the surface to supply the 30% used for reforming CH₄. Modeling and some preliminary experiments suggest that it will be possible to operate the fuel cell with extracted DO in gas or liquid PFC carriers. By doing so, instead of using stored oxidizer to supply all components, the amount of stored oxidizer can be reduced significantly. This is an advantage since large system volumes and masses can complicate deployment to the seafloor.

- The use of stored oxidizer diminishes the autonomy of the seafloor power generation system since it will not operate entirely on ambient resources and its operational life will end when the supply is exhausted. In reality, however, it appears that sufficient oxidizer can be stored such that system lifetime will not be affected; lifetime will probably be limited by other key components, notably the fuel cells. It is proposed, therefore, that the use of stored oxidizer represents a reasonable compromise and practical interim measure that will allow a proof-of-concept prototype to be field tested in the near term. Future breakthroughs in sea water DO collection technology may be applied later to upgrade the system.
- Aqueous solutions of hydrogen peroxide appear to be a good candidate for use as the stored oxidizer. Preliminary experiments have confirmed that H_2O_2 can be employed to reform methane. About 10 m³ of 65% wt. H_2O_2 is sufficient to operate the reformer for 5 years.
- Experiments and analyses were conducted to investigate options to recover DO from ambient sea water. These options included two direct contact mass exchangers based on bubbling carrier gas through sea water or spraying sea water into carrier gas, as well as various configurations of membrane gas extraction.
- Results of the laboratory experiments and analyses of the bubble and spray DO extraction methods indicate that, while they have some potential for application, implementation may be complicated (e.g., providing adequate rise height for a bubble plume; reducing parasitic power consumption to acceptable levels) and performance appears to be marginal.
- Membrane contactors have become the focus of our investigation. These devices eliminate sea water carryover and can be configured to provide high interfacial area and volumetric flows to promote the rate of mass transfer. If micro-porous materials are employed, then membrane transport resistance is negligible, essentially eliminating any advantage of direct contact exchangers. Furthermore, membrane contactors can be applied to liquid carriers such as PFCs as well as gas carriers
- A model of a membrane contactor for DO extraction was developed and calibrated to simulate a commercially-available device. The model was coupled to our AFC model to assess the suitability of DO extraction to supply the fuel cell. Results of simulations performed at conditions representative of locations near the ocean surface and at about 100 m depth were encouraging and provide a basis for the conceptual design of nominal 100 W (gross) modules. These calculations identify DO extraction rates, required sea water flow through the contactor, and the amount of make-up sweep gas methane.
- Power consumed to pump sea water through the contactor is believed to be the primary parasitic loss of the DO extraction system. At a flow rate of 50 gpm (3.15 l/s) pumping power is estimated to fall between 30 and 35 W, assuming pump efficiencies of 60% 70%. Ambient currents could be exploited to reduce pumping power. An actual pump

that meets the requirements of the membrane contactor has not yet been identified; a custom design probably will be necessary.

- The use of high-oxygen solubility liquids, specifically perfluorocarbons such as PFOB, to deliver O₂ to the fuel cell cathode was investigated. The rationale for using these substances is that higher concentrations of extracted oxygen can accumulate in them, as compared to a carrier gas such as N₂ or CH₄. Under certain scenarios, this higher concentration could enhance the rate of O₂ delivery to the fuel cell cathode with an accompanying improvement in limiting current. Additional modeling and experiments must be conducted to determine clearly whether these liquids provide any significant benefit over gas phase O₂ carriers.
- The viability of employing DO extraction in an integrated system that can produce net power needs to be confirmed. As mentioned above, simulations that couple our models of the reformer, membrane contactor, and AFC have generated favorable results; however, the membrane contactor model needs to be validated, estimated parasitic losses associated with pumping sea water must be verified, and additional information is required on fuel cell performance at elevated pressure and low O₂ mole fraction in methane carrier gas. A strategy for the oxygen supply system will be finalized once these issues are addressed.

II.4.4 System layout

Preliminary sketches showing a system layout concept for the AUV/UUV recharging application are provided in Figures 2.4.40 and 2.4.41. This configuration was conceived for use with gas seeps or surface and shallow hydrate deposits.

The gas purification and reforming, O_2 extraction, and fuel cell modules are mounted on the top of a cylindrical structure along with a docking station where an AUV/UUV can recharge its batteries. The bottom end of the cylindrical structure is open and will sit on the seafloor above a gas vent or hydrate mound. The weight of the system will drive the cylinder into the sediment like a gravity core to ensure stability and to seal off the enclosed seep or hydrates. A fin can be installed around the circumference of the cylinder at a selected height to limit the depth of penetration and for stability.

Aqueous solutions of H_2O_2 for the reformer will be stored in a tank constructed of appropriate materials installed around the perimeter of the cylinder. In these drawings, it was assumed that the outside diameter of the cylinder is approximately 2 m and that it stands about 2 m tall. In order to hold the 10 m³ 5-year supply of oxidizer, the diameter of the tank must be about 3.2 m.

Inside the hollow cylinder, an upside down cone will be installed to funnel the seep gas or hydrate methane to an opening at the top where the raw gas will flow into the reformer module. A vent line connected to a pressure relief valve will discharge gas from the plenum at the top of the cone to avoid over-pressurization and excessive buoyancy when the rate of raw gas consumption by the system is exceeded by the supply. Additional vents may be provided slightly above the sediment line to allow water to be pushed out by the buoyant gases. The spaces between the cone and cylinder will be employed to store processed gases (e.g., purified CH_4 , H_2 , or O_2) or reagents.

In the case of hydrate deposits, decomposition must be induced to release the methane gas. Thermal methods appear to be the most feasible for the present application, since the required level of depressurization at deep ocean temperatures will be difficult to implement and methanol of other reagent injection is unlikely to be acceptable from an environmental standpoint. As indicated in the Figures, a matrix of heating tubes that penetrate into the sediment could be employed to channel waste heat (e.g., hot water or steam) from the reformer or fuel cell to melt the hydrates enclosed within the cylinder. Note that the amount of hydrate required to sustain operation for 5 years is rather large. Since 1 m³ of hydrate contains approximately 150 Nm³ = 9.8×10^4 g of CH₄ gas, destabilization and collection of all of the methane could supply a nominal 100 W (net) fuel cell operating at about 10% system efficiency for about 1,400 hours. This presumes a CH₄ utilization rate of a little less than 0.02 g/s. A year of continuous operation would consume 6.4 m³ of hydrate; 5 years would require about 32 m³.



Figure 2.4.40 Sketch of the system layout for AUV/UUV recharging applications.



Figure 2.4.41 Sectional view of the system layout for AUV/UUV recharging applications.

III DISCUSSION AND SUMMARY

A study was conducted to evaluate the technical feasibility of generating electrical power in the deep ocean from seafloor methane and to initiate the design of a first prototype system for field deployment. Although uncertainties remain that warrant additional investigation, information collected to date suggest that it should be possible to produce net power of the order of 100 W employing existing technologies. The lifetime of such a system remains unclear; however, values of 1 - 5 years do not appear to be unreasonable (assuming that component lifetimes, and not the supply of seafloor methane, is the limiting factor), and this probably can be extended through careful design, component redundancy, and future R&D.

A likely configuration for the seafloor power system would thermochemically reform methane fuel gas from seeps or hydrates to H_2 , which would be converted to electricity in a low temperature fuel cell. Although the long-reaching goal is for the system to be self-sufficient, i.e., to run entirely on ambient fuel and oxidizer resources, our study has concluded that some stored oxidizer brought from the surface will be required, since the current level of technology to extract dissolved O_2 from sea water is not adequate to provide the concentrations needed to reform methane. DO extraction does appear to be a viable option to supply the fuel cell cathode. Seafloor methane and DO resources were assessed. It was concluded that the energy density of sediment porewater methane and methane dissolved in sea water was too low to sustain operation of a nominal 100 W system. Gas seeps on the seafloor were ranked as the best option to fuel this system, followed by hydrate outcroppings. This restricts the range of potential operating sites. Although the DO resource is extensive, ambient concentrations limit the maximum partial pressures of O₂ that can be recovered in a mass exchanger to about 8 kPa. Based on our resource assessment, we propose two candidate sites to deploy a prototype for field testing. The first is a shallow site in the Santa Barbara Channel where there are strong and persistent hydrocarbon gas seeps that have been extensively characterized. The second site is in deep water in the Gulf of Mexico (GOM) where hydrate outcroppings (and gas seeps) have been observed. Coordinates and oceanographic conditions for both sites are included in this report. Our preferred strategy is to field test a first prototype at the shallow site off California which would allow diver access and facilitate deployment, on-the-fly modifications and repairs, recovery, and data collection. Lessons learned from this initial testing could then be applied to develop a refined and robust system that would be tested at the deep, relatively inaccessible site in the GOM, where the level of risk is higher and the logistics are much more complicated. This staged approach should enhance the probability of a successful proof-of-concept demonstration.

Models of the methane reforming process, PEM and alkaline fuel cells, and direct mass exchangers and membrane contactors to extract DO were developed and associated laboratory experiments were performed to pursue assessments of candidate technologies and the design of an integrated system. A final conceptual design has not yet been identified, pending validation of the membrane contactor model; estimated parasitic pumping losses; and fuel cell performance at elevated pressure and low O_2 mole fraction in methane carrier gas. Preliminary case studies, that couple the reforming, membrane contactor, and AFC models, however, have produced encouraging results that suggest that net power production may be possible with a system operating at seafloor pressures and utilizing DO extraction to supply the fuel cell and stored oxidizer for the reformer. Our experiments have confirmed that aqueous solutions of H₂O₂ can be used successfully to reform methane and are a good choice for the stored oxidizer.

The obvious next step will be to test and characterize the major components (i.e., reformer; fuel cell; membrane contactor) individually, first on the benchtop, then in pressure chambers at simulated underwater conditions, and finally offshore. Data obtained will then be applied to calibrate and refine our models and for system integration.

In summary, no critical hurdles or fundamental deficiencies in principle or concept were uncovered that would definitively preclude net power production from seafloor methane using existing technologies. It appears possible to develop and deploy a first prototype for field testing within a 5 year time horizon, given appropriate resources. It is recommended that this prototype be tested first in relatively shallow waters and utilize free gas seeps as a fuel resource. The system is expected to utilize a low-temperature fuel cell and a hybrid oxygen supply system comprising stored H_2O_2 solutions and membrane contactors to extract DO from sea water.

Detailed results of this study were recounted previously in Sections II.1.3, II.2.1, II.3.2, II.4.1.4, II.4.2.5, and II.4.3.4. This information is provided again below:

Resource Evaluation Summary

- The minimum methane supply rate needed to attain a target net power of the order of 100 W is approximately 10⁻³ mol/s.
- Methane dissolved in sediment pore water or sea water is not a viable fuel resource for the present application.
- CH₄ gas vents are the first choice to test and demonstrate a proof-of-concept seafloor power system.
- Methane hydrates, like vents, represent a highly concentrated sources of fuel and appear to be a viable option; however, techniques to recover methane gas from hydrates need to be verified.
- Confining the fuel source to vents and hydrates restricts the range of potential operating sites.
- The primary contaminant of concern in vent gas and hydrate gas is H₂S; levels in excess of 1% H₂S by volume have been detected, but a typical concentration which will be employed to test gas clean-up systems is 1000 ppmV.
- Data from the National Oceanographic Data Center of NOAA have been coded to determine DO concentrations at a given depth at locations on a 1 degree latitude x 1 degree longitude grid; the level of accuracy is believed to be acceptable to proceed with a conceptual design study.
- We have not been able conclusively to rule out the possibility that O₂ is depleted locally in regions adjacent to strong seafloor methane sources; this is an important concern since the present system is oxygen-limited.
- Contaminants of concern in the oxidizer supply will depend on the procedures employed to extract DO from sea water and deliver it to the reformer and fuel cell; these procedures have not been finalized so the assessment of oxidizer contaminants has been deferred.
- Additional site-specific data on the ambient methane and oxygen resource will need to be collected during the preliminary and final design phases.

Candidates Sites Summary

• Based primarily on our survey of the methane resource, four sites in two geographical areas within the U.S. EEZ were identified. The first area is off Coal Oil Point in the Santa Barbara Channel. The other three sites overlie seafloor hydrate mounds in the Gulf of Mexico.

- The methane source in the Santa Barbara Channel is free gas vents at relatively shallow depths typically less than 100 m. These vents have been studied extensively, so an excellent database exists on gas composition, contaminants, flow rates, and spatial and temporal properties.
- The GOM sites include deep gas seeps and hydrate mounds. The seeps occur at depths between 500 m and 1000 m; hydrate mounds located in Atwater Valley are located between 1000 m and 1500 m.
- Ambient conditions, including temperature, pressure, density, salinity, DO concentrations and fugacities, have been secured for the candidate sites. This information is believed to be sufficient to conduct a conceptual design study of the power generation system.
- Data on currents at the sites have not been located; while these data are not essential during the conceptual design phase, they will be needed later to develop deployment plans and to address various structural and anchoring issues.
- DO levels and fugacities at the deep sites are approximately half the values at the shallow vents; this is a significant disadvantage for the present oxygen-limited system. Other factors also favor a shallow locale for first prototype deployment and testing.
- It is recommended that the first prototype be sited on a gas vent in the Santa Barbara Channel or similar shallow location to enhance the probability of success. Knowledge and expertise gained from this trial could then be applied to deeper deployments and to systems utilizing hydrate sources, which have greater inherent technical risks.

System Requirements Summary

- The design net power output is of the order of 100 W.
- A target lifetime of 3-5 years would appear to provide adequate benefits over conventional batteries to justify development.
- Although it is not possible at this point to anticipate all possible failure scenarios since specific components have not been selected, the two most vulnerable components appear to be the fuel cell module and reformer catalysts. Other areas of concern include fouling of the fuel gas purification and DO extraction subsystems and failure of various ancillary equipment such as pumps.
- Operating histories for PEMFC and AFC reported in the literature suggest that lifetimes of these devices are less than 1 year; attaining the target lifetime of 3-5 years may require redundant components and/or reduced duty cycle operation.
- Component lifetimes need to be critically assessed once they have been tentatively identified on the basis of performance.

- System lifetimes also depend on the ability to perform repairs or maintenance. Limited access will impose more stringent requirements on components. We propose the following maintenance schedule: no servicing or repair over the mission lifetime below 1,200 fsw depth; annual servicing or repair will be possible at < 300 fsw (military diver scuba limit); longer maintenance intervals with increasing depth up to 1,200 fsw.
- The two primary products for the subsea power generation system are: 1) electricity production for instrument power or AUV/UUV battery recharging; 2) production and storage of fuel (e.g., H₂, pure CH₄, methanol) and, possibly, oxidizer to recharge fuel cell or combustion-driven AUVs or UUVs.
- The system to produce fuel for AUVs constitutes a subset of the one required to generate electrical power. It is recommended, therefore, that the present design effort focus on electricity generation, since those results should provide much of the information needed to respond to a fuel production application.

Fuel Cells for Seafloor Power Generation Summary

- No ideal candidate fuel cell exists for this application; all "commercially available" fuel cells suffer from various disadvantages that significantly compromise their ability to meet the performance requirements for seafloor power generation. Work-arounds to minimize these disadvantages may be possible to adapt conventional fuel cells to this unconventional end use and secure adequate performance. Development of a fuel cell optimized for this application is not believed to be practicable, since it would probably require (much) more than the 5 years allotted to field deploy a prototype, substantial R&D funding, and may depend on major technology breakthroughs.
- Heat losses to the relatively cold environment must be minimized, since these losses ultimately are sustained by methane oxidation—which wastes the limited O₂ resource. Lower operating temperature reduces the driving potential for thermal leakage and was therefore applied as one of the conditions to rank different types of fuel cells.
- With regard to thermal leakage, PEM and alkaline fuel cells are preferable since they operate at the lowest temperatures, typically well below 100°C; phosphoric acid fuel cells operate at temperatures nearly 100°C higher, while molten carbonate and solid oxide fuel cells require temperatures in excess of 600°C.
- The low operating temperatures of PEMFC and AFC necessitate high noble metal catalyst loadings to promote redox reactions on the electrodes. While the associated cost may not be a serious drawback for specialized defense applications, these catalysts are vulnerable to poisoning by certain impurities found in the raw fuel gas (H₂S) or produced during the reforming of methane (CO). This vulnerability to poisoning is a major disadvantage of PEMFC and AFC. The higher temperature fuel cells (phosphoric acid, molten carbonate, and solid oxide) are generally more robust.

- PEMFC membranes must be hydrated and should not be allowed to overheat. Water and thermal management in the PEMFC may be difficult to implement properly and could seriously compromise performance and longevity.
- The KOH electrolyte employed in the AFC is subject to carbonation by CO₂, which is found both in the raw fuel gas and is produced during reforming. Carbonation of the electrolyte is usually cited as a primary factor that degrades performance over time and limits the lifetime of AFCs. CO₂ must be removed from the H₂ and O₂ feedstreams prior to entering the fuel cell. Some of the CO₂ in the fuel gas will condense out, since the AFC operates below the dew point of the reformate and CO₂ is highly soluble in water.
- Reported lifetimes of AFCs and PEMFCs are comparable and of the order of 5000 hours (7 months continuous operation). PEMFC lifetime depends on duty cycle: frequent stops and starts cause high voltage excursions at the cathode that can aggressively corrode the anode catalysts and supports. Failure of the proton exchange membrane due to chemical attack by hydrogen peroxide formed in the cell can be the life-limiting factor. It has been contended that PEMFC lifetimes can increase by an order of magnitude if the fuel cell is run continuously and steadily under optimal conditions; however, evidence confirming this has not been found in the archival literature. AFC lifetime may be limited by corrosion due to the KOH electrolyte that leads to shunt currents and crossover. AFC performance is also degraded over time as a result of carbonation of the electrolyte and re-crystallization of the noble metal black catalysts.
- There is minimal probability that a single fuel cell module will operate successfully over the target 5-10 year period using current AFC and PEMFC technology, especially since the modules will not be easily accessible for periodic maintenance. It may be possible, however, to reach this goal by providing a sufficient degree of redundancy in the system design; i.e., including back-up fuel cell modules that can be switched into service after a predetermined period of operation or upon failure of the module in service.
- In spite of their shortcomings, we propose that AFC and PEMFC represent the best candidates for the subsea power application and that the design strategy should be to continue to focus on these types of fuel cells unless information emerges that clearly precludes their use. If AFC and PEMFC are found to be unacceptable, then high temperature fuel cells can be considered, with phosphoric acid being the first alternative, followed by SOFC.
- Appropriate means must be applied to reduce the level of certain gas impurities (e.g., H₂S, CO, and CO₂) in the fuel and oxidizer streams to acceptable values prior to entering the fuel cell. These values will be determined by reference to the rather extensive body of literature on FC fuel purity standards and experiments that will be performed at elevated operating pressures.
- Limitations in the oxygen supply may require that the selected fuel cell be operated at O_2 partial pressures of ≤ 8 kPa and possibly with oxygen delivered to the cathode either by methane carrier gas or a liquid perfluorocarbon.

- Liquid O₂ carriers do not appear to be feasible for use with PEMFC due to problems with water management. Liquid carriers might be an option for AFC, which produces water on the anode, and a patent exists that supports this concept. Tests were initiated using a small (50 cm²) nominal 3.75W AFC purchased from Astris Energi to explore operation at low oxygen partial pressure and with unconventional O₂ carriers.
- Experiments were conducted at a gas mixture pressure of slightly over 1 bar (absolute), for various mole fractions of O₂ in N₂ supplied to the cathode. Preliminary results suggest that the tested AFC can be operated at oxygen partial pressures as low as about 1 kPa. Limiting current was observed to decline by about 50% as the mole fraction of O₂ was reduced by an order of magnitude, from 21% to 1.6%. While these results are encouraging, they must be interpreted with caution, since the performance claimed by the manufacturer could not be reproduced and the cells appeared to have unusually high IR characteristics. Further testing should be pursued.
- To date, the experiments were unable to distinguish between the effects of mole fraction and partial pressure. It should be possible to extract oxygen from sea water at a partial pressure of 8 kPa at all of the candidate sites identified in Section II.2. Our AFC model predicts that performance will drop precipitously with depth as extracted O₂ mole fraction declines (even though its partial pressure remains constant). Kinetic theory arguments, however, suggest that partial pressure, rather than mole fraction, is the relevant parameter. Experiments must be conducted in which oxygen mole fraction and partial pressure are varied independently, in order to determine how each of these factors influences fuel cell performance.
- The AFC was tested using oxygenated distilled water and perfluorooctylbromide to deliver O₂ to the cathode. Results indicate that operation is possible with liquid carriers, at least over short time periods. The degree of degradation in performance observed with oxygenated water was very similar to predictions of our alkaline fuel cell model. The limiting current was significantly higher for PFOB than oxygenated water, but not to the extent anticipated. Reasons for this discrepancy are being explored.
- Experiments have been devised, but have not yet been initiated, to investigate using methane carrier gas to deliver oxygen to the cathode. Methane is being considered since it is expected that the carrier gas will be lost over time by diffusion into sea water during the extraction of dissolved O₂. A supply of the carrier gas is needed to make up this loss. Methane, unlike N₂, is readily available from the seafloor source.
- Additional long-term tests need to be performed fully to characterize the operation of the selected type of fuel cell (AFC or PEMFC) at elevated pressure and with O₂ levels that can be provided by the oxygen supply system that remains to be identified. These experiments will yield data to calibrate the fuel cell models we have developed that will be integrated with the models of the fuel and oxidizer supply subsystems to perform parametric simulations of the system.

Fuel Supply System Summary

- Catalytic thermochemical reforming, followed by water-shift, of CH₄ to H₂ appears to be a viable option for small subsea power stations employing fuel cells as the energy conversion device.
- Methane reforming tests conducted at operating pressures up to 58 atm. were successful; no significant problems were encountered. Based on our survey of the literature, these experiments may represent the first systematic investigation of high pressure methane reforming.
- Reformate composition data over a range of pressures agree well with equilibrium values calculated using the FACTSageTM 5.1 software package. This suggests that equilibrium models can be employed to estimate performance of the reforming process for system integration and optimization.
- Concentrations of H₂ and CO were observed to decrease with increasing operating pressure; CO₂ concentration was relatively unaffected by pressure, but the amount of unreacted methane increased significantly. Reduced methane conversion also results in reduced gas yield. Over the range of expected pressures, none of these effects is expected substantially to compromise system performance.
- While elevated pressure is known to induce carbon formation and coking of the reformer catalyst, none was observed in our experiments conducted to date. Longer term tests should be performed for verification.
- The amount of O_2 needed for reforming can be shown to be about 30% of stoichiometric O_2 , i.e., 30% of what would be consumed completely to oxidize methane to CO_2 and H_2O . For a nominal 100 W system operating at 10% overall efficiency, this corresponds to approximately 2 x 10⁴ mol O_2 /year. The reformer requires gas-phase O_2 , either in pure form or in a mixture of gases. Gas mixtures with low values of O_2 mole fraction are not suitable for reforming. Furthermore, if O_2 is supplied in a gas mixture of reactive and diluent species, then the composition of the mixture will affect the reforming process and needs to be controlled.
- Equilibrium calculations indicate that the cumulative enthalpy of all steps of the reforming process is negative (i.e., there is a net heat release). This excess would equate to an 18% heat loss from each of the five process steps which include: raising reactants to the selected reforming temperature and pressure; reaction at the selected reforming temperature and pressure; cooling of reformate to the selected temperature and pressure; and cooling of water gas shift products to fuel cell inlet temperature and pressure. The energy to drive the reformer comes from oxidation of a portion of the methane fuel gas; the energy content of the reformate is less than that of the original reactants.

- While, in concept, thermochemical reforming appears to be a good candidate for the present application, engineering studies will need to be pursued to develop simple and robust methods to meter reactants appropriately and to control operating conditions including temperatures and pressures.
- To account for the possibility that extraction of dissolved oxygen from sea water will not be able to provide the high concentrations of gas phase O₂ required for reforming or will impose too high an energy penalty on the system, experiments were conducted to explore the use of liquid hydrogen peroxide as a stored oxidizer.
- H₂O₂ decomposes to provide O₂, H₂O, and heat. Pure H₂O₂ has an oxidizer density of about 21 mol O₂/liter H₂O₂. This compares favorably to pure O₂ gas stored at, say, 80 atm and 5°C, which contains only 3.5 mol O₂/liter.
- Tests were performed at 8-9 atm. and 800°C in which H₂O₂ was used successfully in place of O₂ gas to reform methane to H₂. To our knowledge, these experiments represent the first investigation of hydrogen peroxide reforming of CH₄. Reformate composition predicted by chemical equilibrium agreed within <2% (absolute) for all species. Additional verification testing should be conducted over a range of pressures and oxygento-carbon ratios. Using higher concentration H₂O₂ solutions should also be studied.
- High pressure contaminant removal experiments were initiated. A review of the literature identified H₂S and, possibly, CO₂, as the species found mixed with seafloor methane that pose the greatest threat to the operation of the reformer and fuel cells. H₂S deactivates catalysts and CO₂ can result in carbonation of the AFC electrolyte. Since it has not been determined if AFC will be employed, the present investigation focused on H₂S. Breakout curves were obtained for a commercially-available activated alumina sorbent at two values of pressure (14 and 28 atm.). The bottled gas mixture entering the sorbent bed comprised methane doped with 1043 ppmV H₂S. This value of H₂S concentration was selected based on literature on seafloor methane seeps and released gases from hydrates.
- As configured, our test facility was able easily to reduce H_2S levels to from 1043 ppmV to below 500 ppbV at a mixture flow rate of 1 slpm and temperature = 27°C.
- Increasing pressure serves to increase the time until breakthrough occurs and is likely due to improved penetration of the gas into the pore volume of the sorbent and the increased residence time of the gas in the sorbent bed as indicated by the reduced GHSV (gas hourly space velocity). Additional testing needs to be performed to explore the effects of bed geometry, pressure, temperature, and other sorbent characteristics on system performance.
- Based on these initial, non-optimized results, sorbent bed capacities were estimated for a nominal 100 W system. Approximately 0.6 m³ of sorbent is required for 3 years of continuous operation; 1.2 m³ is required over a 5 year lifetime. Modifications to reactor geometry, sorbent selection, and operating pressure can be expected to improve system

performance, thereby reducing sorbent volume requirements from these preliminary estimates.

Oxygen Supply System Summary

- Extraction of DO from ambient sea water, using existing technologies or those that can reasonably be anticipated to be available for use within a 5 year time horizon, does not appear to be sufficient to meet all the oxidizer requirements for seafloor power generation utilizing methane as a fuel. Specifically, attainable concentrations of extracted DO are less than what is needed to thermochemically reform methane to the H₂ utilized by the fuel cell.
- A possible strategy to address this problem is to employ a hybrid system comprising DO extraction to supply the ~70% of total O₂ partitioned to the fuel cell, and stored oxidizer brought down from the surface to supply the 30% used for reforming CH₄. Modeling and some preliminary experiments suggest that it will be possible to operate the fuel cell with extracted DO in gas or liquid PFC carriers. By doing so, instead of using stored oxidizer to supply all components, the amount of stored oxidizer can be reduced significantly. This is an advantage since large system volumes and masses can complicate deployment to the seafloor.
- The use of stored oxidizer diminishes the autonomy of the seafloor power generation system since it will not operate entirely on ambient resources and its operational life will end when the supply is exhausted. In reality, however, it appears that sufficient oxidizer can be stored such that system lifetime will not be affected; lifetime will probably be limited by other key components, notably the fuel cells. It is proposed, therefore, that the use of stored oxidizer represents a reasonable compromise and practical interim measure that will allow a proof-of-concept prototype to be field tested in the near term. Future breakthroughs in sea water DO collection technology may be applied later to upgrade the system.
- Aqueous solutions of hydrogen peroxide appear to be a good candidate for use as the stored oxidizer. Preliminary experiments have confirmed that H_2O_2 can be employed to reform methane. About 10 m³ of 65% wt. H_2O_2 is sufficient to operate the reformer for 5 years.
- Experiments and analyses were conducted to investigate options to recover DO from ambient sea water. These options included two direct contact mass exchangers based on bubbling carrier gas through sea water or spraying sea water into carrier gas, as well as various configurations of membrane gas extraction.
- Results of the laboratory experiments and analyses of the bubble and spray DO extraction methods indicate that, while they have some potential for application, implementation may be complicated (e.g., providing adequate rise height for a bubble plume; reducing parasitic power consumption to acceptable levels) and performance appears to be marginal.

- Membrane contactors have become the focus of our investigation. These devices eliminate sea water carryover and can be configured to provide high interfacial area and volumetric flows to promote the rate of mass transfer. If micro-porous materials are employed, then membrane transport resistance is negligible, essentially eliminating any advantage of direct contact exchangers. Furthermore, membrane contactors can be applied to liquid carriers such as PFCs as well as gas carriers
- A model of a membrane contactor for DO extraction was developed and calibrated to simulate a commercially-available device. The model was coupled to our AFC model to assess the suitability of DO extraction to supply the fuel cell. Results of simulations performed at conditions representative of locations near the ocean surface and at about 100 m depth were encouraging and provide a basis for the conceptual design of nominal 100 W (gross) modules. These calculations identify DO extraction rates, required sea water flow through the contactor, and the amount of make-up sweep gas methane.
- Power consumed to pump sea water through the contactor is believed to be the primary parasitic loss of the DO extraction system. At a flow rate of 50 gpm (3.15 l/s) pumping power is estimated to fall between 30 and 35 W, assuming pump efficiencies of 60% 70%. Ambient currents could be exploited to reduce pumping power. An actual pump that meets the requirements of the membrane contactor has not yet been identified; a custom design probably will be necessary.
- The use of high-oxygen solubility liquids, specifically perfluorocarbons such as PFOB, to deliver O₂ to the fuel cell cathode was investigated. The rationale for using these substances is that higher concentrations of extracted oxygen can accumulate in them, as compared to a carrier gas such as N₂ or CH₄. Under certain scenarios, this higher concentration could enhance the rate of O₂ delivery to the fuel cell cathode with an accompanying improvement in limiting current. Additional modeling and experiments must be conducted to determine clearly whether these liquids provide any significant benefit over gas phase O₂ carriers.
- The viability of employing DO extraction in an integrated system that can produce net power needs to be confirmed. As mentioned above, simulations that couple our models of the reformer, membrane contactor, and AFC have generated favorable results; however, the membrane contactor model needs to be validated, estimated parasitic losses associated with pumping sea water must be verified, and additional information is required on fuel cell performance at elevated pressure and low O₂ mole fraction in methane carrier gas. A strategy for the oxygen supply system will be finalized once these issues are addressed.

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APPENDIX A: Section III from the 1st Quarterly Report

III TECHNICAL ACTIVITIES

A description of technical activities conducted during this reporting period, broken down by Task, is provided below. Tasks 1, 2, 3, 5, and 7 were initiated during the first Quarter of this project.

III.1 Task 1: Methane and oxygen source assessment

This Task is proceeding slightly behind schedule due to the delay in executing an Agreement between UH and NRL that was reported in Section II. NRL technical personnel, however, have been cooperating informally on this project in anticipation of that Agreement and have provided some of the information needed for this Task. It is anticipated that we will be back on schedule once NRL is contractually engaged to participate fully, presumably sometime during the upcoming Quarter.

During the present reporting period, a review of the technical literature was initiated at UH to begin to establish ranges for available methane and dissolved oxygen quality and volume, and other conditions such as temperature and currents that will be applied as design criteria for the subsea power generation system. A primary goal of this Task is progressively to screen potential methane sources (i.e., seeps; hydrates; methane dissolved in sediment pore water or the water column) and the associated sites, on the basis of their capacity to provide adequate and exploitable fuel and oxidizer resources to attain the target power output with the current level of technology. While we will endeavor to consider the broadest range of operating scenarios possible, to enhance portability of the product system(s) to a variety of mission profiles and locales, the scope will need to be narrowed in order to proceed through final design, and possible deployment, given the anticipated resources.

Information on methane purity and contaminant gas concentrations has been obtained from the literature review for both gas seeps and dissociated hydrates. This information is summarized in Table 3.5.2 of Section III.5.1 below, where it is discussed in the context of fuel clean-up and reforming. We currently are in the process of correlating concentration data with information on methane availability; i.e., methane flux from seeps; vertical flux of methane dissolved in pore water near the seafloor; and the volume and distribution of methane in hydrate outcroppings or hydrate deposits adjacent to the seafloor. Hydrate deposits below a few meters in the sediment have tentatively been excluded from consideration, due to the obvious difficulty of accessing this resource for a small power generation system application.

Methane fluxes from shallow gas seeps offshore California have been reported. Hornafius *et al.* (1999) estimate that more than 1,000 seep vents on the northern margin of the Santa Barbara Channel emit a total of about $1.7 \times 10^5 \text{ m}^3$ /day of hydrocarbon gases that contain up to about 90% by volume of methane (Clark *et al.*, 2003). This corresponds to an average value of approximately 1.8 N liter/s of CH₄ per seep. Information on methane fluxes from deeper seeps in the Gulf of Mexico is being collected and will be reported in a future Quarterly Report along with assessments of temporal stability of this methane source.

While there appears to be sufficient information in the literature to define a representative seep for present design purposes, we need to secure additional data to characterize the methane resource in shallow hydrate deposits and outcroppings; and dissolved in sediment pore water. Toward this end, NRL is expected to provide information during the upcoming Quarter from analyses of piston core samples and heat flow measurements conducted recently at Atwater Valley and Keathley Canyon in the Gulf of Mexico, and at locations on the Cascadia Margin, Nankai Trough, mid-Chilean margin, Blake Ridge, and the Norwegian Greenland Sea. From these data we expect to be able to estimate:

- available methane in hydrate per unit volume of sediment in the upper 2-3 meters of the seafloor at different locations;
- dissolved methane (in pore water) flux (mol/m²-s) in the upper 2-3 meters of the seafloor at different locations.

This will then be applied as design criteria. Securing this information is the major priority for this Task during the upcoming Quarter.

In the research proposal for this project, it was argued that the availability of oxygen may be the primary factor that limits system power generating capacity. During the present reporting period, the available database on dissolved O_2 concentration in the oceans was carefully reviewed to establish ranges of ambient values of this species as a function of depth and location. One issue that has emerged, which we will continue to pursue during the upcoming Quarter, is the correlation between dissolved O_2 and methane levels. There is anecdotal evidence that localized O_2 depletion can occur in regions with elevated methane concentration, such as near seeps or hydrate beds. The mechanisms for oxygen removal can include extraction by contact with a rising bubble plume of methane gas, enhanced microbial metabolism promoted by the methane carbon source, or chemical oxidation. Depletion of dissolved O_2 near the methane fuel source will complicate the development of the power generation system.

During the upcoming Quarter, we will examine the literature for data sets that include measurements of both methane and oxygen in the deep ocean and near gas seeps and hydrate beds in particular. NRL has been asked, and has agreed, to provide dissolved O_2 data that they collected in past surveys of offshore methane hydrates. This information will be reviewed to determine if there is a negative correlation between O_2 and CH_4 .

Finally, effort is ongoing to assemble an adequate database of currents adjacent to the seafloor that can be applied, with the concentration data, to estimate the horizontal flux of dissolved O_2 . This information is needed for the design of the oxygen collection subsystem.

III.2 Task 2: Component selection criteria

This Task was initiated in August 2005 and is proceeding on schedule. As discussed in Section III.1 above, we intend to define ranges of operating conditions for three types of methane resource: 1) seafloor seeps; 2) hydrate deposits from 0-3 m below the seafloor; and 3) dissolved methane in sediment pore water adjacent to the seafloor. Specifically, the conditions of interest are pressure; temperature; salinity; current regime; dissolved O₂ concentrations; O₂ flux;

methane flux (for seeps or pore water) or methane in hydrate per unit volume of sediment; and fuel gas contaminant levels. We anticipate that Task 1, which will provide information on these conditions, will be completed by the end of the upcoming Quarter. The second part of Task 2, identification of potential end uses, is ongoing.

III.3 Task 3: Oxygen supply system

This Task currently is proceeding ahead of schedule and has been expanded to include some laboratory experiments to test potential oxygen extraction systems in order to reduce the uncertainty associated with the viability of this key component, and to address issues that have emerged (see Section III.4) related to integrating it with the fuel cell module.

A review of the literature was conducted during this reporting period to identify relevant O_2 extraction strategies that could be applied to this application. Strategies that appear to have some potential to supply oxygen for the subsea power generation system are described below.

Artificial Gill

Artificial gill systems were designed to extract dissolved oxygen from seawater to meet the respiratory requirements of a person breathing underwater. In these systems, seawater is pumped through hollow fiber membranes and oxygen diffuses from the seawater into a reagent that has higher O_2 solubility. This oxygen carrier is then circulated through another hollow fiber membrane where O_2 is transferred to an air stream to replenish a breathing tank. O_2 capture can be enhanced by heating or by light irradiating different liquid carriers. A schematic diagram of the apparatus is shown in Figure 3.3.1.



Figure 3.3.1 Schematic of artificial gill to extract O₂ from seawater for human respiration while underwater.

Several reagents have been proposed for use as the artifical gill oxygen carrier, including perfluorooctylbromide (PFOB), molybdenum porphyrin, and hemoglobin. PFOB (Haramoto *et al.* 1994; Nagase *et al.* 2005) has a high affinity for O_2 ; the solubility of O_2 in PFOB is about 16.7 times greater than in water. PFOB's affinity for O_2 aids uptake but hinders release of the O_2 .

Nagase *et al.* (2003; 2005) also examined hemoglobin and molybdenum porphyrin as substitutes for PFOB in the artificial gill. It was determined that O_2 partial pressure in these reagents can be increased by heating the hemoglobin and irradiating molybdenum porphyrin with a xenon lamp. These techniques impose an additional energy penalty; however, if hemoglobin is employed in the subsea power generation system, then it may be possible to recover waste heat from the fuel cell or reformer for this purpose. Light irradiating molybdenum porphyrin probably cannot be implemented as easily.

According to the literature, the strong C-F bonds of PFOB make it very chemically stable. PFOB has low toxicity to the extent that it is employed regularly in medical procedures as a source of O_2 to cells and organs (Weers, 1993). Hemoglobin was found to be susceptible to denaturation over time due to increased heat or pH change, though additives and pH control can improve stability (Nagase, 2003). Denaturation would compromise performance of hemoglobin in the artificial gill over time. The stability of molybdenum porphyrin is still being investigated.

Results of laboratory studies of the artificial gill were scaled to estimate membrane areas and seawater flow rates required to meet the O_2 needs of one person underwater. These values are presented in Table 3.5.1. For comparison, about 1 mmol/s (5 times the O_2 supplied by the systems in Table 3.5.1) will be required to produce about 60W net power by a fuel cell system operating at about 12-15% efficiency.

	Haramoto	Nagase PFOB	Molybdenum	Hemoglobin
	PFOB		porphyrin	
P ₀₂ , seawater, kPa	-	20	20	20
Estimated human	0.186	-	0.186	0.223
respiration rate,				
mmol/s				
P ₀₂ , respiratory gas,	-	17.8	20.4	20.7
kPa				
P ₀₂ , carrier liquid at	-	16.3	10.3	9.46
uptake, kPa				(293 K)
P ₀₂ , carrier liquid at	-	18.4	26.9	22.6
release, kPa			(w/ light)	(310 K)
Total membrane SA,	40-60	50.8	123	63.8
m^2				
Seawater flow rate, l/s	-	6.53	5.33	0.117

Table 3.5.1. Artificial gill systems to sustain one person breathing underwater.

The artificial gill was tested at subsurface dissolved O_2 partial pressures of 20 kPa, typical of diving depths. The configuration employing hemoglobin was also tested at 10 kPa O_2 partial pressure. Although this gill could still supply sufficient O_2 to sustain human respiration, the required membrane surface area increased significantly (Nagase *et al.*, 2003). Since dissolved O_2 levels in the deep ocean near methane hydrate beds or methane seeps may be 2 to 5 times less than in the upper ocean mixed layer, the artificial gill results must be applied with caution to the design of the subsea power generation system.

The artificial gill was designed to maintain O_2 levels in the breathing air supply at values suitable for human respiration—typically about 20% by volume. O_2 transfer from the carrier fluid to the air circulated through the membrane oxygenator occurs across a modest concentration gradient. For example, in the tests of the artificial gill using molybdenum porphyrin, air entered the oxygenator at a partial pressure of 20.0 kPa and exited with a partial pressure of 20.4 kPa (Nagase *et al.*, 2005). P_{O2} in the molybdenum porphyrin was about 27 kPa. PFOB performance was evaluated at an even smaller gradient: for this case, the partial pressure of O_2 in the air exiting the oxygenator was about 17.8 kPa, while P_{O2} in the entering PFOB was about 18.4 kPa.

For a subsea fuel cell application, a recycled gas stream leaving the fuel cell could be used as a carrier gas and would have an O_2 partial pressure substantially less than 20% by volume. About 25% of the O_2 in a feedstream of air is consumed in a solid oxide fuel cell, while other configurations such as a Proton Exchange Membrane (PEM) fuel cell can operate at higher O_2 utilization levels (Fuel Cell Handbook 2002). The lower O_2 partial pressures in the carrier gas stream will increase the gradient that drives O_2 transfer in the membrane oxidizer. This is anticipated to enhance the performance of the artificial gill, but needs to be verified by additional experimentation.

Pressure-driven Oxygen Extraction

A novel approach to extract O_2 from seawater for divers by depressurization was recently reported (Genuth, 2005). Figure 3.3.2 shows the process. Seawater is drawn into a cylindrical cell containing a propeller that spins the water, forcing it against the walls, much like a centrifuge. A void is generated along the centerline of the cell and gas diffuses from the water into this region of low pressure, where it is collected into a breathing tank. Approximately 200 L/min of seawater must pass through the system to provide enough O_2 to sustain human respiration. Oxygen recovery efficiency was reported to be about 20%. Technical details of the system have not been published to date, but the concept appears to warrant evaluation. In the upcoming Quarters, we will attempt to estimate the performance characteristics (i.e., O_2 extraction rate; power consumption; etc.) of this approach.



Figure 3.3.2 Depressurization oxygen extraction from seawater for diving applications.

III.3.1 O2 supply system development

The original scope of work for this project did not include any experimentation during the initial 12 month period to reduce uncertainties related to supplying adequate O_2 to meet the targets for power production by oxidation of the methane fuel. It has become clear, however, that the performance of the O_2 supply system is a critical design consideration which should be determined at the earliest opportunity.

A plan to test the viability of candidate O_2 supply strategies that have emerged is being prepared and some simple experiments have been initiated, currently at no cost to this project, utilizing some of the P.I.'s discretionary funds. The focus currently has been placed on employing perfluorocarbons (PFCs), such as PFOB, to extract and transport O_2 from seawater to a fuel cell cathode.

The high oxygen affinity and solubility of PFCs can be exploited to enhance collection of dissolved O_2 from seawater. Two strategies are being considered. In the first approach, which parallels the artificial gill, a PFC will be used to extract O_2 from seawater in one membrane contactor and transport it to a second membrane oxygenator where it is released into a carrier gas that is used to supply the fuel cell cathode. The second approach eliminates the membrane oxygenator and will attempt to employ liquid PFC or a PFC emulsion directly to supply O_2 to the cathode.

Figure 3.3.3 presents the concept of adapting the artificial gill to a subsea fuel cell. System enhancements to promote O_2 extraction in the seawater membrane contactor and O_2 release in the membrane oxygenator are also shown. The enhancements include selective heating or cooling of the seawater and PFC at different points in the process (utilizing waste heat from the fuel cell or reformer, or cold seawater).



Figure 3.3.3 Artificial gill concept adapted to supply O₂ to fuel cell. Heating and cooling employed to enhance mass transfer processes.

The initial series of tests will investigate O_2 transfer across membranes from seawater containing low levels (<100 µmol/L) of dissolved oxygen into PFCs and the release of O_2 from the PFCs into a carrier gas. The viability of utilizing O_2 -laden PFCs directly to deliver oxygen to PEM cathodes also will be explored by circulating these fluids through small single PEM fuel cells fed with H₂ and observing performance. PFC reagents and membranes have been procured along with the necessary PEM fuel cell components.

As a first step, the solubility properties of PFOB will be determined, since O_2 transfer from the seawater is driven by the degree of undersaturation of the PFC. An experimental apparatus was fabricated during the present reporting period. This apparatus measures oxygen solubility by monitoring the change in the volume of the headspace above an initially degassed liquid as the gas in the headspace dissolves in the liquid. Temperature can be selected and controlled. The device was modeled after one that was used to measure Ostwald coefficients for several PFC compounds (Dias, 2004). Figure 3.3.4a is a sketch of the apparatus. A variation of the device, shown in Figure 3.3.4b, will be employed to monitor oxygen diffusion from seawater through a membrane into an oxygen carrier while maintaining a constant O_2 partial pressure in the seawater.



Figure 3.3.4 (a) apparatus to measure O₂ solubility of oxygen carriers such as perflurooctylbromide (PFOB); (b) apparatus to monitor O₂ transfer from seawater through a membrane.

PFOB can be mixed with a surfactant to produce an emulsion that is water soluble. The solubility of O_2 in the PFOB emulsion is lower than in pure PFOB but is still more than 5 times the solubility of O_2 in seawater. The process of oxygen transport to a fuel cell electrode using an emulsion is part of a patent application filed by Markoski *et al.* (2004). Technical publications that detail this approach, however, have not been identified to date.

Figure 3.3.5 presents one possible configuration that employs a PFOB emulsion as an oxygen carrier. O_2 extraction from the emulsion into a carrier gas stream may still need to be implemented to supply the methane reformer. Here, the cathode will be exposed to relatively high O_2 concentrations which has the potential to benefit performance. There are potential drawbacks, however, that need to be assessed and which could eliminate this approach from further consideration. First, water produced at the cathode will dilute the emulsion and reduce oxygen solubility. Second, as discussed in the following Section, O_2 diffusion proceeds much slower in liquids than in gases, which may offset the effect of increased O_2 concentration. These questions will be addressed through some experiments and analysis in next two Quarters.



Figure 3.3.5 O₂ supply to fuel cell cathode using liquid PFC emulsion.

III.4 Task 5: System model

This Task was initiated in August 2005 and is proceeding on schedule. Activities to date have been directed toward acquiring a better understanding of the key parameters that may affect the performance and operation of PEM fuel cells (PEMFCs) in conditions that could be encountered in the deep ocean. During project team meetings, PEMFCs were identified as the most likely candidate technology capable of providing a targeted life of up to five years or longer with no maintenance. Solid oxide fuel cells (SOFCs) remain in contention, but currently represent a secondary option.

Basic parameterization of other primary subsystems (fuel reforming and clean-up, oxygen extraction, etc.) will be underway shortly.

The modeling strategy under development consists of: 1) identifying a set of necessary and sufficient parameters for all systemic elements; and 2) tying these fundamental elements together through appropriate relationships (e.g., via heat and mass balances). This approach will ensure basic compatibility among elements. Depending on results, it may be possible to formulate objective functions that can be optimized.

Two issues related to PEMFC performance as a component of a subsea power generation system were examined during the present reporting period. The first issue relates to diminished performance under low O_2 operating conditions, which could occur given the limited oxygen resource in the deep ocean. The second issue concerns the feasibility of employing a liquid phase carrier, such as the PFOB emulsion discussed in Section III.3, to transport O_2 directly to the fuel cell cathode.

Low O₂ operation of PEMFC

Under worst case scenarios, the limited availability of O_2 dissolved in deep ambient seawater may force operation of the fuel cell module significantly off design. PEMFCs typically operate with the cathode fed by a gas stream containing 20% or more O_2 by volume. O_2 concentrations below this level are expected to result in substantial performance penalties and may possibly exclude the use of fuel cell technology altogether.

Current generation air-blown PEMFCs are designed for high power density and efficiency. Operating the PEMFC at low O_2 partial pressure reduces performance according to the Nernst equation:

$$\varepsilon_o = E_o + \frac{RT}{nF} * \sum \upsilon_j * \ln a_j$$

Where E_o is the standard potential, 1.23 V, and a_j are the respective activities for the reactants and products. At 25°C, the operating potential at equilibrium is 1.18 V at O₂ concentration of 1,000 ppmV and with water assumed to be unity. This suggests that it may be feasible to employ a fuel cell at low O₂ partial pressures.

The kinetics and mass transfer limitations of PEMFCs operated at low oxygen partial pressures can be assessed from data obtained at elevated O_2 level by a first-order approximation. Figure 3.4.1 from Gasteiger & Mathias compares the performance of a PEMFC operating with pure oxygen and air. Figure 3.4.2, reproduced from Suzuki *et al.*, shows the influence of reduced O_2 content and different carrier gases. The data in these two figures indicate that significant reduction of O_2 concentration at the cathode will lower the limiting current, and that this change can be attributed to mass transport limitations. The data also suggest that if the PEMFC is operated at an O_2 concentration of the order of, say, 1,000 ppmV, then the limiting current would fall in the range of 25 mA/cm² to 50 mA/cm². Under these conditions, a fuel cell operating at 2 mA/cm² to 5 mA/cm² would be feasible and could provide a cell voltage of approximately 0.7V. The associated power output of a 100 cm² cell would fall between 0.14 and 0.7 W.



Figure 3.4.1 Comparison of PEMFC performance with O₂ and air supplied to the cathode (reproduced from Gasteiger & Mathias).



Figure 3.4.2 PEMFC performance at 5% O₂ in He and N₂ (reproduced from Suzuki *et al.*).

A major drawback under this scenario would be the hydrogen crossover current observed with commercial grade 50 micrometer thick Nafion® membranes in the PEMFC. This hydrogen crossover current is usually 1 mA/cm², which is nearly equal to the operating current. One possible approach to reduce the hydrogen crossover would be to employ a thicker membrane, e.g., 125 μ m or 175 μ m thickness. While the hydrogen crossover will be lower, the proton conductance of the membrane would also decrease and increase the associated internal resistance. Because, however, the operating current is so low, the increase in voltage loss (i x R) would not be substantial.

Experiments are needed to verify the preceding estimates of downgraded PEMFC performance at low O_2 partial pressures. These experiments can be easily performed using small 50 cm² test cells currently at HNEI's Hawaii Fuel Cell Test Facility.

PEMFC cathode operating in liquid

As discussed in Section III.3.1, an approach that supplies O_2 to the fuel cell cathode with a liquid carrier, such as a PFOB emulsion, is under consideration. The compatibility of the liquid phase with the operation of the cathode is not known and concerns have been raised about diffusive transport of the O_2 to the electrode. A simple analysis was conducted during the present reporting period to explore these issues.

If the cathode of a PEMFC is immersed in a liquid with a bulk concentration $[O_2]_{bulk}$ that can be considered constant at some distance in the oxidant feed stream (z = 0), then the diffusion of O_2 toward the catalyst (at z = l) can be formulated as a steady-state Dirichlet Boundary-Value Problem:

$$-D\frac{d[O_2]}{dz} = \frac{I}{4F}$$

where *D* is the diffusivity of oxygen in the liquid (m^2/s), *I* the current density of the fuel cell (A/m²) and *F* the conversion factor equal to 96487 C per mole- \bar{e} (one mole of oxygen is reduced by 4 electrons).

The solution across the liquid diffusion layer is:

$$[O_2] = [O_2]_{bulk} - \frac{I}{4FD}z$$

Setting z = l in the above equation provides the oxygen concentration at the catalyst layer.

The limiting current density I_{lim} corresponds to a vanishing concentration of reactant where the reaction takes place:

$$I_{\rm lim} = \frac{4FD[O_2]_{bulk}}{l}$$

In liquids, *D* is of the order of 10^{-9} m²/s. With [O₂]_{bulk} of the order of 1 mol/m³ (that could be typical of the extraction of oxygen from ambient seawater with a high-solubility liquid), and *l* of the order of 100 µm, *I*_{lim} would be of the order of a few A/m².

This is four orders of magnitude lower than values of limiting currents typical of mixed-gas cathodes (a pure gaseous O_2 cathode has no limiting current). Although the analysis is more complex in the case of a gaseous feed stream, the difference in the values of limiting currents essentially reflects relatively high binary diffusivities for gas mixtures (order of magnitude 10^{-5} m²/s).

These results corroborate the known problem of electrode flooding: when product liquid water at the cathode overwhelms the porous gas diffusion layer in a standard PEMFC operation, the only diffusion path left for oxygen (liquid water) becomes too slow. Utilizing a liquid carrier to supply O_2 to the cathode may not be feasible, but additional analyses will be conducted to confirm this conclusion.

III.5 Task 7: Fuel clean-up and reforming experiments

This Task currently is proceeding ahead of schedule.

III.5.1 Gas hydrate and seep gas characterization

A literature review was conducted to compile available data on the composition of gases emitted from seeps on the ocean floor and collected from decomposed methane hydrates; both potential fuel sources for seafloor power modules. Data for other sites will be provided by NRL in the future to supplement this review. In addition, a request has been made with Dr. John Ripmeester of the Stacie Institute for Molecular Sciences of Natural Resources Canada to request results of unpublished gas analyses of natural hydrate samples.

Table 3.5.1 presents a summary of the composition information obtained from the literature. Most of the analyses reported levels of CH_4 , N_2 , O_2 , CO_2 , and non-methane hydrocarbons (NMHC). Sampling depths ranged from 1 meter to 3,160 m below the ocean surface. Methane concentrations ranged from 99.1% for hydrates sampled at 3,160 m to 76.7% in seep gas bubbles collected 1 m below the ocean surface. The concentration of H_2S was determined in several cases and ranged from 20 to 2,700 ppmV, with hydrate samples falling at the upper end of this range. The average of 168 gas samples collected above relatively shallow marine seeps at Coal Point, California was reported by Clark *et al.* (2000). The gas composition from this study was selected as an initial baseline for a model seep gas for laboratory tests of gas clean up and reforming.

	Gas Composition										
					NonMethane			Sample	Seafloor		
Ref.					Hydrocarbons	a1	Gas	Depth	Depth		No. of
No.	CH ₄	N ₂	O_2	CO_2	Total	H ₂ S ¹	Source	(m)	(m)	Location ²	Samples
1	79.4	13.8	4.5	>0.1	2.2		seep	1	20	а	4
1	76.7	14.4	6.0	>0.1	-		seep	1	20	а	6
1	79.5	12.6	5.0	>0.1	2.8		seep	1	20	а	2
1	90.8	4.9	1.8	0.2	2.4		seep	10	20	а	2
1	84.4	8.1	3.0	0.1	-		seep	10	20	а	2
1	86.4	7.5	2.8	>0.1	3.2		seep	10	20	а	2
1	84.2	2.5	0.3	10.6	2.3		seep	20	20	а	1
1	81.9	1.4	0.2	13.4	-		seep	20	20	а	4
1	84.0	1.5	0.3	11.2	3.0		seep	20	20	а	4
2	98.0				0.1	ND	seep	123	123	b	
2	98.1				0.004	ND	seep	43	43	с	
2	93.2				0.003	ND	seep	83	83	d	
3 ³	87.5	0.8	0.1	1.3	10.2	0.002	seep	57	67	e	168
4	99.1	0	0	0.83	0.043	0.02	hydrate	~3160	3160	f	
5						0.27	hydrate			g	
						0.04 to					
6						0.15	hydrate			h	
¹ ND=not	1 ND=not detected by odor										
² a= Shane	⁴ a= Shane Seep (Coal Oil Point CA)										
b=Coqui	Ile Bank (Cape I	Blanca O	R)								
c=Bluff	Seep (Eel River	CA)									
d=Hecta	d=Hecta Bank Seep (Florence OR)										
e=Seep	e=Seep Tents (Coal Oil Point CA)										
f=KZR-4	f=KZR-42 Congo-Angola Basin										
g=Cascadia Margin											
n=Blake Klage - East Coast 3 NonMathana Hydrogerhang inglyded 5 19/ C H 2 19/ C H 0 09/ n C H 0 49/ igo C H 0 29/ n C H 0 29/ igo C H 0 29/ C H											
Nonviculatic regulations included 5.1% C ₂ r ₆ , 5.1% C ₃ r ₈ , 0.9% II-C ₄ r ₁₀ , 0.4% ISO-C ₄ r ₁₀ , 0.2% II-C ₅ r ₁₂ , 0.2% ISO-C ₅ r ₁₂ , 0.5% C ₆ r ₁₄ .											
Reference Key (Column 1): No. 1 = Clark et al. (2003); No. 2 = Collier et al. (2005); No. 3 = Clark et al. (2000); No. 4 = Charlou et al. (2004); No. 5 = Milkov et al. (2005); No.											
6 = Paull <i>et al.</i> (1996)											

Table 3.5.1. Summary of gas compositions of seep gas and dissociated hydrates reported in the literature

III.5.2 Equilibrium calculations

Equilibrium calculations for methane reforming were performed using the software package FACTSageTM 5.1. Results will be applied to devise appropriate reforming strategies for the present application and for comparison with upcoming laboratory results. Calculations were performed on a unit mole CH₄ basis, an O₂ to C ratio of 0.55, and a H₂O to C ratio of 1.24. Ratios were selected based on prior reforming experience with other hydrocarbon fuels. Figure 3.5.1 summarizes the equilibrium gas composition at pressures ranging from 1-100 atm and temperature ranging from 500-1000°C. Methane conversion to H₂ is favored at low pressure and high temperature. H₂ approaches a maximum value at temperatures above 975 K (700°C) for the range of conditions investigated.



Figure 3.5.1 Equilibrium prediction of the products of catalytic, autothermal, methane reforming as a function of temperature and pressure with a unit mole of CH₄, oxygen/carbon ratio=0.55, steam/carbon ratio=1.24. Experimental product gas data shown for CH₄ reforming using 20 g of Ni catalyst at 800°C, 1 atm, oxygen/carbon ratio=0.55, and steam/carbon ratio=1.24.

III.5.3 Reforming experiments

Two preliminary experiments were conducted during the present reporting period to explore catalytic conversion of methane to hydrogen using an atmospheric reformer system shown schematically in Figure 3.5.2. The reformer is a lab-scale, fixed-bed, catalytic reactor, 45.7 cm in length and 1.93 cm internal diameter, made from 316 stainless steel. It has been used in previous investigations of LNG reforming and will be applied to this study of seafloor methane power generation. The reactor is heated by an electric tube furnace with a heating length of 30.5 cm. A steam reforming catalyst, G-91 EW from Süd-Chemie, was used. The 20 g catalyst bed was located in the constant temperature zone in the reactor. Temperatures in the reactor were measured at three locations, 7.5 cm in front of the catalyst bed (T1), just before the catalyst bed (T2), and just after the catalyst bed (T3). Air and methane (Grade 5.0) were supplied to the reactor from gas bottles and metered using mass flow controllers. The air and methane mixture passed a vaporizer where water, heated to 100°C, was added before the reactant flow entered the reactor. Downstream of the reactor, water vapor was separated from the product gas in a condenser and then dried further using a coalescing filter. The dry effluent gas was analyzed using a gas chromatograph (Shimadzu 14A). Gas was separated on a Supelco Carbonex 1000 45/60 (1.5 m \times 0.32 mm) packed column and analyzed using a thermal conductivity detector (TCD). The permanent gas species – H₂, N₂, CO, CH₄, CO₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ – were quantified. Test durations were 6 hours. Reactor operating conditions were monitored and recorded on a one minute interval. Composition of the gas exiting the reactor was determined every 35 minutes.



Figure 3.5.2 Automated reformer test system (WGS = water gas shift; GC = gas chromatograph).

The two test conditions were selected based on thermodynamic analysis and the results were compared with equilibrium calculations. The steam-to-carbon (S/C) ratio and oxygen-to-carbon (O/C) ratio chosen for the two tests were: 1) O/C=0.555, S/C=1.24 and 2) O/C=0.122 S/C=1.66.

The first was selected to represent a high-methane conversion condition with low chance for coke formation based on autothermal reforming conditions (no external heating) and a 20% heat loss. The second was selected to simulate a condition where unused hydrogen from the fuel cell could be recycled to provide supplemental heat to the reforming process. The average H_2 and CH_4 concentrations of the product gas stream for the first test condition are shown as data points on the equilibrium curves of Figure 3.5.1 and illustrate close agreement between theory and experiment. The gas composition was stable over the test duration and no catalyst deactivation was observed. The experimental results of the second condition did not agree as closely with equilibrium predictions, indicating that methane conversion was limited by reaction kinetics due to the lower oxygen to carbon ratio compared to the first test condition.

III.5.4 Sulfur removal

It is anticipated that removal of sulfur from a seep or hydrate-derived gas stream will be a critical element of the seafloor power module. A review of techniques for removing sulfur from gas streams was conducted. A summary of the findings is presented in Table 3.5.2. The removal techniques can be categorized into two groups, solid sorbents and membrane based systems, and both reportedly can remove sulfur compounds with > 99% efficiency. In addition to removal efficiency, selection will depend on required operating conditions and the ease with which the removal technique can be integrated into the seafloor power module system.

Table 3	1010 3.5.2 Summary of removal media for cleaning H ₂ S from gas streams.										
Ref. No.	Removal Media	Formula	Surface Area,	Bulk Density,	Particle Shape	Particle Size,	Pressure Range,	Temp Range,	Absorption % Mass	Regenerability.	H ₂ S Removal Efficiency
			m ⁻ /g	g/cm ²		mm	atm	۰C			%
7	Zinc Oxide	ZnO	3.2	0.84	Pellet	d=1	1	400-500			
8	Zinc Ferrite	$ZnFe_2O_4$						550	39.8	>5x	
9	Zinc Ferrite	ZnO/TiO ₂	3.2-3.9		Cylinder	d=4.7, l=11.75	1	565-785	19.8	>15x	
10	SulphaTreat	Fe ₂ O ₃ & Fe ₃ O ₄		1.1	Pellet	4-16 Mesh	1+	10-50	25	no	
11	Sulfa-Bind	Proprietary					1+		3-4 / regen	<14x	99.98
12	Sorb-Z	Proprietary		0.88	Cylinder	d=3.2, l=7.5	10-20	400-500	17	50x	99.99
13	Elec.chem Membrane						1	580-650			<90
14	Pressure Membrane						40+				~97
	Aqueous Sol.										
15	Membrane	Na ₂ CO ₃					1.2-1.6	25			>99.98
16	Zeolite	Mole Sieve MCM-41			Pellet	d=0.5-1.0	1	25		?	99.5

Table 3.5.2 Summary of removal media for cleaning H_2S from gas streams.

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APPENDIX B: Section III from the 2nd Quarterly Report

III TECHNICAL ACTIVITIES

A description of technical activities conducted during this reporting period, broken down by Task, is provided below. Tasks 1, 2, 3, 4, 5, and 7 were scheduled to be undertaken during the second Quarter of this project.

III.1 Task 1: Methane and oxygen source assessment

This Task has been delayed as a result of the complications in executing an Agreement between UH and NRL. Approximately 80% of the NRL effort was to be directed in support of Task 1. As reported previously, we have been attempting to minimize this problem by utilizing, wherever possible, information from the archival literature on seafloor methane and oxygen sources needed to proceed with other Tasks. While this approach has prevented significant slippage in the schedule, compromises have had to be made, since the open literature does not include all the information available in the NRL database and by analysis of their hydrate sample collection.

During the present reporting period, information was collected on the distribution of dissolved O_2 as a function of depth in the oceans, and on seafloor methane fluxes on the U.S. continental shelf. In addition, a model was developed to estimate CH₄ solubility as a function of temperature, pressure, and salinity. This information will be applied to assess the feasibility of strategies to extract dissolved methane from sediment pore water and from the water column for power production.

III.1.1 O2 distribution

Monthly and annual averaged O_2 concentrations at various depths in the ocean are available from the National Oceanographic Data Center of NOAA. These data were coded and we are able to determine the level of dissolved oxygen at a given depth at locations on a 1 degree latitude x 1 degree longitude grid (approximately 60 x 60 nautical miles). As an example, distributions of dissolved O_2 at the surface, 500 m, and 1,000 m, are shown in Figures 3.1.1 - 3.1.3. For the purposes of the present conceptual design study, the only additional information required on the O_2 source is the extent of possible depletion in regions with elevated methane concentration.



World Ocean Atlas 2001 Ocean Climate Laboratory/NODC

Figure 3.1.1 Annual mean distribution of dissolved oxygen at the ocean surface.



World Ocean Atlas 2001 Ocean Climate Laboratory/NODC

Figure 3.1.2 Annual mean distribution of dissolved oxygen at 500 m depth.

Longitude



World Ocean Atlas 2001 Ocean Climate Laboratory/NODC

Figure 3.1.3 Annual mean distribution of dissolved oxygen at 1,000 m depth.

This issue was mentioned in the previous Quarterly Report. NRL has measured water column O_2 above hydrate beds during past research cruises and these data will be analyzed during the upcoming Quarter.

III.1.2 Seafloor methane fluxes III.1.2.1 free gas vents

Hovland *et al.* (1993) attempted to evaluate the global flux of methane from shallow seeps. Their analysis focused on continental shelves, in water depths not much exceeding 200 m. Estimates of mean shelf methane seepage rates along U.S. coastlines are provided in Table 3.1.1.

Location	Source	Depth range	Mean flux (g $CH_4 m^{-2} yr^{-1}$)	
		(m)		
Coal Oil Point (CA)	Thermogenic	20 to 100	400	
Gulf of Mexico	Bacterial	50 to 230	0.01 to 56	
Cape Lookout Bight (NC)	Bacterial	8	69	
Norton Sound (Alaska)	Bacterial	10 to 20	N/A	

Table 3.1.1 Some methane seepage rate estimates along U.S. coastlines

Coal Oil Point is an area of about 18 km² located 3 km offshore in the Santa Barbara Channel. It has been extensively documented as one of the most active known methane seep zone in the world (Hornafius *et al.*, 1999; Leifer *et al.*, 2000; Clark *et al.*, 2000). Because of the thermogenic origin of the gas, substantial amounts of oil and tar also are released. Hornafius *et al.* (1999) revised the mean flux estimate sharply upward, from 400 g CH₄ m⁻² yr⁻¹ to 1600 g CH₄ m⁻² yr⁻¹. Clark *et al.* (2000) reported the following gas composition from the Seep Tents (two large gas capture devices installed by ARCO over very intense seeps in 1982):

Gas	Mol Fraction, %	Plus or Minus		
Methane	87.5	0.9		
Ethane	5.1	0.3		
Propane	3.1	0.3		
Carbon dioxide	1.3	0.3		
N-Butane	0.9	0.1		
Nitrogen	0.8	0.4		
Iso-Butane	0.4	0.06		
Hexane+	0.3	0.22		
Iso-Pentane	0.2	0.04		
N-Pentane	0.2	0.05		
Öxygen	0.1	0.12		
Hydrogen sulfide	0.002	0.001		
Methane/ethane	17	1		
Methane/propane	29	3		

Gas samples were collected after bubbles traveled through approximately 10 m of scawater. Shallow shelf emissions of natural gas are extensive along the coastline of the Gulf of Mexico, with tens of thousands of seeps. They are often associated with salt piercement structures. Typical $C_1/(C_2 + C_3)$ ratios greater than 1000 and methane stable carbon isotope ratios less than -50 ‰ point to a bacterial origin. Sub-bottom pore water methane concentrations were also measured (10 to 40 m below the seafloor); values of the order of 30 ml/l (mole fraction of the order of 2.4 x 10⁻⁵) are high but below saturation.

Hovland *et al.* (1993) assumed that the distribution of shallow methane seepage rates is lognormal with the same geometric standard deviation (about 15) as gas production from California oil and gas fields in 1990. Whether the probability that shelf seepage rates exceed the Coal Oil Point value in Table 1 is 0.1% or 1% leads to mean seepage rates of 4.7 to 38.3 g CH₄ m⁻² yr⁻¹. Hornafius *et al.* (1999) later revised this range, following the same methodology, to 15 to 208 g CH₄ m⁻² yr⁻¹. They also considered the mean rates of the same distributions truncated at 1600 g CH₄ m⁻² yr⁻¹, and obtained mean rates of 10 to 28 g CH₄ m⁻² yr⁻¹. Applied to high seepage potential areas on all continental shelves, i.e., about 1.7 million km², the order of magnitude of worldwide methane shelf seepage is 10^{13} Tg yr⁻¹.

III.1.2.2 seeps near hydrate deposits

Leifer and MacDonald (2003) studied gas bubbles released from three vents off Louisiana at a water depth of about 500 m, in the vicinity of hydrate deposits. The bubbles were oily. They estimated methane releases from 1.64 ('Oily Vent') to 53.2 mmol/s ('Pulsing Vent'). The corresponding bubble streams generated upwelling velocities of less than 2 cm/s to about 20 cm/s. 50% of the methane release appeared to be partitioned around bubble radii of the order of 5.5 mm.

It should be noted that the dynamics of typical buoyancy driven plumes is reasonably well described with entrainment coefficients of 0.12 to 0.15 (top-hat formulation); therefore, the order of magnitude of the radial inward velocity generated by a bubble stream is expected to be about a tenth of the observed upwelling velocity.

Information collected to date from the archival literature is sufficient to define representative ranges of the methane resource from vents and hydrate deposits. Data from additional hydrate sites and on pore water methane fluxes will be provided by NRL. A complete description of the seafloor methane resource, required to design the subsea power systems, will be included in the next Quarterly Report, along with other relevant properties including pressure, temperature, salinity, and current field.

An important question which cannot be answered without additional field studies is the stability of seafloor methane vents over time. We have been unable to locate any studies that provide long-term information on the temporal variations in gas flow rate and lifetimes of vents. It appears difficult, if not impossible, to determine *a priori* if a specific vent will be able to supply sufficient methane to generate the targeted power over a desired mission duration. This complicates site selection unless the system can be easily redeployed or is engineered with the capability to self-relocate.

III.1.3 Dissolved CH4

Although free methane gas from seafloor vents and shallow hydrate deposits appear to be the best candidate sources of fuel for the subsea power systems, a substantial amount of CH_4 also exists dissolved in sediment pore water and in sea water adjacent to these vents and deposits. One objective of this project is to assess the potential of utilizing the dissolved methane resource for power generation.

For the applications under consideration (i.e., powering subsea vehicles, equipment, and instruments) dissolved methane will probably need to be extracted from the water or sea water. The concentration of CH_4 is a critical parameter, since the collection of dissolved gases generally becomes more difficult when the amount of gas in solution is low. A model to predict the solubility limits of CH_4 in water as a function of temperature, pressure, and salinity was developed and some results are shown in Figures 3.1.4 - 3.1.6, which present methane solubility in fresh water and sea water (salinity = 35 ppt) at pressures up to 20 MPa (approximately 2,000 m depth) at 5, 10, and 15°C, respectively.



Figure 3.1.4 Methane solubility at 5°C in freshwater and seawater as a function of pressure.

Methane Solubility (10 C)



Figure 3.1.5 Methane solubility at 10°C in freshwater and seawater as a function of pressure.



Figure 3.1.6 Methane solubility at 15°C in freshwater and seawater as a function of pressure.

Solubility is observed to decrease with increasing salinity. At a given temperature, solubility initially rises with pressure, before attaining a limiting value. For conditions in the ocean, where temperature declines and pressure increases with depth, dissolved CH₄ levels are never expected to exceed about 0.2% by volume (between 1 and 2 gCH₄/liter) and will, in general, be significantly lower. As noted in the proposal for this project, a minimum methane supply rate of about 0.01 g/s is required to produce between 50 to 100 W of net power at conservative levels of system efficiency (between 10% and 20%). Even if only 10% of the dissolved gas is recovered, the amount of methane-saturated water that needs to be processed is a relatively modest 0.1 l/s. It should be noted, however, that even pore water from methane rich sediment may not be saturated. Figure 3.1.7 presents data on pore water CH₄ concentrations collected by NRL in a recent survey of potential seafloor hydrate reservoirs in Atwater Valley in the Gulf of Mexico. The correlation between chloride and methane levels is not relevant to the present discussion; what is important is that methane levels at these and other hydrate sites were rarely observed to exceed 10 mM (0.01 mol/l = 0.16 gCH₄/l), or about 10% of saturation.



Figure 3.1.7 Seafloor pore water methane (and chloride) concentrations from Atwater Valley, Gulf of Mexico.

During the upcoming Quarter, we will analyze the NRL database on pore water methane to determine whether it is worthwhile to attempt to exploit the dissolved CH_4 resource for power generation. Our preliminary assessment is that it is inferior to gas vents and shallow hydrate deposits in terms of achievable methane fuel supply rates, but may represent a more widely available and (temporally) stable resource.

III.2 Task 2: Component selection criteria

Establishing component selection criteria requires information about operating conditions (e.g., ambient CH_4 and O_2 resource) that remains incomplete due to the delay in Task 1. In spite of this complication, most of the work is done and we anticipate concluding this effort once we receive the full database on dissolved methane in pore water and pore water fluxes; contaminant

levels in gas released from dissociated hydrates, and information on ambient dissolved O_2 in the immediate vicinity of hydrate deposits.

III.2.1 Operating conditions

To date, we have been able to define ranges of the following operating conditions from information available in the technical literature:

- ambient pressure, temperature, salinity in the water column as functions of depth;
- typical current regimes as a function of depth; specific current profiles will need to be measured as part of a site selection process;
- monthly and annual averaged ambient dissolved O₂ levels as a function of depth and location (spatial resolution of approximately 1 degree latitude x 1 degree longitude);
- dissolved O₂ flux (O₂ concentration x current velocity)

Resource characterization remains largely incomplete, with the exception of seafloor gas seeps. The status is:

- <u>Dissolved O₂</u>: although average dissolved oxygen levels (and fluxes) within a 60 square nautical mile zone can be estimated from data on hand, we still need to confirm whether O₂ levels in the immediate vicinity of seeps or hydrate deposits may be reduced from these average values, since this would negatively affect the performance of the oxygen supply system.
- <u>Seafloor CH₄ seeps:</u> characterization of this potential resource has been completed to a level adequate for component selection purposes and to pursue development of a conceptual design of a subsea power system. There are questions remaining concerning the lifetimes of these seeps and temporal variations in gas flow rates, but those questions will not be resolved without additional field studies.
- <u>Shallow (0-3 m below the seafloor) hydrate deposits:</u> the ranges of methane content per unit volume of hydrate is reasonably well established as are the phase transition characteristics (i.e., pressure-temperature; heat of dissociation) and relevant thermal properties (e.g., heat capacity; thermal conductivity). Additional information is needed on hydrate gas contaminants and the range of methane in hydrate per unit volume of sediment; however, knowing the amount of hydrate distributed in the sediment may not be essential if we narrow our focus to consider only surface hydrate outcroppings. This option is discussed in Section III.5.2.
- <u>Pore water methane:</u> as noted in Section III.1.3 of this report, this resource probably is inferior to seeps and hydrates with respect to the ability to supply methane at a sufficient rate to generate high levels of power. Furthermore, extraction of the dissolved methane gas appears to present significant technical challenges and will probably impose an

energy burden (parasitic loss) on the system. On the other hand, pore water methane may represent a more widely available and (temporally) stable resource than seeps or hydrate deposits. As reported above, a model has been developed to estimate the limiting solubility of CH₄ in water as a function of pressure, temperature, and salinity. This establishes (barring supersaturation) an upper bound on the resource. Data on hand suggests, however, that pore water may not come close to attaining saturation even in methane-rich sediments. The NRL database on piston and push core pore water properties is expected to contain sufficient information to establish reasonable ranges of dissolved methane concentration and also provide guidance on types and levels of containments (e.g., chloride; sulfur) in the water that must be considered in the selection and design of the system to extract the dissolved CH₄. Corresponding heat probe data, which also will be provided by NRL, will be applied to estimate pore water methane flux, by a mass transfer to heat transfer analogy.

III.2.2 Mission profiles

Selection of individual components and the design of the integrated system will be based on satisfying specific mission profiles (i.e., application, lifetime, and maintenance schedule) under constraints imposed by resource availability and ambient operating conditions. Defining the primary mission profiles of interest to DoD and its contractors was an objective of Task 2.

III.2.2.1 lifetime

This project is part of a larger program to develop means to sustain activities of importance to National security and defense, including surveillance and environmental monitoring, in the littoral zone, beyond limits currently imposed by a number of factors, but primarily the lifetime of conventional energy sources such as marine batteries. The subsea power generating systems using seafloor methane, which are the focus of the present effort, were conceived for application in the deep ocean as well as the shallow littoral region.

The lifetime of conventional energy storage devices for subsea applications, such as marine batteries, typically does not exceed 6 months to a year, depending on ambient conditions, power draw, etc. Furthermore, certain instruments and devices consume too much power to be reliably operated by batteries. Table 3.2.1 from Kurasaki (2004) provides examples of peak and duty cycle power consumption of some typical oceanographic instruments.

Instrument	Peak Power Requirement, W	Duty Cycle Power		
		Budget, W		
Air-Sea Flux	1-2			
Gyroscope	10	0.06		
Seismograph	1.5			
Acoustic Doppler Current	0-100	0.07		
Profiler				

 Table 3.2.1 Power requirements of some seafloor instrumentation.

Assuming that conventional fuel cell technology will be applied in some or all of the systems being designed and that minimal or no servicing will be possible for deeply deployed devices, we tentatively propose that the target lifetime be 3 to 5 years. This appears feasible,--based on operating histories of conventional fuel cells (e.g., PEMFC ~ 3,000 hours life; Alkaline FC ~ 5,000 hours; SOFC > 10,000 hours) and assuming a modest duty cycle (say, 20%),--while still providing a substantial improvement over batteries to justify the anticipated cost premium. Poisoning of the fuel reforming system catalysts and fouling of filters used to remove contaminants from the raw fuel or during the O_2 extraction process can also impact lifetime and these factors will be evaluated as the design process advances.

III.2.2.2 maintenance schedule

Systems utilizing seafloor methane seeps deployed in the shallow littoral zone or at diveraccessible depths (typically < 1,200 feet of sea water--fsw) can be serviced. Except in very cold water, hydrates are found below these depths and power systems supplied with methane from hydrates or deep sediment pore water will need to be designed to operate over their targeted lifetimes with no maintenance. Although ROVs (remotely operated vehicles) could perform some simple repair or recovery operations, the cost is expected to be prohibitively high. The following preliminary maintenance schedule will be adopted for component selection purposes:

- Below 1,200 fsw depth: no servicing or repair over the mission lifetime.
- Above or at 1,200 fsw depth: annual servicing or repair possible at < 300 fsw (military diver scuba limit); longer maintenance intervals with increasing depth.

III.2.2.3 applications

Two primary products have been identified for the subsea power generation systems:

ELECTRICITY GENERATION. The objective is to produce electricity for recharging AUVs (autonomous underwater vehicles) or UUVs (unmanned underwater vehicles), or for underwater instruments or monitoring devices, particularly those with electrical requirements that exceed the capabilities of batteries, or microbial fuel cells that are also under development.

FUEL (AND OXIDIZER) PRODUCTION. The objective is to produce and store fuel (e.g., H₂, pure CH₄, methanol) and, possibly, oxidizer to refuel AUVs or UUVs. Electricity is generated only at levels needed by system equipment such as pumps.

The conceptual design will consider both of these applications and evaluate the feasibility and performance of systems configured to meet these objectives.

During the present reporting period, work was initiated to establish guidelines for an AUV/UUV battery charging station based on a low power seafloor fuel cell.
AUV/UUV Battery Charging Application

Both batteries and fuel cells currently are employed to power AUV/UUV thrusters. Table 3.2.2 lists the different battery technologies.

Technology	Energy Density	Voltage/Cell	
	W-h/dm ³	V	
Lead-acid	10-20	2.8	
NiCd/NiMH	10-30	1.2	
Silver-Zinc	30 - 50	1.45	
Lithium Ion	40 - 70	4.0	

Table 3.2.2 Properties of battery cell technologies used in AUVs (Hasvold et al., 2005)

Batteries packs are composed of combinations of individual cells connected in series and in parallel to achieve the necessary voltage and current. The estimated recharging capability of a 60 W fuel cell is presented in Table 3.2.3. It is assumed that the fuel cell can be operated at any combination of voltage and current. Appropriate circuits will need to be designed to provide the necessary electrical characteristics. Given the power requirements of some of the larger AUVs, an on-site energy storage system comprising batteries or capacitors may be needed to supplement the fuel cell in order to reduce the excessively long recharging times. The fuel cell output would be stored by these devices during the periods between charging events.

				Charging	Recharge
AUV	Energy	Voltage	Capacity	Current	Time
	kWh	V	Ah	А	Н
Duke Robotics	0.5	29.6	16	2.0	7.9
Remus 100	1.0	14	71	4.3	16.7
HUGIN 1	3.6	32	113	1.9	60.0
HUGIN 3000	4.0	8	500	7.5	66.7
HUGIN 1000	15	50	300	1.2	250.0

It appears that AUV/UUV recharging is feasible even with a system based on a low power fuel cell, provided that energy storage is included and appropriate electronics can be designed.

This analysis will be extended in the upcoming Quarters and the feasibility of the fuel and oxidizer production application will also be explored.

III.3 Task 3: Oxygen supply system

This Task is proceeding on schedule. The literature review of candidate oxygen extraction and supply techniques continued during the present reporting period as did preparations for experiments to investigate perfluorooctylbromide (PFOB) as an O_2 carrier for an artificial gill

described in the previous Quarterly Report. In addition, an analysis was conducted to assess the potential for application of an additional strategy to extract dissolved oxygen from sea water using gas bubbles.

III.3.1 O₂ extraction by gas bubbles

Bubblers are used frequently in industrial processes, primarily to transfer components of the bubbles into the liquid solvent, but also to add reagents in the liquid to the gas. During our review (Task 1) of data on methane bubble composition from shallow seafloor seeps, it was observed that the O_2 and N_2 content of the bubbles could increase significantly with rise height as the bubbles scrubbed these dissolved gases from the sea water. Table 3.3.1 presents some of the data collected by Clark *et al.* (2003) from the Coal Oil Point seeps. Gas samples were taken at the vent (20 m depth), at 10 m above the vent, and at 1 m below the surface, and analyzed for CH₄, O_2 , N_2 , CO_2 , and other species.

Table 3.3.1	Gas composition (in mole fraction) of bubbles from Shane Seep in Coal Oil Point,
	CA (from Clark et al., 2003)

Depth (m)	CH ₄	N_2	O ₂	CO_2
1	79.4	13.8	4.5	< 0.1
1	76.7	14.4	6	< 0.1
1	79.5	12.6	5	< 0.1
10	90.8	4.9	1.8	0.2
10	84.4	8.1	3	0.1
10	86.4	7.5	2.8	< 0.1
20	84.2	2.5	0.3	10.6
20	81.9	1.4	0.2	13.4
20	84	1.5	0.3	11.2

Over a 19 m rise, the mole fractions of O_2 and N_2 were observed to increase by about a factor of 10, while CO_2 (which is in significant excess over ambient levels when the gas issues from the vent) drops precipitously.

Given the apparent effectiveness of natural seep bubbles to extract O_2 from sea water, it was decided that this concept warranted consideration for the present application along with the artificial gill approach. Figure 3.3.1 provides a sketch showing how the concept might be implemented. The bubble plume is collected with a conical shaped trap and, after filtering, the gas mixture is used to feed the reformer and the cathode side of a fuel cell. The gas bubbles may originate from two sources: 1) natural methane bubbles from seafloor vents or destabilized hydrates and 2) an artificial bubble plume comprising gases from the power generation system. In the second scenario, the bubble plume could serve both to collect dissolved O_2 and to discharge waste gases like CO_2 .



Figure 3.3.1 Sketch of the concept to extract O₂ using gas bubbles.

A gas exchange model for bubbles ascending through water was developed following the approach of Leifer & Patro (2002). The model was applied to predict the change in O_2 concentration of a single bubble of inert gas (here, assumed to be N_2) as a function of rise height. Two cases were examined in which it was assumed that the bubble was released at depths of 40 m and 500 m, typical of shallow water vents and methane hydrate outcroppings respectively. The maximum bubble rise time was set at 120 seconds and rise height was limited to10 m. Results are presented in Figure 3.3.2 for a bubble with and initial diameter of 1 mm. At 40 m depth, a 10 m rise would yield > 4% O₂ mole fraction. While not shown in the Figure, the model predicts that O_2 mole fraction in the bubble would reach levels between 12% and 14% if the bubble did not exceed 1% for both 10 m rise height and 120 s rise time. At this depth, O_2 diffusion into the bubble is impeded by the elevated gas density in the bubble and low ambient concentrations of dissolved oxygen.

Although the model results suggest that only modest amounts of oxygen can be collected with gas bubbles over practical rise heights and residence times, the relative simplicity of the approach and the fact that, unlike the artificial gill, gas phase O₂ is available directly, without additional processing (e.g., membrane separation from PFOB emulsions or thermal release when bound by other carriers) support further inquiry. Refinement of the model will be pursued during the upcoming Quarter along with the development and evaluation of strategies to integrate the concept with the reformer and fuel cell.

Model calculations: 1 mm radius N₂ bubble





III.3.2 PFOB oxygen supply system

The fabrication and procurement of facilities and instruments required to conduct experiments to explore O_2 capture and transport using perfluorooctylbromide (PFOB) were pursued during the present reporting period. These experiments were added to this Task on the basis of the initial literature search.

As described in the previous Quarterly Report, two experiments will be performed. The first will measure oxygen solubility and mass transfer characteristics of PFOB and PFOB emulsions over a range of conditions (i.e., temperature, pressure, dissolved O_2 concentration) relevant to subsea operation. The second will investigate fuel cell performance when O_2 is supplied to the cathode with liquid PFOB emulsions. There is concern that low oxygen levels in the emulsions and slow diffusive transport of O_2 through the liquid to the cathode could significantly limit performance. A plan has been developed to conduct tests using one of the small 50 cm² PEM cells available at HNEI's Hawaii Fuel Cell Test Facility, contingent on the availability of funds for this experiment which was not included in the original scope of work.

During the ongoing literature search, a patent was discovered (Brokman & Goldstein, 1993) that appears to be directly relevant to the application of perfluorocarbons (PFC) as O₂ carriers for fuel cell applications. This patent, and its implications with regard to fuel cell selection is discussed in the following Section on Task 4.

III.4 Task 4: Fuel reforming system and fuel cell selection

This Task was initiated during the present reporting period. In the previous Quarterly Report, it was noted that PEM fuel cells (PEMFCs) appeared to be the most likely candidate technology capable of achieving the targeted power levels and lifetime with no maintenance. Solid oxide fuel cells (SOFCs) were considered to be a secondary option. Development of the system model (Task 5), fuel gas processing subsystem (Task 7), and oxygen supply subsystem (Task 3) to date have focused on PEMFCs.

In the course of the literature search of oxygen carriers for an artificial gill, we came across a patent on electrodes for metal/air batteries and fuel cells that also included the concept of utilizing an organic fluid to deliver O_2 to the cathode (Brokman & Goldstein, 1993). A copy of this patent is included as an Appendix to this Quarterly Report. Information provided in the patent has compelled us to reassess our preliminary position favoring PEMFCs and to extend the scope of our inquiry to include alkaline fuel cells (AFCs).

III.4.1 Candidate fuel cells

U.S. Patent 5,185,218 (Brokman & Goldstein, 1993) suggests that an electrochemical cell (e.g., fuel cell) can operate using oxygenated PFC (or other organic fluids) by passing the PFC across the back of a heavily wet-proofed substrate. O_2 is released from the PFC and enters water vapor-filled pores to diffuse and react at the catalyst in contact with KOH electrolyte, for the case of an AFC. The example in the patent reports that the performance of this cathode was very similar to that of the same cathode operating conventionally on air, indicating that the partial pressure of oxygen in the pores supplied by PFC, aerated by a bubbler, is the essentially the same as in air. The implication is that a fuel cell cathode configured as described in the patent can operate equally as well with O_2 supplied by a gas mixture or by a liquid PFC equilibrated with the same gas mixture.

Table 3.4.1 provides properties of water and some liquid fluorocarbon O_2 carriers (Lehmler *et al.*, 1999). As indicated in the table, fresh water and PFCs in contact with pure O_2 at 1 atmosphere and 25°C have equilibrium dissolved oxygen concentrations of about 30 and 500 ml/L, respectively. These values decline in proportion to the O_2 mole fraction in the gas; water in equilibrium with air contains approximately 6 ml/L dissolved oxygen (0.21 x 30 ml/L) and PFC in equilibrium with this oxygenated water will have the same dissolved O_2 content that it would have if it were directly in contact with the air (about 105 ml/L = 0.21 x 500 ml/L).

For a PEMFC operating in a similar manner as the alkaline fuel cell described in the patent, the air limiting current density is estimated to be $2A/cm^2$ and the operating current density is 500 mA/cm². If O₂ is supplied to the cathode by liquid PFC equilibrated with surface seawater (which, in turn, is assumed to be in equilibrium with air), then the limiting current density is expected to drop to about 430 mA/cm² with an operating current density of 108 mA/cm². This appears to be in agreement with the AFC operating current densities reported in U.S. Patent 5,185,218.

Solvent	Density, g/mL	Vapor pressure at 37°C, mm Hg	Surface tension, dyn/cm	O ₂ solubility, mL/L	CO ₂ solubility, mL/L
Water	1.0	47	72	30	570
Perfluorooctyl bromide	1.92	10.5	18	530	2100
Perfluorodecalin (APF-40)	1.95	14	15	490	1400
Perfluorooctane (FC 3280)	1.75	NA	12	400	1000
FC-77	1.78	85	15	500	1980
RM-101	1.77	64	15	520	1600
FC-75	1.78	64	15	520	1600

Table 3.4.1 Physical properties of water and some fluorocarbon liquids

Extending the claims of the patent to situations where the power system will be deployed to depths near the O_2 minimum, where the concentration of oxygen in seawater is about 1 ml/L (see, for example, Figures 3.1.2 and 3.1.3), we can anticipate operating current densities of the order of tens of mA/cm². In terms of stack dimensions, the planform area of a 25 W, 10 cell stack operating at the surface would be about 20 cm² to 30 cm². At a few hundred meters below the surface, the planform area of a 10 cell 25 W stack would need to be increased by a factor of 5 to 6 (i.e., in proportion to the reduction in the ambient concentration of dissolved oxygen), to 100 cm² to 200 cm², in order to compensate for the limited availability of O_2 . While these dimensions do not appear to be excessively large, they depend on the validity of the information provided in the patent and their applicability to PEMFC. Toward this end, the PFOB experiments that have been proposed to supplement the Task 3 literature search would provide valuable information.

There is reason to believe that the level of performance reported in the patent may reflect certain characteristics of AFCs that do not apply to PEMFCs. Specifically, AFCs produce water at the anode according to the reaction:

 $H_2 + 2(OH^-) \rightarrow 2H_2O + 2e^-$

and employ a liquid electrolyte, while PEMFCs generate water at the cathode which needs constantly to be removed to avoid flooding that can seriously degrade the limiting current. Using a liquid carrier such as a PFC to deliver O_2 to the cathode may not, therefore, produce the level of performance reported in the patent for the AFC that was tested.

AFC, like PEMFC, operate at relatively low temperature (50° C to 200° C) and are compact. AFC generally has a longer lifetime than PEMFC, but is sensitive to CO₂. In consideration of possible advantages with respect to operation with liquid oxygen carriers, we have decided to include AFC as a candidate for subsea power applications.

III.4.2 Fuel reforming and clean up

Work performed on the selection of the fuel reforming and clean up system is described below in Section III.6.2.

III.5 Task 5: System model

This Task is proceeding on schedule. The major accomplishment during the present reporting period was the development of a sub-model to predict the performance of a PEM fuel cell component as a function of operating conditions. This model will eventually be linked to models of the other modules (i.e., fuel reformer, O_2 extraction system) by the appropriate energy and mass balance relationships to conduct parametric studies of the subsea power generation device.

As discussed in Section III.4, PEM previously was the leading candidate fuel cell for our application and development of the PEMFC model followed accordingly. While we expect to continue to refine the model during the upcoming Quarter and pursue its integration into a comprehensive system model, we will also consider parallel development of a model of an alkaline fuel cell, given its (apparent) better compatibility with liquid PFC oxygen carriers.

III.5.1 PEMFC model

The model considers a PEMFC as a two-dimensional device illustrated in Figure 3.5.1. The two dimensions being resolved are the x-direction along the flow channels and the z-direction across the Membrane Electrode Assembly (MEA).

The model is isobaric under pressure *P*.

The porosity of the gas diffusion layers is taken as a constant.

Transport phenomena through catalyst layers are not included.

In the anode flow channel at x = 0, hydrogen, water, and perhaps inert gases, are supplied at temperature T(0). A typical inert gas may be carbon dioxide, for example, as a product of a reforming process to produce hydrogen.

In the cathode flow channel at x = 0, oxygen, water, and perhaps inert gases, are supplied at temperature T(0). A typical inert gas may be nitrogen, for example, if air is used in the cathode.

The temperature field is assumed to depend upon x only (sections across the MEA are isothermal). Also, heat transfer along the x direction is considered negligible.

The determination of fuel cell characteristics proceeds from x = 0 along the flow channel.



Figure 3.5.1 Diagram of two-dimensional PEM fuel cell.

Solution requires that the following steps be implemented:

- a) The knowledge of temperature and channel inlet molar fluxes per unit width allows the calculation of how much water is in gas (steam) or liquid form; the inlet enthalpy flux per unit width H(0) and gaseous compositions X_i in the flow channels are then available.
- b) A current density *I* and a ratio α of the steam molar flow rate per unit area over the hydrogen molar flow rate per unit area through the anode are arbitrarily picked. The hydrogen molar flow rate per unit area through the anode is I/(2F).
- c) The Stefan-Maxwell equations for the binary diffusion of gas mixtures are then solved across the gas diffusion layer of each electrode. *z*-integration proceeds toward the membrane from either flow channel (i.e., from Point 1 to Point 2 in the anode, and from Point 4 to point 3 in the cathode). This yields the gas compositions X_j on either side of the membrane.
- d) An equation expressing the balance between electro-osmotic drag and back diffusion through the membrane is solved for the water content of the membrane λ . λ is defined as the number of water molecules per sulfonic site and depends upon relative saturation of the gas phase. Since steam composition is known on both sides of the membrane from step c), the solution of the equation is iterative from step b). α is varied until both boundary conditions are satisfied. Once convergence is achieved, the ohmic resistance R_m through the membrane can be calculated (in Ω -cm²).
- e) Ohmic loss through the membrane, activation overpotential at the cathode and concentration overpotentials through the gas diffusion layers are available at this juncture. The potential *V* can therefore be calculated and compared to V_{cell} . A second iteration on *I* is performed from step b) until *V* converges to V_{cell} .
- f) Channel molar fluxes per unit width and enthalpy flux are available for the next *x*-sectional calculations from simple mass and enthalpy balances.
- g) Pick next sectional temperature.
- h) <u>Temperature for the next *x*-section is determined iteratively until the compositions in both channels yield an enthalpy flux equal to the value from step f</u>). The next *x*-sectional calculations can then be initiated from step b).
- i) Calculations end when they reached x = L.

A flow chart of the solution procedure is shown in Figure 3.5.2.



Figure 3.5.2 Flow chart of solution algorithm.

The fuel-cell power per unit width is given by $\{V \int_0^L I dx\}$.

Hydrogen utilization is defined as $\frac{N_{H2}(0) - N_{H2}(L)}{N_{H2}(0)}$.

Oxygen utilization is defined as $\frac{N_{O2}(0) - N_{O2}(L)}{N_{O2}(0)}$.

Input to model includes:

- t_A thickness of anode gas diffusion layer (µm)
- t_C thickness of cathode gas diffusion layer (µm)
- t_M thickness of proton exchange membrane (µm)
- ε porosity of gas diffusion layers

 ρ_{dry} density of dry membrane (g/cm³)

 M_m equivalent weight of membrane sulfonic site (g/mol)

 i_0 exchange current density for pure O₂ at 1 atm (A/cm²)

- *L* length of flow channels
- $N_j(0)$ input molar flow per unit width for species j (mol/s-m)
- T(0) inlet temperature (K)
- *P* overall pressure (atm)

 V_{cell} fuel cell voltage (V)

- T_{ext} exterior temperature (K)
- U heat transfer coefficient between fuel cell and exterior (W/m²-K)

An example is provided to demonstrate some of the capabilities of the model. Values of parameters used in the calculation are provided below and results are presented in Figures 3.5.3 - 3.5.9. For the case examined, fuel cell power per unit width is 292 W/m, hydrogen utilization is 28%, and oxygen utilization 70%.

Example model input

 $t_A = 365 \,\mu m$ $t_{C} = 365 \, \mu m$ $t_M = 183 \ \mu m$ $\varepsilon = 0.20$ $\rho_{dry} = 1.87 \text{ g/cm}^3$ $M_m = 1100 \text{ g/mol}$ $i_0 = 0.01 \text{ A/cm}^2$ $b = \frac{RT}{0.5F}$ varies with x through T L = 100 mm $N_{O2}(0) = 1.797 \text{ mmol/s-m}$ $N_{N2}(0) = 7.188 \text{ mmol/s-m}$ $N_{H2Oc}(0) = 1.015 \text{ mmol/s-m}$ $N_{H2}(0) = 8.985 \text{ mmol/s-m}$ $N_{H2Oa}(0) = 1.015 \text{ mmol/s-m}$ T(0) = 80 CP = 3 atm $V_{cell} = 0.6 V$ $T_{ext} = 10 \text{ C}$ $U = 100 \text{ W/m}^2\text{-K}$

Nomenclature

- *F* electric charge per mole of electron (96487 C/mol- \bar{e})
- h_{jk} specific enthalpy of species *j* in phase *k* (J/mol)
- H(x) enthalpy flow per unit width (W/m)
- I(x) current density (A/cm²)
- $N_j(x)$ molar flow per unit width for species j (mol/s-m)
- $P_{sat}(T)$ saturation pressure (atm)
- *R* gas constant (J/mol-K)
- R_m ohmic resistance across membrane (Ω -cm²)
- T(x) temperature (K)
- V(x) calculated cell potential (V)
- *x* coordinate along the flow channel (m)
- $X_j(x, z)$ gaseous mole fraction for species j
- X_{sat} saturation steam mole fraction
- z coordinate across the MEA (m)
- $\alpha(x)$ ratio of steam flow rate per unit area over hydrogen flow rate per unit area across the anode
- $\lambda(x, z)$ number of water molecules per sulfonic site in membrane

Subscripts

CO2	carbon dioxide
O2	oxygen
H2	hydrogen
H2Oa	water (anode)
H2Oc	water (cathode)
N2	nitrogen
STMa	steam (anode)
STMc	steam (cathode)
INRa	inert gas (anode)
INRc	inert gas (cathode)



Figure 3.5.3 Model results for test case: calculated temperature distribution along flow channel.



Figure 3.5.4 Model results for test case: calculated current density along flow channel.



Figure 3.5.5 Model results for test case: calculated ratio of steam flow rate per unit area to hydrogen flow rate per unit area across the anode along flow channel.



Figure 3.5.6 Model results for test case: calculated oxygen mole fraction along flow channel.



Figure 3.5.7 Model results for test case: calculated H₂ anode flux.



Figure 3.5.8 Model results for test case: calculated O₂ cathode flux.



Figure 3.5.9 Model results for test case: calculated water fluxes.

III.5.2 System layout

Preliminary sketches showing a system layout concept for the AUV/UUV recharging or refueling application are provided in Figures 3.5.10 and 3.5.11. This configuration was conceived for use with gas seeps or surface and shallow hydrate deposits.

The gas purification and reforming, O_2 extraction, and fuel cell modules are mounted on the top of a cylindrical structure along with a docking station where an AUV/UUV can refuel (if power by a fuel cell) or recharge its batteries. The bottom end of the cylindrical structure is open and will sit on the seafloor above a gas vent or hydrate mound. The weight of the system will drive the cylinder into the sediment like a gravity core to ensure stability and to seal off the enclosed seep or hydrates. A fin can be installed around the circumference of the cylinder at a selected height to limit the depth of penetration and for stability.

Inside the hollow cylinder, an upside down cone will be installed to funnel the seep gas or hydrate methane to an opening at the top where the raw gas will flow into the reformer module. A vent line connected to a pressure relief valve will discharge gas from the plenum at the top of the cone to avoid over-pressurization and excessive buoyancy when the rate of raw gas consumption by the system is exceeded by the supply. Additional vents may be provided slightly above the sediment line to allow water to be pushed out by the buoyant gases. The spaces between the cone and cylinder will be employed to store processed gases (e.g., purified CH_4 , H_2 , or O_2) or reagents.

In the case of hydrate deposits, decomposition must be induced to release the methane gas. Thermal methods appear to be the most feasible for the present application, since the required level of depressurization at deep ocean temperatures will be difficult to implement and methanol of other reagent injection is unlikely to be acceptable from an environmental standpoint. As indicated in the Figures, a matrix of heating tubes that penetrate into the sediment could be employed to channel waste heat (e.g., hot water or steam) from the reformer or fuel cell to melt the hydrates enclosed within the cylinder.

When deployed over a shallow hydrate deposit or surface outcropping, the amount of CH_4 gas recoverable is limited by the volume of hydrate enclosed within the cylinder and which can be decomposed by the heating tubes. This is different from a seep, which we presume will supply gas continuously over the mission lifetime. Since 1 m³ of hydrate contains approximately 150 Nm³ = 9.8 x 10^4 g of CH_4 gas, destabilization and collection of all of the methane could supply a nominal 100 W (net) fuel cell operating at about 10% system efficiency for about 1,400 hours. This presumes a CH_4 utilization rate of a little less than 0.02 g/s as calculated in the proposal for the project. Assuming that the system lifetime will be limited by the life of the fuel cell—which, conservatively, is estimated at about 3,000 hours for PEMFC and 5,000 hours for AFC, approximately 3-4 m³ of hydrate will be required over the duration of the mission. Considering that hydrate mounds observed on the Cascadia Margin or in the Gulf of Mexico may be several meters in diameter and more than a meter thick, this requirement does not appear to be excessive and suggests a minimum diameter for the cylindrical platform of about 2 m (or 80 inches as shown in the Figures). Assuming that the platform can penetrate a meter into the seafloor, the enclosed sediment/hydrate volume would then be about 3 m³.

We plan to refine the conceptual layout in the coming months, particularly with respect to material selection and ocean engineering issues related to deployment, but will also continue to explore alternative designs. A more detailed analysis of the available methane in the enclosed sediment volume will be performed and the viability of the heating tube system proposed to destabilize the hydrates will be assessed.



Figure 3.5.10 Sketch of the subsea power generation system.



Figure 3.5.11 Perspective of the subsea power generation system.

III.6 Task 7: Fuel clean-up and reforming experiments

This Task is proceeding on schedule. During this reporting period, preparations were undertaken for gas cleaning and reforming experiments utilizing mixtures of methane and contaminant species representative of the raw gas from seeps and destabilized hydrate. We are awaiting additional input from NRL on the composition of gas released from hydrate samples to supplement the data presented in Table 3.5.1 of the first Quarterly Report.

III.6.1 Reforming experiments

Based on information collected from the archival literature on seep gas composition, cylinders of grade 5 methane and grade 5 methane doped with 1000 ppmV H₂S were ordered to conduct gas cleaning and reforming experiments. By all available accounts, the 99.9:0.1 CH₄:H₂S ratio represents well the relative quantities of these species in typical seep gases; hydrate gases are expected to contain even less sulfur. The laboratory grade gases can be mixed in various proportions with other species (e.g., N₂, CO₂) found in seep and hydrate gases. The cylinders have been received and will be used in experiments in the coming Quarter.

A preliminary design of reforming and gas conditioning systems is shown in Figure 3.6.1. Three possible sulfur removal systems are proposed for preconditioning of the seafloor methane stream. Reforming of desulfurized gas is followed by removal of carbon monoxide using selective oxidation.

III.6.2 Sulfur removal

Possible adsorbents have been explored. Table 3.6.1, provided previously in the first Quarterly Report, lists some candidate media. There is an abundance of literature regarding hydrogen sulfide adsorbents and their use in treating various gas streams. There is not, however, an abundance of commercially available adsorbents as most are in the developmental or testing stage. Commercially available adsorbents are generally targeted at large scale systems such as power generating plants.

A preliminary design worksheet has been set up to model lifespan and adsorption characteristics of an adsorbent packed bed while meeting flow regime requirements. This will lead to the design and fabrication of an adsorbent test bed in the upcoming quarters.

In-house production of zinc oxide adsorbent is underway. This will serve as a starting point to gather data such as hydrogen sulfide removal efficiency, loading capacity, and pressure drop with tests specific to our working parameters.

Hollow fiber membranes for the removal of H_2S were also investigated and may still be an option. It appears that all usage of the hollow fiber membrane to date has been to remove H_2S from N_2 rather than methane. Finding a readily available supply of hollow fiber membranes or a well defined method for producing them has not been fruitful thus far.



Figure 3.6.1 Possible fuel processing set-up: block 1) sulfur removal; block 2) reforming; block 3) CO removal.

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Ref. No	Removal Media	Formula	Surface Area	Bulk Density	Particle Shape	Particle Size	Pressure Range	Temp Range	Absorption % Mass	Regenerability	H ₂ S Removal Efficiency
1.01	1110010	1 01111414	m ³ /g	g/cm ³	Shupe	mm	atm	°C	, 0 112000		%
7	Zinc Oxide	ZnO	3.2	0.84	Pellet	d=1	1	400-500			
8	Zinc Ferrite	ZnFe ₂ O ₄						550	39.8	>5x	
9	Zinc Ferrite	ZnO/TiO ₂	3.2-3.9		Cylinder	d=4.7, l=11.75	1	565-785	19.8	>15x	
10	SulphaTreat	Fe ₂ O ₃ & Fe ₃ O ₄		1.1	Pellet	4-16 Mesh	1+	10-50	25	no	
11	Sulfa-Bind	Proprietary					1+		3-4 / regen	<14x	99.98
12	Sorb-Z	Proprietary		0.88	Cylinder	d=3.2, l=7.5	10-20	400-500	17	50x	99.99
13	Elec.chem Membrane						1	580-650			<90
14	Pressure Membrane						40+				~97
	Aqueous Sol.										
15	Membrane	Na ₂ CO ₃					1.2-1.6	25			>99.98
16	Zeolite	Mole Sieve MCM-41			Pellet	d=0.5-1.0	1	25		?	99.5

Table 3.6.1Summary of removal media for cleaning H2S from gas streams

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APPENDIX C: Section III from the 3rd Quarterly Report

III TECHNICAL ACTIVITIES

A description of technical activities conducted during this reporting period, broken down by Task, is provided below. Tasks 1, 2, 3, 4, 5, and 7 were scheduled to be undertaken during the third Quarter of this project.

III.1 Task 1: Methane and oxygen source assessment

This Task has been completed and the associated milestone, M1, has been reached.

As discussed in the previous Quarterly Report, there were three remaining issues associated with this Task that required input from NRL: 1) the viability of pore water methane as an energy resource; 2) the possible occurrence of dissolved oxygen depletion in the vicinity of strong seafloor methane sources; and 3) confirmation of the levels of contaminants in gas released from hydrates. NRL has been providing information from its data archives and consulting with the UH participants to resolve these issues since execution of its subcontract in December 2005. Draft reports on these and other topics have been received from NRL recently and are being reviewed and edited and will be included in the Final Report.

III.1.1 Methane resource

Table 3.1.1 summarizes the major conclusion about the candidate methane resources. Detailed information on seafloor gas vents, hydrates, and dissolved methane has been presented in previous Quarterly Reports. A full assessment of pore water methane, and the associated NRL report on this resource, will be included in the Final Report.

As indicated in the Table, we propose that seafloor vents of free methane gas provide the best opportunity for the deployment of a proof-of-concept, subsea power generation system. Many of these vents have documented methane gas fluxes well in excess of what is required to produce the target nominal 100 W power. Moreover, they can be found at diver-accessible depths, which would be very advantageous for a test of a first prototype that may require extensive monitoring and service. In the long-term, methane hydrates—particularly surface outcroppings and deposits just beneath the seafloor—need to be considered, since they are much more widely available than vents, albeit at depths below 500 m. Recovery of methane gas from the solid hydrates is the primary technical disadvantage of this resource. Recovery will impose an energy penalty on the system and techniques that have been proposed to accomplish this have not been fully verified.

Although sediment pore water methane and methane dissolved in sea water are available throughout the oceans, concentrations typically are extremely low and, based on our analyses,

Resource	Primary Advantages	Primary Disadvantages	Ranking
Methane gas vents	Large fluxes of gas phase	Not widely available;	Best choice
	CH ₄ ; no energy required to	temporal stability of gas	for proof-of-
	produce gas; found in	vents unknown; gas may	concept
	shallow and deep water	contain high levels of	
		contaminants	
Hydrates	Large amounts of methane	Gas recovery requires	Second
	in hydrates in many areas	energy; recovery	choice
	of the deep ocean;	technologies not verified;	
	relatively clean gas	generally available only at	
		depths $> 500 \text{ m}$	
Pore water methane	Widely available	Concentrations and natural	Unacceptable
		fluxes only capable of	
		sustaining milli- or micro-	
		watts of power; difficult to	
		recover methane	
Dissolved methane in	Widely available	Concentrations too low to	Unacceptable
sea water	throughout the ocean	produce any significant	
		power; difficult to recover	
		methane	

Table 3.1.1 Comparison of seafloor methane resources

cannot be utilized to sustain any significant level of power generation with available or near-term technologies. The NRL heat flow and pore water chemistry data from methane-rich regions were analyzed during the present reporting period and an average natural flux of CH_4 upward through the sediment of approximately 100 mM/m²/year was calculated. This level of flux would produce power of the order of a milliwatt per square meter of seafloor. The concentration of methane dissolved in sea water rarely exceeds a few nanomolar, or six orders of magnitude smaller than in sediment pore water. Near strong seafloor methane sources, concentrations may reach micromolar levels, as shown in Figure 3.1.1 provided by NRL, but this is still too low to be viable.



Figure 3.1.1 Methane concentration history recorded with a Capsum METS oceanographic methane sensor attached to a submersible traversing over a hydrate mound in the Gulf of Mexico. Instrument lower detection threshold ~ 50 nM. Away from the strong seafloor methane source CH_4 levels are below the detection threshold; concentrations rise to between 1 and 10 μ M (0.02 to 0.2 standard cm³/liter) a few meters directly above the source.

III.1.2 Oxygen resource

As reported previously, we have coded a database using information available from the National Oceanographic Data Center of NOAA and developed resources to estimate dissolved O_2 levels throughout most of the world's oceans. The user needs to specify the desired depth and location (on a 1 degree latitude by 1 degree longitude grid). Examples are provided in the following Section. The only unresolved issue is whether O_2 is depleted locally in regions adjacent to strong seafloor methane sources. This was examined in cooperation with NRL during the present reporting period.

A review of the available data revealed no consistent correlation between depleted concentrations of O_2 and elevated levels of methane. Examples of this type of behavior do exist, but the evidence is not sufficient to identify conclusively a cause-and-effect. For the purpose of the present conceptual design exercise, therefore, we assume that we can utilize the aforementioned dissolved oxygen database, with the caveat that O_2 levels must be confirmed at a selected site during the preliminary design phase.

III.2 Task 2: Component selection criteria

This Task has been completed and the associated milestone, M2, has been reached.

As discussed in the previous Quarterly Report, mission profiles, including target lifetimes, maintenance schedules, and applications, have been identified and operating ranges have been defined for gas vent and hydrate methane resources and ambient dissolved oxygen levels. The

plan for the present reporting period was to develop operating ranges for pore water methane and methane dissolved in sea water; determine whether local O_2 depletion needed to be considered; and update the contaminant species profiles developed from information from the archival literature using data to be provided by NRL. It was concluded (see Sections III.1.1 and III.1.2 above) that neither pore water methane nor CH₄ dissolved in sea water represented a viable energy resource and that O_2 depletion would not be considered during the present conceptual design phase. On the remaining issue of contaminant species in the raw methane gas mixture, we had tentatively determined that H₂S was the contaminant of greatest concern and presumed that a representative and conservative level was about 1000 ppmV. During the present reporting period, these points were reassessed, working in cooperation with NRL.

Based on a review of additional data from NRL and several new references, it was concluded that H_2S will continue to be the species of interest, given its potential to poison reformer and fuel cell catalysts. No new insight was provided on sulfide levels in vent gas. Data on gases released from the strong vents offshore Coal Oil Point in the Santa Barbara Channel that have been extensively documented support our assumed representative value of 1000 ppmV. In the case of methane gas released from hydrates, several examples have been reported where H_2S was detected in significant excess of 1000 ppmV. Milkov *et al.* (2005) analyzed hydrates from the Cascadia Margin and determined an average sulfide concentration of 0.27% (i.e., 2700 ppmV). It has been observed that there can be large variations in H_2S over the same general area. Kastner *et al.* (1998) reported sulfide concentrations as high as 18.5% (185,000 ppmV) in hydrates from one location on the Cascadia Margin; however, Milkov (2005) states that this is an unusual exception and their review of the available data for sites throughout the world concludes that contaminants generally are present in released hydrate gas at very low trace levels. He suggests a conservative, representative concentration of sulfide of about 0.1%, which corresponds to our assumed value of 1000 ppmV.

We will continue to use 1000 ppmV H_2S in our development of the fuel clean-up system (Task 7), but will take into consideration the possibility of much higher levels of this contaminant.

III.2.2 Background environmental parameters

Background operating condition profiles (i.e., ambient environmental parameters) have been developed for candidate sites and are being used for component selection. An example is provided below to demonstrate the approach that we have employed to prepare these profiles.

Four candidate sites in two significant geographical areas have identified. The first area is off Coal Oil Point in the Santa Barbara Channel, shown in Figure 3.2.1 reproduced from Leifer *et al.* (2000). Very active and relatively shallow natural gas bubble seeps have been surveyed there. The 1° latitude-by-1° longitude square closest to the Coal Oil Point seeps that was used to determine dissolved O_2 concentrations is shown in Figure 3.2.2.

Three other sites overlying seafloor hydrate mounds have been considered in the Gulf of Mexico. These include the Atwater Valley mounds shown in Figure 3.2.3 and surveyed by NRL. These sites also encompass the three mounds and corresponding gas bubble seeps discussed in Leifer and MacDonald (2003). Figure 3.2.4 provides the coordinates of the three sites.



Figure 3.2.1 Map of natural gas seep field off Coal Oil Point, Santa Barbara Channel.



Figure 3.2.2 1° latitude by 1° longitude square from WOA01 database (NODC) closest to Coal Point seeps.



Figure 3.2.3 Map of Atwater Valley gas hydrate mounds in the Gulf of Mexico.



Figure 3.2.4 Map showing 3 bubble seeps above seafloor hydrate deposits (▲) in the Gulf of Mexico and the Atwater Valley mounds (●); corresponding 1° latitude by 1° longitude square from WOA01 database (NODC) are outlined in red.

Corresponding environmental data are presented in the form of depth-varying profiles. A thick black line always identifies the Santa Barbara Channel site and terminates at 600 m depth (the seafloor is reached before the next WOA01 depth level of 700 m). A thin blue line represents the easternmost site in the Gulf of Mexico (centered at longitude 89.5 W). Thin green and red lines correspond to the two sites in the Gulf of Mexico respectively centered at longitude 91.5 W and longitude 92.5 W; due to the proximity of these two sites, the data are essentially the same.

Annual mean temperature is shown in Figure 3.2.5. Figure 3.2.6 presents the annual mean salinity.

The following equations are used to derive several of the environmental parameters:

$$\sigma_{t}(z) = \rho\{0, T(z), \overline{s}(z)\} - 1000$$

$$p(z) = p_{atm} + g \int_{0}^{z} \rho\{p(z'), \overline{T}(z'), \overline{s}(z')\} dz'$$

$$f_{O_{2}}(z) = [DO] \frac{X_{O_{2};dry}\{p_{atm} - p_{sat}(\overline{T})\}}{C_{0}^{*}(\overline{T}, \overline{s}) \exp\{-v_{liq,O_{2}}(p - p_{atm})\}}$$

Due to the nonlinearity of some physical relationships, these parameters strictly are not annual means. Instead, they are estimates obtained with the annual means of temperature, salinity and Dissolved Oxygen (DO). The topmost equation is a practical definition of potential density (σ_i) where pressure effects on density are excluded. σ_i is sufficient to understand the relative stability of water masses. The second equation, implicit in the pressure *p* allows the simultaneous determination of pressure and density ρ . The last equation relates DO to oxygen fugacity; low oxygen fugacities (of the order of less than one bar) can be interpreted as oxygen partial pressures. In those equations, the functional dependence of density on temperature, salinity and pressure is the formula proposed by Fofonoff (1985). The solubility C_0^* of oxygen in equilibrium with a saturated humid atmosphere of standard composition ($X_{O2;dry} = 0.2095$) is given in García and Gordon (1992).

Figures 3.2.7 and 3.2.8 show σ_t and ρ , respectively. As expected, Figure 3.2.9 exhibits a hydrostatic pressure *p* that is quasi-linear with depth.

DO profiles are provided in Figure 3.2.10. An oxygen minimum is notable in the Gulf of Mexico, while DO levels plummet with depth in the Santa Barbara Channel; this latter feature is typical along coastlines where upwelling and oxygen utilization are substantial. For the purpose of possible oxygen extraction from seawater, however, the true measure of useful oxygen content is oxygen fugacity, shown in Figure 3.1.11. It is observed that the relatively higher DO near-surface values in Santa Barbara merely reflect colder seawater temperatures in Northern California. The slightly lower near-surface oxygen fugacities for the Gulf of Mexico represent the effect of higher vapor pressures with higher temperatures.

These ambient profiles are being applied to select components and develop the conceptual design.



Figure 3.2.5 Annual mean temperature profiles from WOA01 database for the selected 1° latitude by 1° longitude squares.



Salinity (ppt)

Figure 3.2.6 Annual mean mean salinity profiles from WOA01 database for the selected 1° latitude by 1° longitude squares.


Sigma-t (kg/m³)

Figure 3.2.7 σ_t estimates for the selected 1° latitude by 1° longitude squares



Density (kg/m³)

Figure 3.2.8 Density estimates for the selected 1° latitude by 1° longitude squares.



Pressure (bar)

Figure 3.2.9 Pressure estimates for the selected 1° latitude by 1° longitude squares.



Dissolved Oxygen (ml/l)

Figure 3.2.10 Annual mean DO profiles for the selected 1° latitude by 1° longitude squares.



Oxygen Fugacity (kPa)

Figure 3.2.11 Oxygen fugacity estimates for the selected 1° latitude by 1° longitude squares.

III.3 Task 3: Oxygen supply system

This Task is proceeding on schedule. Models of the membrane exchanger and gas bubbler oxygen extraction process were completed. Tests of the membrane exchanger were initiated during the present reporting period. An additional oxygen extraction technique was explored that consists of spraying fine droplets of sea water containing dissolved O_2 into a carrier gas stream to enhance mass transfer. Preliminary experiments were performed and results are provided below.

III.3.1 Evaluation of O2 extraction using high solubility liquids and membrane contactors

To fix ideas with little loss of generality, a "generic" membrane contactor is selected as a basic mass exchanger module. Such modules are widely used in industrial processes and several examples have been designed and tested in the context of artificial gill development. Nagase *et al.* (2003) have proposed artificial gill modules that employ bundles of hollow fibers made of a micro-porous membrane material (e.g., polypropylene). Typically, a cross-flow arrangement is preferred wherein the fluid with lower mass transfer characteristic' flows outside of the hollow fibers (shell side) and the fluid with higher mass transfer characteristics flows inside the hollow fibers (lumen side).

Mass transfer from one fluid to another is driven by a difference in partial pressures and not concentrations, since solubilities can be very different. For a given contact area and partial pressure difference (across that area), the mass transfer performance can be evaluated by film theory. In the present context, there are typically three films in series: one for each fluid on either side of the membrane, and one consisting of the membrane itself. Each film has a mass conductance, which generally is the product of solubility $s \pmod{m^3-Pa}$ and mass transfer coefficient $k \pmod{s}$; s is a measure of how densely the species is packed in the film and k of how fast it moves across the film.

For micro-porous membranes, the solubility concept does not apply since the species migrates through the membrane pores; theoretical and experimental evidence shows that the mass transfer resistance through typical micro-porous membranes is negligible.

When a gas phase is involved, and assuming ideal gas behavior, solubility simply is 1/(RT). This is of the order of 4×10^{-4} mol/m³-Pa. For standard cool sea water, the solubility α is about 1.4×10^{-5} mol/m³-Pa. Moreover, the mass transfer coefficient *k* typically is proportional to $D^{2/3}$ where *D* is diffusivity (m²/s). Diffusivities in gases are of order 10^{-5} m²/s versus 10^{-9} m²/s in liquids. With a combination of high solubility and very fast mass transfer the mass transfer resistance in a gas film is negligible when a liquid film also is present.

For a gas-water mass exchanger, it follows that water typically should flow on the shell side and gas on the lumen side. The overall mass transfer coefficient is αk_W . Similarly, in a gas-liquid mass exchanger, where a liquid with a high oxygen solubility β is considered, the liquid is expected to flow on the shell side and the overall mass transfer coefficient is βk_{CS} . In a water-liquid module, water would flow on the shell side and the O₂-carrying liquid on the lumen side. The overall mass transfer coefficient is $\{1/(\alpha k_W) + 1/(\beta k_{CL})\}^{-1}$.

Nomenclature

- A exchange area per module (m^2)
- D diffusivity (m²/s)
- k mass transfer coefficient (m/s)
- k_{CL} mass transfer coefficient for lumen side O₂-carrying fluid (m/s)
- k_{CS} mass transfer coefficient for shell side O₂-carrying fluid (m/s)
- k_G mass transfer coefficient for gas (m/s)
- k_W mass transfer coefficient for seawater (m/s)
- *n* number of gas-seawater mass exchanger modules per unit O₂ production
- n_L number of O₂-carrying-fluid-seawater mass exchanger modules per unit O₂ production
- n_S number of gas-O₂-carrying-fluid mass exchanger modules per unit O₂ production
- N O₂ transfer rate per gas-seawater mass exchanger module (mol/s)
- N_L O₂ transfer rate per O₂-carrying-fluid-seawater mass exchanger module (mol/s)
- N_S O₂ transfer rate per gas-O₂-carrying-fluid mass exchanger module (mol/s)

 P_{CMAX} maximum O₂ partial pressure in O₂-carrying fluid loop (Pa)

- P_{CMIN} minimum O₂ partial pressure in O₂-carrying fluid loop (Pa)
- P_{GIN} O₂ partial pressure in inlet gas (Pa)
- P_{GOUT} O₂ partial pressure in outlet gas (Pa)
- P_{WIN} O₂ partial pressure in inlet seawater (Pa)
- P_{WOUT} O₂ partial pressure in outlet seawater (Pa)
- *P* total pressure (Pa)
- Q_{CL} lumen-side volume flow of O₂-carrying fluid per mass exchanger module (m³/s)
- Q_{CS} shell-side volume flow of O₂-carrying fluid per mass exchanger module (m³/s)
- Q_G inlet volume flow of gas per mass exchanger module (m³/s)
- Q_W volume flow of seawater per mass exchanger module (m³/s)
- *R* gas constant (J/mol-K)
- *s* solubility (mol/m³-Pa)
- T temperature (K)
- α O₂ solubility in seawater (mol/m³-Pa)
- β O₂ solubility in O₂-carrying fluid (mol/m³-Pa)

In this preliminary analysis, it is assumed that only oxygen is transferred in the mass exchanger modules. Other dissolved gases, such as N_2 , are not considered. Micro-porous membranes, however, are not species selective. In other words, they allow the transfer of most species as long as a partial pressure difference is applied across the membrane. It is very likely that species other than oxygen (nitrogen, methane, etc.) would be subject to a partial pressure gradient in our application. The mass transfer coefficient for these other species is expected to be similar to that for oxygen since diffusivities in liquids are generally of order 10^{-9} m²/s. The most realistic possibility that the above assumption would hold is if oxygen were very soluble in a given liquid while other species were not. Water is not such a liquid. The implications and limitations of the oxygen-only assumption will be evaluated when the present model is developed further during the upcoming quarter.

Figure 3.3.1 shows a schematic diagram of a gas-seawater mass exchanger. The three equations for oxygen conservation in each fluid stream and oxygen transfer within this mass exchanger are presented in Figure 3.3.2. The gas volume flow is allowed to change as a result of oxygen transfer from seawater. This results in a more complex expression of average partial pressure difference than the traditional logarithmic mean. This correction is only significant if the gas outlet partial pressure is not much smaller than the total pressure.

Figure 3.3.3 shows a schematic diagram of coupled gas-liquid and liquid-seawater mass exchangers. Note that the O_2 -carrying liquid volume flow rates are allowed to be different in the gas-liquid module (shell side) and in the liquid-seawater module (lumen side). Coupling is enforced by matching the inlet and outlet oxygen partial pressures of the O_2 -carrying liquid (labeled *maximum* and *minimum* without ambiguity). For a given overall oxygen transfer target, the overall flow rate of O_2 -carrying liquid must be the same throughout the system; this is accomplished by selecting an appropriate number of gas-liquid and liquid-seawater modules.

The solution procedure employed was to fix the inlet seawater O₂ partial pressure P_{WIN} at 10 kPa, the inlet gas O₂ partial pressure P_{GIN} at 4 kPa and the outlet gas O₂ partial pressure P_{GOUT} at 8 kPa. The selected value of P_{WIN} represents environmental conditions corresponding to about 50% oxygen depletion from atmospheric equilibrium. P_{GIN} and P_{GOUT} may be target values that should be compatible with the operation of other system components (e.g., fuel cell). Also fixed at 0.1 m³/s (100 cm³/s) were the volume flow rates Q_W and Q_{CS} ; the strategy here consists of assigning moderately high flows on shell sides where mass transfer and potential power penalties are both relatively low. According to the performance evaluation of *Modules C and D* in Nagase *et al.* (2003), this approximately corresponds to $k_W = 10^{-4}$ m/s (100 µm/s). For lack of better knowledge, we took $k_{CS} = k_W$. To fix ideas, the solubility of oxygen in the O₂-carrying liquid was assumed to be 10 times that in seawater: $\beta = 10\alpha = 1.4 \times 10^{-4}$ mol/m³-Pa. The lumen-side mass transfer coefficient k_{CL} was selected as $1.5 \times 10^{-5} \times (10^5 \times Q_{CL})^{1/3}$, i.e., 15 µm/s at 10 cm³/s. A temperature of 283.15 K (10° C) and a pressure of one bar (10⁵ Pa) were considered.

With the above choices, the system of three equations shown in Figure 3.3.2 has three unknowns: Q_G , P_{WOUT} and N. Therefore, it has a unique solution. The system of six equations shown in Figure 3.3.4 has seven unknowns: Q_G , Q_{CL} , P_{CMAX} , P_{CMIN} , P_{WOUT} , N_L and N_S . Consequently, there is a one-parameter family of solutions.



Figure 3.3.1 Schematic of oxygen transfer from seawater to gas.

$$\begin{cases} \frac{Q_G}{RT} (P_{GOUT} - P_{GIN}) = N(1 - \frac{P_{GOUT}}{P}) \\ Q_W \alpha (P_{WIN} - P_{WOUT}) = N \\ \alpha k_W A \frac{P_{WIN} - P_{WOUT}}{\int_{P_{WOUT}}^{P_{WIN}} \frac{dx}{x - P \frac{Q_G P_{GIN} + Q_W \alpha RT(x - P_{WOUT})}{Q_G P + Q_W \alpha RT(x - P_{WOUT})}} = N \end{cases}$$

Figure 3.3.2 Mass transfer equations for a gas-seawater mass exchanger module.



Figure 3.3.3 Schematic of oxygen transfer from seawater to gas via a liquid O₂ carrier.

$$\begin{cases} \frac{Q_{G}}{RT} (P_{GOUT} - P_{GIN}) = N_{S} (1 - \frac{P_{GOUT}}{P}) \\ Q_{CS} \beta (P_{CMAX} - P_{CMIN}) = N_{S} \\ \beta k_{CS} A \frac{P_{CMAX} - P_{CMIN}}{\sqrt{P_{CMIN}}} \frac{dx}{x - P \frac{Q_{G} P_{GIN} + Q_{CS} \beta RT (x - P_{CMIN})}{Q_{G} P + Q_{CS} \beta RT (x - P_{CMIN})}} \\ Q_{W} \alpha (P_{WIN} - P_{WOUT}) = N_{L} \\ Q_{CL} \beta (P_{CMAX} - P_{CMIN}) = N_{L} \\ A \frac{1}{\frac{1}{ck_{W}} + \frac{1}{\beta k_{CL}}} \frac{(P_{WIN} - P_{CMAX}) - (P_{WOUT} - P_{CMIN})}{Log\{\frac{P_{WIN} - P_{CMAX}}{P_{WOUT} - P_{CMIN}}\}} = N_{L} \end{cases}$$

Figure 3.3.4 Mass transfer equations for coupled gas-liquid and liquid-seawater mass exchanger modules.

Equations for both configurations, with and without an oxygen-carrying fluid loop, were solved. Since results concern single mass exchanger modules, a comparison between configurations required the choice of an overall oxygen transfer rate target to allow an estimation of the number of modules. An arbitrary overall O_2 transfer rate of 1 liter STP per minute was chosen. No attempt was made at this stage to arrange modules in series for either fluid. In other words, the simplest assumption of a parallel/parallel system was made. The number of modules needed to reach the overall O_2 transfer rate target can then be calculated immediately from the O_2 transfer rate per module. It should be noted that this assumption is not conservative.

With a gas-seawater system, it was found that 171 modules would be necessary, corresponding to a seawater flow rate of 17.1 l/s and a gas flow rate of 0.4 l/s (*in situ* conditions). The seawater oxygen partial pressure would drop from 10 kPa to 6.89 kPa.

If an intermediate O_2 -carrying liquid is used, the minimum and maximum oxygen partial pressures within the liquid loop are shown in Figure 3.3.5. Figure 3.3.6 presents the corresponding oxygen partial pressure at the seawater outlet. Note that the maximum liquid-loop partial pressure was arbitrarily selected as the free parameter in the family of solutions for plotting purposes; in practice, an operational degree of freedom may likely be the overall sea water flow rate or the overall O₂-carrying liquid flow rate. Figures 3.3.7 and 3.3.8 show the number of parallel modules required for the gas-liquid and liquid-seawater oxygen exchange, respectively. Replacing seawater with an O₂-carrying liquid markedly improves oxygen transfer to the gas phase, but the mass exchange constraints from seawater to the liquid more than offset such a gain: for the range of P_{CMAX} considered (8.1 to 9.9 kPa), between 49 and 18 modules would suffice to transfer 1 liter O₂ STP/minute from the O₂-carrying liquid to the gas, but between 379 and 1178 modules would then be needed from seawater to the O₂-carrying liquid. Within this range, the overall liquid and seawater flow rates would vary from 4.9 l/s to 1.8 l/s and from 37.9 l/s to 117.8 l/s, respectively.

III.3.1.2 model of oxygen extraction involving multiple gas species

The methodology and analysis described above can be extended to the case where multiple gas species are allowed to be exchanged between the fluid carriers. This situation is more realistic for exchanger membranes that are not species selective. To date, the simpler configuration of a gas/seawater mass exchanger configuration was considered without intermediate high-O₂-solubility liquid loop presently is in the process of being incorporated into the model.

We consider the gas outlet and the seawater inlet to coincide as the origin of integration for all differential variables. Integration as needed would proceed toward the other end of the mass exchanger, i.e., the gas inlet and seawater outlet. Although the mass exchanger would be more accurately represented with a cross-flow arrangement, we effectively adopt here a counter-flow representation more amenable to one-dimensional analysis.

When only oxygen was allowed to be exchanged at prevailing oxygen partial pressures significantly less than one bar, it was practical to consider the exchange to be driven by oxygen partial pressure differences. With other species being considered, and pressures potentially much higher than one bar, a more accurate formulation based on partial fugacity should be offered.



Figure 3.3.5 Minimum and maximum oxygen partial pressures in the O₂-carrying-liquid loop.



Figure 3.3.6 Oxygen partial pressure in seawater outlet after transfer to an O₂ carrying liquid.

Parallel Module Requirement - Gas-Liquid Exchange



Figure 3.3.7 Number of parallel modules required for the gas-liquid oxygen exchange.



Parallel Module Requirement - Seawater-Liquid Exchange

Figure 3.3.8 Number of parallel modules required for the sea water-liquid oxygen exchange.

Figure 3.3.9 presents the fundamental equations of mass conservation for the process. Subscript *i* is for each species. Notation is largely the same as that in the preceding sections. N_W represents a molar flow in seawater (m/s), N_G a molar flow in the gas phase (m/s), *C* is the sea water concentration (mol/m³), and f_{Wi} and f_{Gi} are partial fugacities (Pa).

Sea water is considered to be an ideal solution of the dilute species under consideration (activity coefficients equal to one). It follows that $C_i = \alpha_i f_{Wi}$ and concentration can be eliminated. The actual set of ordinary differential equations to be solved is shown in Figure 3.3.10.

The equations for N_{Gi} are coupled via f_{Gi} . This is more obvious with the ideal gas and

ideal mixture approximations where
$$f_{Gi} \approx P_i = \frac{N_{Gi}}{\sum_i N_{Gj}} P$$
.

The sea water fugacities at the origin are inferred from the environment.

For specified temperature and pressure, the initial conditions for the gas phase may be derived from a trial value $N_{GO2}(0)$ for oxygen and a given gas composition (mole fractions) at the origin (gas outlet). This composition is subject to the constraint that for oxygen, $f_{GO2}(0)$ must be less than $f_{WO2}(0)$. The equations are solved repeatedly by varying $N_{GO2}(0)$ until a target stoichiometric ratio for oxygen is reached. The target stoichiometric ratio (oxygen outlet molar flow over oxygen inlet molar flow) and the outlet composition reflect oxygen utilization through external processes (e.g. a fuel cell operation).

As an example, a two-gas system was considered where only O_2 and N_2 are present with the gas/seawater mass exchanger module described in the previous sections. The following typical values were adopted for seawater of 10° C and 35 ppt salinity: as before, $\alpha_{O2} \approx 1.4 \times 10^{-5}$ mol/m³-Pa while $\alpha_{N2} \approx 7.0 \times 10^{-6}$ mol/m³-Pa. Owing to the slightly smaller diffusivity of nitrogen in seawater, $k_{shell;N2} \approx 0.88 k_{shell;O2}$. The sea water inlet fugacities were taken to be 10 kPa and 80 kPa for O_2 and N_2 , respectively. The equations were solved assuming an ideal gas mixture with little loss of generality. The target oxygen stoichiometric ratio was set at 2.

At first, calculations were performed for a total pressure of 1 bar. In this case, the gas outlet composition was fixed with an oxygen molar fraction of 0.08; this choice satisfies the requirement $f_{GO2}(0) = 8$ kPa $< f_{WO2}(0) = 10$ kPa. Under these conditions, it was found that 166 mass exchanger modules would be needed to extract 1 liter-STP O₂ per minute from seawater. Outlet seawater fugacities were 6.8 kPa and 89.8 kPa for oxygen and nitrogen, respectively. A troublesome point is that 1.5 liter-STP N₂ per minute would have to be supplied upstream of the gas inlet to compensate for losses of this inert carrier species into the seawater.

These calculations were repeated for a total pressure of 10 bars. To satisfy the constraint on oxygen fugacities at the origin, an oxygen molar fraction of 0.008 was selected. It was found that 139 mass exchanger modules would be needed to extract 1 liter-STP O_2 per minute from seawater. Outlet seawater fugacities were 6.2 kPa and 704.9 kPa for oxygen and nitrogen, respectively. The need for makeup nitrogen in this case is as high as 81.5 liter-STP N_2 per minute.

$$-\alpha_{i}k_{shell;i}(f_{Wi} - f_{Gi})dA = dN_{Wi}$$
$$Q_{W}dC_{i} = dN_{Wi}$$
$$dN_{Gi} = dN_{Wi}$$

Figure 3.3.9 Basic process equations.

$$\frac{dN_{Gi}}{dA} = -\alpha_i k_{shell;i} (f_{Wi} - f_{Gi})$$
$$\frac{df_{Wi}}{dA} = \frac{1}{Q_W \alpha_i} \frac{dN_{Gi}}{dA}$$

Figure 3.3.10 Basic differential equations.

These preliminary results have significant implications with regard to the design of a practicable dissolved oxygen extraction system for the subsea power generation application. In addition to the large number of gas exchange modules predicted to be needed to supply the required amount of O_2 , the rate of loss of inert carrier gas into the sea water pose major design hurdles. Replenishing the carrier gas will be problematic. Methane could be considered in place of an inert species, since it will be available from the seafloor sources (i.e., vents or hydrates) in excess of what will be consumed in the reformer; however, a mixture of methane and oxygen will result in coking in the reformer if the mole fraction of CH₄ is too high.

The reforming system requires gas phase O_2 . The fuel cell module, on the other hand, may be able to utilize oxygen supplied directly by a liquid carrier, which would eliminate the need for associated (to service only the fuel cell) liquid-gas exchangers and makeup carrier gas. As reported previously, PEM fuel cells probably cannot be used with liquid O_2 carriers due to cathode flooding issues. Alkaline fuels cells produce water at the anode and therefore may be compatible with liquid carriers. This issue currently is being investigated.

Alternative approaches to supply oxygen to the reformer also are being evaluated. A tank of oxidizer could be brought down from the surface when the device is deployed. Since oxygen consumption for a nominal 100 W system could reach 1 to 2 metric tones per year, it would be desirable to utilize high density oxidizers (to minimize the size of the storage tank) and to supplement the stored oxidizer supply by applying the artificial gill where possible. One concept under consideration would utilize hydrogen peroxide or some other liquid oxidizer for the reformer and the artificial gill to provide O_2 to an alkaline fuel cell.

III.3.2 Membrane exchange experiments

Experiments were initiated to complement the O_2 mass exchange modeling activities described above. These experiments are not included in the original scope of work for this Task. Figure 3.3.11 presents a schematic diagram of the facility that is being employed. Oxygenated sea water, that can also contain dissolved N_2 or other gas species, is circulated through a membrane mass exchanger where the O_2 is transferred to a carrier fluid. The carrier fluid can be a gas such



Figure 3.3.11 Schematic diagram of the O₂ exchanger.

as N_2 , as shown in the Figure, or a liquid PFC. Dissolved oxygen concentration in the sea water upstream and downstream of the mass exchanger is monitored continuously with in-line oxygen probes (DO). The flow rate of sea water can be varied and is measured with a liquid flow meter (FM). A paramagnetic oxygen analyzer (Sable Systems model PA-1b) is used to determine O_2 concentration in gas-phase carrier fluids.

Various membranes of known surface area and thickness currently are being tested over a range of operating conditions. These results will be applied to verify the model predictions and to design the O_2 extraction system. The oxygen mass exchanger module will also be coupled to small single cell alkaline and PEM fuel cells during the upcoming quarter.

III.3.3 O₂ exchange from sprays

Direct contact heat and mass exchangers are often used in industrial processes where fluid purity is not an issue, since these devices usually have lower transport resistances and are relatively simple to implement. During the second quarter of this project, we conducted a study of dissolved oxygen extraction by bubbles of carrier gas. A confined bubble plume of O₂-depleted carrier gas would rise through the sea water, scrubbing up dissolved oxygen. The bubbles would be collected after ascending an adequate distance and the O₂-replished gas would then be directed into the reformer and fuel cell to supply these components with oxygen. As reported previously, calculations indicated that the rise height of the bubble plume may need to be large (>10 m) in order to extract sufficient oxygen. This would complicate the design and operation of such a system.

Direct contact mass transfer can also be accomplished by spraying the sea water into the carrier gas. Compact exchangers are possible using this approach, since residence time is not linked to bubble rise height. Some power would be consumed to generate the liquid spray, except in scenarios where the reformer and fuel cell are operated at pressures below ambient. In this case, the spray could be driven by the pressure difference. Operating at reduced pressure inside a containment hull offers some advantages including higher reformer efficiencies (see Section 3.6.4; equilibrium favors the formation of more H_2 from methane as pressure is reduced) and lower uncertainties regarding fuel cell performance and lifetime (since most extended testing has been conducted at near atmospheric operating pressure). Disadvantages include the energy penalty of discharging waste products, particularly gases, into the sea water to maintain the reduced pressure.

During the present reporting period, some experiments were conducted to explore mass transfer of dissolved O_2 from water sprayed into a carrier gas. A sketch of the concept is shown in Figure 3.3.12. Tests were conducted using the facility shown in Figure 3.3.11 with a direct contact spray exchanger substituted for the membrane exchanger. In these initial tests, tap water in equilibrium with air was pumped at a fixed rate through a nozzle to produce a spray of fine droplets that discharged into a small enclosed canister. According to the nozzle specifications, the water droplets had diameters between 18-40 μ m at the operating conditions of the tests. N₂ gas was circulated through the spray canister and the O₂ concentration in that closed gas loop was monitored with the paramagnetic oxygen analyzer to determine the mass transfer rate.



Figure 3.3.12 Sketch of spray exchanger to extract dissolved O₂ from sea water.

Figure 3.3.13 presents the time history of the O_2 partial pressure (in kPa) in the gas loop. In this test, water was pumped through the nozzle at 27 ml/min. The gas loop had an estimated total volume of 121 ml at room temperature (296 K) and pressure and was circulated through the spray canister at 27 ml/min. The O_2 mass transfer rate determined from the data in Figure 3.3.13 is plotted as a function of the O_2 partial pressure in the gas stream. The Figure also shows the calculated rate that excess dissolved O_2 is brought into the canister; i.e., the difference between the dissolved oxygen concentration at equilibrium with air and at equilibrium with a gas mixture at the indicated O_2 partial pressure, multiplied by the water flow rate into the canister. This corresponds to the rate that oxygen would need to be transferred out of the water into an infinite gas reservoir (i.e., O_2 partial pressure remains constant) at steady state to reach equilibrium with the gas at the point of discharge.



Figure 3.3.13 Increasing oxygen partial pressure in the closed gas loop due to mass transfer from a spray of water equilibrated with air.



Figure 3.3.14 Oxygen accumulation rate in the gas (•) determined from the data in Figure 3.3.13 and plotted vs. O_2 partial pressure. The solid line is the calculated steady state rate of oxygen transfer from the water (at the experimental flow rate) required to reach equilibrium with a gas at the indicated O_2 partial pressure.

Complementary modeling and design analyses are underway to evaluate the potential of this approach to collect and supply oxygen to the reformer and fuel cell.

III.4 Task 4: Fuel reforming system and fuel cell selection

This Task is proceeding on schedule. Reformer and fuel cell selection has been complicated somewhat by the level of uncertainty regarding the attainable amount of O_2 that can be provided by a dissolved oxygen extraction system. Alternative O_2 supplies are being explored as part of Tasks 3 and 7 and will be included in the selection parameters.

III.4.1 Candidate fuel cells

As reported previously, PEM and alkaline fuel cells have been identified as the primary candidates for the subsea power generation application. DJW Technology is conducting a comparison of the advantages and drawbacks of these two types of fuel cells under the anticipated operating conditions. The results of this assessment will be applied to the conceptual design and will be included in the Final Report.

III.4.2 Fuel reforming and clean up

Work performed on the selection of the fuel reforming and clean up system is described below in Section III.6.2.

III.5 Task 5: System model

This Task is proceeding on schedule. Models of all major components (i.e., reformer, fuel cell, and oxygen extraction systems) have now been developed. During the previous reporting period, a model was devised to predict the performance of a PEM fuel cell as a function of operating conditions. During the present reporting period, a similar model of an alkaline fuel cell (AFC) was constructed since, as discussed in the previous Quarterly Report, AFC appear to have much better potential than PEMFC for coupling with O_2 supply systems utilizing liquid oxygen carriers. The PEMFC and AFC models are in the process of being linked to models of the reformer and O_2 extraction system by the appropriate energy and mass balance relationships to conduct parametric studies of the subsea power generation device. As discussed in Section III.3, a model of the oxygen extraction system has also been developed during this reporting period. The milestone, M4, for this Task is therefore expected to be attained shortly.

III.5.1 AFC model

The model considers an alkaline fuel cell as a one-dimensional device illustrated in Figure 1. The model architecture is derived from Vargas & Bejan (2004). Its implementation necessitated several important corrections to Vargas & Bejan's work and an extension to mixed reactants. The latter development required the consideration of Stefan-Maxwell diffusion within the gas diffusion layers (in addition to Knudsen diffusion).

The fuel cell is divided into seven control volumes. Seven time-dependent ordinary differential equations are formulated for the temperatures in each control volume, assumed to be uniform. Although it may be of potential interest, the transient phase of the solution is not discussed here; instead, the steady-state values reached after a short time will be illustrated. At this stage of development, the model was run for two-gas systems: hydrogen and carbon dioxide in the anode, oxygen and nitrogen in the cathode. Ideal gas behavior was assumed. A partial list of model input parameters is provided below. Also required are the standard anodic and cathodic open-cell potentials (V); the standard anodic and cathodic enthalpies of reaction (J/mol-H₂); and specific enthalpies of gas constituents, liquid water and hydroxyl ion.

The model was first run for sample input values listed below. The effect of porosity on the diffusion coefficients in the gas diffusion layers was represented by a multiplicative factor $\varepsilon^{I.5}$. Figure 3.5.2 demonstrates the calculation of polarization curves as the current *I* varies for fixed stoichiometric ratios of the reactants (another possible way to set up calculations would be to fix the inlet molar flows of reactants). The thick black line represents a baseline. As Figure 3.5.3 shows, temperatures become excessive at high currents.



Figure 3.5.1 Diagram of one-dimensional alkaline fuel cell.

Model Input

- A_s cross-sectional area of fuel cell (m²)
- c_{pa} specific heat of solid anode material (J/kg-K)
- c_{pc} specific heat of solid cathode material (J/kg-K)
- c_{pKOH} specific heat of KOH (J/kg-K)
- h_{12} convective heat transfer coefficient from anode flow channel to gas diffusion layer (W/m²-K)
- h_{67} convective heat transfer coefficient from cathode flow channel to gas diffusion layer (W/m²-K)
- i_{0a} exchange current density for the anode reaction (A/m²)
- i_{0c} exchange current density for the cathode reaction (A/m²)
- k_a heat conductivity of solid anode material (W/m-K)
- k_c heat conductivity of solid cathode material (W/m-K)
- k_L heat conductivity of electrolyte (W/m-K)
- K_i permeability of gas diffusion and reaction layers (i = 2, 3, 5, 6)
- *H* height of fuel cell (m)

I current (A)

- L_i width of ith Control Volume (m)
- P_a inlet pressure in fuel stream (Pa)
- P_c inlet pressure in oxidant stream (Pa)
- $T_i(0)$ initial temperature of ith Control Volume (K)
- T_{inf} ambient temperature (K)
- T_a inlet temperature in fuel stream (Pa)
- T_c inlet temperature in oxidant stream (Pa)
- U_{wi} heat transfer coefficient between ith Control Volume and exterior (W/m²-K)
- X_a inlet hydrogen mole fraction in anode
- X_c inlet oxygen mole fraction in cathode
- *y*_{sol} mass fraction of KOH in electrolyte solution
- α_a anode charge transfer coefficient
- α_c cathode charge transfer coefficient
- ε_i porosity of gas diffusion and reaction layers (i = 2, 3, 5, 6)
- ρ_a density of solid anode material (kg/m³)
- ρ_c density of solid cathode material (kg/m³)
- σ electrical conductivity of electrolyte (Ω -m)⁻¹
- ζ_a hydrogen stoichiometric ratio in anode
- ζ_c oxygen stoichiometric ratio in cathode

A very slight change in the modeling of diffusion may have a substantial effect. By simply replacing the exponent in the porosity corrective factor by 1.6, from 1.5, one reaches a limiting current at about 125 A (oxygen starvation in the cathode). The modeling of the activation overpotential also has profound effects. The lower thin red curve shows a formalism where the number of electrons participating in the reactions (2) is omitted in the Butler-Volmer equations. This may not be correct, but can be found in many references including Vargas and Bejan (2004). Doing so exactly doubles the activation overpotentials, all other things being equal. To fix ideas, a cross in Figure 3.5.3 shows the operating point of a typical commercial alkaline fuel cell (pro-rated with A_s), even though the input that would accurately match this commercial unit is not known at this time.

Figure 3.5.4 shows the effect of lowering the inlet oxygen mole fraction from the baseline value of 0.2 to 0.08, for a total pressure of 1 bar. This corresponds to an oxygen partial pressure of 8 kPa and could be representative of a system extracting oxygen from seawater with a background oxygen partial pressure of 10 kPa. The polarization curve for the reduced inlet oxygen mole fraction is represented by a thin blue line. Figure 3.5.5 shows the same results in terms of fuel cell power. If we arbitrarily target a power output of 100 W, one fuel cell unit operating at baseline conditions could achieve this goal at a potential of 0.82 V with a current of 122 A; the corresponding inlet reactant molar flow rates are 1.27 mmol/s (hydrogen) and 0.63 mmol/s (oxygen). When the inlet oxygen partial pressure drops to 8 kPa, two fuel cell units would be required to supply 100 W; assuming each unit delivers 50 W in an ideal parallel configuration, the operating potential and current for each unit would be 0.85 V and 58.8 A, respectively; the corresponding overall inlet reactant molar flow rates would be 1.22 mmol/s (hydrogen) and 0.61 mmol/s (oxygen).

The same results were derived when the total pressure is 10 bars. Figure 3.5.6 shows the polarization curves for the baseline as well as for an inlet oxygen mole fraction of 0.008, which still corresponds to an oxygen partial pressure of 8 kPa. The higher total pressure raises the baseline polarization curve since it corresponds to a higher open-cell potential difference, as long as reactant concentrations remain sufficient. Unfortunately, this relative benefit cannot be sustained when the inlet oxygen mole fraction is as low as 0.008; here, we both have an increase in the cathodic activation overpotential and a small limiting current from O₂ starvation. Figure 3.5.7 shows the power curve for the oxygen-poor inlet oxidant stream. Typically, 100 W could be supplied with 20 fuel cell units delivering 5 W each; the operating potential and current for each unit would be 1.11 V and 4.5 A, respectively; the corresponding overall inlet reactant molar flow rates would be 0.94 mmol/s (hydrogen) and 0.47 mmol/s (oxygen).

Sample Input

A_s	0.0225 m^2
c_{pa}, c_{pc}	133 J/kg-K
C _{pKOH}	1159.3 J/kg-K
h_{12}, h_{67}	25 W/m ² -K
$i_{0a,}$ i_{0c}	10 A/m^2
k_a, k_c	71.6 W/m-K
k_L	0.6071 W/m-K
K_2, K_6	$4 \ge 10^{-10} \text{ m}^2$
K_3, K_5	$4 \ge 10^{-12} \text{ m}^2$
Н	0.15 m
Ι	variable
L_{1}, L_{7}	1 mm
L_2, L_6	2.97 mm
L_3, L_5	0.03 mm
L_4	2 mm
P_a	10^5 Pa
P_c	10^5 Pa
$T_i(0)$	283.15 K
T _{inf}	283.15 K
T_a	283.15 K
T_c	283.15 K
U_{wi}	200 W/m ² -K, $i = 1$ through 7
X_a	0.9
X_c	0.2
Ysol	20%
α_a, α_c	0.5
\mathcal{E}_i	0.05, i = 2, 3, 5, 6
$ ho_a, ho_c$	2145 kg/m ³
σ	$4000 (\Omega-m)^{-1}$
5a, 5c	2



Figure 3.5.2 Sample polarization curves.



Figure 3.5.3 Control-volume steady-state temperatures (baseline conditions).



Figure 3.5.4 Polarization curves when P = 1 bar: baseline (thick black line) and inlet O₂ mole fraction of 0.08 (thin blue line).



Figure 3.5.5 Power curves when P = 1 bar: baseline (thick black line) and inlet O₂ mole fraction of 0.08 (thin blue line).



Figure 3.5.6 Polarization curves when P = 10 bars: baseline (thick black line) and inlet O₂ mole fraction of 0.008 (thin blue line).



Figure 3.5.7 Power curve when P = 10 bars and inlet O₂ mole fraction is 0.008.

III.5.2 System layout

During the present reporting period, we continued engineering development of the system layout for AUV/UUV recharging or refueling applications that was introduced in the previous Quarterly Report and is shown in Figure 3.5.8. Various materials for construction of the cylindrical structure and interior gas funnel were considered, estimates of wet weights were initiated, and deployment strategies were explored. These preliminary concepts will be refined during the upcoming quarter and will be incorporated into the conceptual design.



Figure 3.5.8 Sketch of the system layout for AUV/UUV recharging applications.

III.6 Task 7: Fuel clean-up and reforming experiments

This Task is proceeding on schedule. One additional activity may be added to the scope of work in response to concerns regarding the ability of the proposed oxygen extraction system (i.e., artificial gill) to provide sufficient gas-phase O_2 to the reformer. As discussed in Section III.3.1, a supply of oxidizer brought down from the surface may be necessary. Liquid oxidizers, such as hydrogen peroxide, offer certain advantages over compressed or liquefied O_2 . An investigation of the suitability of liquid oxidizers for the methane reforming process would yield valuable information for our study. Addition of this activity to the scope of work may require a 2-3 month no-cost extension to provide adequate time to complete the investigation.

During this reporting period, work continued on the procurement, fabrication, and assembly of the high pressure reformer and the raw gas clean-up test bench. These facilities are expected to be operational soon and the initial risk mitigation experiments identified in the scope of work for this Task are expected to be conducted during the final Quarter of this project. Following execution of their subcontract, NRL has provided information on contaminant species contained in gas released from hydrates that supplement the information we have already collected from the archival literature. These data largely confirm results presented in Table 3.5.1 of the first Quarterly Report; however, levels of H₂S in excess of 1% by volume have been reported at a few sites, which is much larger than the 1000 ppmV we previously assumed to be typical. This new information will be applied in the upcoming experiments.

In coordination with Tasks 3 and 5, analyses were conducted to estimate the oxygen and energy requirements. This information is being applied to design the O_2 supply system and as input to the system modeling and integration activity.

III.6.1 Reforming experiments

The selection of system components for reforming experiments to be carried out at elevated pressure is nearly complete. Reactor tubes able to withstand 1200 psi at 1500 F have been selected, ordered, and received. Other components, such as high pressure gas regulators and mass flow controllers, have been identified and orders are being processed. A schematic presented in Figure 3.6.1 shows the reformer system layout.

III.6.2 Sulfur removal

A sulfur removal system was selected during the last quarter. The heart of the sulfur removal system is a bubble column partially filled with a mixture of water, zinc oxide and zinc acetate. By weight, the slurry consists of approximately 89% water and 10% zinc oxide and 1% zinc acetate. A design worksheet has been set up to model adsorption characteristics and system size requirements to meet both the lifespan of the lab test set up and also lifespan of the real system. The system components have all been specified and all but a few components have been ordered. All system components should be ordered by the end of March.

A lab test stand has been designed and fabricated. A system schematic presented in Figure 3.6.2 shows the layout as it will appear on the test stand. All components have been chosen to withstand a minimum of 1200 psi and are constructed from type 316 stainless steel. After all components are pre-fit on the test stand they will be dismantled and sent to a vendor for a Sulfinert[®] coating to prevent sulfur compounds from being adsorbed on working surfaces of the system. Preventing adsorption losses will help to ensure accurate balances on sulfur compounds and system performance evaluation.



Figure 3.6.1 Schematic of system for investigating methane reforming at pressures up to 80 bar.



Figure 3.6.2 Schematic of system for investigating the removal of hydrogen sulfide from methane at pressures up to 80 bar.
III.6.3 Assessment of reformer oxygen requirements

The amount of oxygen required to reform methane was estimated based on the target power output from the fuel cell module, i.e., approximately 100 W. A methane flow of 151 ml CH₄ per minute contains 100 W of power based on its heat of combustion (complete oxidation) at standard temperature and pressure. If an overall system efficiency of 10% is assumed, the methane flow rate to produce 100 W of power would increase ten fold to 1.51 slpm. The amount of O₂ needed for (partial oxidation) reforming can be shown to be about 30% of stoichiometric O₂, i.e., 30% of what would be consumed to oxidize methane to CO₂ and H₂O. Since two moles of O₂ are needed to oxidize a mole of CH₄, the estimated oxygen requirement for methane reforming is $0.30 \times 2 \times 1.51$ slpm ~0.9 slpm or about 0.02 g/s. Whereas it may be possible to supply oxygen directly to the fuel cell module with a liquid carrier, such as PFOB (which is a focus area of Task 3), the reformer requires gas-phase O₂, either in pure form or in a mixture of the mixture will affect the reforming process and needs to be controlled. This has significant implications with regard to the design of the dissolved oxygen extraction system.

III.6.4 Assessment of reformer energy requirements

An assessment of energy requirements for fuel reforming was conducted during the present reporting period. Reforming was modeled as a series of five sequential process steps comprising (1) raising reactants to the selected reforming temperature and pressure (which includes phase change of liquid water to vapor); (2) reaction at the selected reforming temperature and pressure with products predicted by chemical equilibrium; (3) cooling of reformate to the selected water gas shift reaction temperature and pressure; (4) water gas shift reaction at the selected temperature and pressure with products predicted by equilibrium; and (5) cooling of water gas shift products to fuel cell inlet temperature and pressure.

The energy budgets of these steps were evaluated for selected values of reforming temperature, water gas shift temperature, and system pressure. Product compositions of reactions assumed that chemical equilibrium was achieved. As reported in the first Quarterly Report, experimental results suggest that this assumption is reasonable. With the objective of maximizing H₂ yield, and under the constraint of a neutral or negative (heat releasing) system energy balance, steam to carbon (S/C) and O_2 to carbon (O_2/C) ratios were varied to identify optimal reactant inputs. System performance indicators at reforming temperatures of 800° C and 1000° C, a range of system pressures from 1 to 80 atm (bar), and a heat loss of 18% are shown in Figure 3.6.3. Efficiencies presented in the figure are defined as the enthalpy of H₂ in the reformate divided by the enthalpy of the methane supplied to the reformer. Note that H_2 yield is favored at low pressure and that as pressure increases, both S/C and O₂/C ratios increase but result in declining H₂ production per mole methane. Increasing reformer operating temperature to 1000° C (the two bar groupings on the right of the figure) results in improved H_2 yield with lower S/C and O_2/C ratio than at 800°C. This indicates that increasing reformer temperature is more effective than increasing steam as an excess reactant to increase H₂ yield. This is borne out by the energy balances for three cases shown in Figures 3.6.4-3.6.6. These results summarize the energy requirements of the five process steps. At each condition, the cumulative enthalpy is negative (i.e., heat release) as required. This excess would equate to an 18% heat loss from each of the five process steps.



Figure 3.6.3 Predicted conversion efficiency (enthalpy of H_2 in reformate/enthalpy of CH_4 in fuel feed), O_2 to carbon ratio, steam to carbon ratio, and H_2 production per mole of methane for various reforming temperatures and pressures and optimized S/C and O_2/C ratios. A heat loss of 18% is included in the calculation.



Figure 3.6.4 Energy balance for methane reforming at 1 atm., 800° C, S/C = 1.1, and O₂/C = 0.6. Numbered bars on abscissa are defined as: (1) enthalpy required to raise reactants from 4° C to reformer temperature (including heat of vaporization of liquid water), (2) enthalpy of reforming reaction with products predicted by chemical equilibrium, (3) enthalpy rejected to cool reformate to the selected water gas shift reaction temperature and pressure, (4) enthalpy of reaction for the water gas shift at the selected temperature and pressure with products predicted by equilibrium, and (5) enthalpy rejected to cool water gas shift products to fuel cell inlet temperature and pressure.



Figure 3.6.5 Energy balance for methane reforming at 80 atm., 800° C, S/C = 3.5, and $O_2/C = 0.9$. Numbered bars represent same quantities as in Figure 3.6.4.



Figure 3.6.6 Energy balance for methane reforming at 80 atm., 1000° C, S/C = 2.4, and $O_2/C = 0.8$. Numbered bars represent same quantities as in Figure 3.6.4.

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APPENDIX D: Sediment Porewater Methane Survey

D.1 Overview

The following document provides an overview of vertical methane diffusion through sediment and the sulfate methane interface (SMI) depth at four coastal regions, above methane hydrate beds; two locations on the Texas-Louisiana Shelf are included, as well as sites on the Mid Chilean Coast and the Cascadia Margin. These data are compared with results from other published sources to provide a range of methane concentrations in porewaters and to assess the potential for this methane to support fuel cell power requirements.

D.2 Site Description

The following sites have been selected for assessing methane concentrations in porewaters because of the high concentrations of methane hydrates that were originally predicted in shallow and deep beds with geochemical and geophysical data sets.

D.2.1 Texas-Louisiana Shelf Sites

The coastal locations of Atwater Valley and Keathley Canyon are presented in Figure D.1. The physiography of the continental margin in the northern Gulf of Mexico is controlled by salt tectonics, in which hummocky bathymetry consists of basins created by salt withdrawal and intervening structural highs created by salt diapirism. Terrigenous siliciclastic deposition has filled and blanketed these subsiding basins and highs during Pleistocene and Holocene, and continued tectonism has resulted in abundant faulting around the basin edges associated with fluid venting. Research on these areas resulted in a thorough data base on seismic profiles, heat flow and shallow piston core geochemistry. Subsequent deep drilling by Chevron-Texaco JIP indicates that large volumes of deep sediment methane do not exist. This situation is believed to result from deep sediment salt diapirs increasing salinity around hydrate beds and inhibiting formation. This region does have high methane concentrations in porewaters.

Piston core sites, on Atwater Valley, on the Texas-Louisiana Shelf, in the Gulf of Mexico, were selected with evaluation of a USGS seismic line (AV65) and a 3.5 kHz echo sounder profile collected during the cruise. Through this survey, piston cores were collected across two mound structures. This region is a shallow trough on the continental slope south of the Mississippi Delta . Atwater Valley lies at 1,200 to 1,500 meters water depth. Several small mound structures occur in the valley, rising less than 50 meters above the surrounding seafloor. Coring locations are presented in Figures D.2 and D.3.

On Keathley Canyon, coring lines were taken across previous USGS seismic profiles (D. Hutchinson, USGS Woods Hole) with a total of 59 lines over 600 km, during May 2003 (Figure D.4). Piston cores (NRL/VIMS) were collected on the R/V Gyre in August 2003. Seismic data consist of 2-D high-resolution multichannel seismic reflection profiles. This survey found a strong pattern of unconformities, pinch-outs, and faults between the basin centers and edges (Figure D.5). The cores, heat flow stations and seismic data were collected along the eastern side of a salt withdrawal minibasin and the adjacent structural high. Relief from the floor of the minibasin to the structural high is about 250 m. The transects of interest lie along lines KC01, KC11 and KC57 from the previous USGS survey. On each of these transects, 5-7 piston cores were collected.



Figure D.1 Gulf of Mexico coring regions Atwater Valley and Keathley Canyon.



Figure D.2 Piston core and heat flow sample positions on Atwater Valley. Geochemical data from piston cores was organized along USGS seismic lines.

D.2.1 Cascadia Margin

The northern Cascadia margin, off Vancouver Island (Figure D.6) is located in an area with a large distribution of hydrates on the seafloor and in the sub seafloor sediments. The observation of a bottom-simulating reflector (BSR) was first observed in seismic data collected in the site survey for the Ocean Drilling Program (ODP) Leg146 (Hyndman & Spence, 1992). The strongest BSR at Site 889 was surveyed during ODP Leg 146. Data from Cl⁻ concentrations in interstitial waters were interpreted to indicate dissociation of gas hydrates in the cores (Kastner *et al.*, 1995). In the area of Sites 889 and 890, prominent seismic blanking zones of reduced seismic reflection amplitude were observed in three-dimensional seismic reflection data (Riedel *et al.*, 2002). The width of the zones range from 80 to several hundred meters. Zones 2-4 are east-west linear features probably associated with near-surface faults, while Zone 1 (also called Bullseye Vent) is approximately spherical with a diameter of 400 m. Massive gas hydrate was



Figure D.3 NRL piston core and heat flow transect sites presented over a 3.5 kHz transect through the sample region.



Figure D.4 Keathley Canyon coring locations taken along USGS seismic lines KC11, KC57 and KC01.



Figure D.5 Seismic profiles of Keathley Canyon presented through key core locations for the comparison in the variation of the SMI and vertical methane diffusion.



Figure D.6 Coring location on the Bullseye Vent, Cascadia Margin.

recovered in piston cores located near the center of the blanking zone, at 4 sites in 2000 and at 3 sites in 2001. The zone is associated with a seafloor mound of height ~6 m and is interpreted as a mud/carbonate feature that resulted from fluid and methane venting. Core locations for Bullseye Vent presented in this text are outlined in Figure D.7.

D.2.3 Mid-Chilean Coast

Methane hydrate exploration was conducted off the Mid-Chilean margin, along the coast of Chile, west of Concepción, during October 2004 (Figure D.8). The goal of the field work was to integrate data from seismic surveys identifying the BSR to outline probable regions of hydrate formation, data from heat flow probes to determine vertical fluxes of methane above the BSR, and geochemical analyses of porewater samples from piston coring to predict hydrates in the deep sediments. Piston cores were collected at 13 sites along a NE-SW trending transect which ran between 36°10.38S, 73°35.72W and 36°12.50S, 73°3976W. This sampling line was determined from a previous DTAGS seismic survey, during March 2003. There was a strong correlation between the seismic, heat flow and geochemical data. Core locations were selected for a comparison of strong BSRs, 'BSR wipeouts', and a BSR drift to the sediment water column interface (Figure D.8).

D.3 Data Analysis

The data presented below are vertical profiles of sulfate concentrations in piston core porewaters. All cores were sub-sampled and pressed on board. Subsequent onboard analysis of porewater samples was performed with a DIONEX DX-120 Ion Chromatograph. A quantitative estimate of vertical methane diffusion is determined with an analysis of the vertical sulfate gradient. Piston core methane samples do not provide accurate data for concentrations because the loss of gas during the reduction of pressure from transport to the deck. With the 1:1 molar ratio of methane to sulfate during methane oxidation, sulfate is used as a proxy for the methane gradient. Sulfate and methane profiles in piston core porewaters are used to determine anaerobic methane oxidation (AOM) in the shallow sediments. The variation in the slopes of these parameters, coupled with seismic and heat flow data, are reviewed to predict the location of hydrate beds deep in the sediment, at locations with the necessary water column pressure and temperature for hydrate stability. AOM occurs through the following reaction:

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^{-1} + HS^{-1}$$

This bacterial cycle occurs in sediments at the sulfate-methane interface (SMI) where downward diffusing seawater sulfate encounters dissolved methane diffusing or advecting upward (Borowski *et al.* 1997). This process is prevalent in hydrate-bearing marine sediments where porewater methane concentrations are high. Sulfate and methane concentration slopes through vertical profiles vary with increases due to on-site methanogenesis or diffusion and advection from deeper microbial or thermogenic sources. Linear profiles are associated with the vertical diffusion of methane.



Figure D.7 Specific core sites through Bulleye Vent on the Cascadia Margin.

Vertical methane diffusion through piston core profiles is calculated with measurements of sulfate gradients. Sulfate is conservative during the core sampling and provides a 1:1 ratio during the oxidation of methane. Diffusive flux calculations from the linear sulfate porewater profiles are applied according to Fick's first law assuming steady state conditions (Berner, 1980):

$$J = -\phi \cdot D_s \cdot \frac{dc}{dx}$$

where J represents the sulfate flux (mmol m⁻² a⁻¹), ϕ is the sediment porosity, D_s is the sediment diffusion coefficient, c is the range in sulfate concentration and x is the range of the linear section of the sulfate profile in the piston core. D_s is calculated assuming a tracer diffusion coefficient for sulfate where,



Figure D.8 Mid Chilean Coast coring locations, including heat flow data and seismic profiles that were used to select locations for piston coring.

$$D_s = \frac{D_0}{1 + n(1 - \phi)}$$

 D_0 is assumed to be 8.7 x 10⁻⁵ cm² s⁻¹ (Iversen & Jørgensen, 1993), n = 3 for clay silt sediments, and ϕ , the sediment porosity, was measured for sub-samples through the sediment cores.

D.4 Data Comparison

The sulfate methane interface and vertical sulfate diffusion are compared between the Gulf of Mexico, Mid Chilean Margin, and Cascadia Margin (Table D.1). These sites were selected for this comparison because they are known to be active regions for shallow and deep methane hydrate deposits and are likely to have the highest methane concentrations in the porewaters. The SMI for these sites ranged from 270 cm to 523 cm, with Atwater Valley in the Gulf of Mexico being the shallowest. Vertical sulfate diffusion values did not consistently vary with changes in the depth of the SMI because of variations in sediment properties, changes of seawater sulfate diffusion rates into the sediments and, in some cases, because high vertical methane diffusion at the four sites was -64 to -121 mmol SO_4^{-2} m⁻² a⁻¹, with the highest rates at Cascadia Margin and Keathley Canyon.

For a conservative estimate of the porewater methane energy capacity to supply a fuel cell, an average of the vertical methane diffusion for all cores is calculated to be approximately -100 mmol $SO_4^{-2} \text{ m}^{-2} \text{ a}^{-1}$ (-95.99 ± 76.08 mmol $SO_4^{-2} \text{ m}^{-2} \text{ a}^{-1}$, n = 51) or 100 mM CH₄ m⁻² a⁻¹ with a 1:1 conversion during anaerobic oxidation. If this vertical methane flux is trapped across a 100 m² sediment region, the methane available would be 10 moles CH₄ a⁻¹ or 40 moles H₂ a⁻¹. In a fuel cell with maximum theoretical efficiency, 1 mole H₂ is converted to 237,000 J and would provide a maximum power of 0.3 W (237,000 J x 40 moles H₂ a⁻¹ divided by a time scale conversion of 365.25 x 24 x 3600).

An initial review of porewater sulfate and methane profiles suggests that the SMI is from 10 - 400 cm deep in 3 to 20 m cores taken from estuarine and coastal waters. The SMI observed in deeper waters, 455 to 1122 m, range from 10 - 200 m (Borowski *et al.*, 1999). Substantially shallower SMIs and corresponding high vertical methane diffusion fluxes were measured in the three coastal regions presented for this survey. This data is consistent with similar published results for coastal waters. A thorough data set is presented for coastal waters ranging from 1228 to 5480 m deep off the coast of Uruguay with a range of methane diffusion from 6.3 to 162 mmol m⁻² a⁻¹ (Hensen *et al.*, 2003). Off the western coast of Africa, methane diffusion values are reported with water column depths from 1312 to 2060 m to vary from 21.5 to 61.5 mmol m⁻² a⁻¹ (Niewöhner *et al.*, 1998). Finally, similar methane diffusion rates were also measured at three sites along the southern Chilean coast with a range between 46.0 to 99.7 mmol m⁻² a⁻¹. For all of the data summarized in this review the power available from methane in porewater would be less than 1 W.

Table D.1	A summary of the SMI and vertical fluid diffusion measured at Atwater Valley (AV)
	and Keathley Canyon (KC), in the Gulf of Mexico (GOM), the Mid Chilean Coast
	(MCM), and Bulleye Vent (BV) in Cascadia Margin (CM) along the southwestern
	coastal region of Canada.

	AV-		KC-				BV-	
	GOM		GOM		MCM		СМ	
Core		Sulfate		Sulfate		Sulfate		Sulfate
ID	SMI	flux	SMI	flux	SMI	flux	SMI	flux
		(mmol -2 $-1)$		(mmol -2 $-1)$		(mmol -2 $-1)$		(mmol -2 $-1)$
	(cm)	m - a -)	(cm)	m - a -)	(cm)	m a -)	(cm)	m - a -)
1	288	-13.4	570	-94.2	555	-22.9	504	-87.7
2	410	-20.4	680	-66.7	212	-63.1	386	-72.2
2	no	7 0 7	(20)	100.0	104	74.0	107	22.7
3	SMI	-/.0/	620	-108.3	194	-/4.8	106	-32.7
Δ	no SMI	-30.5	/30	_201	248	-57.8	308	_07 1
+ 5	224	-50.5	4J0 640	-201	240	-57.0	297 287	-)7.1
5	224 45	-30	460	-00.2	255	-39.2	207	-300
0	43 no	-249	400	-123.2	292	-43.5	274	-31.5
7	SMI	-2.57	290	-1501	275	-50.1	625	-139
8	59	-167	480	-165.6	246	-64.2	020	103
9	291	-77	500	-133 3	189	-78.5		
10	385	-41 5	470	-135.5	33 3	-362		
11	246	-126	550	-172.4	266	-56.4		
12	317	-48.7	650	-120.7	200	20.1		
13	260	-63.5	340	-65.1				
14	504	-8 69	440	-148.6				
15	215	-44 5	550	-70.4				
16	215		640	-109.8				
17			740	-109.8				
17			270	-140.0				
18			3/0	-03.3				
Ave.	270	-63.7	523	-120	250	-84.9	369	-121
s.d.	132	68.5	124	40.9	123	93.1	168	113

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APPENDIX E: Sulfide Concentrations in Sediment Porewater and Gas Hydrates

E.1 Overview

Sulfide concentrations in sediment porewater and gas hydrate are important factors in the evaluation of ocean floor fuel cell installations. Fuel cell performance is inhibited by sulfur compounds such as hydrogen sulfide and carbonyl sulfide because they disable the anode catalyst. Even trace sulfide concentrations can degrade the cell stack performance over time. Generally fuel cell manufacturers recommend that sulfur content of hydrogen fuel be less than 0.01%. During the proposed hydrate dissociation, sulfide from hydrate and porewater may be collected with the fuel gas stream and decrease the performance of the anode catalyst. Careful survey of the sulfide content of sediment porewater and gas hydrate is required to ensure that the sulfide collection is minimized and sulfide removal processes are adequate for the levels that will be encountered at the targeted seafloor locations.

E.2 Sulfide in Sediment Porewater

Porewater sulfide data is presented from NRL fieldwork in the Gulf of Mexico and mid Chilean Margin and from a data review of literature on methane hydrate exploration at different locations through the world's coastal margins (Table E.1). In deep methane and petroleum beds, sulfide is associated with thermogenic conversion of certain organic matter to methane (Elshahawai *et al.* 2005). In shallow sediment, sulfate is reduced to sulfide through anaerobic methane oxidation:

$$CH_4 + SO_4^{-2} \rightarrow HCO_3^{-1} + HS^{-1}$$

This process occurs at the sulfate-methane interface (SMI) where the downward diffusion of seawater sulfate encounters an upward diffusion or advection of dissolved methane (Borowski, 1998). Above this sediment layer, sulfate concentration increases to the seawater concentration at the sediment-water interface, while below, the methane concentration increases due to on-site methanogenesis or mass transfer from deeper microbial or thermogenic sources.

Large sulfide availability in shallow sediment porewater is evident in many regions with the active biological communities, e.g. tube worms, mussels, vesicomyid clams and giant sulfide-oxidizing bacteria (MacDonald *et al.*, 1989; Sibuet & Olu, 1998; and Sahling *et al.*, 2002). For example benthic communities at Hydrate Ridge on the Cascadia Margin are found to be supported by chemo-autotrophic, symbiotic microbial communities that primarily oxidize sulfide (Sahling *et al.* 2002). A review of porewater sulfide concentrations from various regions around the world is presented in Table E.1. Porewater sulfide concentrations are controlled by the rates of reduction during organic carbon degradation, anaerobic methane oxidation, and diffusion through sediment. The values for the regions reviewed ranged from 0 to 11, 000 mmol 1^{-1} (Table E.1). Low values are characteristically measured at locations below the sulfate-methane interface and in samples that are rich in iron and related elements that precipitate sulfide from porewater, e.g., iron to pyrite (Coffin *et al.*, In press; D'Hondt and Jorgensen, 2002). The lowest values were in the range of the analytical detection limits to 0.1 mmol 1^{-1} . Anodic exposure to sulfide will depend in part on the diffusion of porewater sulfide into the gas collected from dissociated hydrate.

Location	Sulfido	Comments	Deference	
Location	$(\text{mmol } \mathbf{I}^{-1})$	Comments	Kelefence	
Son Francisco			Vyyyzhora et al. 1000	
San Francisco	10-980		Kuwabara et al., 1999	
Bay				
Gulf of Mexico	0.1	Minimum concentration in	Cordes et al. 2005	
		region of sulfide oxidation		
Costa Rica Coast	0-11,000		Schmidt et al. 2005	
Blake Ridge	0.1 -11	Sites 994-997	Wallace & Masamoto, 2000	
Hydrate Ridge,	2.0 - 11	Through 2 seep regions	Valentine et al., 2005	
Oregon			,	
Keathley Canyon,	0.1 - 54	Range through piston core	Pohlman, In prep	
Gulf of Mexico				
Mid Chilean	0.0 - 99	Range through piston core	Coffin et al. In press	
Margin				
Peruvian Margin	0.04 - 0.70	High iron concentration	D'Hondt & Jorgensen, 2002	
-		results in pyrite		
Mariana	1.2 - 30		Komors and Mottl, 2004	
Subduction				
Complex				
Cascadia Margin	0-26	Surface sediments	Sahling et al., 2000	
Blake Ridge	0.01 - 0.12	Off methane seep regions	Paull et al. 1996,	
			Borowski et al. 1998	

Table E.1 Review of sediment porewater sulfide data from several methane hydrate sites.

E.3 Gas Hydrate Sulfide Concentrations

The sulfide content of the hydrate depends on the following factors that affect hydrate stability: sulfide concentration in porewater, carbon gas composition, overlying water column depth, and sediment temperature. There is not a large data base for the hydrate sulfide content published in the literature. The data that is available is listed in Table E.2. Preliminary surveys of sulfide in 7 hydrate samples from the Eel River Basin off the coast of Northern California were made with qualitative observations based on odor (Brooks *et al.*, 1991). Cascadia Margin sulfide content was reported to average 0.27% of the total hydrate gas content (Milkov *et al.* 2005). On Blake Ridge similar low concentrations of hydrates were observed with a range of 0.04 - 0.15% sulfide (Paull *et al.*, 1996). In contrast Kastner *et al.* (1998) reported 18% sulfide concentration in hydrates from a region on the Cascadia Margin. Milkov *et al.* (2005) state that this is an unusual exception. A review of available data shows an average conservative concentration of 0.1%. There is also a concern that the measured hydrate sulfide concentration is skewed with porewater sulfide contamination.

Region	% H ₂ S	Reference
Northern California	odor	Brooks et al., 1991
Hydrate Ridge Cascadia Margin	<3	Bohrmann et al., 1998
Blake Ridge	0.04 - 0.15	Paull et al., 1996
Hydrate Ridge, Cascadia Margin	18	Castner et al. 1998
Cascadia Margin	0.27	Milkov et al. 2005
Green Canyon, Gulf of Mexico	0.51	Milkov et al. 2005
Congo Angola Basin	0.05	Milkov et al. 2005
Southern Summit, Oregon	0.06 - 1.20	Milkov et al. 2005
Black Sea	0.25	Milkov et al. 2005
Caspian Sea	0.05	Milkov et al. 2005

Table E.2 Sulfide content of gas hydrates from different regions.

Sulfide content within the gas hydrate also increases the stability of the hydrate and affects the energy necessary to dissociate the hydrate to provide methane for fuel cell operation. Theoretical calculations on methane hydrates with 10% sulfide content predict a substantial shift in the hydrate stability zone to include conditions of lower temperature and shallower depths as shown in Figure E.1. The validity of this prediction is also reinforced by field observation. Along the coast of Australia, hydrates with enriched sulfide concentrations have been observed at water column depths of 200-400 m and at temperatures of 11-14 °C (Swart *et al.*, 2000). The presence of sulfide increases hydrate stability and results in higher sulfide concentrations in gas hydrates in more shallow coastal regions.



Figure E.1 Theoretical gas hydrate stability curves for 100% methane and methane/sulfide at 90%/10% (data plotted from Colorado School of Mines interpretations).

E.4 Summary

The following summary provides key points that pertain to sediment porewater and gas hydrate sulfide concentrations and the resulting impact on *in situ* fuel cell application.

The data review shows a large variation in the sulfide concentrations of porewater and gas hydrate. Estimates of the sulfide content of both sources are necessary because dissociation of the gas hydrate for methane collection will expose the hydrate gas to the surrounding porewater. Sulfide diffusion from the porewater into the gas phase is likely. The collected gas will then be contaminated with sulfide from both gas hydrates and porewater.

The general estimate of the sulfide concentration in hydrates is 0.1% (Milkov, 2005). This is a factor of 10 greater the suggested limits for fuel cell operation.

Sulfide inclusion in the gas hydrate allows the hydrate to be stable at higher temperatures and shallower ocean depths than pure methane hydrates. Shallow hydrates will likely have significant sulfide content.

Biological production of sulfide and vertical migration patterns generate sulfide gradients within the sediment. In biogenic methane hydrate formation, sulfide is produced by anaerobic methane oxidation at the SMI. Generally the SMI is located between 3-20 m of depth in the sediment. Shallow sites, 3-5 m SMI, include mid Chilean Margin, Gulf of Mexico and Cascadia Margin. Development of methods to extract methane from below the SMI could provide feedstock to the fuel cell with lower sulfide concentrations.

With this data review there is a need for the in situ fuel cell application to develop an inline sulfide filter. Patents have been established for gas separation procedures to remove sulfide from gas mixtures. One method applies an inclusion hydrate of a hollow crystal structure, containing alkyl ammonium salt, in the flow line (Dokuritsu *et al.* #JP2003138281-A). Another method is the development of an inline heating system (Mitsui Engine and Ship Building CO LTD, #JP2003282121-A).

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