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Carbon Dioxide Release from OTEC Cycles

Herbert J. Green¹ and Peter R. Guenther²

Abstract

This paper presents the results of recent measurements of CO₂ release from an open-cycle ocean thermal energy conversion (OTEC) experiment. Based on these data, the rate of short-term CO₂ release from future open-cycle OTEC plants is projected to be 15 to 25 times smaller than that from fossil-fueled electric power plants. OTEC systems that incorporate subsurface mixed discharge are expected to result in no long-term release. OTEC plants can significantly reduce CO₂ emissions when substituted for fossil-fueled power generation.

Introduction

OTEC technology uses the temperature difference between warm, surface seawater and deep, cold seawater to generate electricity, usually in a Rankine cycle heat engine. In an open-cycle system, warm seawater is introduced into a chamber in which the pressure is below the seawater vapor pressure. Flash evaporation of the seawater produces steam, which then passes through a turbine. The steam is condensed in either a direct-contact condenser or a surface condenser that also produces desalinated water (Penney and Bharathan, 1987). In a closed-cycle system, a working fluid such as ammonia or Freon is circulated in a closed loop consisting of an evaporator, a turbine, a condenser, and feed pump. Warm seawater provides heat to the evaporator, and cold seawater is used to cool the condenser. A hybrid-cycle system combines the flash evaporator of the open cycle with a closed-cycle loop. The steam flashed from warm seawater in the evaporator passes into a surface heat exchanger that is a combination steam condenser/ammonia evaporator. In this

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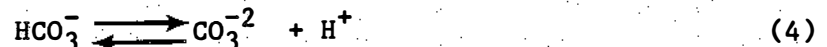
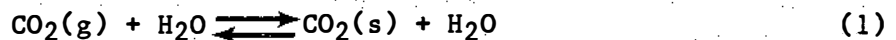
manner the condensing steam provides heat to the closed-cycle loop and produces desalinated water (Panchal and Bell, 1987). Open cycle will be the focus of this paper because it has greater potential for CO₂ release than other OTEC cycles.

There are three types of CO₂ release to consider from OTEC cycles. The first occurs during construction of an OTEC plant and during production of the building materials used in that construction. Second, there may be short-term release from the OTEC plant during power generation. Third, there may be long-term release from the CO₂-rich cold seawater discharged from an OTEC plant.

Short-term release will occur in open- or hybrid-cycle components such as flash evaporators and direct-contact condensers. In these components, seawater is exposed to subatmospheric pressures that will promote outgassing of CO₂ (as well as N₂ and O₂) from both warm and cold seawater. A closed-cycle plant, on the other hand, is expected to have no immediate CO₂ release because the seawater passes through surface heat exchangers.

CO₂ Chemistry of Seawater

Carbon dioxide in seawater participates in the following reactions:



where (g) denotes gas and (s) denotes solute. Riley and Chester (1971) and Sverdrup, Johnson, and Fleming (1970) provide thorough treatments of this chemistry.

The concentrations of dissolved molecular carbon dioxide, CO₂(s), and carbonic acid, H₂CO₃, are commonly added together because there is very little H₂CO₃ in seawater. This sum will be called the dissolved CO₂ or DCO₂. The sum of DCO₂ plus the bicarbonate ions, HCO₃⁻, and the carbonate ions, CO₃⁻², will be called total CO₂ or TCO₂ (sometimes called dissolved inorganic carbon). The partial pressure of CO₂ in the seawater will be called PCO₂ and will be expressed in units of parts per million (ppm) by volume. Only DCO₂ contributes to PCO₂ in seawater. Most CO₂ in seawater exists as HCO₃⁻ with only small concentrations of DCO₂ and CO₃⁻². Figure 1 shows the TCO₂ concentration as a function of depth for the North Pacific Ocean. The depths of interest for supplying cold seawater to OTEC cycles are nominally between 0.5 and 1.0 km. The warm seawater is supplied from near the ocean surface at depths less than 50 m.

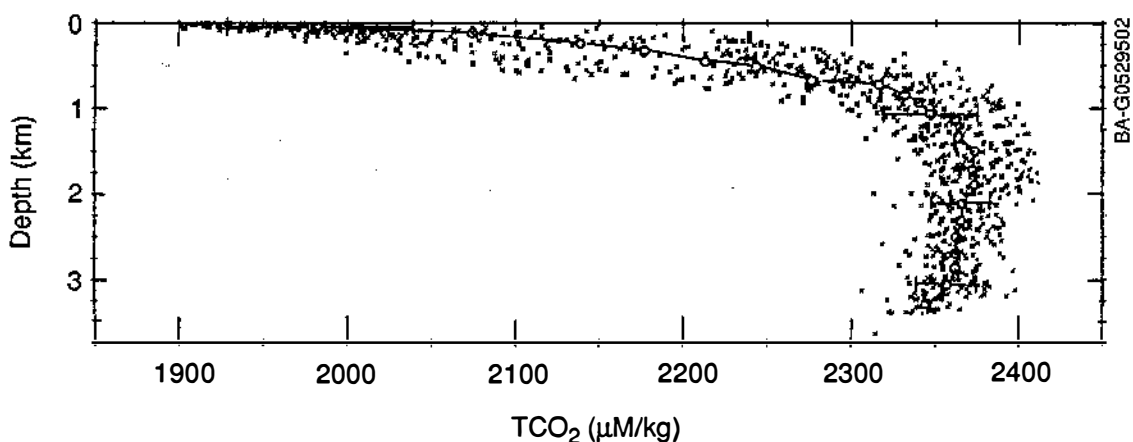


Figure 1. Total CO₂ concentration in the North Pacific Ocean (Takahashi, Broecker, Bainbridge)

The CO₂(s) in seawater, along with the dissolved N₂ and O₂, should be readily released at subatmospheric pressures. The loss of CO₂(s) creates a nonequilibrium condition in the seawater that causes bicarbonate ions to be converted to CO₂(s) by reactions (2), (3), and (4). The kinetics of the hydration reaction (2), are sufficiently slow that CO₂(s) has a half-life in seawater on the order of minutes (Riley and Chester, 1971). This would indicate that only a small fraction of the bicarbonate ions will be converted to CO₂(s) and released in the brief time, 1 to 2 s, required for seawater to pass through a direct-contact condenser or a flash evaporator.

Description of Experiment

The CO₂ emissions were measured during open-cycle experiments at the Natural Energy Laboratory of Hawaii (NELH). These experiments were conducted by the Solar Energy Research Institute (SERI) with funding from the U.S. Department of Energy (DOE). Link (1989) describes the experimental Heat- and Mass-Transfer Scoping Test Apparatus (HMTSTA). The seawater supply system at NELH delivers warm seawater from a 20-m depth and the cold seawater from 675 m (Daniel, 1989).

The CO₂ released from a flash evaporator and a direct-contact condenser was measured by sampling the supply and discharge seawater from these components and performing laboratory analysis for CO₂ content. The source seawater was also sampled as it came directly from the offshore pipes into sumps in a pump station. The sampling locations are noted in the schematic of the HMTSTA seawater supply system (Figure 2). These locations were the same for the warm and cold supply systems. Duplicate samples were obtained at each location to provide a check on the sample integrity and on the repeatability of the measurements. Thus, 12 samples were taken, two each from six locations.

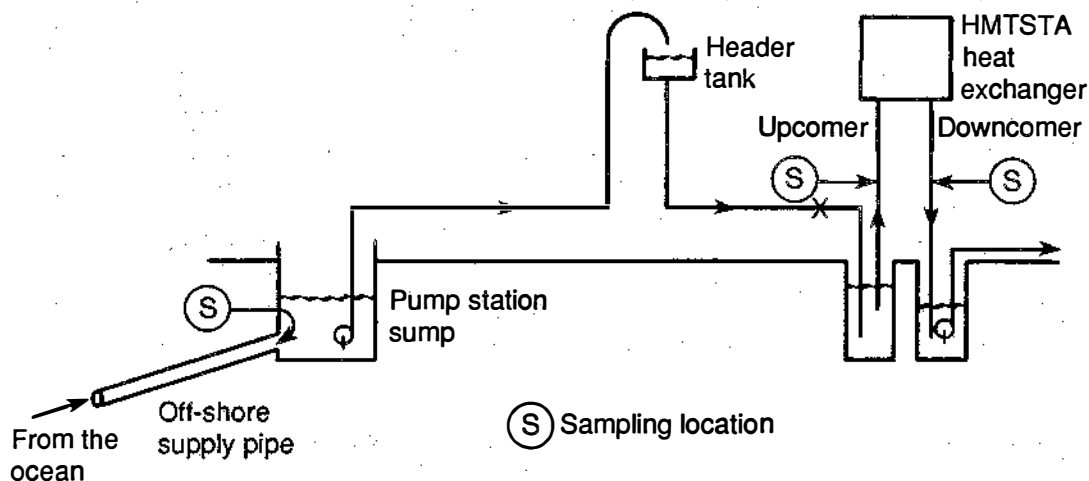


Figure 2. HMTSTA seawater supply system, typical for warm and cold seawater

The HMTSTA was maintained in steady-state operation while the samples were taken. The flash evaporator had a single, 20.3-cm-diameter, vertical spout. The flow rate of seawater through the spout was 28.9 kg/s, which resulted in an evaporator liquid loading of 32.2 kg/s-m². The direct-contact condenser was in a two-stage configuration with a total seawater flow rate of 15.0 kg/s. The first stage was operating with a liquid loading of 24.3 kg/s-m²; the second stage was at 32.1 kg/s-m². The configuration of these components and their operating conditions are both projected to be prototypical of future open-cycle OTEC power plants (Zangrando et al., forthcoming).

The Carbon Dioxide Research Group at the Scripps Institution of Oceanography provided a sampling kit with all the equipment required to preserve, seal, and ship the samples. Scripps also performed the laboratory analysis of the samples. The TCO₂, alkalinity, and salinity were measured on each sample. Several additional parameters, including PCO₂ and DCO₂, were calculated using the three measured parameters and appropriate thermodynamic constants. A cryogenic vacuum extraction technique was used to measure TCO₂. Scripps has demonstrated repeatability of 0.8 μM/kg (one standard deviation) with this technique. Scripps estimates that the accuracy is within ±2.0 μM/kg based primarily on calibrations with measured quantities of carbonates.

Experimental Results

Scripps' initial inspection revealed that one sample bottle appeared to have an air leak past the stopcock. The data from this sample from the cold water sump are not included in the following results. The data from the remaining 11 samples are shown in Table 1. For those five sampling locations where there are duplicate samples, the data were averaged to give one set of data for each location. The standard deviation of the residuals for the pairs of TCO₂ measurements was 1.15 μM/kg. This is a good result compared with the

Table 1. Results of CO₂ Measurements in Warm and Cold Seawater Samples

Source of Sample	Temperature (°C)	TCO ₂ (μM/kg)	DCO ₂ (μM/kg)	PCO ₂ (ppm)	STCO ₂ (μM/kg)	Measured Salinity (ppt)	Calculated Salinity (ppt)	Alkalinity (μequ/kg)
Warm-Water Sump	24.9	1928.6	9.4	326.7	1928.6	34.351	34.351	2261.3
Evaporator Upcomer	24.9	1931.2	9.3	323.7	1931.2	34.352	34.351	2267.0
Evaporator Downcomer	21.2	1929.9	8.8 ^a	279.8 ^a	1918.3 ^b	34.393	34.559	2268.7
Cold-Water Sump	6.5	2320.1	56.2	1133.7	2320.1	34.402	34.402	2340.5
Condenser Upcomer	6.5	2308.6	53.0	1072.0	2308.6	34.307	34.402	2336.1
Condenser Downcomer	13.8	2228.3	36.0 ^a	925.3 ^a	2254.5 ^c	33.985	34.003	2311.3

^aThese data may not reflect actual conditions in the experiment.

^bNormalized to the salinity in the warm water sump.

^cNormalized to the salinity in the cold water sump.

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measurement repeatability of 0.8 $\mu\text{M}/\text{kg}$ noted above. The measurement repeatability reflects the random error in measurements of identical samples, i.e., samples taken from the same sampling bottle. The current data are expected to have some additional random errors because the sample pairs were taken sequentially from a flowing system and, thus, are not identical samples.

The values obtained for TCO_2 and DCO_2 in both the warm and cold seawater coming from the ocean are consistent with other sources of CO_2 data such as Krock (1981) or the data in Figure 1. The warm seawater PCO_2 is 326.7 ppm, just below the current atmospheric partial pressure of CO_2 , which is about 350 ppm. The cold seawater PCO_2 is more than three times higher at 1133.7 ppm. The values for DCO_2 and PCO_2 in the evaporator and condenser downcomers must not be considered to reflect the actual conditions in those components. The seawater just leaving the evaporator and condenser should not be at equilibrium because of the slow reaction kinetics. However, during the 9 days between sampling and analysis, the samples would have come to equilibrium with a replenished content of DCO_2 . These values are not used to calculate CO_2 release.

The TCO_2 data were normalized to constant salinity, designated STCO_2 , to compensate for the removal or addition of pure water resulting from evaporation or condensation:

$$\text{STCO}_2 = (\text{TCO}_2 \times S_{\text{initial}}) / (S_{\text{final}})$$

where S_{initial} is initial salinity and S_{final} is final salinity.

Table 1 shows salinity data from two sources. The salinity of each sample was measured directly as above. Salinity was also calculated from the operating conditions of the evaporator and condenser. The temperature changes and flow rates in these components were used to calculate the steam flow rate. This, in turn, was used to calculate a salinity change in the seawater passing through these components. The calculated salinities for the upcomers were assumed to be the same as for the sumps. This may not be strictly true but is a reasonable assumption because the salinity changes in the seawater supplies are expected to be small.

These two methods of measuring salinity did not agree totally. First, the measured salinity change in the evaporator is much smaller than the calculated change. Second, the measured salinity change between the cold water sump and the condenser upcomer is unexpectedly large. It is unlikely that condensation of atmospheric moisture could cause this change because the resulting cold seawater temperature rise would be 1.7°C. The overall cold seawater salinity change, sump to downcomer, is essentially the same for the two methods. The STCO_2 data noted in Table 1 were normalized by the calculated salinity because this method indicates a larger CO_2 release from the evaporator.

The data show a slight gain in TCO_2 between the warm water sump and the evaporator upcomer. However, the change is barely larger than the repeatability of the measurements. A gain in TCO_2 is reasonable because the warm seawater is not saturated with CO_2 and is exposed to ambient air in the supply system. In the flash evaporator itself, there is a small drop in STCO_2 , $12.9 \mu\text{M}/\text{kg}$. This is about 39% greater than the $9.3 \mu\text{M}/\text{kg}$ of DCO_2 in the evaporator upcomer. This indicates that all the DCO_2 in the seawater was released and an additional quantity of HCO_3^- was converted to DCO_2 and released as well.

There was a drop in TCO_2 between the cold water sump and the condenser upcomer. Some CO_2 release to the atmosphere is expected because the cold seawater is supersaturated with CO_2 . Condensation of atmospheric moisture will result in dilution of the cold seawater, which, in turn, also reduces the TCO_2 . In the direct-contact condenser, the drop in STCO_2 is $54.1 \mu\text{M}/\text{kg}$. This loss is 2% greater than the DCO_2 in the seawater coming into the condenser.

Short-Term CO_2 Release

With this data set, the short-term CO_2 emissions for future open-cycle OTEC plants can be estimated. Assumptions for seawater requirements for commercial-sized plants are based on a system model developed at SERI for a land-based, 10-MW, open-cycle plant. This model predicts that 5710 kg/s-MW of warm seawater and 2580 kg/s-MW of cold seawater will be needed for plant operation. The flow rates for a given plant may differ from these assumptions, depending on many factors, including cycle type, available temperature difference, and cold-water pipe length.

The largest emissions from the data set were used in our projections. For the warm seawater, the largest release of CO_2 is between the evaporator upcomer and downcomer-- $12.9 \mu\text{M}/\text{kg}$. For the cold seawater, the release from the cold-water sump to the condenser downcomer was used, $65.6 \mu\text{M}/\text{kg}$. The resulting CO_2 emission rate is $38.5 \text{ g CO}_2/\text{kWh}$ for the plant, with most of the CO_2 being released from the cold seawater (see Table 2). This rate is significantly lower than was estimated by San Martin (1989) who projected a rate of $300.3 \text{ g CO}_2/\text{kWh}$ for open-cycle plant operation. This comparison points out the uncertainty that previously existed as to CO_2 emissions from an open-cycle system.

Table 2. Projected Short-Term CO_2 Emissions from a Land-Based Open-Cycle OTEC Plant Using Seawater Direct-Contact Condensation

CO_2 Source	CO_2 Emissions ($\mu\text{M}/\text{kg}$)	Flow Rate (kg/s-MW)	CO_2 Emission Rate ($\text{g CO}_2/\text{kWh}$)
Warm Seawater	12.9	5710	11.7
Cold Seawater	65.6	2580	26.8
TOTAL			38.5

Marland (1983) determined average CO₂ emission rates from the burning of natural gas, fuel oil, and coal as shown in Table 3. The Electric Power Research Institute (EPRI) (1986) gives nominal heat rates for current technology power plants for each of these fuel types. These heat rates are given in Table 3 along with the calculated CO₂ emissions for the three fuels per kilowatt-hour of electricity. The emissions from the fossil-fueled plants are substantially greater than the projected emissions from an open-cycle OTEC plant. The OTEC emissions are only 7.3% of those from a gas-fired plant and 4.1% of those of a coal-fired plant.

Table 3. Short-Term CO₂ Emission Rates from Fossil-Fueled Electric Power Plants

Fuel	CO ₂ Emission Rate for Burning ^a (kg CO ₂ /10 ⁹ J)	Plant Heat Rate ^b (kJ/kWh)	CO ₂ Emission Rate for Power Production (g CO ₂ /kWh)
Natural Gas (delivered to the customer)	60.0	8,865	531
Fuel Oil (at the refinery)	81.7	8,970	730
Coal (at the minehead)	90.4	10,340	934

^aMarland, 1983

^bEPRI, 1986

The OTEC emission rates presented earlier apply to an open-cycle plant in which all the condensation is direct contact. If the open-cycle plant is designed for producing desalinated water as well as electricity, some or all of the cold seawater will be routed to a surface heat exchanger, which will release little, if any, CO₂. Thus, coproduction of electricity and desalinated water will reduce the CO₂ emissions of an open-cycle plant. A hybrid-cycle plant will produce CO₂ emissions from the warm seawater only. Assuming a similar flow rate, the emissions will be 11.7 g CO₂/kWh, or 2.2% of the emissions of a gas-fired power plant. A comparison of the short-term CO₂ emission rates for OTEC and fossil-fueled cycles is found in Figure 3.

Construction and Long-Term CO₂ Release

Emissions during construction must be considered in the assessment of CO₂ emissions from any power plant. The experimental effort reported here does not speak to this issue directly. However, a qualitative comparison can be made between fossil-fueled and OTEC plant construction by comparing the respective capital costs. As the capital cost increases, more materials are needed for plant construction, and a larger CO₂ release will result.

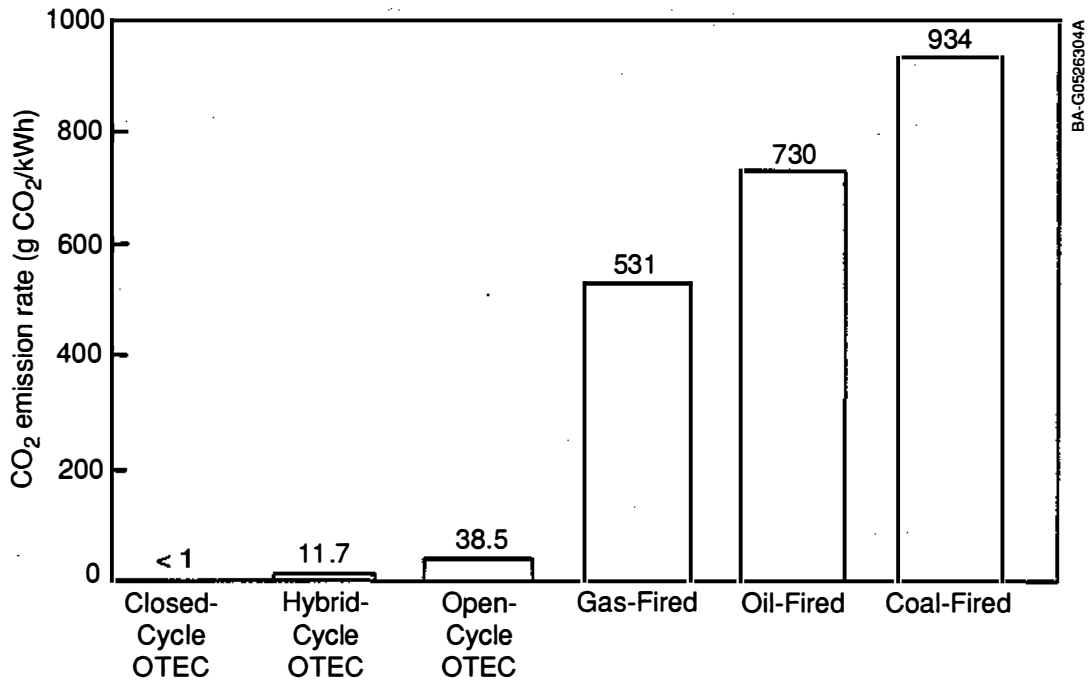


Figure 3. Short-term CO₂ emission rates for electricity production

Given that OTEC plants are expected to have larger capital costs per unit of capacity than are fossil-fueled plants, it follows that OTEC plant construction CO₂ emissions will be larger as well. This is consistent with San Martin (1989) who predicts that construction emissions for OTEC will be equivalent to a rate of 3.7 g CO₂/kWh over the life of the plant. For fossil-fueled plants, a rate of 1 g CO₂/kWh was predicted. However, these rates are quite small compared with the short-term, operating emissions for either open-cycle OTEC or fossil-fueled plants (Figure 3).

The cold seawater discharged to the ocean from any OTEC plant, whether open, hybrid, or closed cycle, will have a higher partial pressure of CO₂ than the atmosphere, creating the possibility of long-term CO₂ release. However, this release can be avoided by a plant design that incorporates subsurface mixed discharge of the warm and cold seawater. This is illustrated in Figure 4, which shows the CO₂ concentration vs. depth for seawater near Oahu, Hawaii. This site has 1910 μM/kg TCO₂ in the warm seawater and 2315 μM/kg in the cold seawater at a depth of 700 m. Based on the data in Table 1 and the specific flow rates in Table 2, an open-cycle OTEC plant at this site would produce a mixed discharge with TCO₂ of 2007 μM/kg. Seawater with the same TCO₂ is found at a depth of 195 m, as shown in Figure 4. Discharge at this depth or lower will result in no long-term CO₂ release.

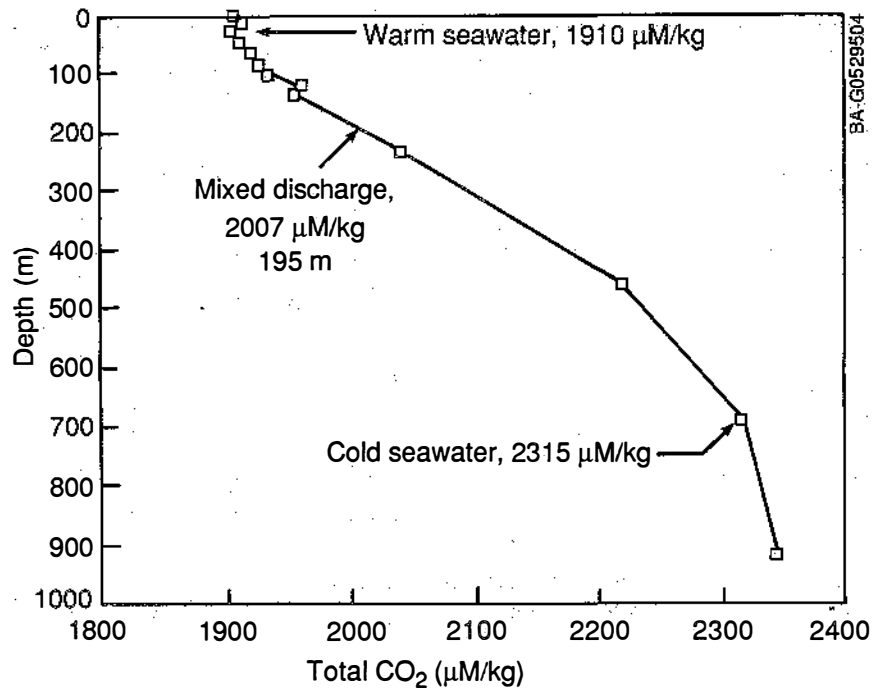


Figure 4. Total CO₂ concentration vs. depth near Oahu, Hawaii (Krock, 1981)

These depths are also below the surface mixed layer of the ocean in relatively stable layers that have virtually no contact with the atmosphere. The surface mixed layer has an average depth of only 75 m, which varies with location and season (Riley and Chester, 1971). Because the discharge is below the mixed layer, the ecology of the surface mixed layer is not disturbed, and the warm seawater supply temperature to the plant is not affected. Subsurface discharge also avoids adding nutrients from the cold seawater to the euphotic zone, where it could promote algae blooms. The euphotic zone is that part of the upper ocean that has adequate sunlight to support plant growth. This zone extends to a depth of at least 80 m (Sverdrup, Johnson, and Fleming, 1970).

The cold seawater from an OTEC plant may be used for mariculture instead of being discharged directly into the ocean. This seawater will be low in oxygen and will likely require reaeration before it can be used to grow marine animals. Such use could result in extended exposure to the atmosphere and some long-term release of CO₂. As for mariculture of marine plants, the cold seawater discharge will be directly usable. It still has a large CO₂ content, as these data indicate; however, the excess CO₂ is likely to be rapidly consumed by the cultured plants, thus limiting its release into the atmosphere.

Conclusion

Measurement of the immediate CO₂ emissions from open-cycle OTEC flash evaporators and direct-contact condensers indicates that the release of CO₂ is slightly greater than the quantity of dissolved molecular CO₂, CO₂(s), in the incoming seawater. This is consistent with the known slow reaction kinetics of the conversion of bicarbonate ions, HCO₃⁻ to CO₂(s). Additional experiments are recommended to confirm the associated salinity measurements and to obtain data over a range of operating conditions.

OTEC plants, whether closed, hybrid, or open cycle, will produce significantly lower CO₂ emissions during operation than will fossil-fueled electric power plants. The rate of these short-term CO₂ emissions per unit of electricity generated in a land-based, open-cycle OTEC electric power plant are projected to be 15 to 25 times smaller than from fossil-fueled electric power plants. OTEC systems that incorporate subsurface, mixed discharge are expected to result in no long-term CO₂ release. The CO₂ released during OTEC plant construction is expected to be small compared with that released over the lifetime of a fossil-fueled power plant.

Acknowledgments

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