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Herbert J. Green (SERI)  
Peter R. Guenther (Scripps Institution of  
Oceranography)

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## Carbon Dioxide Release from OTEC Cycles

Herbert J. Green<sup>1</sup> and Peter R. Guenther<sup>2</sup>

### Abstract

This paper presents the results of recent measurements of CO<sub>2</sub> release from an open-cycle ocean thermal energy conversion (OTEC) experiment. Based on these data, the rate of short-term CO<sub>2</sub> 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 CO<sub>2</sub> 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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<sup>1</sup>Solar Energy Research Institute, 1617 Cole Blvd., Golden, CO 80401

<sup>2</sup>Scripps Institution of Oceanography, 2314 Ritter Hall, A-020, LaJolla, CA 92093

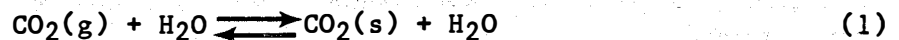
manner the condensing steam provides heat to the closed-cycle loop and produces desalinated water (Panchal and Bell, 1987). Open cycle will be the focus of this paper because it has greater potential for CO<sub>2</sub> release than other OTEC cycles.

There are three types of CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub> (as well as N<sub>2</sub> and O<sub>2</sub>) from both warm and cold seawater. A closed-cycle plant, on the other hand, is expected to have no immediate CO<sub>2</sub> release because the seawater passes through surface heat exchangers.

### CO<sub>2</sub> 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, CO<sub>2</sub>(s), and carbonic acid, H<sub>2</sub>CO<sub>3</sub>, are commonly added together because there is very little H<sub>2</sub>CO<sub>3</sub> in seawater. This sum will be called the dissolved CO<sub>2</sub> or DCO<sub>2</sub>. The sum of DCO<sub>2</sub> plus the bicarbonate ions, HCO<sub>3</sub><sup>-</sup>, and the carbonate ions, CO<sub>3</sub><sup>-2</sup>, will be called total CO<sub>2</sub> or TCO<sub>2</sub> (sometimes called dissolved inorganic carbon). The partial pressure of CO<sub>2</sub> in the seawater will be called PCO<sub>2</sub> and will be expressed in units of parts per million (ppm) by volume. Only DCO<sub>2</sub> contributes to PCO<sub>2</sub> in seawater. Most CO<sub>2</sub> in seawater exists as HCO<sub>3</sub><sup>-</sup> with only small concentrations of DCO<sub>2</sub> and CO<sub>3</sub><sup>-2</sup>. Figure 1 shows the TCO<sub>2</sub> 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.

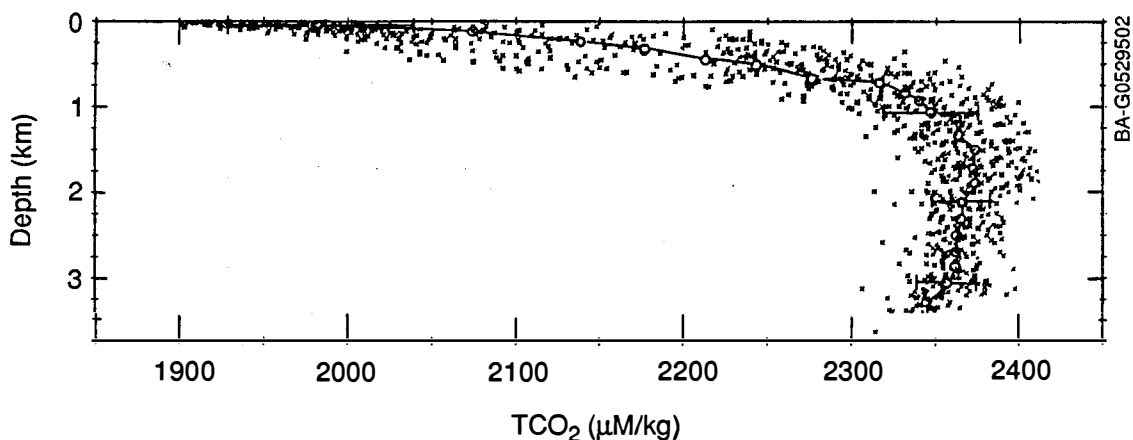


Figure 1. Total CO<sub>2</sub> concentration in the North Pacific Ocean (Takahashi, Broecker, Bainbridge)

The CO<sub>2</sub>(s) in seawater, along with the dissolved N<sub>2</sub> and O<sub>2</sub>, should be readily released at subatmospheric pressures. The loss of CO<sub>2</sub>(s) creates a nonequilibrium condition in the seawater that causes bicarbonate ions to be converted to CO<sub>2</sub>(s) by reactions (2), (3), and (4). The kinetics of the hydration reaction (2), are sufficiently slow that CO<sub>2</sub>(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 CO<sub>2</sub>(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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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.

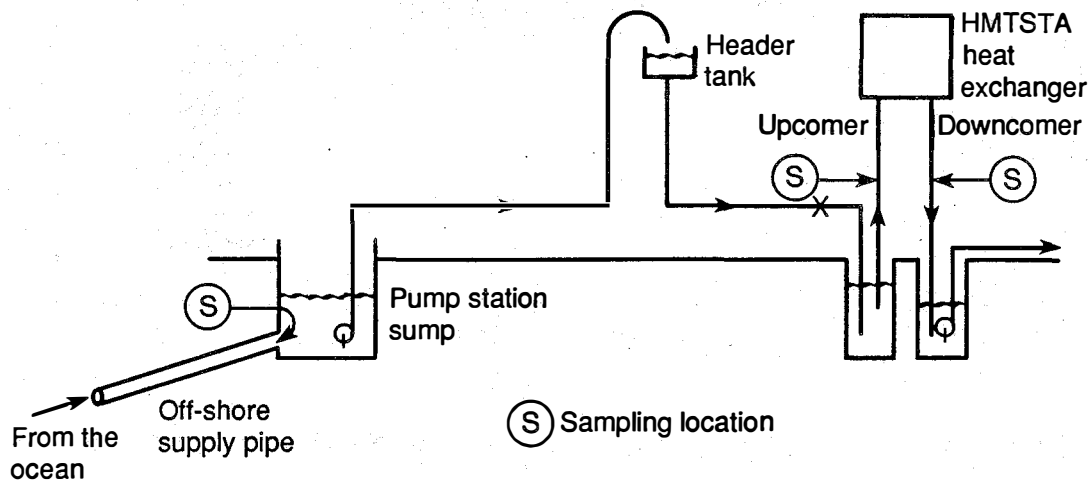


Figure 2. HMTSTA seawater supply system, typical for warm and cold seawater

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-m<sup>2</sup>. 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-m<sup>2</sup>; the second stage was at 32.1 kg/s-m<sup>2</sup>. 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 TCO<sub>2</sub>, alkalinity, and salinity were measured on each sample. Several additional parameters, including PCO<sub>2</sub> and DCO<sub>2</sub>, were calculated using the three measured parameters and appropriate thermodynamic constants. A cryogenic vacuum extraction technique was used to measure TCO<sub>2</sub>. 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 TCO<sub>2</sub> measurements was 1.15 μM/kg. This is a good result compared with the

**Table 1. Results of CO<sub>2</sub> Measurements in Warm and Cold Seawater Samples**

Source of Sample	Temperature (°C)	TCO <sub>2</sub> (μM/kg)	DCO <sub>2</sub> (μM/kg)	PCO <sub>2</sub> (ppm)	STCO <sub>2</sub> (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 <sup>a</sup>	279.8 <sup>a</sup>	1918.3 <sup>b</sup>	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 <sup>a</sup>	925.3 <sup>a</sup>	2254.5 <sup>c</sup>	33.985	34.003	2311.3

<sup>a</sup>These data may not reflect actual conditions in the experiment.

<sup>b</sup>Normalized to the salinity in the warm water sump.

<sup>c</sup>Normalized 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  $\text{TCO}_2$  and  $\text{DCO}_2$  in both the warm and cold seawater coming from the ocean are consistent with other sources of  $\text{CO}_2$  data such as Krock (1981) or the data in Figure 1. The warm seawater  $\text{PCO}_2$  is 326.7 ppm, just below the current atmospheric partial pressure of  $\text{CO}_2$ , which is about 350 ppm. The cold seawater  $\text{PCO}_2$  is more than three times higher at 1133.7 ppm. The values for  $\text{DCO}_2$  and  $\text{PCO}_2$  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  $\text{DCO}_2$ . These values are not used to calculate  $\text{CO}_2$  release.

The  $\text{TCO}_2$  data were normalized to constant salinity, designated  $\text{STCO}_2$ , 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  $S_{\text{initial}}$  is initial salinity and  $S_{\text{final}}$  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  $1.7^\circ\text{C}$ . The overall cold seawater salinity change, sump to downcomer, is essentially the same for the two methods. The  $\text{STCO}_2$  data noted in Table 1 were normalized by the calculated salinity because this method indicates a larger  $\text{CO}_2$  release from the evaporator.



The data show a slight gain in  $\text{TCO}_2$  between the warm water sump and the evaporator upcomer. However, the change is barely larger than the repeatability of the measurements. A gain in  $\text{TCO}_2$  is reasonable because the warm seawater is not saturated with  $\text{CO}_2$  and is exposed to ambient air in the supply system. In the flash evaporator itself, there is a small drop in  $\text{STCO}_2$ ,  $12.9 \mu\text{M}/\text{kg}$ . This is about 39% greater than the  $9.3 \mu\text{M}/\text{kg}$  of  $\text{DCO}_2$  in the evaporator upcomer. This indicates that all the  $\text{DCO}_2$  in the seawater was released and an additional quantity of  $\text{HCO}_3^-$  was converted to  $\text{DCO}_2$  and released as well.

There was a drop in  $\text{TCO}_2$  between the cold water sump and the condenser upcomer. Some  $\text{CO}_2$  release to the atmosphere is expected because the cold seawater is supersaturated with  $\text{CO}_2$ . Condensation of atmospheric moisture will result in dilution of the cold seawater, which, in turn, also reduces the  $\text{TCO}_2$ . In the direct-contact condenser, the drop in  $\text{STCO}_2$  is  $54.1 \mu\text{M}/\text{kg}$ . This loss is 2% greater than the  $\text{DCO}_2$  in the seawater coming into the condenser.

### Short-Term $\text{CO}_2$ Release

With this data set, the short-term  $\text{CO}_2$  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  $5710 \text{ kg}/\text{s-MW}$  of warm seawater and  $2580 \text{ kg}/\text{s-MW}$  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  $\text{CO}_2$  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  $\text{CO}_2$  emission rate is  $38.5 \text{ g CO}_2/\text{kWh}$  for the plant, with most of the  $\text{CO}_2$  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  $\text{CO}_2$  emissions from an open-cycle system.

**Table 2. Projected Short-Term  $\text{CO}_2$  Emissions from a Land-Based Open-Cycle OTEC Plant Using Seawater Direct-Contact Condensation**

$\text{CO}_2$ Source	$\text{CO}_2$ Emissions ( $\mu\text{M}/\text{kg}$ )	Flow Rate ( $\text{kg}/\text{s-MW}$ )	$\text{CO}_2$ 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> Emission Rates from Fossil-Fueled Electric Power Plants**

Fuel	CO <sub>2</sub> Emission Rate for Burning <sup>a</sup> (kg CO <sub>2</sub> /10 <sup>9</sup> J)	Plant Heat Rate <sup>b</sup> (kJ/kWh)	CO <sub>2</sub> Emission Rate for Power Production (g CO <sub>2</sub> /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

<sup>a</sup>Marland, 1983

<sup>b</sup>EPRI, 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, CO<sub>2</sub>. Thus, coproduction of electricity and desalinated water will reduce the CO<sub>2</sub> emissions of an open-cycle plant. A hybrid-cycle plant will produce CO<sub>2</sub> emissions from the warm seawater only. Assuming a similar flow rate, the emissions will be 11.7 g CO<sub>2</sub>/kWh, or 2.2% of the emissions of a gas-fired power plant. A comparison of the short-term CO<sub>2</sub> emission rates for OTEC and fossil-fueled cycles is found in Figure 3.

### Construction and Long-Term CO<sub>2</sub> Release

Emissions during construction must be considered in the assessment of CO<sub>2</sub> 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 CO<sub>2</sub> release will result.

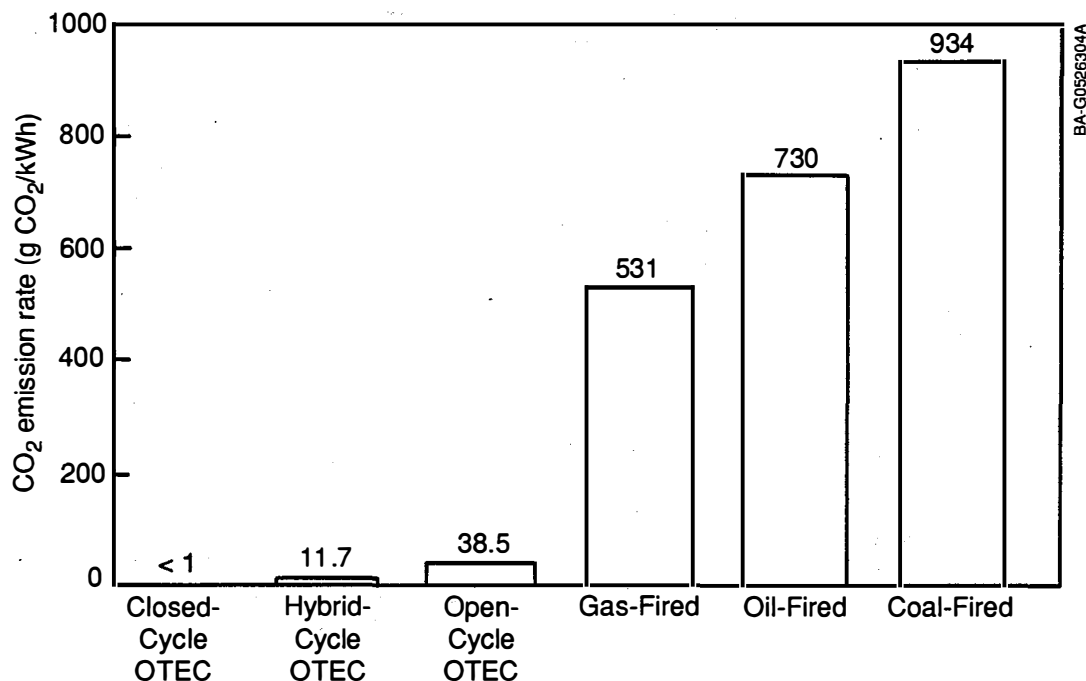


Figure 3. Short-term CO<sub>2</sub> emission rates for electricity production

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 CO<sub>2</sub> 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 CO<sub>2</sub>/kWh over the life of the plant. For fossil-fueled plants, a rate of 1 g CO<sub>2</sub>/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 CO<sub>2</sub> than the atmosphere, creating the possibility of long-term CO<sub>2</sub> 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 CO<sub>2</sub> concentration vs. depth for seawater near Oahu, Hawaii. This site has 1910 μM/kg TCO<sub>2</sub> 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 TCO<sub>2</sub> of 2007 μM/kg. Seawater with the same TCO<sub>2</sub> 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 CO<sub>2</sub> release.

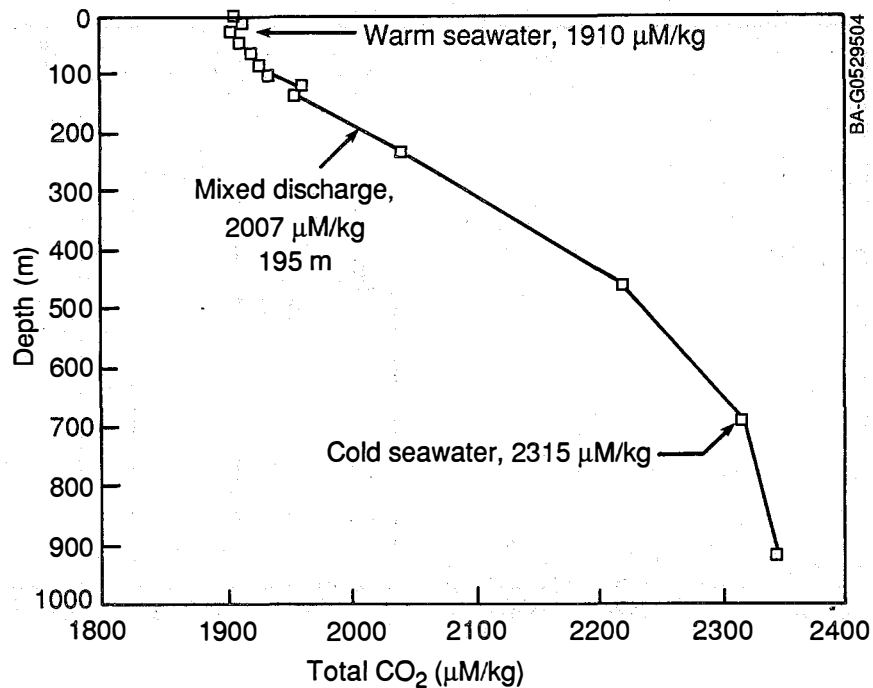


Figure 4. Total CO<sub>2</sub> concentration vs. depth near Oahu, Hawaii (Krock, 1981)

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 CO<sub>2</sub>. As for mariculture of marine plants, the cold seawater discharge will be directly usable. It still has a large CO<sub>2</sub> content, as these data indicate; however, the excess CO<sub>2</sub> is likely to be rapidly consumed by the cultured plants, thus limiting its release into the atmosphere.

## Conclusion

Measurement of the immediate CO<sub>2</sub> emissions from open-cycle OTEC flash evaporators and direct-contact condensers indicates that the release of CO<sub>2</sub> is slightly greater than the quantity of dissolved molecular CO<sub>2</sub>, CO<sub>2</sub>(s), in the incoming seawater. This is consistent with the known slow reaction kinetics of the conversion of bicarbonate ions, HCO<sub>3</sub><sup>-</sup> to CO<sub>2</sub>(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 CO<sub>2</sub> emissions during operation than will fossil-fueled electric power plants. The rate of these short-term CO<sub>2</sub> 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 CO<sub>2</sub> release. The CO<sub>2</sub> released during OTEC plant construction is expected to be small compared with that released over the lifetime of a fossil-fueled power plant.

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