

CESARE MARCHETTI

*International Institute for Applied Systems Analysis, Laxenburg, Austria*

**Abstract.** The problem of CO<sub>2</sub> control in the atmosphere is tackled by proposing a kind of 'fuel cycle' for fossil fuels where CO<sub>2</sub> is partially or totally collected at certain transformation points and properly disposed of.

CO<sub>2</sub> is disposed of by injection into suitable sinking thermohaline currents that carry and spread it into the deep ocean that has a very large equilibrium capacity.

The Mediterranean undercurrent entering the Atlantic at Gibraltar has been identified as one such current; it would have sufficient capacity to deal with all CO<sub>2</sub> produced in Europe even in the year 2100.

## 1. Introduction

The problem of climatological effects of CO<sub>2</sub> has recently attracted much attention, but the related question of how much fossil fuel we can still burn without burning our fingers is yet open. It may turn out that burning fossils 'à gogo' will have no really important consequences at least for our generation; yet reports on the subject, following the spirit of the time perhaps, tend to be more and more pessimistic [1, 2].

The first order effects are thought to be caused by the intense absorption bands of this gas in the infrared window of the atmosphere, i.e. in the region between approximately 8 $\mu$  and 12 $\mu$ . Calculations show that the isotropic scattering and absorption-re-emission of infrared radiation by CO<sub>2</sub> molecules in the atmosphere reduce the diffusiveness of infrared radiation, consequently producing a so-called greenhouse effect (greenhouses do in fact operate on different principles).

As water is competing with CO<sub>2</sub> in the same window, the effect will be larger where water concentration is lowest; this is so in the anticyclonic areas over the deserts, for example, and especially over the poles where due to the very low temperatures the water content is at a minimum. This can produce a second order effect, namely a decreased horizontal lapse rate between the poles and the equator, which would directly influence the circulation cells and the precipitation regime.

A third order effect may come from the increased photosynthetic rate of plants for which atmospheric CO<sub>2</sub> tends to be a limiting factor [3, 4]. This increase may induce a higher level of plant coverage, thus tendentially decreasing the earth's albedo and consequently working in much the same way as the greenhouse effect but with a concentrated influence upon temperate zones and tropical savannas.

An increase in temperature in the polar regions would bring about a similar positive feedback as it would induce a reduction in the snow cover and floating ice coverage, thus reducing the albedo and increasing the energy input.

These effects have been analyzed mainly at the level of total energy balance [1] with

some attempts at quantifying latitudinal effects, but to my knowledge there has been none to introduce the albedo-vegetation feedback. For these reasons, and the still rudimentary state of the models, the results given in the literature should be taken at their face value when we try to derive general consequences from them. The personal opinion of people working in the area, however, is that refinement of the models and consideration of all possible feedbacks will probably force us to draw a bleaker picture.

As the CO<sub>2</sub> problem could, in the short and medium term, impose substantial restrictions upon the burning of fossil fuels, any energy strategy that is framed in present day technology may be strongly conditioned by them.

An interesting analysis of the consequences of imposing a maximum ceiling on the CO<sub>2</sub> level in the atmosphere (e.g. at 300 ppm), for a world economy that would have to adjust by limiting CO<sub>2</sub> emissions has been done by Nordhaus [5]. He uses as a basic tool a model on allocation of energy resources, with extra constraints imposed by CO<sub>2</sub>, that leads to a qualitative supply readjustment intensifying the shift from coal to natural gas and to nuclear. The model permits a calculation of the extra costs induced by the constraints, reflected in an increase in price of industrial and final products, and puts

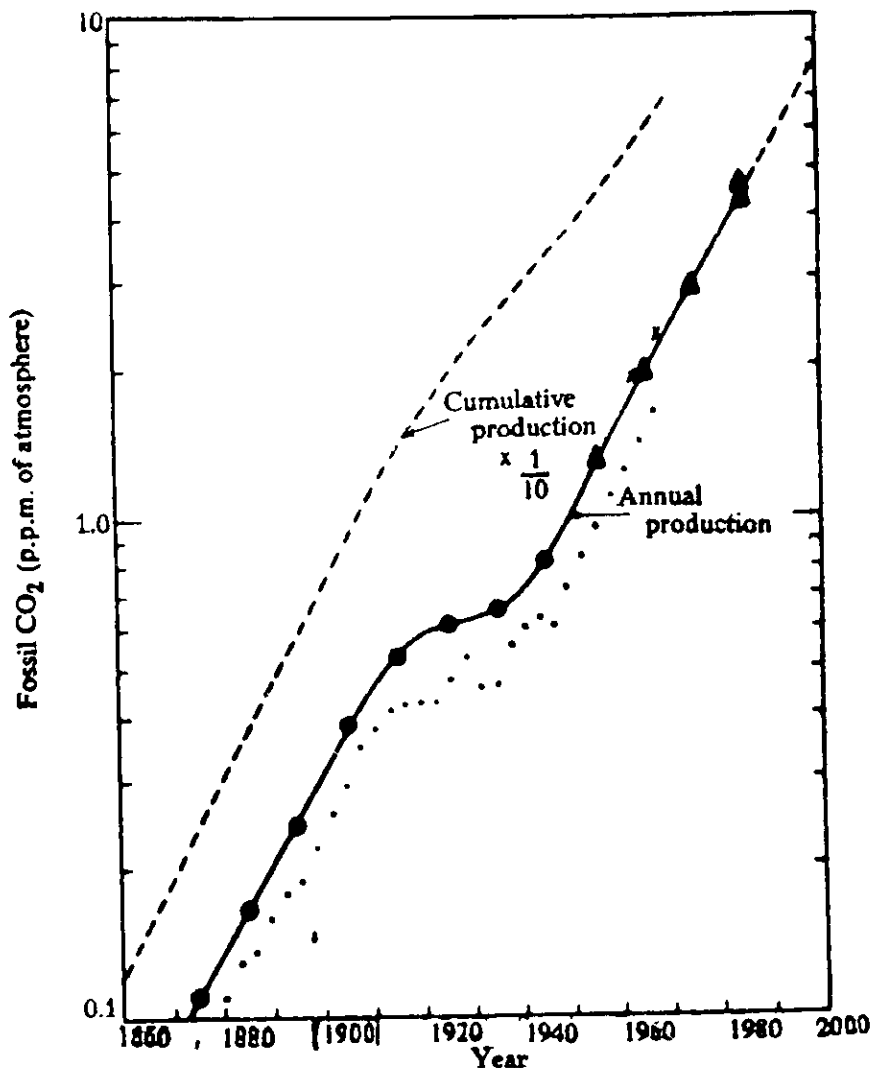


Fig. 1. Annual and cumulative production of CO<sub>2</sub>. The solid circles are the estimates of R. Revelle and H. E. Suess (1957) extended to 1980 by OECD estimates, the dots are estimates of Keeling (1973).

shadow prices on different fuels and CO<sub>2</sub> disposal levels (atmosphere, ocean mixed layer, deep ocean) providing an economic frame for possible CO<sub>2</sub> management techniques. One of these techniques is analyzed in the following. It must be clear that the spirit of the operation is to provide a possible alternative, in order to broaden the spectrum of tools available to society to tackle the problem.

Now, if we analyse the process of burning fuels with an eye on the fate of carbon, we see that:

- We start from a very concentrated form of carbon;
- We go to a dilution of carbon of two or three orders of magnitude in the combustion gases;
- We dilute it again perhaps by three or four orders of magnitude by dispersing these gases into the atmosphere;
- We have to wait for this very dilute stuff to diffuse through the surface of the sea into the thin mixed upper layer of the ocean;
- We have to wait for the mixed upper layer of the ocean to mix with the bulk of the semidormant oceanic mass.

The capacity of the final sink, the oceanic mass, is very large indeed and we may safely assume that once the dissolved CO<sub>2</sub> is completely equilibrated its level in today's atmosphere would be imperceptibly different from the 'historical' one of 290 ppm [6, 7].

The problem appears, at least for the next 100 or 200 years, to be essentially a problem of global kinetics: so kinetics is the place where the cure has to be applied.

The obvious line of attack would be to avoid the whole chain of dilutions and interfaces and to put CO<sub>2</sub> directly into the deep ocean. This may seem more easily said than done, but as I will show later the basis for a technologically and economically feasible operation does exist.

We will logically divide the operation into three steps: the collection of CO<sub>2</sub>, its transportation and disposal.

## 2. CO<sub>2</sub> Collection

This is not the place to think of each consumer filling his own little balloons with CO<sub>2</sub> to be processed by his municipality. The program has to be tackled upstream.

*Coal:* Today roughly 80% of coal is used in large installations such as *power stations* and *blast furnaces*. The combustion product in the first case is CO<sub>2</sub>, in the second it is a mixture of CO<sub>2</sub> and CO. In both cases one of the numerous (a dozen) processes of stripping CO<sub>2</sub> from other gases (e.g. to strip CO<sub>2</sub> from steam-reformed methane in order to purify hydrogen) which are currently used in industry could be employed. They are usually based on a scrubber where CO<sub>2</sub> is first dissolved in hot potassium carbonate water solutions or in other solvents weakly binding it and is later liberated by heating or pressure changes [8, 9, 10].

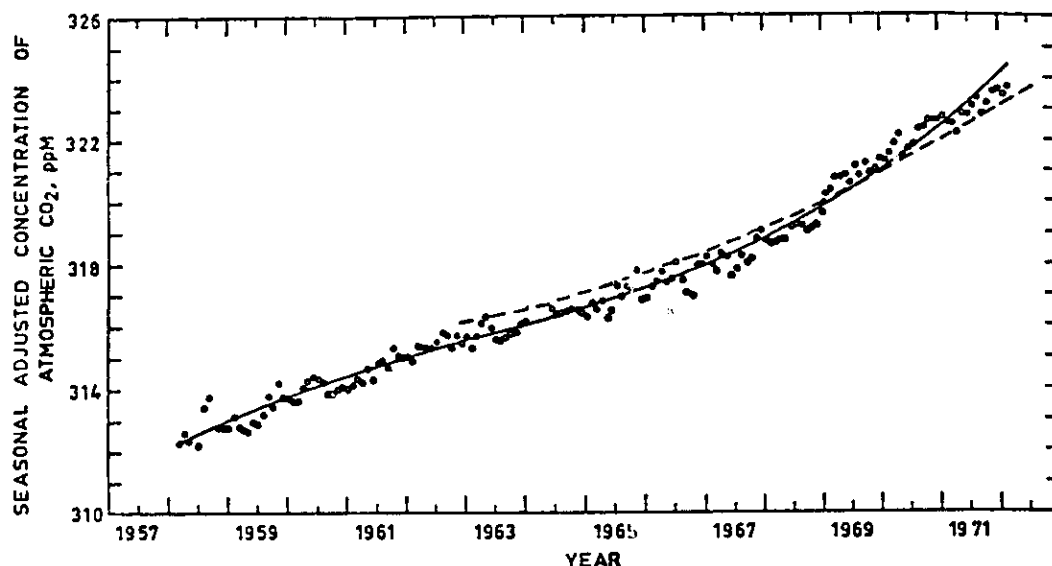


Fig. 2. Evolution of  $\text{CO}_2$  concentration in the atmosphere 1957 to 1972. Figure illustrates changes of the  $\text{CO}_2$  content of the atmosphere 1957 to 1972 (smoothed values) as given by C. A. Ekdahl and C. D. Keeling (1973), data points are seasonally adjusted, and solid line (smoothed curve) by B. Bolin and W. Bischof (1970), including unpublished data from the recent years (dashed line).

In power stations this process could be associated with  $\text{SO}_2$  scrubbing so that only nitrogen is finally released to the atmosphere. The final purification level can be adjusted in a tradeoff with cost.

If coal is used to make synthetic natural gas, given today's efficiencies, about two thirds of the carbon appear as  $\text{CO}_2$ , mostly already collected in the process itself.

*Oil:* Practically 100% of all crude oil is processed today through the refinery. As the hydrogen-carbon ratio is generally increased in the refining, a certain fraction of the carbon (20%?) appears as  $\text{CO}_2$ , most of which has already been collected in the process.

New processes have been developed recently to produce SNG from medium-light oil fractions at a high energy efficiency ( $\sim 95\%$ ). Roughly 50% of the carbon appears as already collected  $\text{CO}_2$  in this case. Similar processes using crude oil as feed are at the prototype stage. The fraction of carbon collected as  $\text{CO}_2$  is of the same order [11, 12].

*Gas:* Natural gas is often processed in order to condense out heavier hydrocarbons, but it is essentially burnt as such.  $\text{CO}_2$  could be separated in large plants as for coal, but this is barely thinkable for small ones.

Looking at the way fuels are transformed and used now, collecting and scrubbing in large plants could permit sequestering probably 50% of the  $\text{CO}_2$  actually rejected into the atmosphere, part of it at marginal cost, and part of it at a relatively low cost of a few dollars per ton of carbon contained [10]. In the set of hypotheses of Nordhaus [5] the shadow price of the operation would be in the range of 50 to 100\$/ton if the  $\text{CO}_2$  is properly disposed of, indicating that this first part of the operation makes sense economically.

The following step of completely controlling  $\text{CO}_2$  emission, down to zero if necessary would be technically more drastic and presumably more costly. It calls for a transformation of the primary fuel into a final fuel to a point where it carries no more carbon. This fuel can be  $\text{H}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{H}_4$  or else. The problems and merits of an energy

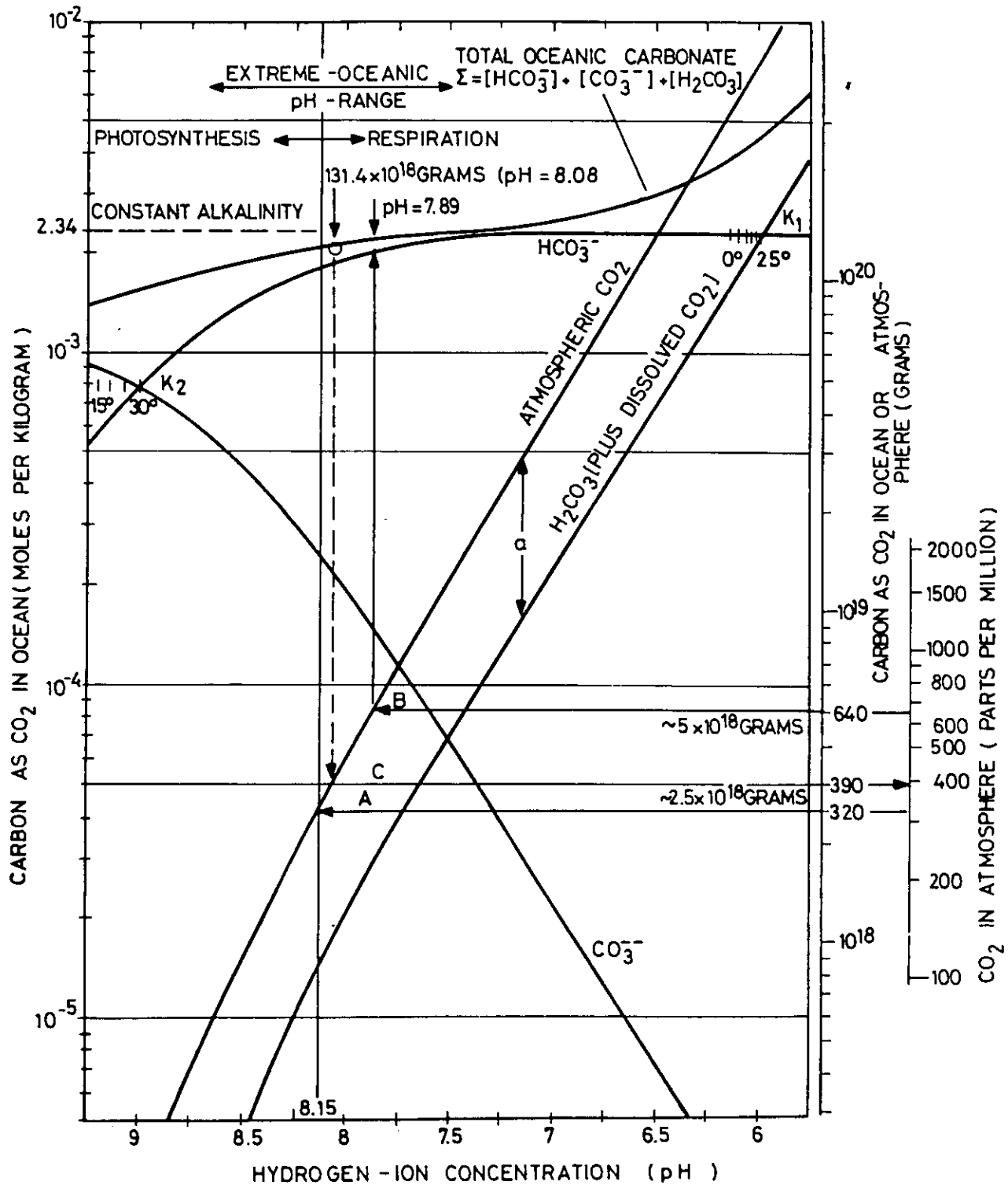


Fig. 3. Bjerrum diagram to calculate equilibrium distribution of CO<sub>2</sub> between atmosphere and ocean. It shows e.g. that injecting into the system an amount of CO<sub>2</sub> equal to that present in the atmosphere or 2.5 × 10<sup>18</sup> grams, the CO<sub>2</sub> level in the atmosphere at equilibrium would rise only by 2%. (From [7]).

system based on hydrogen as a fuel have been analyzed and widely discussed during the last five years, especially in relation to a widespread use of nuclear reactors as primary energy sources [13]. I assume that it is a feasible and highly advantageous proposition which will probably be the inevitable conclusion of two hundred years of evolution of the energy system.

If hydrogen will be the final energy vector, all  $\text{CO}_2$  can be collected at the transformation point where hydrogen is generated, probably using a mix of fossil and nuclear fuels [14].

### 3. $\text{CO}_2$ Transportation

$\text{CO}_2$  can be easily compressed to a liquid of 60–70 atm at room temperature. This liquid has a low viscosity and pumps like water. It can be transported in pipelines that are essentially the same as those for methane.

The high pressures needed to carry  $\text{CO}_2$  in a liquid form, even if it is moderately chilled, make the use of normal oil tankers improbable. But the problem has not been examined in detail and simple tricks may be discovered to do that. Solid  $\text{CO}_2$ , for example, can be piled on barges.

For the sake of the discussion I will assume that only liquid  $\text{CO}_2$  is carried overland in pipelines. I am also confident that the cost of transporting it anywhere will finally be lower than the cost of 'forward' fuel transportation which could be taken as a reference.

### 4. $\text{CO}_2$ Disposal

This could be done in the form of a permanent underground storage, e.g. by using exhausted gas fields. This possible storage of liquid  $\text{CO}_2$  at pressure lower than 100 atm guarantees a large storage capacity than for the original methane, although the solubility of  $\text{CO}_2$  in water and the solubilization of carbonate rocks do not guarantee a similar

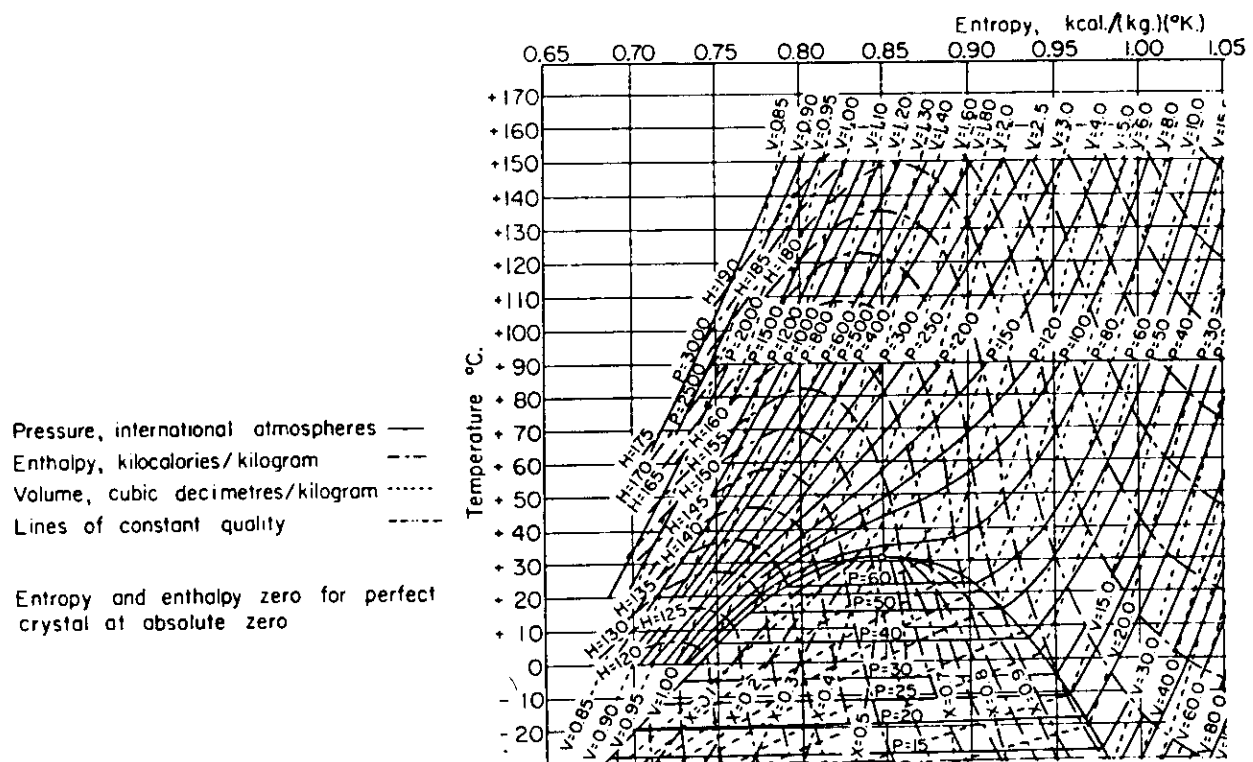


Fig. 4. Temperature entropy diagram for carbon dioxide. From 'Thermodynamic Functions of Gases', Vol. 1, Butterworth, London, 1956.

stability over time. The same could be said for exhausted oil fields and other types of natural or artificial cavities.

I did not go into the details of this system on the grounds that the capacity of natural structures which is available at reasonable cost may be insufficient. The question, however, certainly merits a second thought. The analysis of Nordhaus [5] shows that even temporary storages producing delays of some tens of years have no negligible shadow prices, as they partially release the main constraint.

The system on which I focussed shortcuts the atmospheric-ocean surface links, going directly to the deep ocean. The disposal method should also shortcut the very slow mixing of oceanic waters and should consequently avoid dumping over restricted areas.

The solution I find most promising is what I christened the *Gigamixer*. In the Mediterranean, the rate of evaporation largely exceeds the inflow of water from rivers and rain, thus leading to an increase in salinity and to a net inflow from the Atlantic. At Gibraltar, at the bottom of the Strait, a current of dense and warm (13°) Mediterranean water flows into the Atlantic, being at the same time substituted by slightly larger amounts of lighter and colder Atlantic water. The through-put of each current is of about  $1-2 \times 10^6 \text{ m}^3/\text{s}$ . The outgoing water has a density quite different from that of the Atlantic and it sinks gently, like a huge and slow waterfall, moving westwards and finally spreading at an equilibrium buoyancy level of  $\sim 1500 \text{ m}$ . The spread is flat and wide and covers practically all the Atlantic. Mediterranean water can be detected also in the Indian Ocean.

The phenomenon has been extensively studied in the thirties by G. Wüst, in the fifties by Defant [15], and was recently modelled by Sender [16]. This middle water then diffuses up and down and part of it is caught by the sinking currents in the Weddell Sea. It will presumably not see the light before a good thousand years, and by then will be thoroughly mixed with the rest.

Assuming that our CO<sub>2</sub> is injected e.g. in the neighborhood of the Strait of Gibraltar at the proper pressure, depth and amount, the current would spread and mix it with the core of the oceanic middle waters.

The next question is the matching of scale. This is linked to the maximum allowable concentration of CO<sub>2</sub> in the water. One can find values in the literature which are meant to be safe because they do not interfere with the shell-forming capacity of molluscs and

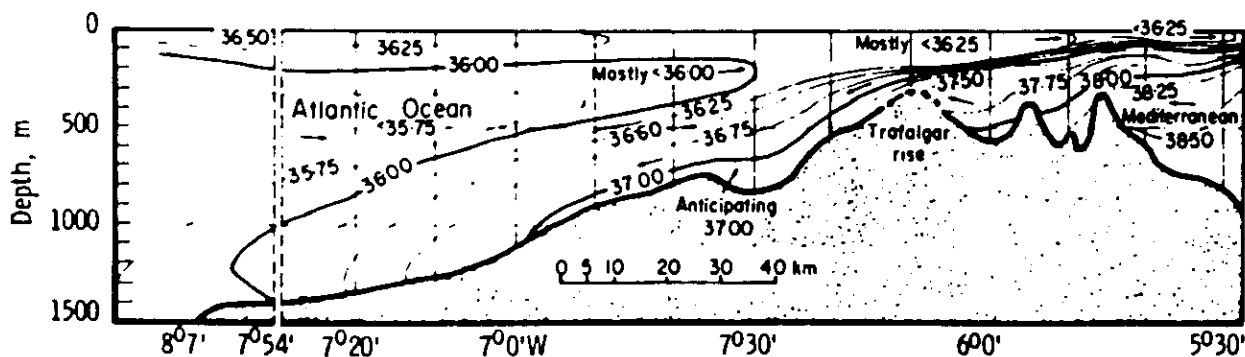


Fig. 5. Schematic diagram of the flow of Mediterranean water into the Atlantic through the salinity profile (From A. Defant).

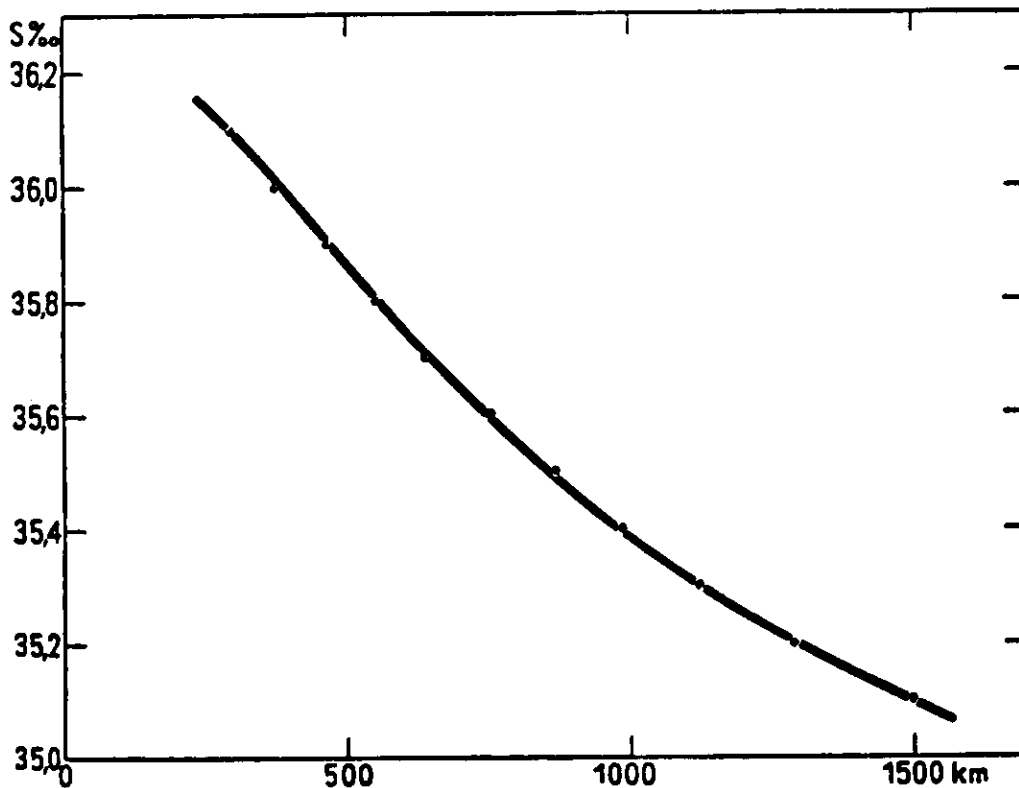
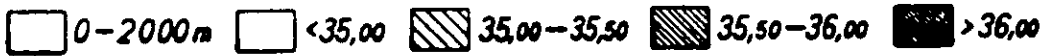
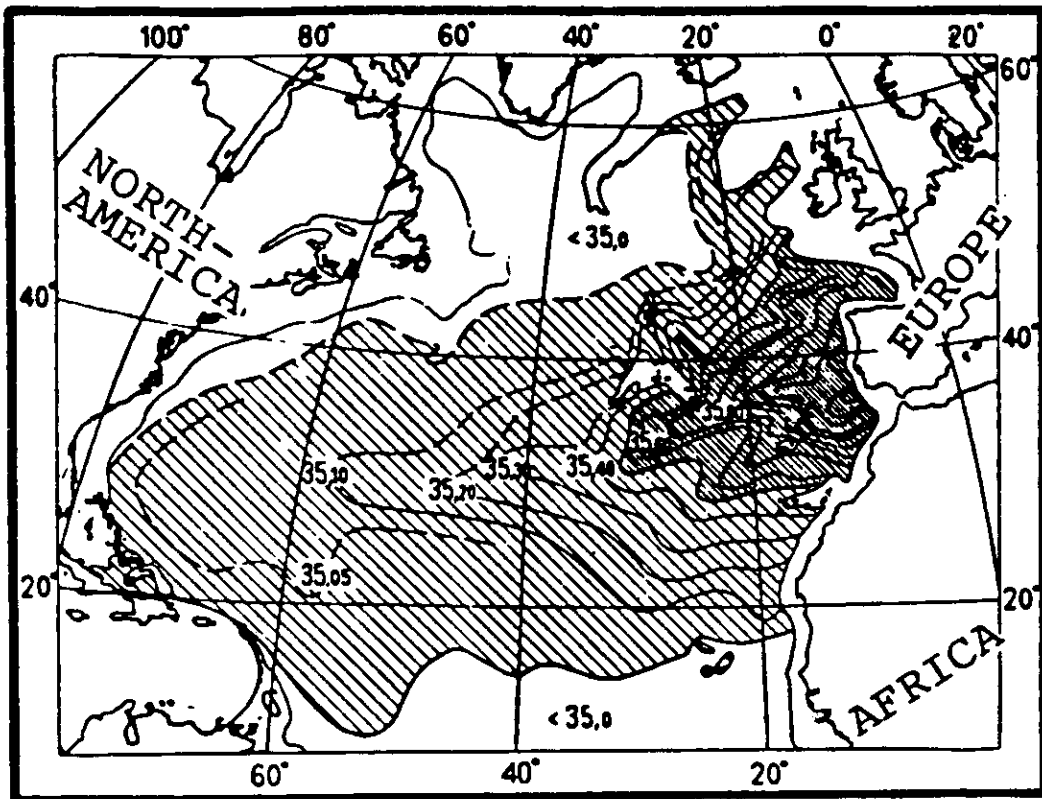


Fig. 6. Horizontal spread of mediterranean water through the atlantic middle waters, as indicated by salinity contours (Data from G. Wüst, 1935). The graph shows the fitting of Wüst data by H. Sender's diffusion model [16].



other creatures precipitating CaCO<sub>3</sub> for their private use. According to Broecker [17], 1% can be quite acceptable. Leaving the question of the maximum allowable level to further discussion, let us define some links between this concentration and the energy use of CO<sub>2</sub>. The amount of industrial CO<sub>2</sub> produced in the world today is, according to Keeling [18], approximately 10<sup>10</sup> tons per year. The amount of water passing through the Strait of Gibraltar at 2MT/s is about 10<sup>14</sup> tons per year. The ratio of 10<sup>-4</sup> is ten times lower than the safety limit. Thus the scale of the carrier seems to match well with that of the source.

The following question is of a logistic character. Should all the CO<sub>2</sub> be sunk there? The first thing to do obviously is to look for other places of analogous properties that are possibly located near energy transformation and consumption points. The Red Sea currents in Bab el Mandeb closely simulate those of Gibraltar although in a lower scale. The poles have gigantic sinking regions, those in the Weddell Sea and the Norwegian Sea which produce ocean bottom water. The three sites do not conform with the second condition of proximity to energy consumption points. The search is open, however.

Another much more drastic solution has been proposed by W. D. Nordhaus. The CO<sub>2</sub> phase diagram shows a small region for temperatures between 0 °C and 10 °C, where the density is somehow higher than 1, e.g. 1.05. The corresponding pressures are in the range of 150 to 300 atm. This means that after injection with a long pipe into the deep sea, the liquid CO<sub>2</sub> would come out to be slightly *denser* than sea water and would fall down to the bottom. There it would make a 'lake' of LCO<sub>2</sub> that is somewhat analogous to the hot brine lakes at the bottom of the Red Sea. If the depression where the LCO<sub>2</sub> collects is narrow and deep, this form of containment may well have a half life of centuries, as only the slowly moving bottom currents carry away the CO<sub>2</sub> that is diffused into the water covering the LCO<sub>2</sub> pool. The analysis of the behavior of the Red Sea brine pools and of others may provide a trace for evaluating the behavior of this kind of storage.

## 5. Conclusion

The problem of the atmospheric CO<sub>2</sub> level as a consequence of fuel burning appears much eased if equilibrium conditions with the whole oceanic mass are taken into consideration.

In order to shortcut the sluggish kinetics of that equilibrium, a CO<sub>2</sub> management system is proposed where CO<sub>2</sub> is collected at proper fuel transformation points and finally injected into the deep seas taking advantage of natural thermohaline circulations.

A back of the envelope evaluation indicates a cost to the consumer of 10% of the fuel cost for a recovery of 50% of the CO<sub>2</sub> and 20% of the fuel costs for a recovery of 90%. These figures should be supported by the detailed design of such a system for a sufficiently large area, e.g. for Europe, and this is currently underway at IIASA.

## References

- [1] S. H. Schneider, 'On the Carbon Dioxide-Climate Confusion', *J. Atmos. Sci.* 32, II, 2060, November 1975.

- [2] S. H. Schneider and R. Dennett, 'Climatic Barriers to Long Term Energy Growth', *Ambio* 4, 65 (1975).
- [3] C. C. Black and R. H. Burris (eds.), *Carbon Dioxide Metabolism and Productivity in Plants*, University Park Press, Baltimore, Maryland (1976).
- [4] M. I. Budyko, *Climate and Life*, Academic Press (1974).
- [5] W. D. Nordhaus, 'Can We Control Carbon Dioxide?' IIASA-Working Paper WP-75-63, June 1975.
- [6] G. N. Plass, 'Relationship Between Atmospheric Carbon Dioxide Amount and Properties of the Sea', *Environmental Science and Technology* 6, 736 (1972).
- [7] F. MacIntyre, 'Why the Sea is Salty', *Scientific American* 223, 104 (1970).
- [8] D. M. Considine, *Chemical and Process Technology Encyclopedia*, McGraw Hill (1974), e.g. p. 112.
- [9] D. K. Beavon *et al.*, 'CO<sub>2</sub> Removal by "Heatless" Process', *Chemical and Process Engineering*, p. 32 (January 1972).
- [10] Benfield Corporation, 'The Way to Low Cost Scrubbing of CO<sub>2</sub> and H<sub>2</sub>S from Industrial Gases' – A Progress Report.
- [11] J. F. McMahon, 'Fluidized Bed Hydrogenation Process for SNG', *Chem. Eng. Progress* 68, 51 (December 1972).
- [12] R. N. Tennyson and P. A. Buckingham, 'What It Will Cost to Make SNG from Light Hydrocarbons', *The Oil and Gas Journal* 99, April 16 (1973).
- [13] *Hydrogen Energy*, ed. Veziroglu, 2 Vols., Plenum Press 1975.
- [14] *Einsatzmöglichkeiten neuer Energiesysteme: Wasserstoff*, Weiss Verlag, Monschau-Imgenbroich, F.R.G., 1975.
- [15] Defant, A., 'Die Ausbreitung des Mittelmeerwassers im Nordatlantischen Ozean', *Deep-Sea Research* 3, 465 (1956).
- [16] Joseph, J. and H. Sender, 'Über die horizontale Diffusion im Meere', *Deutsche Hydrographische Zeitschrift* 11, 2 (1958), Deutsches Hydrographischen Institut, Hamburg.
- [17] Broecker, W. S., Lamont-Doherty Geological Observatory of Columbia University, Palisades, N.Y., private communication.
- [18] Keeling, C. D., 'Industrial Production of Carbon Dioxide from Fossil Fuels and Limestone', *Tellus* 15, 2, pp. 174–198 (1973).

(Received 10 April, 1976)