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Environmental Control Technology For Atmospheric Carbon Dioxide

Final Report

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and Meyer Steinberg**

May 1980

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**Process Sciences Division
Department of Energy and Environment**

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ABSTRACT

The impact of fossil fuel use in the United States on worldwide CO₂ emissions and the impact of increased coal utilization on CO₂ emission rates are assessed. The aspects of CO₂ control are discussed as well as the available CO₂ control points (CO₂ removal sites).

The primary factor affecting the practicability of a CO₂ control system is the energy required by the control system. Of the three potential CO₂ control points, removal from the stacks of fossil fuel power plants appears to require the least amount of energy. Estimates of the energy required to capture and recover CO₂ from coal-fired power plant stacks by various processes are presented.

Although capture and recovery of CO₂ is an important consideration in the overall scheme of CO₂ control, disposal or reuse of recovered CO₂ may be the weakest link in the CO₂ control chain. Of the several options considered, deep ocean storage appears to be the most promising.

Two control scenarios are evaluated, one based on the absorption of CO₂ contained in power plant flue gas by seawater; the other, based on absorption of CO₂ by MEA. Captured CO₂ is injected into the deep ocean in both cases. Our analyses indicate that capture and disposal by seawater is not feasible, whereas capture and disposal using MEA is a possibility. However, the economic penalties of CO₂ control are significant; for example, at a CO₂ removal efficiency of 50%, it is estimated that the power generation efficiency of a conventional coal fired power plant would be reduced from 34% to about 25%. The cost of power generation would be expected to double. For 90% CO₂ removal, power

generation efficiency is reduced to between 15 and 6% and the cost of power generation increases by a factor of from 4 to 7.

The use of non-fossil energy sources, such as nuclear or solar energy, to control the CO₂ emissions resulting from fossil energy usage is not considered in this study.

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INTRODUCTION

During the last one hundred years or so, the release of fossil carbon as CO_2 has increased at an exponential rate as shown in Fig. 1.¹ As a result, the concentration of CO_2 contained in the atmosphere has grown by about 12%, increasing from about 295 ppm by volume in 1860 (pre-Industrial Revolution) to the current level of 331 ppm. Except for short periods during World Wars I and II and the Depression, the release rate of fossil carbon has increased at the rate of about 4.3% per year.² At present, with no CO_2 emission controls, about 5×10^9 metric tons of carbon per year as CO_2 are emitted to the atmosphere by the burning of fossil fuels from worldwide sources. About 50% of this carbon can be accounted for by the increased CO_2 concentration in the atmosphere. The remaining carbon is presumably absorbed by the oceans and by the land biomass; however, the actual quantities of CO_2 absorbed by the land biomass and by the oceans are still undetermined. Deforestation considerations tend to complicate the issue even further.

If the use of fossil fuels continues to grow at 4.3% per year until the estimated supplies are exhausted, the use rate at the end of this period (about 100 years) would be almost 64 times the current use rate, and the total CO_2 injected into the atmosphere during this period would be about 12 times the pre-industrial content of the atmosphere. Based on more reasonable assumptions, it is predicted that the concentration of atmospheric CO_2 relative to the pre-industrial value could increase by a factor of from about 2 (low-use case) to about 5 (high-use case) during the next one hundred years.² The low-use case corresponds to a fossil fuel growth rate of 2% per year until the year 2025, followed by a

symmetrical decrease as alternative and renewable energy sources become more available and the use of fossil fuel is discouraged. The high-use case corresponds to an initial annual growth rate of 4.3% with subsequent reductions in proportion to the ultimate fossil fuel supply that has been consumed. In both cases, about 50% of the emitted fossil carbon is assumed to be taken up by the oceans and land biomass.

Of primary concern is the warming ("greenhouse effect") which may be produced by these increased CO₂ concentrations due to the absorption by CO₂ of a portion of the infrared radiation returning to space from the earth. The amount of warming produced by a given CO₂ concentration increase is estimated at 1° to 5°K per doubling of the CO₂ concentration. For the low-use case described above, this corresponds to a mean global temperature rise of from about 1° to 5°K over the next one hundred years and from about 2° to 10°K for the high-use case. A temperature rise of 1° or 2°K during this period may be acceptable; however, a rise of 10°K would probably cause catastrophic climatic and environmental effects.

Increased concentrations of particulate matter in the global air mass might produce a cooling effect by backscatter of incoming solar radiation and thus counteract, to some degree, the warming produced by increasing CO₂ levels. However, environmental emission regulations on particulates, as well as on other identified pollutants, have become more and more stringent during recent years and the trend is expected to continue. Furthermore, to deliberately attempt to counteract the effects of CO₂ by allowing increased emissions of particulate pollutants does not appear to be a prudent strategy. Besides, it is not certain whether the net effect of man-made dust is one of cooling or warming of the atmosphere.

Thus, since there is a chance that naturally occurring and/or anthropogenic opposing factors will not just counter the effects of increasing CO₂ levels, it may be necessary to limit industrial CO₂ emissions in the not too distant future. Up to the present, there has been practically no concern about the environmental effects of CO₂; accordingly, there are no regulations applicable to CO₂ emissions. Options for CO₂ control have received little attention and although preliminary evaluations indicate that control is theoretically possible, it may not be technically or economically practicable. It is thus important at this time to determine the technical feasibility and economic costs of CO₂ control should the need arise for regulating the quantity of CO₂ contained in the atmosphere.

IMPACT OF U.S. EMISSIONS

In order to determine the impact of fossil fuel use in the United States on overall (worldwide) CO₂ emissions, we have superimposed several points on Figure 1, based on U.S. fuel use data for the years 1950, 1955, 1960, 1965, 1970, 1973,³ and 1976.¹ The points were obtained by subtracting the estimated emissions of carbon (as CO₂) by U.S. sources from the corresponding worldwide emissions for each of the above years, and thus indicate the quantities of carbon that would have been emitted if the U.S. had not burned any fossil fuels during these years. The reduction in carbon (and thus in CO₂) by this hypothetical non-use of fossil fuels in the U.S. ranges from 0.32 ppm in 1950 to 0.64 ppm in 1973 (and in 1976) as given in Table 1. However, during this period the percentage of the total yearly emissions contributed by the U.S. decreased from 43% in 1950 to 27% in 1976. Furthermore, it is projected

that the contribution to global CO₂ production by the U.S. and Canada will decrease to about 8% by the year 2025. Developing nations will account for 36% of the CO₂ production, the USSR and Eastern Europe 27%, Asia 19%, Western Europe 7%, and Japan and Australia 3%.¹ Thus, it appears that a worldwide effort would be required to effectively control the level of atmospheric CO₂.

IMPACT OF COAL UTILIZATION

Table 2 contains a source distribution of the carbon (CO₂) produced from major worldwide sources during the years 1970 through 1976.¹ For the year 1976, using the heating values of 18,000 Btu/lb of contained carbon for coal, 22,400 Btu/lb carbon for fuel oil, and 31,500 Btu/lb carbon for natural gas, and assuming that all fossil energy was produced by the burning of solid coal, the carbon released to the atmosphere would have been roughly 6×10^9 metric tons or about 1.2 times the quantity actually emitted (energy differences required in mining versus drilling, preparation, transportation, etc. and in combustion efficiencies were not taken into account). If we had assumed that the natural gas and petroleum consumed in 1976 had been replaced by coal-derived gaseous and liquid fuels, the quantity of carbon released to the atmosphere would have been even greater than 6×10^9 metric tons because of inefficiencies in the gasification and liquefaction processes. Thus, added reliance on coal for energy production could compound the atmospheric release rate of CO₂, depending upon the extent to which coal displaces oil and natural gas and future energy use patterns.

Table 3 shows the quantities of CO₂ produced per unit energy released for various naturally occurring and synthetic fuels. In determining the CO₂ generated by synthetic fuels such as SNG, the CO₂ generated in the production process is included. It is noted that natural gas produces about one third the amount of CO₂ per unit energy released in comparison to synthetic natural gas derived from coal, and about half the CO₂ from the direct burning of coal.

CO₂ CONTROL OVERVIEW

Perhaps the most significant difference between the control of CO₂ and that of other pollutants is that the amount of CO₂ generated by the activities of mankind is so much greater--currently about 20×10^9 metric tons per year from the use of fossil fuels. Effective control would therefore require an extremely large-scale application of technology and the expenditure of large amounts of energy and capital. Methods for removing CO₂ from gases and liquids are currently available⁴; however, reuse or storage/disposal alternatives are extremely limited. Pretreatment options are obviously nonexistent.

Although there are several key factors to consider in assessing the practicability of a prospective control methodology, the most important consideration is the energy required by the control system. As this energy increases, assuming that the energy required to drive the control system is furnished by fossil fuel, overall power plant efficiency decreases and the quantity of CO₂ emitted to the atmosphere per kWh(e) generated increases. Therefore, in the extreme a point is reached where the only effect produced by the CO₂ control system is a decrease in power plant efficiency with no net reduction in CO₂ emissions.

Conventional coal-fired power plants operate at efficiencies of between 30 and 38%. At an efficiency of 30%, 0.43 kWh of electricity is produced per pound of CO₂ generated; at 38% about 0.55 kWh. Table 4 shows the effect of CO₂ control system energy requirements and CO₂ removal efficiency on overall power plant efficiency and on net CO₂ emissions for an initial power plant efficiency of 38%.

Three potential control points (CO₂ removal sites) are available for regulating the concentration of CO₂ in the atmosphere: (1) the atmosphere itself, (2) the surface waters of the oceans, and (3) the stacks of fossil fuel power plants. The last site has the advantage of providing a source of relatively high CO₂ concentration, while the first two provide more flexibility for site selection and simpler disposal or recovery and reuse logistics. A choice of control point limits the available choices of CO₂ removal processes and will reflect on the size of operation, the number of required sites, energy requirements, the comparative economics, and the overall feasibility of operation.

The CO₂ concentration ranges of the three control points are listed in Table 5. Since the concentration of CO₂ in flue gas is significantly greater than that in the atmosphere or the oceans, the energy required to remove CO₂ from flue gas should be appreciably lower than for the other two control points. The minimum theoretical energies required to separate CO₂ from each of the three sources are also listed in Table 5. Based on these theoretical values, it would take about three times more energy to separate CO₂ from the atmosphere than from flue gas.

Although removal or capture of CO_2 from a particular source is an important consideration in devising a CO_2 control system or scenario, CO_2 disposal (storage) and reuse potentials are equally or perhaps more important, for unless a control scenario produces a net near-term decrease in the rate of buildup of atmospheric CO_2 it will be of no value. This means that the captured CO_2 must be stored or recycled until large-scale non-fossil energy sources become available.

A block diagram showing the relationship between the various aspects of CO_2 control is presented in Figure 2.

CO_2 REMOVAL AND RECOVERY

Atmosphere and Oceans

The present concentration of CO_2 contained in the atmosphere is about 331 ppm by volume. Therefore, in order to remove 1 mole of CO_2 from the atmosphere a minimum of 3021 moles of air must be processed. This is equivalent to about one pound of CO_2 per 2000 pounds of air. The equation for calculating the air horsepower of a fan can be simplified to⁵

$$\text{Air h.p.} = 157 \times 10^{-6} Q \Delta P, \quad (1)$$

where Q is the volume handled in cfm and ΔP is the pressure drop across the fan in inches of water. For air at standard conditions, this equation may be converted to

$$\text{Air h.p.} = 34.9 \times 10^{-6} W \Delta P, \quad (2)$$

where W equals the mass flow rate of air in pounds per hour. Assuming a fan efficiency of 75%, the required shaft horsepower of the fan is

$$\text{Shaft h.p.} = 46.5 \times 10^{-6} W \Delta P. \quad (3)$$

Converting horsepower to kilowatts yields

$$\text{kW fan} = 34.7 \times 10^{-6} W \Delta P = 34.7 \times 10^{-6} (m/\theta) P. \quad (4)$$

Dividing by pounds of CO₂ and substituting 2,000 pounds of air per pound of CO₂ for m yields the following equation:

$$\frac{\text{kWh(e)}}{\text{lb CO}_2} = 0.0694 \Delta P . \quad (5)$$

Assuming an overall power plant efficiency of 38% and a coal heating value of 18,000 Btu per pound of contained carbon, the pounds of CO₂ produced per kilowatt generated calculates to 1.83. Setting 1/1.83 (0.5464) equal to Eq. (5), and solving for ΔP yields $\Delta P = 7.9$ inches of water. Thus, if the pressure drop across a CO₂ absorption or adsorption unit is equal to about 8 in. of water (assuming a 100% removal efficiency and electricity generation by the combustion of coal), as much CO₂ will be generated in supplying electricity to the air-handling fan as will be removed from the atmosphere by the CO₂ removal system. For electricity generation by the combustion of natural gas instead of coal, ΔP maximum calculates to 14 in. of water. Since a maximum allowable pressure drop of from 8 to 14 in. of water is a rather stringent constraint to impose on such equipment (actually the pressure drop would have to be much less than the calculated maximum allowable for the process to be of value), and since there are other system energy requirements to satisfy, e.g., sorbent pumping energy in absorption systems, it is unlikely that a practicable system can be designed for removing CO₂ from the atmosphere unless non-fossil energy sources are considered. Note that Steinberg and Dang⁶ determined that the energy required to remove CO₂ from the atmosphere by refrigeration techniques was greater than that required for removal by atmospheric absorption or adsorption processes.

From the work of Steinberg and Dang and because of the low concentration of CO_2 in seawater, it is also concluded that removal of CO_2 from the oceans by a fossil fuel energy source is not a promising alternative.

Flue Gas

The concentration of CO_2 in fossil fuel power plant flue gas is about 500 times greater than its concentration in the atmosphere, therefore, CO_2 removal should be greatly facilitated. Furthermore, commercial processes, i.e., absorption/desorption processes, are currently available for removing CO_2 from flue gas and other gaseous mixtures. For example, in the manufacture of liquid CO_2 and dry ice, CO_2 resulting from the burning of a carbonaceous material is absorbed from flue gas with sodium carbonate, aqueous potassium carbonate, or amines. CO_2 removal systems are also employed in the production of synthesis gases for ammonia and methanol, and in hydrogen gas production. Thus, removal of CO_2 from flue gas appears to be much more promising than removal from the atmosphere or oceans.

Estimates of the energy requirements for removing CO_2 from flue gas are given in Table 6. Values range from 0.15 kWh(e)/lb CO_2 for 50% absorption with monoethanolamine (MEA) to 0.8 kWh(e)/lb CO_2 for 90% absorption with seawater. The most effective solvent appears to be MEA; however, even the use of MEA will significantly reduce overall power plant efficiency.

CO_2 DISPOSAL (STORAGE)

Four ways of disposing of captured CO_2 have been considered: (1) injection in the deep ocean, (2) terrestrial burial (3) storage in plants and trees, and (4) extraterrestrial disposal. The last method is considered impractical because of the large quantities of CO_2 involved.

Injection in the Deep Ocean

In the two-box model, the world ocean is represented by two reservoirs, separated by a thermocline. One reservoir consists of surface layers to a depth of about 100 meters; the other, of deeper layers from the 100-meter depth to the ocean floor. Mixing is assumed to occur rapidly within each box or reservoir, but exchange between the two boxes proceeds slowly. Thus, the deep ocean is a potential sink for CO_2 since there is no direct exchange between the atmosphere and deep ocean waters. Only the surface layers are in CO_2 equilibrium with the atmosphere. The main discrepancy between the simple two-box model and the real ocean is that in some regions (e.g., Arctic, Antarctic, and Gibraltar) convection currents extend from the ocean surface to the ocean bottom.

One proposal for disposing of collected CO_2 is to inject it into the sea at the Strait of Gibraltar.⁷ Presumably, the current would carry it to the deeper ocean waters where it would remain for centuries. Another proposal is to inject liquid CO_2 into the deep sea at a density greater than that of deep sea water via a long pipe.²⁴ The CO_2 would sink to the bottom of the ocean forming a liquid CO_2 lake within the ocean. CO_2 could also be injected into the deep ocean as a gas, provided the injection depth is deep enough to permit dissolution of the CO_2 before it rises to the upper layers.

The current release rate of fossil carbon to the atmosphere is about 5×10^{15} g/yr, whereas the current carbon content of the deep ocean is estimated to be at 0.373×10^{20} g. Therefore, if all this fossil carbon was captured and deposited in the deep ocean, its carbon content over a

one-year period would increase by only about 0.013%. However, the effects of this injected carbon on the deep ocean ecosystem have not been assessed.

Terrestrial Burial

Storage in abandoned mine shafts or wells and fixation in natural clays are two options that were considered. The latter has been dismissed as impractical because of the large quantities of clays that would have to be handled, even if they were available and effective in fixing CO₂. In the case of below ground storage the rate at which CO₂ would re-enter the atmosphere is an important consideration as well as the available storage capacity of the below-ground cavities. A related disposal scheme is to use captured CO₂ for enhanced oil recovery, in which case, the CO₂ would be injected into depleted oil wells to effect additional oil recovery. Captured CO₂ would thus have an economic value. However, the effectiveness of such a method in controlling atmospheric CO₂ does not principally depend on economics but upon (1) the energy requirements of the CO₂ removal and disposal system, (2) how much CO₂ can be injected into depleted wells, and (3) the length of time the CO₂ would remain underground. These factors have not been studied in enough detail to draw any firm conclusions.

Storage in Plants and Trees

It has been suggested that in the event of a CO₂ worldwide emergency, corrective measures to halt or reverse the growth of atmospheric CO₂ could be instituted by planting fast-growing long-lived trees which are left unharvested and/or by growing short-lived plants

which are converted to humus or allowed to accumulate in artificial peat bogs. However, this action would be limited by the availability of fertilizer.⁸ Furthermore, additional CO₂ would be generated by the reforestation activities and in supplying energy for increased fertilizer production, which would reduce the effectiveness of the method.

CO₂ CONVERSION

Although a number of commercial CO₂ products can be made for the economy, e.g., dry ice, the quantity of these products produced and consumed yearly is extremely small in comparison to the quantity of fossil CO₂ emitted to the atmosphere. Therefore, atmospheric CO₂ levels will not be significantly affected by the way in which these products are made.

A suggested method^{6,9,10} for reducing the buildup of CO₂ in the atmosphere is to recover and convert CO₂ to synthetic liquid and gaseous carbonaceous fuels using a non-fossil energy source such as nuclear or solar energy. The use of non-fossil energy to control the CO₂ emissions resulting from fossil energy usage is not considered in this study.

REMOVAL AND DEEP OCEAN DISPOSAL OF FLUE GAS CO₂ USING SEAWATER

Scenario Formulation and Description

In light of the previous considerations, control point 3 (power plant stacks) has been selected as the initial control point of interest. Accordingly, a scenario based on the absorption of CO₂ generated by coal-fired power plants has been formulated. A block diagram of the system is presented in Figure 3. Seawater from the surface of the ocean is pumped to the top of a CO₂ absorber (packed tower). The seawater flows downward through the packing by gravity, absorbing CO₂ from the

power plant flue gas which flows countercurrent to the seawater. The water exits at the bottom of the absorber and is pumped to the deep ocean while the treated flue gas is discharged to the atmosphere. The flue gas is fed to the absorber, subsequent to SO_2 removal, by an auxiliary blower. Such a system is perhaps the simplest for one-step absorption and disposal of CO_2 . No CO_2 desorption step is required and no additional handling of recovered CO_2 ; the captured CO_2 is discharged directly into a CO_2 reservoir. Furthermore, seawater is readily available in large quantities at a zero purchase price. However, the scenario does impose constraints on power plant location.

In evaluating the subject scenario, it was assumed that the power plant under consideration has a capacity of 200 MW(e) and an efficiency of about 34% (subsequent to SO_2 removal), is located near the U.S. coastline at sea level, and that deep ocean waters are accessible at a distance of about 10 miles from the power plant site.

Flue Gas Composition

A summary of the composition and conditions of the flue gas upon which this evaluation is based is presented in Table 7. Flue gas composition was calculated on the assumption that combustion is carried out with 20% excess air. It was also assumed that the gaseous feed to the CO_2 absorber is saturated with water vapor at 120°F (48.9°C) and is free of sulfur dioxide.

CO_2 Solubility Data

CO_2 solubility data for pure water¹¹ and for seawater at a salinity of 3.5%¹² are summarized in Table 8, for a temperature of 64.4°F (18°C). From these data, the equilibrium relationships between the partial

pressure of CO₂ in atmospheres as a function of its molar concentration in pure water and in seawater (3.5% salinity) are $P = 1390x$ and $P = 1620x$, respectively. Plots of CO₂ partial pressure versus mole fraction for pure water and for seawater are presented in Figure 4 along with two absorber operating lines, one for a CO₂ removal efficiency (η) of 0.6 (60%); the other, for a removal efficiency of 0.9. The operating lines were determined by material balance and are given by¹³

$$L'_m (X_1 - X) = G'_m \left(\frac{p_1}{P - p_1} - \frac{p}{P - p} \right),$$

where

L'_m = liquor rate, lb/mole solute-free solvent/(hr)(ft² tower),

G'_m = superficial molar mass velocity of inert gas,
lb-mole/(hr)(ft²),

X = solute concentration in liquid, lb-mole solute/lb-mole solvent,

X_1 = solute concentration in liquid leaving the tower, lb-mole solute/
lb-mole solvent,

P = total pressure on system, atm,

p = partial pressure of solute in gas stream, atm,

p_1 = partial pressure of solute in gas entering the tower, atm.

The effects of pressure drop across the column and of condensation of water vapor from the flue gas during passage through the absorber are not taken into account in the above equation. For the system under consideration, the lb-mole solute/lb-mole solvent (X) is about equal to the mole fraction of solute in the liquid stream (x).

Transfer Units

When the resistance to mass transfer is principally in the liquid phase, as in the case of physical absorption of a slightly soluble gas (e.g., CO_2), it is customary to base tower calculations on liquid-phase transfer units. Following this convention, the applicable equation for calculating the number of overall liquid-phase transfer units is

$$N_{OL} = \int_{x_2}^{x_1} \frac{dx}{x^* - x}$$

where

N_{OL} = number of overall liquid-phase transfer units,

x_1 = mole fraction of solute in liquid stream at concentrated end of countercurrent apparatus,

x_2 = mole fraction of solute in liquid stream at dilute end of countercurrent apparatus,

x^* = mole fraction of solute in liquid at equilibrium with bulk of gas,

x = mole fraction of solute in liquid stream.

For straight operating and equilibrium lines, the equation can be written

$$N_{OL} = \frac{x_1 - x_2}{(x^* - x)_{LM}}$$

where

$$(x^* - x)_{LM} = \frac{(x^* - x)_2 - (x^* - x)_1}{\ln [(x^* - x)_2 / (x^* - x)_1]}$$

For $\eta = 0.60$, $x_2 = 0.2 \times 10^{-6}$ (fresh seawater), and $x_1 = 70 \times 10^{-6}$ (spent seawater), N_{OL} calculates to 3.3. For $\eta = 0.90$, $x_2 = 0.2 \times 10^{-6}$, and $x_1 = 80 \times 10^{-6}$, N_{OL} is 16.3.

Tower Design

Following the conventional technique for tower design, $(L/G)(\rho_G/\rho_L)^{1/2}$ was calculated and G determined from the Generalized Pressure Drop Correlation for Packed Towers [Figure 5] (Norton Chemical Process Products Division)], relating $G^2 F \psi^{0.2} / \rho_G \rho_L g_c$ to $(L/G)(\rho_G/\rho_L)^{1/2}$, where

L = liquid rate, lb/sec-ft²,

G = gas rate, lb/sec-ft²,

ρ_L = liquid density, lb/ft³,

ρ_G = gas density, lb/ft³,

F = packing factor,

μ = viscosity of liquid, centipoise,

ψ = ratio, density of water/density of liquid,

g_c = gravitational constant = 32.2 .

Two-inch Raschig rings and a pressure drop of 0.5 inches of water per foot packing were assumed. Note that it was necessary to extrapolate the curves of the subject pressure drop correlation because of the high L/G ratios required by the CO₂ absorber. Operating, a tower at high $(L/G)(\rho_G/\rho_L)^{1/2}$ values could result in tower instability.

For the $\eta = 0.6$ case, the value of G was determined to lie between 0.018 and 0.02 lb/sec-ft². Based on the flow of flue gas indicated in Table 7 and the above values of G , between 84 and 90 towers of 20-ft

diameter would be required to achieve the 60% removal efficiency. For $\eta = 0.9$, between 100 and 107 towers of 20-ft diameter are required.

Packing Height

With m (slope of equilibrium line), L , G , and tower diameter established, the height of an overall liquid-phase transfer unit (H_{OL}) was estimated for each of the cases under consideration from data appearing in ref. 11, p. 221. For $\eta = 0.60$, H_{OL} was estimated to be 7 ft and for $\eta = 0.90$, at 8 ft. For the former case the required height of packing, given by $h = N_{OL} H_{OL}$, is 23 feet and for the latter 130 ft. The corresponding pressure drops across the absorbers (with some contingency) are 15 and 70 in. of water, respectively. A summary of the two cases appears in Table 9. Note that it was necessary to calculate h before energy requirements could be assessed.

Energy Requirements

A flow sheet of the subject CO_2 control system is shown in Figure 6; pumping distances and pipe sizes are also included in the diagram. The energy requirements of both the 60 and 90% cases are summarized in Table 10. The major energy requirement, as would be expected, is due to the high seawater pumping load. A relatively minor quantity of energy is required to pump the flue gas through the absorbers. For each of the CO_2 removal efficiencies considered, more CO_2 would be produced in supplying electricity to the control system (assuming coal-derived power and electrically driven equipment) than would be extracted from the power plant flue gas. For the 60% efficiency case, about 0.6 kWh(e)/lb CO_2 captured is required and for the 90% case, about 0.8 kWh(e)/lb CO_2 .

At an overall power plant efficiency of 34% and a coal heating value of 18,000 Btu per pound of contained carbon, only 0.5 kWh of electricity is produced per pound of CO₂ generated.

It should be mentioned that the high horsepower and thus energy requirements of the seawater pumps are due to the large quantities of seawater (about 3×10^6 gpm) that must be supplied to and exhausted from the CO₂ absorption towers (because of the low solubility of CO₂ in seawater); friction loss (for the selected pipe sizes) and static head requirements are not excessive (about 100 psi overall). Furthermore, static head is dictated by absorber height and not by the depth to which the spent seawater must be pumped because the head against which the spent seawater is pumped is balanced by the static head gain of the spent seawater in flowing from sea level to the deep ocean. However, the deeper the injection point the greater the friction loss (for a given pipe size and flow rate) because a greater length of pipe is required.

System Costs

Estimates of the equipment requirements, fixed capital investments, and operating costs of the 60 and 90% removal systems are summarized in Table 11. The total fixed investment for the 60% system is estimated at about \$123,300,000, and for the 90% system at \$226,800,000. Yearly operating costs (utilities only) are \$35,500,000 and \$72,200,000, respectively, assuming an electricity cost of 30 mills/kWh and 8,000 hours of plant operation. For comparison, the fixed capital investment and yearly operating costs (utilities and raw materials only) of a lime slurry SO₂ scrubbing system for a 200-MW(e) plant are roughly \$20,000,000 and \$1,700,000, respectively, assuming 3.3% sulfur coal (dry basis), an 80% SO₂ removal efficiency, and on-site disposal of spent slurry.

30 mills/kWh corresponds to the approximate cost of electricity purchased from an external source, that is, from a power plant without CO₂ control. For a power plant that uses its own electrical output to drive its CO₂ control system (self-contained plant), the revenue requirements and thus cost of generating electricity will depend upon the net electrical output of the plant. Therefore, as net output approaches zero (because of excessive demands by the CO₂ control system), revenue requirements will approach infinity, which is the case for seawater absorption/disposal of CO₂ from power plant flue gas.

Discussion

Although the subject scenario offers the following advantages as compared, for example, to a scenario based on absorption by a chemical solvent - (1) simple plant design (no heat exchangers, desorption equipment and reboilers), (2) no heat load, (3) inexpensive, readily available solvent, (4) no solvent vapors introduced into the gas stream, and (5) direct disposal of captured CO₂ - it is not a promising alternative because of excessive energy and equipment requirements. Furthermore, site location is restricted and absorber stability may be a problem.

For the two CO₂ collection efficiencies considered, the CO₂ produced in supplying energy to the control system would be greater than the CO₂ removed from the flue gas. The energy requirements of the control system can be reduced somewhat by increasing the sizes of the seawater transfer lines and/or by lowering CO₂ collection efficiency. However, equipment requirements would remain substantial. The system may be more attractive if used in combination with an ocean thermal energy conversion (OTEC) system; but, OTEC systems are highly speculative at the present time.

REMOVAL OF CO₂ FROM FLUE GAS USING MEA, FOLLOWED BY DEEP OCEAN DISPOSAL

MEA Absorption/Stripping

Of the several processes evaluated for removing CO₂ from stack gases (Table 6), monoethanolamine (MEA) absorption/stripping requires the least amount of energy per unit of CO₂ recovered. MEA absorbs CO₂ rapidly and efficiently at low partial pressures and is therefore well suited for removing CO₂ from power plant flue gas. Impurities such as COS, CS₂, HCN, and SO₂ react nonregenerably with MEA so SO₂ must be removed from the flue gas prior to treatment with SO₂. Flue gas does not normally contain COS, CS₂, or HCN.

A flow sheet of the MEA process for CO₂ absorption recovery from power plant flue gas is shown in Figure 7.^{19,20} Flue gas at 120°F and 14.7 psia (water saturated) from bulk SO₂ removal is fed to the suction of a blower which compresses the flue gas to about 16 psia and feeds it to the MEA absorber. As the flue gas passes through the absorber, CO₂ is removed by reaction with lean MEA solution, flowing countercurrent to the flue gas, in accordance with the following reaction:

The reaction takes place to the right (forward direction) at temperatures between about 100° and 175°F.

Spent MEA solution is pumped from the bottom of the absorber through a filter, for removal of solid impurities, to the top of the regenerator. Before entering the regenerator, the cold spent MEA solution is heated by heat exchange with the hot regenerated (lean) solution from the bottom of the regenerator. Carbon dioxide is stripped from the MEA as the solution flows downward through the regenerator. A steam-heated reboiler

supplies the necessary heat for regeneration. The bottom of the regenerator is maintained at about 250°F. Elevated temperature combined with steam stripping favors the reverse of the absorption reaction.

The stripped carbon dioxide exits the regenerator at the top and flows to a condenser for removal of water vapor. Most of the condensed water is returned to the generator as reflux; a portion of the remainder is pumped to the top of the absorber to reduce MEA losses. Excess water is pumped to disposal.

Regenerated MEA solution from the bottom of the stripping tower is first cooled by heat exchange with spent MEA solution flowing to the stripper, and then by water. The cooled lean solution is then fed to the top of the absorber tower.

A reclaimer for recovering MEA which has reacted with residual flue gas SO₂ is shown at the bottom of the regenerator. A slipstream of MEA is withdrawn from the regenerator reboiler and cooled by heat exchange with the reclaimed solution returning to the reboiler. Sodium carbonate is added to the stream to liberate MEA. The slipstream is then cooled and filtered to remove precipitated sodium sulfate and sulfite and other degradation products. Purified MEA solution is returned to the reboiler. The reclaiming system is speculative at the present time and further development work is required before a final design can be prepared.²⁰

Deep Ocean Disposal of Recovered CO₂

Three methods of disposing of the recovered gaseous CO₂ from the MEA absorption/stripping process were considered: (a) gaseous disposal via a deep ocean pipeline, (b) liquid disposal via a deep ocean pipeline, and (c) deep ocean solid disposal.

(a) Gaseous Disposal. In gaseous disposal, CO₂ recovered by the MEA process is compressed and fed to the deep ocean via a pipeline. A 500-meter injection depth was assumed even though ocean surface layers usually extend to a depth of only about 100 meters. The additional 400 meters was provided to allow for dissolution of the injected gas in the deep ocean. Any injected CO₂ which reaches the well-mixed surface layers will eventually equilibrate with the atmosphere and thus reduce the effectiveness of disposal. Ocean depths of 500 meters are accessible at distances of about 100 miles from the shoreline of the northeast United States (approximate width of the continental shelf); therefore, a pipeline of about 100 miles in length was assumed (no allowance was made for inland distance).

For 90% recovery of the CO₂ generated by a 200-MW(e) coal-fired power plant, an 18-in. line was selected; for 50% recovery, a 14-in. line was selected. Most of the energy required by the CO₂ compressor is expended in overcoming the seawater static head between the CO₂ injection point and the surface of the ocean. A compressor discharge pressure (third stage) of about 800 psia is required.

A block diagram of the overall absorption/recovery disposal system is shown in Figures 8 and 9.

(b) Liquid Disposal. In order to produce liquid CO₂ from the gaseous CO₂ product of the MEA system, the gaseous CO₂ must be compressed, cooled, and dried. This is done in a three-stage compression system equipped with coolers, water knockout drums, and a dryer. The gas is compressed to 920 psia in the third stage, passed through a cooler, and liquefied in a condenser at about 27°C²² (the critical pressure and

temperature of CO₂ are 1073 psia and 31°C). For deep ocean disposal, the liquefied CO₂ would then be piped to an appropriate location in the deep ocean.

In order to store CO₂ as a liquid pool in the deep ocean it must be injected to a depth where the density of CO₂, at the pressure corresponding to the seawater static head and the prevailing seawater temperature, is greater than the density of the seawater at the injection point. The specific gravity of CO₂ is approximately equal to 1 at pressures between 150 and 300 atmospheres and temperatures between 3° and 15°C. For the subject evaluation, an injection depth of 3000 meters was selected which corresponds to a pressure of about 300 atmospheres; the temperature of the ocean at this depth is about 3°C. The specific gravity of CO₂ (liquid) at these conditions is 1.05. At a salinity of 3.5%, a temperature of 3°C, and a pressure of 300 atmospheres, the specific gravity of seawater is about 1.04.

Ocean depths of 3000 meters are accessible at distances of about 200 miles from the shoreline of the northeast United States and thus a pipeline of about 200 miles in length is required (no allowance is made for inland distance since the required offshore distance is quite variable with respect to the U.S. coastline). For 90% recovery of the CO₂ generated by a 200-MW(e) plant, a 12-in. line was selected; for 50% recovery, a 10-in. line. For these line sizes, the liquid CO₂ will flow to the deep ocean under the influence of the CO₂ liquefaction pressure. Pumps are not required. In the subject evaluation it was assumed that the liquid would be cooled from about 27°C to the temperature of the deep ocean injection point during its journey to the deep ocean. If this is not the case, additional cooling of the liquid CO₂ will be required.

A block diagram of the overall absorption/recovery disposal system is shown in Figures 8 and 9.

(c) Solid Disposal. In the production of commercial solid CO₂, the liquid CO₂ produced by compression and cooling, as described under (b) above, is expanded through a nozzle, forming "snow," and fed to a press. The vapors given off during expansion are used to precool the liquid carbon dioxide prior to expansion. The gas is then recompressed and reliquefied. The "snow" is compressed into 220 pound blocks and then quartered by band saws. The 55-pound blocks are wrapped in Kraft paper and either stored or shipped in insulated cars.²² The density of the blocks is about 100 lb/ft³. The temperature of saturated CO₂ ice at 1 atmosphere pressure is -78.5°C.

Since the density of the CO₂ blocks is much greater than that of seawater, they should readily sink to the ocean bottom when dropped into the surface waters of the ocean. The settling velocity of a 10-in. cube of solid CO₂ in seawater is roughly estimated at 5 ft/sec. For a disposal depth of 500 meters (the depth selected for gaseous CO₂ disposal) it would take about 5.4 minutes for a block to reach bottom; for a disposal depth of 3000 meters (the depth selected for liquid CO₂ disposal) it would take about 32 minutes. Based on the phase diagram for CO₂ and assuming the blocks are heated by the seawater to prevailing ocean temperatures, the final state of the blocks for both the 500- and 3000-meter disposal depths is liquid. The liquid formed for the 3000-meter disposal depth will have a density greater than that of seawater and therefore should remain at the bottom of the ocean. For the 500-meter depth, the liquid will be less dense than seawater and would

therefore tend to rise. Upon rising, some of the liquid CO_2 may dissolve in the seawater and some may flash into vapor which in turn will rise and dissolve. Depending upon the relative rates of heat and mass transfer and the rate of ascent of the CO_2 liquid droplets and gaseous bubbles, some CO_2 may reach the surface layers of the ocean. CO_2 reaching these layers may eventually end up in the atmosphere. Losses may also occur as the blocks descend to the ocean bottom as a result of gas and liquid formation and dissolution. Without experimental data or a detailed analysis of the physics of deep ocean disposal of solid CO_2 , it is not possible to confidently predict the fate of the solid CO_2 blocks or accurately determine the extent of losses.

The energy required to transport the solid CO_2 blocks a distance of 100 miles offshore (500-meter disposal depth) by barge is estimated at 0.005 kWh(e)/lb CO_2 and for 200 miles (3000 meter depth) at 0.010 kWh(e)/lb CO_2 . The energy to produce solid CO_2 blocks from gaseous CO_2 is about 0.17 kWh(e)/lb CO_2 . Therefore, barging distance does not have a significant effect on the overall energy requirements of the system, assuming no CO_2 losses during transport; however, disposal costs for the 200-mile distance would be almost twice that of the 100-mile distance.

A block diagram of the overall absorption/recovery disposal system is shown in Figures 8 and 9.

Energy Requirements

Total system energy requirements for CO_2 recovery efficiencies of 50 and 90% and for gaseous, liquid, and solid disposal are summarized in Figures 8 and 9, respectively. At 50% efficiency, gaseous or liquid disposal require the equivalent of about 0.20 kWh(e)/lb CO_2 recovered and

at 90% efficiency about 0.32 kWh(e)/lb CO₂. For solid disposal at 50% recovery, assuming no sublimation losses during handling and transportation, about 0.33 kWh(e)/lb CO₂ are required, whereas about 0.45 kWh(e)/lb CO₂ are needed at 90% recovery.

Assuming a power plant efficiency of 34% after sulfur dioxide removal, 0.49 kilowatt-hours of electricity is produced per pound of CO₂ generated. With no CO₂ removal, 2.04 pounds of CO₂ are discharged to the atmosphere per net kilowatt-hour of electricity produced. At 50% recovery and gaseous or liquid disposal, overall power plant efficiency would be reduced to 27% and for 90% recovery to 14%. The corresponding pounds of CO₂ discharged to the atmosphere per net kWh(e) generated are 1.3 and 0.5, respectively. For 50 and 90% recoveries and solid disposal, power plant efficiency would be reduced to 23 and 6%, respectively. The corresponding pounds of CO₂ discharged per net kWh(e) produced are 1.5 and 1.1.

Investment and Power Generation Costs

Rough estimates of the required fixed capital investments for 50 and 90% CO₂ recovery using MEA and for gaseous, liquid, and solid disposal are presented in Tables 12 and 13. On the basis of these estimates and those of the capital and operating costs of a 200-MW(e) coal-fired power plant with flue gas desulfurization (FGD), electricity generation costs have been calculated. These are presented in Table 14 along with an estimate of the cost of generation without CO₂ control.

Revenue requirements in mills/kWh were calculated on the basis of net electricity output assuming an initial plant capacity of 200 MW(e) (after SO₂ removal) and assuming that the electricity required to drive

the CO₂ control system is supplied internally by the subject power plant. Thus, the net output of the power plant (e_{net}) is equal to gross output [$e_{\text{gross}} = 200 \text{ MW(e)}$] minus the electricity consumed by the control system (e_{control}). A schematic of the overall system is presented in Figure 10.

For a CO₂ removal efficiency of 50%, the costs of generating electricity for gaseous, liquid, and solid disposal are approximately equal. The net power generated and yearly operating costs for gaseous and solid disposal are about the same and, therefore, so are power generation costs. Solid disposal requires more energy but less capital. For 50% removal of CO₂, these two factors balance one another and the cost of power generation for solid disposal turns out to be about the same as for gaseous and liquid disposal.

For 90% CO₂ removal, in comparison to 50%, the cost of power generation roughly doubles for both gaseous and liquid disposal, whereas it increases by a factor of about 4 for solid disposal. This marked increase in generation costs for solid disposal is due to excessive control system energy requirements at the 90% CO₂ removal efficiency.

If the above analysis had been based on a net power plant output of 200 MW(e) rather than a gross output of 200 MW(e) the costs of power generation, particularly at the higher CO₂ removal efficiencies, might have been somewhat lower because of economies of scale.

Discussion

If we accept the previous results and evaluation, removal and recovery of flue gas CO₂ using MEA is technically and energetically feasible; however, economic penalties are significant. Disposal also appears to be feasible provided the effects of injected CO₂ on the deep ocean ecosystem are not prohibitive.

MEA absorption/stripping in combination with either gaseous or liquid disposal requires appreciably less energy than an MEA-solid disposal combination. On the other hand, the capital investments required by the former combinations far exceed those of the latter, offsetting, to some degree, the economic benefits of the lower energy requirements. For gaseous or liquid disposal, the major portion of the capital investment is due to pipeline costs, which are probably understated in the cost estimates.

A possible way to reduce the capital investment for a liquid disposal system is to barge liquid CO₂ to the required offshore distance (about 200 miles) and then inject the liquid into the deep ocean via a pipe extending from the ocean surface to the injection point. With this arrangement the required length of injection piping would be substantially reduced (from about 330,000 to about 3000 meters) as well as the required pipe size. Unfortunately, CO₂ cannot be shipped as a liquid at atmospheric pressure as can LNG, therefore, high pressure barges or tankers, or numerous high pressure cylinders, would be required for transport. Gaseous CO₂ could also be shipped under pressure and then injected into the deep ocean.

For direct gaseous or liquid deep ocean injection (via pipeline), essentially no losses of recovered CO₂ would be incurred during transport. For solid disposal by barging, losses during handling and transportation could be significant. For 10-in. cube blocks of about 55 pounds each, shipping losses (based on transport by truck) could be as high as 8 pounds during the first 24 hours in summer.²³ To reduce

handling losses and improve handling logistics for inland power plants, it may be better to pump the flue gas to the dock site and remove/recover and solidify at that point.

CONCLUSIONS

(1) The contribution by the United States to worldwide CO₂ emissions has been decreasing during the last 25 years and it is projected that it will decrease even further during the next 50 years. Therefore, a worldwide effort will be required to control the buildup of atmospheric CO₂.

(2) Increased utilization of coal for producing heat, electric power, and/or synthetic gaseous and liquid fuels will increase the rate of CO₂ emissions. The magnitude of this increase may or may not be significant depending upon the extent to which coal displaces oil and natural gas, and future energy use patterns.

(3) Direct capture of CO₂ from the atmosphere or capture from the surface waters of the oceans do not appear to be feasible if a fossil energy source is used to drive the CO₂ control system.

(4) For 60 to 90% absorption of the CO₂ contained in the flue gas of a coal-fired power plant using seawater and deep ocean disposal, more CO₂ would be generated in supplying energy to the control system than would be recovered from the flue gas.

(5) Removal and recovery of CO₂ from the stacks of fossil fuel plants by commercially available processes is feasible, e.g., by absorption/stripping with MEA. However, large quantities of energy are required which will substantially reduce the efficiency of power generation and thus increase the cost of producing electricity.

(6) Disposal of captured and recovered CO₂ will be a problem. Of the disposal/reuse options considered, deep ocean disposal appears to be a possibility. However, the costs of disposal are substantial. The effects of injected CO₂ on the ocean ecosystem have not been assessed.

(7) Of the processes considered, absorption by MEA is the least energy intensive. For a 50% CO₂ removal efficiency, the equivalent of 0.15 kWh(e)/lb captured CO₂ is required; and for 90% removal, 0.27 kWh(e)/lb CO₂. Gaseous or liquid disposal of the captured CO₂ requires an additional 0.05 kWh(e)/lb CO₂, whereas solid disposal requires about 0.18 kWh(e)/lb CO₂ (discounting transportation and handling losses). The required capital investments for gaseous and liquid pipeline disposal are substantially greater than for solid disposal. Low energy consumption and high capital investment have offsetting effects on the cost of power generation.

(8) For effective control of atmospheric CO₂ by removal from flue gases, it would be advantageous and perhaps necessary to centralize the use of fossil fuels, such as in an all electric economy, since it would be almost impossible to remove, recover, and dispose of CO₂ from the numerous small sources, i.e., from the flues of home heating units, process plants, and automobile exhausts. In the U.S. today, about 30% of the total CO₂ released to the atmosphere from the use of fossil fuels comes from large stationary sources (electric power plants).

For direct removal of CO₂ from the atmosphere or from the surface layers of the ocean, centralized use of fossil fuels is not required. However, removal of CO₂ directly from the atmosphere or from the oceans does not appear to be feasible unless the energy required to drive the CO₂ control system is supplied by a non-fossil energy source.

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REFERENCES

1. R.M. Rotty, Global CO₂ production from fossil fuels and cement, AD 1950-AD 2000, Proc. Mtg. at Univ. Hawaii on Fate and Fossil Fuel CO₂ in the Ocean, Sponsored by Office of Naval Research Jan. 1976, Plenum Press, pp. 167-181, Oct. 1977.
2. C.F. Baes Jr., H.E. Goeller, J.S. Olson, and R.M. Rotty, Carbon dioxide and climate: The uncontrolled experiment, Am. Sci. 65, 310 (1977).
3. Statistical Abstract of the United States, U.S. Department of Commerce, 1975.
4. A. Albanese and M. Steinberg, Environmental Control Technology for Atmospheric Carbon Dioxide, BNL 50877, (Apr. 1978).
5. Chemical Engineers Handbook, R.H. Perry and C.H. Chilton, Editors, 5th Ed., McGraw Hill, 1973.
6. M. Steinberg and Vi-Duong Dang, Use of Controlled Thermonuclear Reactor Fusion Power for the Production of Synthetic Methanol Fuel from Air and Water, BNL 20016R, Apr. 1975.
7. C. Marchetti, On geoengineering and the CO₂ problem, Climatic Change 1, 59 (1977).
8. F.J. Dyson, Can we control the carbon dioxide in the atmosphere, Energy 2, 287-291 (1977).
9. M. Steinberg, Nuclear Power for the Production of Synthetic Fuels and Feedstocks, BNL 21330, Apr. 1976.
10. M. Steinberg, Synthetic Carbonaceous Fuels and Feedstocks from Oxides of Carbon and Nuclear Power, BNL 22785, Mar. 1977.
11. Gas Purification, F.C. Reisenfeld and A.L. Kohl, 2nd Ed., Gulf Publishing Co., 1974.
12. Chemical Oceanography, Vol. 2, J.P. Riley and G. Skirrow, Editors, 2nd Ed., Academic Press, 1975.

13. Absorption and Extraction, T.K. Sherwood and R.L. Pigford, Editors, 2nd Ed., McGraw Hill, 1952.
14. T.B. Reed, Efficiencies of Methanol Production from Gas, Coal, Waste or Wood, Lincoln Laboratory, MIT.
15. R. Detman, Factored Estimates for Western Coal Commercial Concepts, C.F. Braun & Co., Interim Report, FE-2240-5, Oct. 1976.
16. R. Detman, Factored Estimates for Eastern Coal Commercial Concepts, C.F. Braun & Co., Interim Report, FE-2240-31, Sept. 1978.
17. A.S. Albanese and M. Steinberg, Environmental Control Technology for the Flash Hydropyrolysis of Coal, Progress Report No. 3, BNL 50983, Feb. 1979.
18. P.J. Rogoszewski, Standards of Practice Manual for the Solvent Refined Coal Liquefaction Process, Hittman Associates, EPA-600/7-78-091, June 1978.
19. A.W. Pappano et al., Availability and Economics of CO₂ for Enhanced Oil Recovery in Appalachia, Dept of ChE, West Virginia University, TID-22787, Aug. 1976.
20. W.M. Rump et al., The Supply of Carbon Dioxide for Enhanced Oil Recovery, Pullman Kellog, Final Report, FE-2515-10, Sept. 1977.
21. R.M. Guthrie, Process Plant Estimating Evaluation and Control, Craftsman Book Company of America, 1974.
22. Industrial Chemicals, W.L. Faith, D.B. Keyes, and R.L. Clark, Editors, 4th Ed., John Wiley & Sons, Inc. 1975.
23. E.L. Quinn and C.L. Jones, Carbon Dioxide, Reinhold Publishing Company, 1936.
24. W.D. Nordhaus, Can We Control Carbon Dioxide? IIASA-Working Paper WP-75-63, June 1975.

Table 1

U.S. Contribution to Atmospheric CO₂ Emissions
Compared to All Other Worldwide Sources^{1,3}

Year	Incremental atmospheric CO ₂ concentration in ppm		% U.S. contribution	% Others
	Worldwide	U.S.		
1950	0.74	0.32	43	57
1955	0.92	0.36	39	61
1960	1.18	0.39	33	67
1965	1.47	0.46	31	69
1970	2.00	0.58	29	71
1973	2.27	0.64	28	72
1976	2.38	0.64	27	73
2025 Est.			8	92(1)

(1) Developing nations estimated to account for 36% of total worldwide emissions.

Table 2

Worldwide CO₂ Emissions by Source
All entries in 10⁶ metric tons carbon as CO₂

Source	1970	1971	1972	1973	1974	1975	1976	1976 Distribution %
Coal	1497	1479	1499	1527	1550	1626	1676	33.2
Lignite	237	239	243	246	246	249	260	5.1
Crude petroleum & N.G. liquids	1803	1907	2011	2203	2213	2107	2224	44.1
Natural gas	545	583	614	646	659	665	675	13.4
Natural gas flared	90	94	100	110	113	105	113	2.2
Cement	82	88	93	95	95	100	99	2.0
Total carbon as CO ₂	4254	4390	4560	4827	4876	4852	5047	
Incremental atm CO ₂ conc. (ppm)	2.00	2.07	2.15	2.27	2.29	2.28	2.38	
U.S. emissions contribution	0.58			0.64			0.64	

Table 3

CO₂ Generation for Various Fuels

Fuel type	Chemical Formula	Higher heating value Btu/lb	CO ₂ generated lb CO ₂ /lb fuel	CO ₂ generated lb CO ₂ /1000 Btu	Energy generated kWh(e)/lb CO ₂ generated(1)
Coke (ashless C)	C	14,000	3.67	0.26	
Bituminous coal	CH _{0.85} O _{0.1}	12,700	2.59	0.204	0.55(2)
Fuel oil & gasoline (petrol. dist.)	(CH ₂) _n	19,600	3.14	0.16	0.70
Benzene	C ₆ H ₆	18,000	3.38	0.19	
Acetylene	C ₂ H ₂	21,500	3.38	0.16	
Methanol (wood alc)	CH ₃ OH	10,000	1.38	0.14	
Methanol (syn. from coal)	CH ₃ OH	10,000	3.3	0.33(3)	0.34
Biomass (wood, cellulose)	(CH ₂ O) _n	8,000	1.47	0.18	
Carbon monoxide	CO	4,350	1.57	0.36	0.31
Natural gas	CH ₄	24,000	2.75	0.115	0.97
SNG from coal gasification	CH ₄	24,000	7.9	0.33(4)	0.34
Synthetic liquid fuels (from coal by FHP process)	--	--	--	0.34(5)	
Synthetic liquid & gaseous fuels (mixed products from FHP or SRC-II plants)	--	--	--	0.26(6)	

(1) Assuming a power plant efficiency of 38%.

(2) For a power plant with FGC, assuming power plant efficiency is reduced from 38% to 35%, the kWh(e)/lb CO₂ generated is reduced to 0.50.

(3) Estimated from ref. 14.

(4) Estimated from ref. 15 and 16.

(5) Estimated from ref. 17.

(6) Estimated from ref. 17 and 18.

Table 4

Effect of CO₂ Control System Energy
Requirements on Power Plant Efficiency

Energy required by CO ₂ control system kWh(e)/lb CO ₂	CO ₂ removal efficiency, %	Net power plant efficiency %	lbs CO ₂ discharged to atmosphere per net kWh(e) generated
0	100	38.0	0
0.1	100	31.0	0
	75	32.8	0.53
	50	34.5	1.01
	25	36.3	1.44
	0	38.0	1.83
0.2	100	24.1	0
	75	27.6	0.63
	50	31.0	1.12
	25	34.5	1.51
	0	38.0	1.83
0.3	100	17.1	0
	75	22.4	0.78
	50	27.6	1.26
	25	32.8	1.59
	0	38.0	1.83
0.4	100	10.2	0
	75	17.1	1.01
	50	24.1	1.44
	25	31.0	1.68
	0	38.0	1.83
0.5	100	3.2	0
	75	11.9	1.46
	50	20.6	1.69
	25	29.3	1.78
	0	38.0	1.83
0.55	100	0	0
	75	9.5	1.83
	50	19.0	1.83
	25	28.5	1.83
	0	38.0	1.83

Table 5

CO₂ Concentrations at Control Points and Minimum
CO₂ Separation Energies

Control point	CO ₂ concentration		Min separation energy ⁽¹⁾ kWh/lb CO ₂
	% by vol	% by wt	
(1) Atmosphere	331x10 ⁻⁴	502x10 ⁻⁴	0.0570
(2) Ocean	--	100x10 ⁻⁴ (2)	0.0570
(3) Fossil fueled power plant stacks	7-20	11-28	0.0259-0.0179

(1) Minimum energy based on free energy of mixing:

$\Delta F = RT \sum n_i \ln(P_i/P_i^0)$, where P_i^0 and P_i are the initial and final partial pressures of the i^{th} species, respectively. R is the gas constant, T is temperature in degrees absolute, and n_i is the number of moles of the i^{th} species.

(2) ΣCO_2 (total carbon dioxide content) = $C_{\text{H}_2\text{CO}_3} + C_{\text{CO}_2(\text{aq})} + C_{\text{HCO}_3(\text{T})} + C_{\text{CO}_3(\text{T})}$.

Table 6

Energy Required To Remove and Recover
CO₂ (Gaseous) From Flue Gas

Process	CO ₂ removal efficiency %	kWh(e) lb/CO ₂ (1,2,3) recovered
1. Amine (MEA) absorption/Stripping	50	0.15
	90	0.27
2. Potassium carbonate absorption/stripping	90	0.32
3. Molecular sieves	90	0.40
4. Refrigeration	90	0.40
5. Seawater absorption ⁽⁴⁾	60	0.60
	90	0.80

(1) Energy required to recover CO₂ (as a gas) from flue gas of coal-fired power plant subsequent to SO₂ removal. Inlet conditions to CO₂ removal process are 120°F and 14.7 psia, assuming flue gas is saturated with water vapor and free of SO₂. Reheat of flue gas accounted for by SO₂ system.

(2) All energy requirements have been converted to the equivalent amount of electrical energy.

(3) To liquefy the recovered CO₂ gas, an additional 0.05 kWh(e)/lb CO₂ is required; to solidify the CO₂ gas, about 0.17 kWh(e)/lb CO₂ is required.

(4) Including deep ocean disposal of captured CO₂.

Table 7

Summary of Flue Gas from 200 MWe Coal
Fired Power Plant at 20% Excess Air

Component	M.W.	lb/hr	lb-mol/hr	Mole percent
O ₂	32	70,873	2,214.8	3.155
N ₂	28	1,401,550	50,055.4	71.295
H ₂ O	18	153,552	8,530.7	12.150
CO ₂	44	<u>413,967</u>	<u>9,408.3</u>	<u>13.400</u>
		2,039,942	70,209.2	100.0

MW(avg): 29.06

P(psia): 14.7

T (°F): 120°

Basis : Flue gas composition at discharge of SO₂ scrubbers -
flue gas assumed to be SO₂ free and saturated with
water vapor at 120°F.

Table 8

CO₂ Solubility Data for Pure Water and
Sea Water (3.5% Salinity), at 64.4°F (18°C)

<u>Water</u> ¹¹			
Partial pressure CO ₂ , mm Hg	Partial pressure CO ₂ , atm	lb CO ₂ /100 lb H ₂ O	Mole fraction x10 ⁶
0	0	0	0
100	0.1316	0.022	90
200	0.2632	0.047	192.3
300	0.3947	0.070	286.4
400	0.5263	0.094	384.4
500	0.6579	0.116	474.3

Seawater¹²

Basis: 3.429×10^{-2} mol/kg-atm.

0	0	0	0
100	0.1316	0.020	81.2
200	0.2632	0.040	162.4
300	0.3947	0.060	243.5
400	0.5263	0.079	324.6
500	0.6579	0.099	405.8

Table 9

Summary of CO₂ Absorber Design Data
and Results for CO₂ Removal Efficiencies
of 60 and 90 Percent
Seawater Absorption/Disposal

	CO ₂ removal efficiency	
	60%	90%
x ₁ , mf CO ₂ in outlet seawater	70x10 ⁻⁶	80x10 ⁻⁶
x ₂ , mf CO ₂ in inlet seawater	0.2x10 ⁻⁶	0.2x10 ⁻⁶
y ₁ , mf CO ₂ in inlet gas	0.1340	0.1340
y ₂ , mf CO ₂ in outlet gas	0.0536	0.0134
N _{OL} , number of overall liquid-phase transfer units	3.3	16.3
m, slope of equilibrium line	1620	1620
L _m /G _m , molar ratio of liquid to gas	1217-1493	1533-1981
L/G, mass ratio of liquid to gas	754-927	949-1271
G, mass velocity of gas, lb/(sec) (ft ²)	0.020-0.018	0.017-0.014
H _{OL} , height of overall liquid-phase transfer unit, feet	7	8
h, packing height, feet	23	130
ΔP/foot packing, inches water	0.5	0.5
ΔP/tower, inches water	15	70
Tower diameter, feet	20	20
Overall tower height, feet (approx.)	42	150
No. towers	84-90	100-107

Table 10

Summary of Energy Requirements for CO₂
Removal Efficiencies of 60 and 90 Percent
Seawater Absorption/Disposal

	Energy requirements, kWh(e)/Lb CO ₂ captured	
	60%	90%
Seawater pump #1	0.2235	0.4839
Seawater pump #2	0.3688	0.3087
Flue gas exhaust blower	<u>0.0045</u>	<u>0.0136</u>
Total	0.5968	0.8062

Table 11
Estimated Equipment Requirements and Investment and
Operating Costs for CO₂ Removal and Disposal Systems
200-MW(e) Power Plant
Seawater Absorption/Disposal

	No. units	Size/capacity	(Millions of dollars)	Yearly operating ⁽²⁾ costs (millions of dollars)
<u>Case I ($\eta = 0.6$)</u>				
Towers	87	20'Dx42'H	16.9	—
Piping (principal)	—	48" I.D.x10 mi	15.8 ⁽¹⁾	—
Pumps	174	36,000 GPM	89.3	35.3
Blowers	1	500,000 SCFM	<u>1.3</u>	<u>0.2</u>
			123.3	35.5
<u>Case II ($\eta = 0.9$)</u>				
Towers	104	20'Dx150'H	94.6	—
Piping (principal)	—	48" I.D.x10 mi	15.8 ⁽¹⁾	—
Pumps	208	36,000 GPM	113.0	70.9
Blowers	1	500,000 SCFM	<u>3.4</u>	<u>1.3</u>
			226.8	72.2

(1) @ \$300 per ft.

(2) Utilities only - labor, maintenance, etc. not included; 8000 hours of operation per year; electricity at 30 mills/kWh. Refer to discussion under system costs on page 19 of this report.

(3) The fixed capital investment and yearly operating cost (utilities and raw materials only) of a lime slurry SO₂ scrubbing system (200 MWe plant) are roughly \$20,000,000 and \$1,700,000, respectively, assuming 3.3% sulfur coal (dry basis), an 80% SO₂ removal efficiency, and on-site disposal of spent slurry.

Table 12

Investment and Operating Costs for MEA Absorption
and Deep Ocean Disposal of Flue Gas CO₂ From
200-MW(e) Coal-Fired Power Plant

Case I ($\eta = 0.5$)

	Fixed capital investment ⁽¹⁾ (millions of dollars)
<u>A. Gaseous disposal</u>	
Removal & recovery	18(2)
Compression	3
Piping (14 in. x 100 mi)	<u>106</u>
	127
<u>B. Liquid disposal</u>	
Removal & recovery	18(2)
Liquefaction	4
Piping (10 in. x 200 mi)	<u>158</u>
	180
<u>C. Solid disposal</u>	
Removal & recovery	18(2)
Solidification	20
Barging	<u>--</u>
	38

(1) Plant investment does not include costs of equipment for reclaiming degraded MEA.

(2) Estimated from ref. 19, 20, and 21.

Table 13

Investment and Operating Costs for MEA Absorption
and Deep Ocean Disposal of Flue Gas CO₂ From
200-MW(e) Coal-Fired Power Plant

Case II (n = 0.9)

	Fixed capital investment ⁽¹⁾ (millions of dollars)
<u>A. Gaseous disposal</u>	
Removal & recovery	25(2)
Compression	5
Piping (18 in. x 100 mi)	<u>132</u>
	162
<u>B. Liquid disposal</u>	
Removal & recovery	25(2)
Liquefaction	6
Piping (12 in. x 200 mi)	<u>211</u>
	242
<u>C. Solid disposal</u>	
Removal & recovery	25(2)
Solidification	32
Barging	<u>—</u>
	57

(1) Plant investment does not include costs of equipment for reclaiming degraded MEA.

(2) Estimated from ref. 19, 20, and 21.

Table 14

Costs of Generating Electricity
With and Without CO₂ Control
for Initial Power Plant Capacity
of 200-MW(e)

	SO ₂ removal with no CO ₂ control	SO ₂ removed plus 50% CO ₂ control			SO ₂ removed plus 90% CO ₂ control		
		Gaseous disposal	Liquid disposal	Solid disposal	Gaseous disposal	Liquid disposal	Solid disposal
Net capacity, ⁽¹⁾ MW(e)	200	161	159	134	86	83	37
Capital investment MM\$							
(a) Power plant ⁽²⁾	160	160	160	160	160	160	160
(b) CO ₂ control system ⁽³⁾	—	152	216	46	194	290	68
Total	160	312	376	206	354	450	228
Operating costs, ⁽⁴⁾ MM\$/year							
(a) Coal @ \$30/ton	18.9	18.9	18.9	18.9	18.9	18.9	18.9
(b) O&M	4.8	5.8	5.8	7.2	5.8	5.8	7.2
(c) Barging costs ^(5,6)	—	—	—	5.0	—	—	5.0
(d) Capital charges @ 15% of Capital investment	24.0	46.8	56.4	30.9	53.1	67.5	34.2
Total	47.7	71.5	81.1	62.0	77.8	92.2	65.3
Electricity generation costs, Mills/kWh (revenue requirements)	30	56	64	58	113	139	221

(1) Electrical energy to drive the CO₂ control system is assumed to be obtained from the electrical output of the power plant, therefore:
 $e_{\text{net}} = e_{\text{gross}}(200 \text{ MWe}) - e_{\text{control}}$

(2) Total capital investment @ \$800/kW(e) including FGD.

(3) Total capital investment @ 1.2 times fixed capital investment (Tables 12 and 13).

(4) Based on 8000 hours of operation per year.

(5) Dry ice barging costs @ \$15,000 per day; costs for transporting dry ice from power plant to barge are not included.

(6) Barging costs are based on a 100-mile barging distance (500-meter disposal depth); for a 200-mile distance (3000-meter disposal depth), barging costs are estimated at 9 million dollars per year.

Figure 1. CO₂ Production from Fossil Fuels and Cement.

— worldwide
 - - - - - Worldwide less U.S. Sources

Figure 2. Logic Diagram for CO₂ Control.

Figure 3. Absorption and Disposal of CO₂ Generated by Coal-Fired Power Plants, Using Seawater.

Figure 4. Equilibrium Partial Pressure of CO₂ Versus Mole Fraction in Water and in Seawater (3.5% salinity).

Figure 5. Generalized Pressure Drop Correlation for Sizing Packed Towers.

Figure 6. Flowsheet for CO₂ Absorption Disposal from Power Plant Flue Gas Using Seawater.

Case I ($\eta = 0.5$)

A. Gaseous Disposal

B. Liquid Disposal

C. Solid Disposal

Note:

(1) Equivalent energy requirement in KWH(e) per pound of CO₂ recovered.

Figure 8. Energy Requirements for MEA Absorption and Deep Ocean Disposal of Flue Gas CO₂ from 200 MW(e) Coal Fired Power Plant.

Case II ($\eta = 0.9$)

A. Gaseous Disposal

B. Liquid Disposal

C. Solid Disposal

Note:

(1) Equivalent energy requirement in KWH(e) per pound of CO₂ recovered.

Figure 9. Energy Requirements for MEA Absorption and Deep Ocean Disposal of Flue Gas CO₂ from 200 MW(e) Coal Fired Power Plant.

$$e_{\text{net}} = e_{\text{gross}} - e_{\text{control}}$$

Figure 10. Schematic of Self-Contained Power Plant with FGD and CO_2 Control.

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