



CAPTURE OF CO₂ USING WATER SCRUBBING

**Report Number PH3/26
July 2000**

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Title: Capture of CO₂ using water scrubbing
Reference number: PH3/26
Date issued: July 2000

Other remarks:

Background to the Study

The leading options for CO₂ capture are based on scrubbing with regenerable solvents. A potentially simpler alternative would be once-through scrubbing with seawater, followed by direct discharge of the CO₂-laden seawater into the deep ocean. This would avoid the cost, complexity and energy losses associated with regenerating the scrubbing solvent and compressing the CO₂ gas.

This report presents the results of a scoping study on options for CO₂ capture using water scrubbing. The study was carried out for IEA GHG by URS New Zealand Ltd. (formerly Woodward Clyde (NZ) Ltd.)

Approach Adopted

A range of power generation processes involving seawater scrubbing has been examined. A scoping assessment has been carried out to identify the most promising processes based on coal and natural gas fuels. Outline designs of CO₂ capture processes have been prepared and comparative plant performances and costs estimated. From this, the key parameters that influence the potential for water-based capture processes are identified and the sensitivity of costs and performance to variations in these parameters assessed.

CO₂-laden seawater would normally need to be discharged at depths greater than about 1500m, to minimise environmental impacts and to ensure that the CO₂ remained in the ocean for a long period of time. A survey of the world's coastline was carried out to identify sites that are close to 1500m deep ocean and that are also close to major areas of population and power demand. Preliminary estimates of the global potential of seawater scrubbing are then made.

Results and discussion

Screening study

A preliminary screening study was carried out to assess water scrubbing of CO₂ from the flue gas of a pulverised coal fired power station. This was found to be not feasible. The partial pressure of CO₂ in power station flue gas means that an excessively large amount of water would be needed, resulting in very large costs for scrubbers and water pipes. The flue gas could be compressed prior to scrubbing, to increase the CO₂ partial pressure and reduce the quantity of water required, but the resulting costs and energy losses were also found to be excessively high. The situation would be even worse for a natural gas fired plant, where the CO₂ concentration in the flue gas is much lower.

An alternative to scrubbing flue gas would be to scrub shifted fuel gas in a coal-IGCC or a natural gas pre-combustion decarbonisation plant. The partial pressure of CO₂ in shifted fuel gas is at least 50 times higher than in combustor flue gas. The study therefore focussed on water scrubbing of shifted fuel gas.

Reference cases

The reference coal and gas fired power plants for this study are taken from a recent study carried out for IEA GHG by Stork Engineering (report PH3/14). In the reference plants, CO₂ is scrubbed from shifted fuel gas to leave a hydrogen-rich gas for use as fuel in a gas turbine. These reference plant designs were modified by replacing the solvent scrubber unit by a seawater scrubber. CO₂ is separated from shifted fuel gas in packed scrubber columns by contact with a counter-current flow of seawater. The CO₂-laden seawater from the scrubber is piped to a discharge location at a depth of 1500m. The water from the scrubber is at high pressure, sufficient to overcome the pressure drop through the pipeline and differences in hydrostatic head.

In the reference plants, 85% of the CO₂ is captured using regenerable Selexol solvent. Some of the CO in the fuel gas is not converted in the shift reactor but is burnt in the gas turbine. Seawater is a less effective solvent for CO₂ than Selexol. In order to achieve the same overall percentage capture of CO₂ as in the reference plants, more CO needs to be converted to CO₂ in the shift converter. This is achieved by adding more steam to the feed gas to the shift converter. It may be preferable to accept a lower percentage capture of CO₂ in plants with seawater scrubbing, to avoid the need for more shift conversion and/or to reduce the costs of the scrubbers. However, such optimisation was beyond the scope of this study.

Base case results

The assessment showed that water scrubbing is more competitive for coal fired plants than gas fired plants. This summary will therefore concentrate on coal fired plants. The results for the main coal-fired IGCC cases evaluated in this study are summarised in table 1 - these include one base case and 3 sensitivity cases, which are described below. The efficiencies and costs in Table 1 are relative to a reference IGCC plant with Selexol scrubbing and pipeline disposal of pure CO₂ to the ocean.

The efficiency, capital cost and cost of CO₂ emission avoidance are almost identical for the seawater scrubbing base case and the Selexol reference case. The differences are all within the level of accuracy of the estimates. The main advantage of seawater scrubbing (i.e. avoiding the energy consumption for CO₂ compression) is offset by the energy demand for pumping water.

Table 1 Efficiencies and costs of seawater scrubbing relative to Selexol scrubbing in an IGCC

Case	Pipeline length (km)	Efficiency, (percentage points)	Capital cost (\$/kW _e)	Cost of emission avoidance (\$/t CO ₂)
Seawater base case	25	+0.1	0	0
Short pipeline	10	+0.1	-60	-2
Long pipeline	100	+0.1	+360	+12
High pressure scrubber	25	-0.9	-40	-1

The quantity of seawater fed to the scrubber in the base case plant (383MW_e) is 6 tonnes/s. This is less than the quantity of seawater that would be required as cooling water for the steam turbine condenser.

These cases are all based on a seawater temperature of 12°C, in line with IEA GHG's standard assessment criteria. As discussed later, the sea water temperature will be higher at most of the potential sites for plants with seawater scrubbing. As the solubility of CO₂ in water decreases with increasing temperature, a higher seawater temperature would result in somewhat higher water flows and costs.

Sensitivity cases

The capital costs of water scrubbing plants are very sensitive to the length of the water disposal pipeline. Reducing the disposal pipeline length from 25 km to 10 km results in a cost advantage for seawater scrubbing, compared to a reference plant with a 10 km CO₂ disposal pipeline. However, the

cost advantage is still less than 10% of the overall cost of capture and storage. With a pipeline length of 100 km, seawater scrubbing is much more expensive than a Selexol scrubbing reference case with the same length of CO₂ disposal pipe.

The amount of CO₂ that can be dissolved in seawater depends on the operating pressure of the scrubber. The effects of compressing the scrubber inlet gas to 50 bar were assessed in the high pressure scrubber sensitivity case. The water flow and capital cost of the scrubbers and pipelines is lower in this case but this is offset by the capital and energy costs of the gas compressor, so the overall cost of capture is similar to that of the base case. The reference study was based on a dry-feed gasifier. It would be possible to operate a slurry-feed gasifier at a substantially higher pressure and this could improve the competitiveness of water scrubbing.

Low operating temperatures make water scrubbing more attractive, because the solubility of CO₂ increases significantly as the temperature is reduced. A further advantage is that, compared to CO₂, hydrogen becomes much less soluble in water at lower temperatures, so operating the scrubber at low temperature reduces the amount of hydrogen lost with the seawater. Most of the potential locations for seawater scrubbing, where deep ocean is available close to the shore, are in tropical and subtropical locations where the surface ocean is relatively warm. Methods for providing cold water for the scrubber at these locations were assessed. One option is to pipe cold water from below the thermocline but this was shown to be uncompetitive because it requires a long inlet water pipe. Another option is to chill the water before the scrubber. This was shown to be infeasible, because of the high energy consumption for the chiller.

Environmental impacts

Dissolution of CO₂ in seawater forms carbonic acid. The water from the base case IGCC scrubber would have a pH of about 4.2. Seawater with a pH of less than 6.5 is lethal to most coastal marine organisms and oceanic species are expected to be more sensitive. The pH of the water from the scrubber could be raised by partial neutralisation with calcium carbonate prior to discharge but very large quantities of limestone would be required and further dilution would still be needed to avoid adverse environmental impacts.

There are several possible ways of injecting pure CO₂ into the ocean, including injection from a shore-based pipeline, a fixed floating platform or a moving ship. Water scrubbing has the disadvantage that it is restricted to using a shore-based pipeline but it has the advantage that the CO₂ is already dissolved and partially diluted. Detailed studies would be needed to determine the relative environmental impacts of water scrubbing and injection of concentrated CO₂.

Potential sites

The water discharge pipe length would need to be short, preferably less than 25km, to make water scrubbing competitive. A simple survey of the world's coastline was carried out to identify potential sites which are within 100km of 1500m deep ocean and which are also close to large centres of population and power demand. Most of the locations where 1500m deep ocean is close to the coast are in tropical and subtropical regions. There are a few exceptions, in Japan, Spain, Portugal and California.

A major uncertainty is how many power plants with water scrubbing could be built on a given site, which depends on how quickly the CO₂-rich water disperses and local environmental factors. If there are no constraints on dispersion of CO₂-laden seawater it is estimated that about 35 GW of power generation capacity could be installed with seawater discharge pipe lengths of 25 km or less. More capacity could be installed if the electricity could be transmitted long distances to consumers.

Capture of CO₂ as a hydrate

Much higher loadings of CO₂ in water could be achieved by formation of CO₂ hydrates. These are ice-like materials that form by combination of CO₂ and water at high pressures and low temperatures.

Hydrates could potentially be pumped as a slurry into the ocean or they could be decomposed to give CO₂ for more conventional storage.

A process based on capturing CO₂ as a hydrate has been patented and development work is underway with support from the US Department of Energy. The contractor has pointed out that to achieve a percentage capture of CO₂ comparable to that in other capture processes, hydrates would need to form readily at CO₂ partial pressures substantially lower than those shown in published phase diagrams for water / pure CO₂. However, there are many uncertainties about the formation of hydrates, particularly for multi-component gas mixtures, not least because the emphasis of most research to date has been on inhibiting hydrate formation, for example during natural gas production, not enhancing it. In the absence of published data on hydrate formation under the conditions expected in the IGCC application, the contractor has been unable to evaluate the cost-effectiveness of using hydrates for CO₂ separation.

Expert Reviewers' Comments

The draft version of this report was sent to experts including members of the Programme's Power Generation and Capture expert group and the holder of patents on a hydrate capture process. Following receipt of the comments it was not thought to be necessary to make any major changes to the report.

Main Conclusions

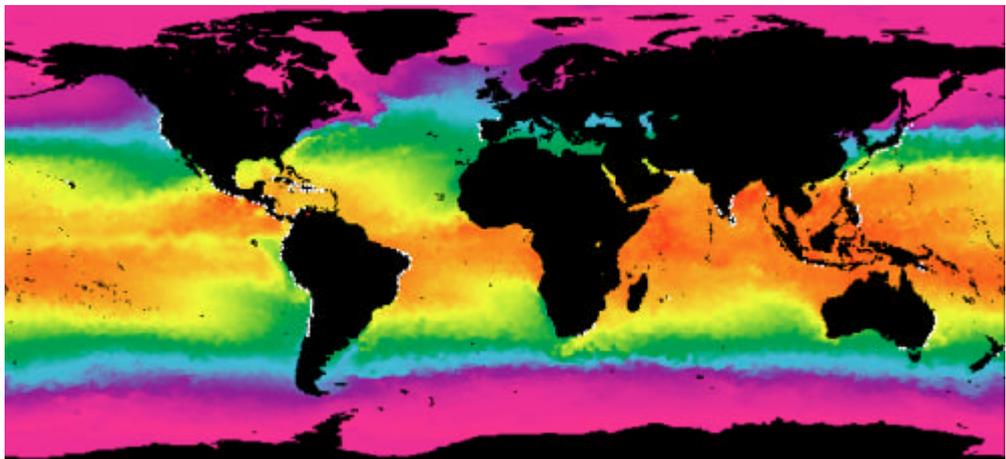
- Seawater scrubbing of flue gas from atmospheric pressure combustion processes would not be feasible because very large quantities of water would be required.
- The most appropriate process streams for seawater scrubbing would be shifted fuel gas in a coal fired IGCC or a natural gas pre-combustion decarbonisation plant.
- The thermal efficiency of an IGCC or pre-combustion decarbonisation power plant with CO₂ capture by seawater scrubbing (in a suitable coastal location) would be similar to that of a plant with conventional Selexol regenerable solvent scrubbing for CO₂ capture.
- The cost of a seawater scrubbing plant depends greatly on the length of the water pipeline. If the discharge pipeline is 25 km long, the overall cost of avoiding CO₂ emissions is predicted to be very similar for seawater scrubbing and conventional Selexol solvent scrubbing. If the discharge pipeline is 10 km long, the overall cost of avoiding CO₂ emissions is predicted to be about \$2/t less than in a Selexol-based plant. If the pipeline is 100 km long the cost is predicted to be about \$12/t higher than in a Selexol based plant.
- A review of the coastline of the world has identified potential power plant locations that are within 10, 25 and 100 km of adequately deep ocean. Most of the sites are in tropical and subtropical regions.
- The number of power stations that could be built with seawater scrubbing would depend on the rate of dispersion of CO₂-rich seawater. The water discharged into the deep ocean would have an acidity of about pH 4.2. This would require extensive dilution to avoid local environmental impacts.
- Public domain information concerning the use of water/hydrate mixtures for CO₂ capture has been considered in detail. To achieve an adequate capture of CO₂, hydrates would need to form readily at CO₂ partial pressures substantially lower than those shown in published phase diagrams for water and pure CO₂ but there are many uncertainties about the formation of hydrates from multi-component gas mixtures. Consequently, no firm conclusion has been reached about the use of water/hydrate mixtures for CO₂ capture.

Recommendations

- A more detailed assessment of seawater scrubbing should be carried out if other studies on the environmental impacts of ocean injection of CO₂ show that injection of CO₂-laden seawater has significant environmental advantages compared to injection of pure CO₂.
- Hydrate-based CO₂ capture processes should be re-evaluated by IEA GHG if it is demonstrated that hydrates can be formed from gas mixtures at low CO₂ partial pressures.

FINAL REPORT

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21 October 2003

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The International Energy Agency Greenhouse Gas R&D Programme (IEA GHG) has carried out studies on a variety of methods of capturing CO₂ in power stations, for example by scrubbing with physical and chemical solvents and by using membrane and cryogenic processes. The aim of this scoping study is to assess alternative methods of capturing CO₂, which involve the use of water or water/hydrate mixtures.

The use of water as a once-through CO₂ capture medium has potential advantages over conventional processes because it involves a simple process scheme with no requirement for solvent regeneration and CO₂ compression. These are the source of the principal energy losses associated with other CO₂ capture processes.

An assessment of leading technology options for abatement of CO₂ emissions has been carried out for IEA GHG by Stork Engineering Consultancy B.V, (PH3/14)¹. The full power plant systems evaluated in PH3/14 are taken as a framework within which CO₂ capture using water is considered in this report. Therefore this study evaluates water-scrubbing technologies on the basis of substitution for the conventional scrubbing technologies evaluated in PH3/14 and does not rework the full power plant technical and economic assessment.

A range of water-based capture processes are identified. A preliminary assessment of these is carried out to identify the most promising processes based on coal and natural gas as power generation fuels. The key parameters that influence the potential for water based capture processes are identified and the sensitivity of the technical and economic assessment to these parameters is carried out.

The discharge of a solution of carbon dioxide in water to a sensitive receiving environment has the potential to cause a major environmental impact. The pH of the discharged solution is determined and the potential environmental impact is discussed.

The economics of the use of water as a once-through solvent for CO₂ is strongly dependent on the proximity of a suitable deep discharge point for large volumes of acidic water. A review of the world coastline is carried out to identify potentially suitable locations. Based on this survey, an estimate is made of the approximate quantities of CO₂ that may be captured using seawater scrubbing processes for three different discharge pipeline lengths.

¹ Leading Options for the Capture of CO₂ Emissions at Power Stations. February 2000 Stork Engineering Consultancy B.V. IEA GHG report PH3/14

The selection of processes for evaluation is discussed and assessed in Appendix A.

2.1 HOST POWER GENERATION PROCESSES

The PH3/14 includes an assessment of leading technology options for abatement of CO₂ emissions. A literature review has not identified any other potential host power generation processes better suited to the application of water scrubbing processes than those studied in PH3/14.

2.1.1 Coal based processes

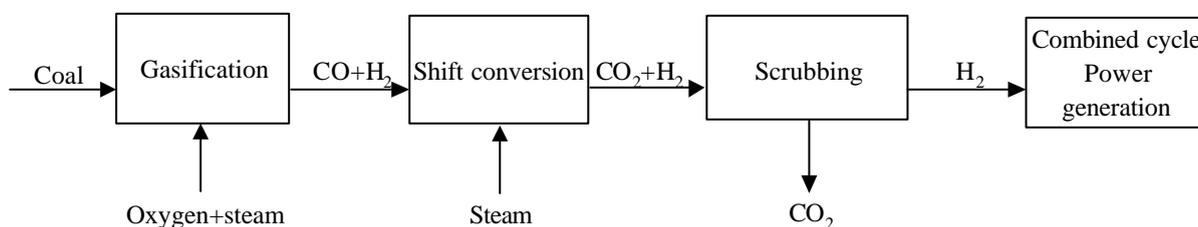
Conventional PF coal fired power generation with Flue Gas Desulphurisation (PF+FGD) is considered in PH3/14 as a host power generation process from which CO₂ may be abated by amine scrubbing of the flue gas at atmospheric pressure. The partial pressure of CO₂ in the flue gas is low, therefore the substitution of water scrubbing for amine scrubbing would result in excessively large amounts of water being required, resulting in excessive capital costs for the water supply, scrubbing and disposal system.

A detailed evaluation of the application of water scrubbing to PF+FGD is presented in Appendix A. In this evaluation the compression of the flue gas, to increase the partial pressure of CO₂, is considered. Compression of the flue gas prior to scrubbing would result in excessive energy penalties. It is concluded from the detailed evaluation presented in Appendix A, that direct scrubbing of flue gas from a PF+FGD plant is not appropriate for further investigation.

A preliminary technical and economic assessment of water scrubbing for the capture of CO₂ from shifted fuel gas in a coal-fired Integrated Gasification Combined Cycle (IGCC) scheme is also presented in Appendix A. This preliminary assessment does not exclude cases based on IGCC from further consideration. The PH3/14-C2w case is adopted as a basis for further study of the application of water scrubbing for CO₂ capture from coal fired power generation.

Figure 2-1 shows a simplified schematic of the integration of CO₂ abatement with a coal-fired IGCC process. The basic IGCC process involves coal gasification and combined cycle power generation. For CO₂ capture shift conversion and CO₂ scrubbing processes need to be added.

Figure 2-1 Outline of coal-fired IGCC with CO₂ scrubbing



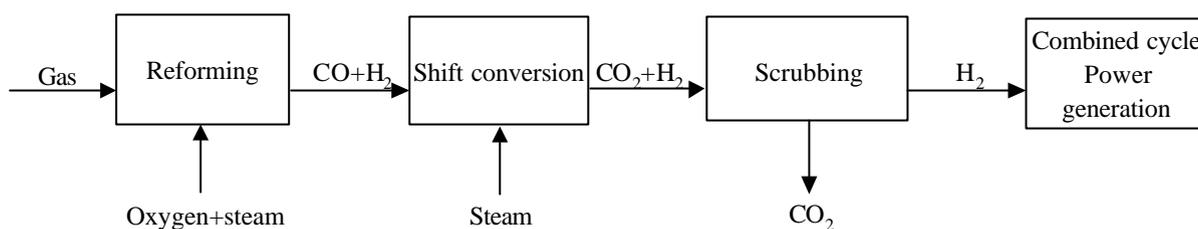
2.1.2 Natural gas based processes

Natural gas is less carbon intensive than coal. Therefore CO₂ concentrations in process streams are lower, making natural gas based power plants less amenable to the application of CO₂ abatement than coal based processes. In particular, the flue gas from a state-of-the-art gas fired combined cycle power plant, containing less than 5% CO₂ at atmospheric pressure is not suitable for seawater scrubbing.

Pre-combustion decarbonisation schemes for natural gas fired power plants were considered in IEA GHG studies PH2/19 and PH3/14. The merits of these schemes are considered in Appendix A, where it is concluded that case PH3/14-G2w is the most suitable for further evaluation.

Figure 2-2 shows a simplified schematic of the integration of CO₂ abatement with a natural gas combined cycle (NGCC) process. In the basic NGCC process natural gas is directly fired in a gas turbine in a combined cycle power plant. Precombustion decarbonisation involves reforming of natural gas (CH₄) to syngas (CO + H₂) followed by shift conversion and CO₂ scrubbing processes.

Figure 2-2 Outline of gas-fired NGCC with gas conversion and CO₂ scrubbing



2.1.3 Revision of reference case data

The PH3/14 cases C2w and G2w, which are adopted as the reference cases for this study, both involve shift conversion for increasing the CO₂ content of the fuel gas prior to scrubbing. In both cases Selexol solvent is nominated in PH3/14 for CO₂ scrubbing, with 97% CO₂ removal. Hence a high degree of shift conversion is not required to enable an overall CO₂ abatement of 85% to be achieved.

In the case of scrubbing with water, which is a much less effective CO₂ solvent than Selexol, less complete CO₂ capture can be achieved in the scrubber. Therefore a higher degree of shift conversion is required to achieve an overall carbon capture of 85%. The adaptation of the shift conversion section of the PH3/14 schemes and the determination of the consequent fuel loss penalties are presented in Appendix D.

2.2 WATER SCRUBBING PROCESSES

The concept of seawater scrubbing as an alternative to solvent scrubbing for the purpose of capture of CO₂ from an IGCC process was first published in 1993². This concept is based on a single process to replace a more complex scheme. The PH3/14-C2w scheme for power plant CO₂ recovery with ocean disposal involves solvent scrubbing of CO₂ from fuel gas, regeneration of the solvent with recovery of CO₂, CO₂ compression and liquefaction ready for CO₂ disposal to the deep ocean. The single water scrubbing process involves direct scrubbing of CO₂ from gases using seawater as a non-regenerable solvent. This process concept involves the discharge of large volumes of CO₂-laden seawater into the deep ocean, and is therefore best suited to a coastal power plant adjacent to steeply-shelving ocean floor.

² Costs of CO₂ Disposal Options. IR Summerfield, SH Goldthorpe, N Williams, A Sheikh. Paper to IEA Carbon Dioxide Disposal Symposium, Oxford. March 1993.

An extension of the seawater scrubbing concept has been proposed and patented³. This is a CO₂-hydrate capture concept, which involves chilling both the seawater and the gas to be scrubbed so that CO₂-hydrates form as a slurry in seawater at high pressure. This would have the potential to increase the CO₂ loading in the seawater to be piped to the deep ocean, thereby reducing the pumping and piping requirements significantly. Public domain information concerning the proposed CO₂-hydrate capture concept is discussed in detail in Appendix E. Based on that information, it is concluded that the necessary extent of formation of hydrates would not occur. Therefore further assessment of the concept is not included in this study.

The seawater scrubbing concept could also be considered in the context of fresh water pumped from and returned to a very deep lake or a deep aquifer. It is identified in Section 4 that there are no open freshwater resources of adequate depth and capacity to accommodate water scrubbing for CO₂ abatement. Aquifers are not suitable because the fast flows of water that would be required for extraction and reinjection would result in impracticably high pressure drops across water bearing strata. Therefore only scrubbing with seawater is considered in this study.

2.3 STEP-OFF CASES

The two reference cases are based on operating conditions in the scrubber of 12°C and 22 bar and a disposal pipeline length of 25 km. These are identified as key parameters influencing the potential for water based capture processes. Step-off cases are evaluated to quantify the sensitivity to these parameters, as described in Appendix A. Step-off values of 5°C, 20°C, 50 bar, 10 km and 100 km are used.

It is particularly noted that a low operating temperature enhances CO₂ capture via water scrubbing, because the solubility of CO₂ in water increases significantly as the temperature is reduced. In addition, the solubility of hydrogen is much less sensitive to temperature than CO₂, therefore the reduced water requirement at low temperature reduces the loss of fuel as dissolved hydrogen.

It is identified in Appendix F that most potential locations for seawater scrubbing are in tropical and sub-tropical regions where cold seawater is not readily accessible. A supply of cold sea water at 5°C might either be obtained by the water intake pipe being positioned in the deep ocean layer below the thermocline, or by chilling the water prior to use in the scrubber. The use of a chiller is evaluated in Appendix A and it is concluded that the consequent energy consumption would rule out this option. Therefore the cold water step-off case is evaluated on the basis of a long suction pipe drawing water from below the thermocline.

2.4 POWER PLANT EFFICIENCY IMPROVEMENT CONCEPT

The cold water step-off case involves the discharge of a large volume of cold water, at about 5°C into the deep ocean. Prior to disposal of this water it could potentially be used as the cooling medium for the power plant, resulting in process efficiency improvements and reduction in overall capital cost. An outline assessment of this concept is presented in Appendix A.

³ Hydrate Process Design for Extracting and Sequestering Carbon Dioxide from Power Plant Flue Gases or Shifted Synthesis Gas. Submitted to United States Department of Energy (IGCC/hydrate) – Fossil Energy Office of Coal and Power technology by Dwain F Spencer, Principal, SIMTECHE and J.S. White, Parsons Energy and Chemicals Group Inc. 16th February 1998.

This large heat sink would be at a substantially lower temperature than other sources of cooling likely to be available, particularly in a tropical climate. Thus a significant improvement in the thermal efficiency of an IGCC power plant might be obtained by reducing the condenser temperature in the power plant steam cycle. The amount of cooling water available is estimated to be sufficient to meet all of the cooling requirements of an IGCC power plant without reaching a temperature at which CO₂ would start to evolve from solution.

It is possible that a process scheme could be devised in which full integration of the seawater scrubbing process with the power plant cooling system might result in a significant improvement in the power plant thermal efficiency, particularly in a warm climate. This improvement may partly offset the energy penalty associated with CO₂ capture.

2.5 ACIDITY NEUTRALISATION WITH LIMESTONE

It is identified in Appendix G that the solution of CO₂ in seawater discharged into the deep ocean would be acidic, in the region of pH 4. As discussed in Appendix H, this acidity is likely to be a major environmental barrier to the use of seawater scrubbing as a means of CO₂ capture. In particular, the capacity of the discharged solution to dissolve calcium carbonate would be likely to result in adverse environmental effects at the point of discharge from the seawater scrubbing system into the deep ocean.

It is suggested by Rau and Caldiera⁴ that the discharge of CO₂ in the form of a solution of calcium bicarbonate would be likely to be more environmentally acceptable than the discharge of CO₂ as carbonic acid into the ocean. Therefore the concept of acidity neutralisation with limestone prior to discharge is briefly considered for the reference IGCC-coal case.

- A solution of CO₂ in seawater will react with calcium carbonate (limestone) to form calcium bicarbonate according to the equation



- Table B-3 in Appendix B indicates that the effluent from the reference case seawater scrubbing scheme would comprise 6.1 m³/s of water with a loading of 1.24% CO₂ by weight.
- Figure G-2 in Appendix G indicates that, at 1.24% CO₂ by weight in water, the effluent would have the capacity to dissolve up to 3.5 grams of CaCO₃ per litre of solution and in doing so would increase the pH of the solution from about pH 4.2 to about pH 5.6. The solution would then be saturated with bicarbonate and unable to dissolve more limestone.
- At pH 5.6 the discharged water would still probably be unable to sustain marine life until further diluted after discharge.
- The rate of dissolution of limestone would be 77 tonnes per hour, which is about half of the flowrate of coal to the power plant. Very large equipment and finely ground limestone would be required.
- Impurities in the limestone would tend to build up in the acid neutralising equipment and thereby would inhibit the rate of reaction and would contaminate the discharged solution.

⁴ Enhanced carbonate dissolution: a means of sequestering waste CO₂ as ocean bicarbonate. G.H. Rau and K Caldiera. Energy Conversion and Management (40) 1999 1803-1813.

These preliminary considerations indicate that partial neutralisation with limestone of the acidity of the discharged solution of CO₂ in sea water would not completely eliminate the problem of acidity. It is also likely to incur some major economic penalties. Therefore this process concept is not evaluated further.

Technical and economic evaluations of the two reference cases and twelve step-off cases are presented in Appendix B. Figure 3-1 shows a simple schematic process flow diagram of the seawater scrubbing process area, with mass balance data for the two reference cases. A simple process schematic illustrating the additional plant required for the high-pressure step-off cases is included in Appendix B.

3.1 PROCESS DESCRIPTION

CO₂ is removed from shifted fuel gas in packed scrubber columns by contact with a counter current flow of seawater. The scrubbed fuel gas is subsequently used in a gas turbine for power generation. Prior to use in a gas turbine the hydrogen-rich gas would need to be conditioned by scrubbing with clean water. This gas conditioning process step is included in the process definitions for the framework cases PH3/14 C2w and G2w. However, some modification to the gas conditioning stage might be required to ensure any carry-over of alkaline salts from the seawater is dealt with.

The scrubber column nominal design is based on the use of multiple columns that are a maximum of 4 m diameter. The calculated column heights range from 18 to 25 m. The number of columns required range from 4 for the coal case using cold water at high pressure, through to 13 for the natural gas case using warm water without additional gas compression.

The scrubber effluent is piped to a discharge point 1500 m deep in the ocean. The pipeline length is site specific. Cases are evaluated based on disposal pipeline lengths of 10 km, 25 km and 100 km. The diameter of the single disposal pipeline is determined to utilise the pressure at the base of the column to overcome the pipeline pressure drop, thereby avoiding the need for booster pumps. The required disposal pipeline diameters range from 700mm for the 10 km pipeline for the high pressure case based on coal, through to 2.0 m diameter for the 100 km pipeline for the natural gas case. Pipelaying constraints may alternatively require the use of multiple pipelines.

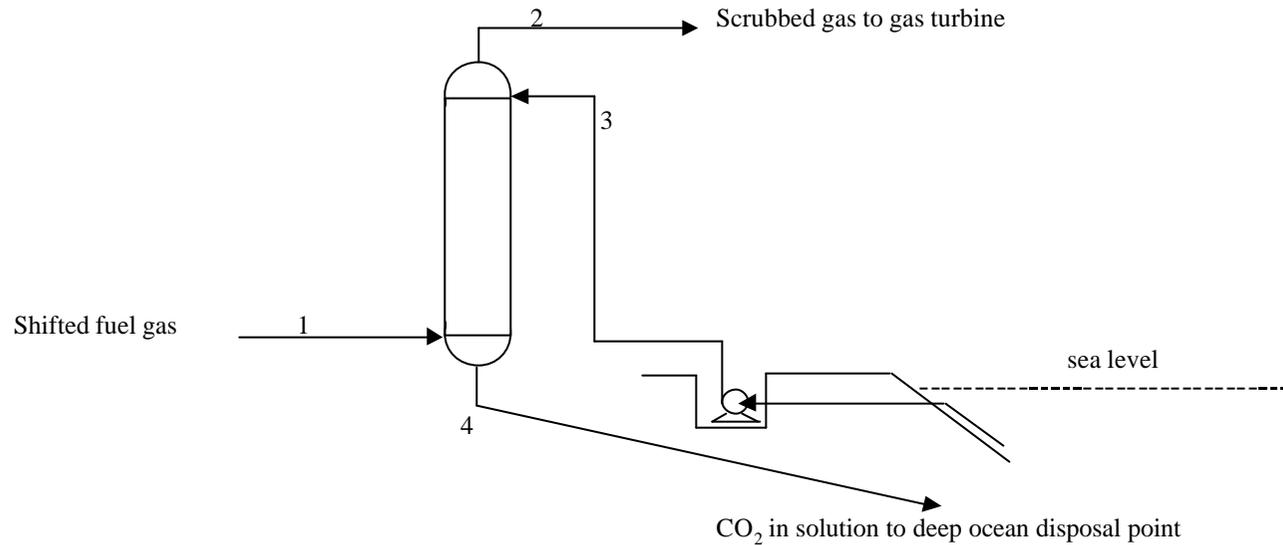
The water supply is assumed to be pumped from a point 200 m deep in the ocean via a single pipe. The suction pump is located 20 m below sea level to avoid cavitation. The required suction pipeline diameters range from 1 m to 1.7 m. There is significant advantage to be obtained by the use of cold water. Therefore some cases are evaluated in which cold water is supplied from 1000 m depth. In the gas case, the suction pump would have to be 25m deep to keep the required single pipeline diameter within the 2 m criterion.

In the cases where the operating pressure of the scrubber column is elevated to 50 bar there would be consequential impacts on other aspects of the power plant design. However, for comparability with the 22 bar cases, the high pressure scrubbing cases are evaluated on the basis of compression of the fuel gas from 22 bar to 50 bar, cooling against the scrubber product gas, scrubbing at 50 bar, reheating the product gas against the compressor output and recovery of some of the pressure energy in an expander from 50 bar back down to 22 bar. This process variant is described in Appendix B.

3.2 ASSESSMENT RESULTS

Tables 3-1 and 3-2 show a summary of the detailed assessment results, which are presented in full in Appendix B. In Tables 3-1 and 3-2 the contributions to the energy penalty and the capital cost penalty are compared with equivalent data for the reference cases, C2w and G2w from PH3/14.

Figure 3-1 Outline process flow diagram for seawater scrubbing reference cases



	Reference case based on coal				Reference case based on gas			
	1	2	3	4	1	2	3	4
Mass flow (kg/s)	100.04	22.15	6269.5	6347.4	110.0	26.6	9236.9	9320.3
Pressure (bar)	22	21.35	21.35	22	22	21.48	21.48	22
Temperature (C)	35	12	12	12	35	12	12	12
Component flows (kg/s)								
H ₂ O	-	-	6269	6269	-	-	9237	9237
CO ₂	87.65	9.87	-	77.78	92.95	9.76	-	83.19
H ₂	5.83	5.74	-	0.09	11.44	11.27	-	0.17
CO	1.87	1.84	-	0.03	2.92	2.88	-	0.04
N ₂ etc.	4.68	4.68	-	0.00	2.70	2.70	-	0.00

Table 3-1 CO₂ scrubbing and disposal - Coal fired power generation

	PH3/14 Case C2w	Seawater scrubbing reference case	Warm water supply	Cold water supply	High pressure scrubber	Long disposal pipe	Short disposal pipe	Short pipe high pres cold water	Least cost high pres. short pipe
Electricity output reduction - MW									
Due to additional LT shift	-	4.1	4.1	4.1	4.1	4.1	4.1	4.1	4.1
Due to fuel gas loss in scrubber	2.5	5.6	7.0	4.7	6.2	5.6	5.6	5.2	6.2
CO ₂ scrubber pumping	5	21.9	27.6	17.4	21.5	21.8	21.8	17.2	21.5
CO ₂ /fuel gas compression	25	0	0	0	10.1	0	0	10.1	10.1
Total electricity penalty - MWe	32.5	31.6	38.7	26.2	41.9	31.6	31.6	36.5	41.9
(for CO ₂ scrubbing and disposal)									
Net power output - MWe	382	383	376	388	373	383	383	378	373
Capital costs - US\$ million									
Capture system (excluding shift)	42.5	20.2	24.4	16.8	14.2	20.2	20.2	11.9	14.2
CO ₂ /gas compression	27.9	0.0	0.0	0.0	5.8	0.0	0.0	5.8	5.8
Water pumps	-	16.9	18.2	15.9	16.9	16.9	16.9	15.9	16.9
Water supply pipeline	-	2.9	3.2	41.3	2.0	2.9	1.7	7.5	1.2
Disposal pipeline	6	34.9	38.2	31.7	21.0	192.7	11.4	6.1	6.6
Total capital cost penalty - US\$M (for CO ₂ scrubbing and disposal)	76.4	75.0	83.9	105.7	59.8	232.7	50.3	47.1	44.7

Table 3-2 CO₂ scrubbing and disposal - Gas fired power generation

	PH3/14 Case G2w	Seawater scrubbing reference case	Warm water supply	Cold water supply	High pressure scrubber	Long disposal pipe	Short disposal pipe
Electricity output reduction - MW							
Due to additional LT shift	-	6.5	6.5	6.5	6.5	6.5	6.5
Due to fuel gas loss in scrubber	16.5	10.8	13.4	8.9	11.4	10.8	10.8
CO ₂ scrubber pumping	5	32.9	41.5	26.6	31.0	32.9	32.9
CO ₂ /fuel gas compression	27	0	0	0	14.6	0	0
Total electricity penalty - MW	48.5	50.1	61.4	42.0	63.5	50.1	50.1
(for CO ₂ scrubbing and disposal)							
Net power output – MWe	820	818	807	827	805	818	818
Capital costs - US\$ million							
Capture system (excluding shift)	45.2	35.0	42.3	29.2	23.6	35.0	35.0
CO ₂ /gas compression	29.4	0.0	0.0	0.0	8.2	0.0	0.0
Water pumps	-	19.2	20.9	17.9	18.8	19.2	19.2
Water supply pipeline	-	3.4	3.9	46.8	4.1	3.4	2.2
Disposal pipeline	6	41.4	46.5	36.5	24.0	227.2	13.3
Total capital cost penalty - US\$M (for CO ₂ scrubbing and disposal)	80.6	99.1	113.5	130.6	78.7	284.8	69.7

Table 3-3 Comparison of CO₂ abatement cost with case PH3/14-C2w

	PH3/14 C2w	Seawater scrubbing reference case	Warm water supply	Cold water supply	High pressure scrubber	Long disposal pipe	Short disposal pipe	Short pipe high pres cold water	Least cost high pres. short pipe
MWe sent out	382	383	376	388	373	383	383	378	373
Total investment (US\$million)	807	806	816	842	788	992	777	773	770
Capital charge (US\$/kWh)	3.26	3.25	3.29	3.40	3.18	4.00	3.13	3.12	3.11
Fuel and other costs (US\$/kWh)	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65	3.65
Production costs (US\$/kWh)	6.91	6.90	6.94	7.05	6.83	7.65	6.78	6.77	6.76
Prod. cost w/o CO ₂ rem (US\$/kWh)	4.78	4.78	4.78	4.78	4.78	4.78	4.78	4.78	4.78
Production cost increase (US\$/kWh)	2.13	2.12	2.16	2.27	2.05	2.87	2.00	1.99	1.98
CO ₂ emitted (kg/sec)	14	14	14	14	14	14	14	14	14
CO ₂ emitted (kg/MWh)	134	134	136	132	137	134	134	135	137
CO ₂ emitted w/o CO ₂ rem (kg/MWh)	710	710	710	710	710	710	710	710	710
CO ₂ reduction (kg/MWh)	576	576	574	578	573	576	576	575	573
Cost of CO₂ capture (US\$/ton CO₂)	36.9	36.8	37.7	39.2	35.7	49.8	34.7	34.6	34.5

Table 3-4 Comparison of CO₂ abatement cost with case PH3/14-G2w

	PH3/14 Case G2w	Seawater scrubbing reference case	Warm water supply	Cold water supply	High pressure scrubber	Long disposal pipe	Short disposal pipe
MWe sent out	820	818	807	827	805	818	818
Total investment (US\$million)	712	734	751	771	710	953	699
Capital charge (USc/kWh)	1.10	1.14	1.16	1.20	1.10	1.48	1.08
Fuel and other costs (USc/kWh)	2.34	2.34	2.34	2.34	2.34	2.34	2.34
Production costs (USc/kWh)	3.44	3.47	3.50	3.53	3.44	3.81	3.42
Prod. cost w/o CO ₂ rem (USc/kWh)	2.16	2.16	2.16	2.16	2.16	2.16	2.16
Production cost increase (USc/kWh)	1.28	1.31	1.34	1.37	1.28	1.65	1.26
CO ₂ emitted (kg/sec)	14.9	14.9	14.9	14.9	14.9	14.9	14.9
CO ₂ emitted (kg/MWh)	65	66	66	65	67	66	66
CO ₂ emitted w/o CO ₂ rem (kg/MWh)	370	370	370	370	370	370	370
CO ₂ reduction (kg/MWh)	305	304	304	305	303	304	304
Cost of CO₂ capture (US\$/ton CO₂)	42.0	43.1	44.1	44.9	42.0	54.3	41.4

These cost and energy loss comparisons relate only to the CO₂ capture and disposal components on the process scheme and do not include shift conversion or other common elements of the whole power plant modification which would be required for the integration of CO₂ abatement.

The data in Table 3-1 show that the seawater scrubbing reference case based on coal has a slightly lower energy loss and capital cost penalty than the comparable cases based on the use of Selexol scrubbing. The smallest energy penalty is obtained for the case based on the use of cold water without gas compression. However in this case the capital costs of the suction pipeline becomes a significant item.

The lowest capital costs are obtained for the cases involving gas compression where the additional equipment costs are more than offset by reduced column and pipeline costs, but the energy penalty is increased.

The data in Table 3-2 show that the seawater scrubbing reference case based on natural gas has a slightly higher energy loss and capital cost penalty than the comparable case reported in PH3/14. In the case of the use of cold water an improvement in energy penalty is noted, but the capital cost penalty is greater.

The energy penalties and the capital cost penalties are generally higher for the cases based natural gas compared with those based on coal. However Case G2w has a power output of 820 MW compared with 382 MW for Case C2w.

Tables 3-3 and 3-4 show the combined impacts of energy loss, capital cost and power plant scale to give a net cost of CO₂ capture in comparison with values for the cases based on solvent scrubbing. The absolute values of the bottom line costs of CO₂ capture are subject to significant uncertainty due to the assumptions made in the contributing studies. However, when compared on a relative basis, these assessment results indicate that the seawater scrubbing cases based on a short pipeline are estimated to have a lower cost of CO₂ abatement than a comparable solvent scrubbing process.

To maintain the CO₂ in solution, thereby preventing its release to the atmosphere, the CO₂-laden water would need to be discharged at a depth where the CO₂ would be diluted and dispersed so that it would not come out of solution and be released to the atmosphere. To meet this requirement, this study is based on a discharge depth of 1500 m, where the hydrostatic pressure is about 150 bar.

The requirement for the CO₂-laden water to be discharged at a depth of 1500 m excludes freshwater lakes as potential storage sites. The only freshwater lake that exceeds this depth is Ozero Baykal in Russia, which reaches 1940 m at its deepest point but is mostly less than 1000 m deep. Also water contained in aquifers is excluded because the fast flow of water that would be required is likely to be incompatible with the slow water movements which occur in aquifers. Therefore only seawater scrubbing is considered in this study.

A major capital cost item for a seawater scrubbing scheme would be the disposal pipeline used to transport the effluent to a deep-water location. There is also a significant energy loss associated with pumping water down a long pipe. Therefore a limit of 100 km as the length of a disposal pipeline has been adopted for this study. There are many locations in the world where the 1500 m ocean floor contour is less than 100 km from land. Appendix F details a survey of the world's coastline, which has used this criterion and others to identify potential opportunities for application of the seawater scrubbing concept.

The key criteria used to identify potentially suitable states and locations for coastal seawater scrubbing installations are:-

- A maximum distance of 100 km to the 1500 m contour and water deeper than 2000 m beyond the 1500 m contour
- Direct deep level connection to the deep water of a major oceans
- At least one million population in the state per 500 MW power plant installation
- Proximity of a large center of population within reasonable access, via transmission lines
- Spacing of location on a coastline to allow exclusive access to 25,000 cubic kilometers of deep ocean water
- At least 4 TWh of thermal power generation in 1991/92 per 500 MW power plant installation

On the basis of these criteria, 89 potential locations are identified in Appendix F. Table 4-1 shows a summary of this world coastline survey.

Table 4-1 Summary of results of world coastline survey

Pipe length range	Number of locations	Average pipe length	Average sea temp.
Up to 10 km	11	5.5 km	27°C
11 km to 25 km	20	16 km	21°C
26 km to 50 km	28	39 km	21°C
51 km to 100 km	30	70 km	20°C

A significant outcome of this world coastline survey is illustrated in Table 4-1 and discussed further in Appendix F. All of the 11 locations where the 1500m deep water is within 10km of land are in tropical regions where the sea temperature is above 25°C. Therefore it is unlikely that a source of cool seawater could readily be obtained. In general, the lower latitude locations where cooler water would be available correspond to longer distances to the 1500m contour.

However, Table F-2 in Appendix F shows that there are six locations where the pipeline length would be less than 20 km, where the sea surface temperature is less than 20°C and where there is a large local population to provide a demand for electricity. These are at Matsukaki, Shiono-misaki and Nojima-Zaki in Japan, Santander in Spain, Sagres in Portugal and Monterey in California. These locations are probably the most favourable for the implementation of seawater scrubbing.

The solution of CO₂ in seawater forms carbonic acid. Acidification of seawater is a potentially significant adverse environmental effect. Appendix G presents a prediction of the effect of the dissolution of pressurised CO₂ on the pH of seawater. It is estimated that the acidity of the CO₂ solution discharged into the deep ocean will be about pH 4.

Seawater with a pH less than 6.5 is lethal to most coastal marine organisms. Oceanic species are likely to be more sensitive to environmental change due to the stability of their deep-sea environment. Sub-lethal effects on reproduction, growth, metabolic rates and longevity would be experienced with smaller decreases in pH from the normal value of about pH 8. Limited knowledge of the physiological tolerance of inshore coastal species indicates that a pH of 7.5 would be the lower limit for many species.

Consideration of chemical equilibria in Appendix G indicates that seawater is generally super saturated in calcium carbonate and that reduction of pH to below about 7.8 would eliminate super saturation. Since marine life is adapted to its super-saturated environment, it is reasonable to assume that environmental effects would begin to occur if seawater ceases to be supersaturated in calcium carbonate. It is estimated in Appendix G that dilution of the discharged seawater by a factor of about 4000 would be required to avoid crossing this threshold. This level of dilution is used as the basis for the capacity estimates discussed in Section 6.

These considerations indicate that the environmental consequences of discharges of CO₂ into stationary deep-ocean water are unlikely to be considered to be environmentally acceptable.

The capacity of the world's oceans as a sink for dissolved CO₂ is immense. However, some deep ocean currents are slow moving and may not be able to disperse injected CO₂-laden water quickly. As a worst case, the deep ocean is considered as a stationary body of water into which acidic water is injected and remains in the locality of the injection point. It is identified in Section 5 that dilution of the discharged CO₂ solution by a factor of 4000 would be required to reduce the acidity to a potentially acceptable level.

The dispersion of a plume of discharged water in the deep ocean would be very uncertain and site specific. For the purpose of providing a basis for estimating the minimum spacing between CO₂ seawater scrubbing installations, a 4000 fold dilution within the local body of water is assumed. On this basis, the maximum capacity for worldwide CO₂ abatement via seawater scrubbing is estimated in Appendix I.

The installation of one 500 MW power plant with seawater scrubbing at each of the 89 locations identified in Appendix F would result in the capture of 260 million tonnes of CO₂ per year corresponding to about 3% of the world emissions from coal fired power generation. However, this estimate is very uncertain due to dispersion considerations.

The environmental impact of the discharge of acidic CO₂ into a stationary body of water is unlikely to be acceptable. Therefore seawater scrubbing could probably only be installed where deep ocean currents exist with the capacity to dilute and disperse the injected solution of CO₂ immediately.

The existence of suitable deep ocean currents adjacent to the identified locations for seawater scrubbing installations could increase their capacity of seawater scrubbing plants up to the point where it is constrained by the demand for electricity. These issues are discussed further in Appendix I.

This wide-ranging study of CO₂ capture using water scrubbing has involved outline assessment of many issues for the purpose of identifying whether the concept of water scrubbing is worth further investigation. A number of possible avenues of investigation have been ruled out and some significant uncertainties have been identified. The following topics are proposed for further site-specific investigations, with a view to establishing the contribution that water scrubbing might make to the availability of CO₂ abatement technologies.

- Further evaluation of the integration of water scrubbing with power plant cooling
- Investigation of deep ocean currents and dispersion
- Study of the environmental impacts of acidified water on marine biota and deposits

- A preliminary assessment of host power generation processes indicates that the most appropriate process streams for the application of seawater scrubbing are shifted fuel gas in a coal fired IGCC power plant and shifted reformed natural gas in an NGCC power plant with pre-combustion decarbonisation.
- Parameters that have a major influence on the performance and cost of a seawater scrubbing process include the operating temperature and pressure of the scrubbing columns and the length of the disposal pipeline.
- The use of cold water has significant advantages for seawater scrubbing and may provide opportunities for additional beneficial process integration.
- Public domain information concerning the use of water/hydrate mixtures for CO₂ capture has been considered in detail. Based on that information, it is concluded that the necessary extent of formation of CO₂ hydrates would not occur.
- A review of the coastline of the world has resulted in identification of 89 potential sites for installation of 500 MW power plants with seawater scrubbing. These are subject to the principal criteria that the disposal pipeline should be no longer than 100 km and that the spacing of installations should avoid compounding environmental effects.
- 13% of the potential power plant disposal sites are within 10 km of the corresponding deep ocean disposal point and 35% of the potential sites are within 25 km of the disposal point.
- If deep ocean mixing currents are sufficient, such that dispersion is not a limiting factor, then the world wide-capacity for CO₂ abatement via seawater scrubbing would be significantly increased.
- The estimated capacity for seawater scrubbing to contribute to CO₂ emission mitigation corresponds to about 3-14% of the projected world coal-fired power generation in the year 2020.
- The water discharged into the deep ocean would have an acidity of about pH 4. Therefore the water in the vicinity of the disposal pipeline would be unable to support marine life.
- The environmental requirement for the acidic water to be diluted and dispersed in the oceans could be an overwhelming constraint preventing application in locations where there are no deep ocean currents.
- The locations of the potential seawater scrubbing sites are predominantly in tropical and subtropical regions.
- Comparison of assessment results indicates that the seawater scrubbing cases based on a short disposal pipeline are estimated to have lower costs of CO₂ abatement than comparable conventional scrubbing processes.

Appendix A
Process Selection

Appendix B
Technical and Economic Assessment

Appendix C
Solubility of CO₂ in Seawater

Appendix D
Definition of Modelling Boundary Conditions

APPENDIX D

Definition of Modelling Boundary Conditions

D.1 PURPOSE

The objective of this study of the capture of CO₂ using water scrubbing is to assess the implications of seawater scrubbing as a means of removing carbon dioxide from a high pressure fuel gas, as an alternative technology to conventional scrubbing processes. This assessment is to be comparable with the CO₂ scrubbing component of the whole of system studies that have been carried out by Stork Engineering Consultancy B.V. (IEA GHG report PH3/14). It is identified in Appendix A that PH3/14 cases C2w and G2w are the most appropriate to use as a basis for this study.

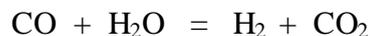
The PH3/14 cases C2w (coal-based) and G2w (gas based) incorporate a Selexol scrubbing process for removing CO₂ from the shifted fuel gas, followed by a CO₂ compression and liquefaction section. A CO₂ disposal system would also be required to complete the abatement scheme, but was not included in PH3/14. These are the process components that are to be replaced by a direct-contact seawater scrubbing system. The fuel gas process streams into and out of the scrubbing system are identified as the boundary points for the purposes of comparative assessment.

The purpose of this Appendix is to define the PH3/14 data in a form that can be compared with the seawater scrubbing option.

D.2 REVISION OF SCRUBBER FEED STREAM DATA

Table D-1 shows the Selexol scrubber inlet and outlet streams for PH3/14 cases C2w and G2w at the “scrubbing” boundary points. These data show that 85% overall removal of CO₂ from the power plant is achieved by partial conversion of CO to CO₂ in the shift reactor, followed by 98% removal of CO₂ in the Selexol scrubbing system.

In the case of seawater scrubbing such a high level of CO₂ removal in the scrubber is not achievable. Therefore, to obtain an overall removal of 85% of the carbon from the fuel gas, a greater conversion of CO to CO₂ must first be obtained in the shift conversion stage prior to the scrubber. The shift reaction replaces the carbon monoxide component of the fuel with hydrogen fuel according to the equilibrium reaction:-



The extent of conversion of CO to CO₂ via the shift equilibrium can be increased either by a reduction in temperature, which affects the equilibrium position, or by addition of extra steam.

In PH3/14-C2w the shift conversion process is modelled as two stages with extensive heat recovery between the stages. Table D 2 shows key features of the low temperature shift reported in PH3/14. The values for the G2w case are in line with the minimum practicable shift exit temperature and shift equilibrium approach.

Appendix D – Definition of Modelling Boundary Conditions

These data indicate that there is no scope for further reduction in the shift exit temperature. Therefore increased CO conversion must be achieved by steam addition.

Table D-1

PH3/14 scrubber stream data

	C2w inlet	C2w outlet	G2w inlet	G2w outlet
Mass flow – kg/s	97.06	19.28	106.4	23.4
Temperature – C	37	34	37	45
Pressure – bar	20	20	20	20
Fuel content (MW – lhv)	733	728	1438	1405
Mass flows – kg/s				
CO	7.35	7.21	7.68	7.40
H ₂	5.48	5.45	11.13	10.88
CO ₂	79.12	1.58	84.17	1.64
CH ₄	0	0	0.49	0.48
H ₂ O	0.55	0.48	0.51	0.44
N ₂	3.25	3.25	0.61	0.60
Ar	1.31	1.31	2.0	1.95
Composition – mole %				
CO	5.29	8.11	3.5	4.54
H ₂	54.85	85.24	70.44	92.68
CO ₂	36.24	1.13	24.4	0.64
CH ₄	0	0	0.39	0.51
H ₂ O	0.61	0.84	0.36	0.42
N ₂	2.34	3.65	0.28	0.37
Ar	0.66	1.03	0.64	0.84

Table D-2 – LT shift data from PH3/14 study

Case	C2W	G2W
LT shift exit temp	177	206
Equilibrium temperature corresponding to LT shift exit composition	207	240
Extent of CO conversion in LT shift	64%	72%

Appendix D – Definition of Modelling Boundary Conditions

For the purpose of defining a basis for revision of the boundary conditions, a minimum LT shift exit temperature is assumed to be 230°C. At that temperature, a temperature approach to shift equilibrium of 5 degrees is assumed. Hence the equilibrium temperature corresponding to LT shift exit composition is assumed to be 235°C. On this basis additional steam must be added to the LT shift feed so that the extent of conversion of carbon monoxide can be increased to more than 90%.

A revised process scheme has been devised for the low temperature shift process area of the PH3/14 C2w and G2w cases, in which some of the rejected heat is used to raise process steam for injection prior to the low temperature shift reactor. Additional shift conversion results in the release of additional heat. In this revised configuration, the heat recovery scheme has been arranged to match the supply of heat to the steam cycle in the PH3/14 as far as possible, whilst ensuring that adequate temperature differentials are maintained throughout the process area. The effects of this revision external to the low temperature shift process area are shown in Table D3.

Table D-3
Effects of revision of LT shift process area

	C2w PH3/14	C2w revised	G2w PH3/14	G2w revised
CO conversion in LT shift	64%	91%	72%	92%
%CO in scrubber feed	5.3	1.3	3.5	1.0
%CO ₂ in scrubber feed	36.2	38.7	24.4	26.3
% H ₂ in scrubber feed	54.9	56.7	70.4	71.2
Fuel energy in scrubber feed - MW-lhv	732.9	724.9	1438.7	1430.6
High temp. heat to steam cycle – MW	31	31	57	57
Low temp. heat to steam cycle – MW	52	52	96	80
Electricity required for pumping - MW	0	0.013	0	0.018
Overall penalty as electricity loss* - MW		4.1		6.5

*Assuming fuel gas to electricity conversion of via CCGT of 50% and low temperature heat to electricity conversion via steam cycle of 15%.

Table D-3 shows that the net external effects of arranging additional CO conversion prior to fuel gas scrubbing are equivalent to a loss of 4.1 MW of electricity for the C2w case and 6.5 MW of electricity for the G2w case. In addition, the equipment configuration required for the low temperature shift process area might result in an increase in capital cost.

Appendix D – Definition of Modelling Boundary Conditions

D-3 OTHER REFERENCE DATA

Table D-4
Reference data from IEA GHG PH3/14 report

	Case C2w	Case G2w
Mass of CO ₂ captured – kg/s	77.54	82.53
CO ₂ discharged to atmosphere – kg/s	13.05	15.54
CO ₂ capture fraction	85.6%	84.2%
Net power generation – MWe	382	820
Total CO ₂ /MWh	854	431
Electricity required for CO ₂ recovery – MWe	5	5
Electricity required for CO ₂ compression - MWe	25	27
Capital costs – US \$ million		
Total CO ₂ capture system	106.5	296.9
Shift conversion etc. (60%)*	64	251.7
CO ₂ scrubbing process area (40%)*	42.5	45.2
Capital cost of CO ₂ compression - \$m	27.9	29.4
CO ₂ disposal pipeline	6	6

*PH3/14 does not include a capital cost breakdown for the additional CO₂ capture plant, which essentially comprises a shift conversion process area and a CO₂ scrubbing process area. A capital cost breakdown of equipment for CO₂ removal from a coal fired IGCC power plant is included in the 1994 IEA Greenhouse Gas Full Fuel Cycle Study. In the Full Fuel Cycle study the ratio of the capital cost of the shift conversion and CO₂ scrubbing process areas was 60%:40%.

In the case of the NGCC power plant with precombustion decarbonisation the CO₂ capture system includes an additional air separation plant and reformer. This accounts for the higher capital cost of the total CO₂ capture system for Case G2w. The portion of the total cost which is attributable to CO₂ scrubbing is determined from Case C2w, pro-rata on the amount of CO₂ removed.

D-4 DISPOSAL COSTS

PH3/14 does not address the issue of disposal of the separated CO₂. It is based on delivering a stream of pure CO₂ at 110 bar pressure to the plant boundary. For

Appendix D – Definition of Modelling Boundary Conditions

consistency with this seawater scrubbing study, it is assumed that this CO₂ would be disposed of via a 25 km pipeline to an ocean disposal point at a depth of 1500m. Since the volume of pure CO₂ is much less than CO₂ in solution, the disposal of 80 kg/s of supercritical CO₂ could be achieved with a 300 mm diameter pipeline. Using the approximate pipeline costing formula defined in Appendix A, the capital cost of this CO₂ disposal facility would be \$6 million for a 25km long disposal pipe. For comparison with step-off cases, the liquid CO₂ disposal pipeline is estimated to cost \$2.4 million for 10 km or \$24 million for 100 km.

Appendix E
Discussion of a CO₂-hydrate Formation Process

APPENDIX E

Discussion of a CO₂-Hydrate Formation Process

E.1 INTRODUCTION

This report on capture of CO₂ using water scrubbing investigates the potential for once-through water scrubbing technologies to contribute to CO₂ emission mitigation. This potential is constrained by the solubility of CO₂ in water, resulting in the need for large volumes of water, high plant cost and significant consumption of energy. The solubility of CO₂ in water is enhanced by a high partial pressure of CO₂ in the gas phase. Therefore this study of a CO₂ emission mitigation technology focuses primarily on potential practical applications involving the scrubbing of CO₂ from shifted synthesis gas at high pressure.

If a higher loading of CO₂ in water could be achieved then substantial benefits would result. The solubility of CO₂ in water is enhanced at low temperature and high pressure. These conditions also favour the formation of CO₂-hydrates, which would have the potential to provide a substantially higher loading of CO₂ in water than can be obtained by solubility alone. The formation of CO₂-hydrate, (CO₂)₈·(H₂O)₄₆ also known as CO₂ clathrate, is the basis of a patented¹ proprietary process, referred to hereafter as a CO₂-hydrate formation process.

E.2 PROCESS DESCRIPTION

A CO₂-hydrate formation process is described in detail in a report submitted to US DOE². This report describes a hydrate formation process for integration with an IGCC process and is referred to hereafter as the "IGCC/hydrate" report. The principles of the CO₂-hydrate formation process, and some of the claims made in the IGCC/hydrate report for CO₂ removal from shifted synthesis gas using water in an IGCC application, are discussed here. Other variants of the concept are identified in reports and patents listed in Appendix J.

The CO₂-hydrate formation process comprises two stages referred to as a CO₂ nucleation reactor and a CO₂-hydrate reactor. In the CO₂ nucleation reactor cold water is contacted in a counter-current scrubber tower with about 30% of the shifted synthesis gas.

¹ US patents 5,562,891 (8th Oct 1996) and 5,700,311 (23rd December 1997)

² Hydrate Process Design for Extracting and Sequestering Carbon Dioxide from Power Plant Flue Gases or Shifted Synthesis Gas. Submitted to United States Department of Energy (IGCC/hydrate) – Fossil Energy Office of Coal and Power technology by Dwain F Spencer, Principal, SIMTECHE and J.S. White, Parsons Energy and Chemicals Group Inc. 16th February 1998.

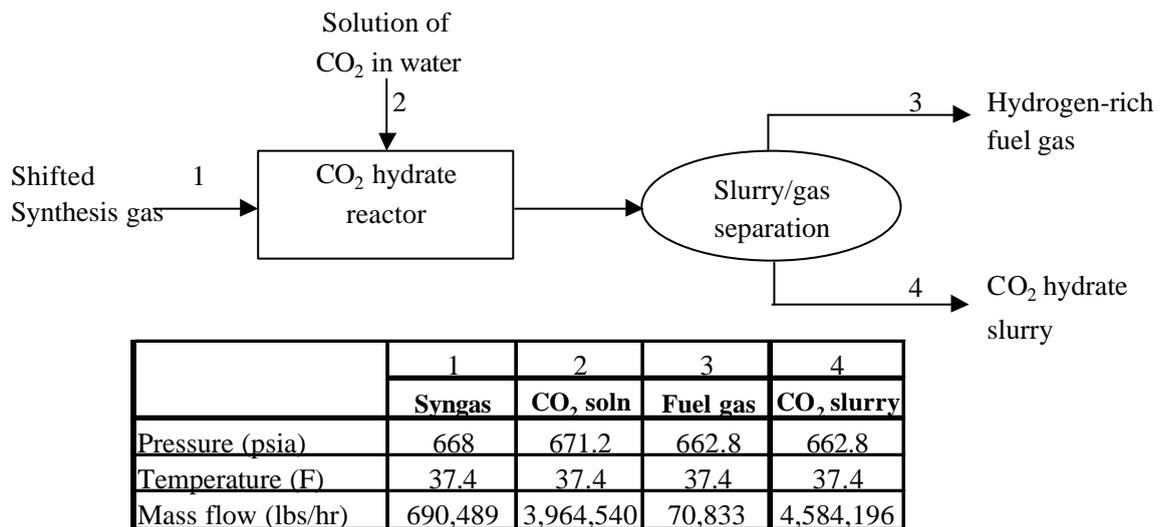
Appendix E – Discussion of a CO₂-Hydrate Formation Process

This process is carried out at a temperature of approximately 3°C and at a system pressure of approximately 45 bar. The scrubber tower is cooled by an ammonia refrigeration cycle. The CO₂ nucleation reactor saturates the water with CO₂ at the partial pressure of CO₂ in the feed gas and produces CO₂ nucleated water³.

In the CO₂-hydrate reactor, the cold CO₂ nucleated water is contacted with the remaining 70% of the shifted synthesis gas in a turbulent externally cooled co-current reactor. This process also occurs at approximately 3°C and 45 bar. Heat is extracted by an external ammonia refrigeration cycle. Further details of this process are proprietary.

The IGCC/hydrate report presents a conceptual plant design for a hydrate production system for integration with an IGCC plant. The CO₂-hydrate reactor element and the slurry/gas separation element of this conceptual design are reproduced in Figure E-1.

Figure E-1 – Outline of conceptual design for CO₂-hydrate formation process



The component mass balances corresponding to this part of the CO₂-hydrate formation conceptual design can be derived with the following additional information provided in the IGCC/hydrate report.

- CO₂ in the shifted synthesis gas is 39 volume percent
- H₂/CO ratio in the shifted synthesis gas is approximately 30
- The water solubilities of other gas species present in the fuel gas are low
- The amount of gas dissolved in the nucleation reactor is 268,565 lbs/hr
- The extent of CO₂ removal from the shifted synthesis gas is 90%.

³ CO₂ nucleated water is a term used in the IGCC/hydrate report to refer to a saturated solution of CO₂ in water at a low temperature from which CO₂ hydrates can readily be formed.

Appendix E – Discussion of a CO₂-Hydrate Formation Process

90% CO₂ removal corresponds to an overall carbon removal of 87% when carbon monoxide is taken into account. This is in line with the level of carbon capture that is studied in this report. The mass flow of fuel gas of 70,833 lbs/hr, shown on Figure E-1, corresponds to 99% CO₂ removal or 96% overall carbon capture. With 90% CO₂ removal, the mass flow of fuel gas would be 153,150 lbs/hr.

The concentration of fuel hydrogen in the scrubber output and hydrate slurry streams is calculated from the solubility of hydrogen in water at 3°C, where the partial pressure of hydrogen in the gas phase is 5.96×10^4 times the mole fraction of hydrogen in the liquid phase.⁴

A component mass balance is presented in Table E-1 for the streams shown in Figure E-1.

Table E-1 – Component balances across CO₂-hydrate reactor and slurry gas separator

Stream	1 Shifted synthesis gas	2 Solution of CO ₂	3 Hydrogen-rich fuel gas	4 CO ₂ -hydrate slurry	
Phase	gas	Liquid	gas	liquid	hydrate
Mass flows (Tonnes/hr)					
CO ₂	284	122	40.6	13.2	352
H ₂ O	0	1676	0	847	829
H ₂	19.7	0.09	19.7	0.07	0
CO	9.1	0.07	9.1	0.05	0
Total	313	1798	69.5	860	1181
Mole fractions					
CO ₂	39%	2.9%	8.4%	0.63%	14.8%
H ₂ O	0	97.1%	0	99.3%	85.2%
H ₂	59%	0.05%	89%	0.07%	0%
CO	2%	0.002%	3%	0.004%	0%
Partial pressure (bar)					
CO ₂	17.7		3.8		
H ₂	26.8		40		
CO	0.9		1.3		

The data in Table E-1 show that the calculated molar concentration of CO₂ in the gas phase reduces from 39% to 8.4% as the gas is processed through the CO₂-hydrate reactor and the

⁴ Gas purification, p 154. A.L. Kohl & F.C. Riesenfeld. McGraw Hill 1960.

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separator. Since the system pressure is approximately 45 bar in this conceptual scheme, the partial pressure of CO₂ in the gas phase would reduce from 17.7 bar down to 3.8 bar as CO₂ is removed from the gas phase into the liquid/hydrate phases.

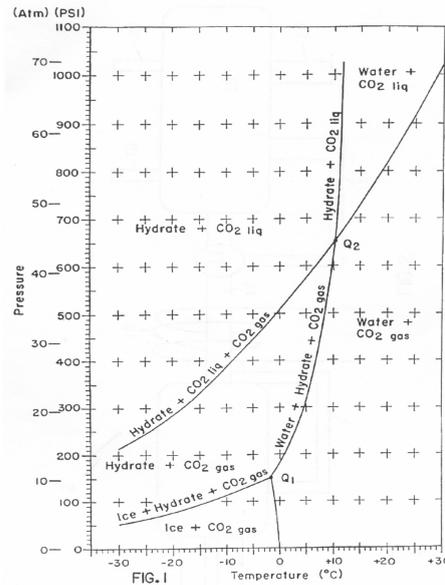
Coal slurry gasification can be operated at up to 80 bar pressure. This could provide a feed gas pressure of up to 75 bar at the scrubber inlet. Under these conditions the hydrate formation process would need to occur at pressures down to 6.3 bar to achieve 86% CO₂ removal.

For the CO₂-hydrate formation process to achieve 90% CO₂ removal, as described in the IGCC/hydrate report for the conceptual IGCC scheme, CO₂-hydrates must be able to be formed under all CO₂ partial pressures from 17.7 bar down to 2.7 bar. For 99% removal, CO₂-hydrates must be able to form at a CO₂ partial pressure less than 0.3 bar.

E.3 DISCUSSION

The formation of CO₂-hydrate is the key feature of the process that would enable a CO₂ loading substantially in excess of the solubility of CO₂ in water to be obtained at the process conditions. Figure E-2 shows the CO₂/H₂O phase diagram.

Figure E-2 – CO₂/H₂O phase diagram⁵



The CO₂/H₂O phase diagram shows the stable phase conditions for a two-component system for a range of temperature and pressure conditions. Regions are shown where two phases are the stable state. Lines are shown where three phases can coexist during transition between two-phase stable-state conditions.

⁵ Source:- US Patent 5,562,891 – Method for the production of carbon dioxide hydrates. Dwain F Spencer.

Appendix E – Discussion of a CO₂-Hydrate Formation Process

This phase diagram shows a curve, Q1 to Q2, which indicates the limiting conditions for hydrate formation in a CO₂-gas/water system. The phase diagram indicates that at 3°C hydrates would be able to form when the pressure of CO₂ is in excess of about 17 bar (atmospheres), but that at lower CO₂ pressures the stable state would be water+CO₂-gas. At lower temperatures the minimum hydrate formation pressure reduces down to a limit of about 10 bar CO₂ pressure at a temperature of about -2°C (point Q1). At even lower temperatures the water would turn to ice. The phase diagram indicates that stable coexistence of CO₂-gas, CO₂-hydrate and water cannot occur at CO₂ pressures below about 10 bar, in a CO₂/H₂O system.

As shown in Table E-1, the partial pressure of CO₂ in the feed gas is 17.7 bar. At the system temperature of 3°C, the minimum hydrate formation pressure would be about 17 bar according to the phase diagram. Therefore hydrate formation may occur at the CO₂-hydrate reactor inlet conditions, because the partial pressure is above the minimum hydrate formation pressure.

However, as CO₂ in the multi-component gas phase is depleted, the partial pressure of CO₂ in the gas phase would reduce until the minimum hydrate formation pressure is reached. When the partial pressure of CO₂ in the gas phase is at the minimum hydrate formation pressure, the rate of formation of CO₂-hydrate would be expected to be equal to the rate of decomposition according to the principles of chemical equilibrium. On this theoretical basis, it is expected that there would be no further net CO₂-hydrate formation.

The assessment described in the IGCC/hydrate report for the IGCC case indicates that the CO₂-hydrate reactor would continue to produce CO₂-hydrate until the residual gas had a CO₂ concentration of 8.4%, as determined via Table E-1. This corresponds to a CO₂ partial pressure that is four to five times less than the minimum hydrate formation pressure, which is indicated on the CO₂/H₂O phase diagram. This CO₂-hydrate formation process is described in US Patent 5,700,311⁶ as follows:-

Upon contact of the gaseous stream with the CO₂ nucleated water, CO₂ is selectively absorbed from the gaseous stream into the CO₂ nucleated water liquid phase. The absorbed CO₂ is concomitantly fixed as solid CO₂ clathrates in the liquid phase. Contact between the gaseous and liquid phases results in the production of a CO₂ depleted multi-component gaseous stream and a slurry of CO₂ clathrates. In the CO₂ depleted multi-component gaseous stream the CO₂ concentration is reduced by at least about 50%, usually by at least about 70%, and more usually by at least about 90%, as compared to the untreated multi-component gaseous stream. In other words, contact of the multi-component gaseous stream with the CO₂ nucleated water results in at least a decrease in the concentration of the CO₂ of the gaseous phase, where the decrease will be at least about 50%, usually at least about 70%, more usually at least about 90%. In some instances the concentration of CO₂ in the gaseous phase may be reduced to the level

⁶ US Patent 5,700,311 Methods of selectively separating CO₂ from a multi-component gaseous stream. Dwain F Spencer

Appendix E – Discussion of a CO₂-Hydrate Formation Process

where it does not exceed 1% (v/v), such that the treated gaseous stream is effectively free of CO₂ solute gas.

The published information referring to the CO₂-hydrate formation process indicates that experiments with pure-CO₂/water systems have shown that the mechanisms of CO₂-hydrate formation and decomposition may differ. A study of hydrate formation from gaseous CO₂ and water⁷ notes that “*The hydrate phase diagram is based on hydrate decomposition pressures and should not be used as an indicator of formation pressures*”. Experimental data presented in that report show that hydrate formation requires a higher pressure than hydrate decomposition, but that repeated cycling of hydrate formation and decomposition can result in a reduction in that pressure differential.

The hydrate formation report⁷ demonstrates the possibility of a reduction in the actual hydrate formation pressure towards the lower hydrate decomposition pressure. However, it does not explain the basis for claiming that hydrates can form below the hydrate decomposition pressure. In particular, this research report⁷ does not indicate that hydrates can be formed at a CO₂ partial pressure that is four to five times less than the hydrate decomposition pressure, as would be required for 90% CO₂ removal in a multi-component gas/water system.

The author of this report has found no public domain literature describing experimental tests of CO₂-hydrate formation with multi-component systems. A test programme with multi-component mixtures is proposed by the process developers.

The IGCC/hydrate report describes a CO₂-hydrate formation process that is proprietary technology and has patents pending. The details of the devices, concepts, and any supporting experimental evidence are confidential and have not been disclosed to the author of this public domain report.

E.4. CONCLUSION

The application of the CO₂-hydrate formation process to the scrubbing of 90% of CO₂ from shifted synthesis gas in an IGCC scheme depends on CO₂-hydrate formation being achieved at a CO₂ partial pressure less than 4 bar in a multi-component gas. This is four to five times lower than the minimum theoretical CO₂-hydrate formation pressure indicated by the phase diagram for water and pure CO₂. Despite extensive enquiries, the author of this report has found no evidence or scientific theory to support the claim that this can be achieved. Therefore further assessment of the CO₂-hydrate formation process is not included in this report.

⁷ Hydrate formation from gaseous CO₂ and water, paper submitted to Environmental Science and Technology, James J Morgan, Veronica R Blackwell, Don E Johnson, Dwain F Spencer and Wheeler J North. California Institute of Technology.

Appendix F
World Coastline Survey

APPENDIX F

World Coastline Survey

F.1 INITIAL SCREENING

An initial survey of the coastline of the world was carried out on a country-by-country basis, to identify locations where seawater scrubbing could potentially be implemented. The following criteria were used to identify countries, or states within countries, with potentially suitable coastline.

- Only states with a population in excess of about 1 million people were considered. This criterion was adopted to eliminate small island states where the demand for thermal electricity would be unlikely to be sufficient to justify a large base-load coal or gas fired power plant.
- Sections of mainland coastline within 100 km of the 1500 m contour and with water deeper than 2000 m beyond the 1500 m contour.
- Direct connection to the deep water of the oceans. This criterion was adopted to exclude seas that are only connected to the oceans via relatively shallow water. The potential for discharge into such seas is discussed in Appendix I.
- Proximity of a large centre of population within reasonable access, via transmission lines, to a potential power plant site.

F.2 EXCLUSIONS

The coastline of many countries was excluded by the screening criteria described in Section F.1. However, site-specific studies might identify opportunities to apply seawater scrubbing CO₂ mitigation to these excluded countries. Reasons for some of the exclusions are explained as follows.

The West Coast of Canada is adjacent to deep water of the Pacific Ocean. However the shortest distance from the mainland to the 1500 m contour is about 100km. Closer proximity to deep water is available only from Vancouver Island and the Queen Charlotte Islands.

Many of the countries on the African continent border the South Atlantic and Indian Oceans. Adequate proximity to the 1500 m contour exists on the coasts of Somalia, Tanzania, Mozambique, Madagascar, South Africa, Angola, Nigeria, Benin, Togo, Ghana, Cote d'Ivoire, Liberia and Morocco. However, for most of these countries the required pipe length would be in excess of about 50km. Furthermore, the population in these countries is generally dispersed and adequate electricity transmission infrastructure is unlikely to be viable. In the case of South Africa, the coast between Durban and East London is the closest to the 1500 m contour of the whole African continent and the

Appendix F – World Coastline Survey

adjacent land is probably suited to power transmission infrastructure. Therefore South Africa is included to represent seawater scrubbing opportunities which may be found on the African continent.

The Black Sea and the Mediterranean Sea have adequately deep regions adjacent to highly populated areas providing potential disposal sites for CO₂ saturated water. However, these seas only communicate with the Atlantic Ocean via the relatively shallow waters of the Bosphorous and the Straits of Gibraltar. Similarly, the Sea of Japan, the South China Sea, the Celebes Sea and the Banda Sea are isolated from the Pacific Ocean by shallow waters. Hence CO₂ dissolved in these seas would not be able to disperse in the deep oceans. These seas have therefore been excluded. In contrast, the Caribbean Sea is connected via deep-water channels between the Caribbean islands with the Atlantic Ocean. Therefore the southern and western coasts of the Caribbean islands have been included.

On the basis of this initial assessment 42 coastal states were identified for further investigation. These states are listed in Table F-1.

Table F-1 – Initial identification of coastal states

Brazil	Haiti	New Zealand	Portugal
Burma	USA Hawaii	Nicaragua	Puerto Rico
USA California	Honduras	USA North Carolina	Aus. Queensland
Chile	India	Oman	South Africa
Colombia	Indonesia	USA Oregon	South Australia
Costa Rica	Jamaica	Pakistan	Spain
Cuba	Japan	Panama	Sri Lanka
Dominican Republic	Mauritius	Papua New Guinea	Taiwan
Ecuador	Mexico	Peru	Aus. Victoria
El Salvador	New South Wales	Philippines	USA Washington
Guatemala			

F.3 DETAILED COASTLINE REVIEW

Maps of the coastline and local bathymetry for each of the countries listed in Table F-1 were examined to identify potential specific locations for seawater scrubbing power plants. The following additional criteria were adopted to determine the number and location of potential 500 MWe coal-fired power plants with seawater scrubbing.

- Specific locations were identified on the basis of minimum distance from the mainland coast to the 1500 m ocean-depth contour.

Appendix F – World Coastline Survey

- The spacing of power plants along suitable coastline was arranged so that each plant had exclusive access to 25,000 cubic kilometers of deep-ocean water. The derivation of this value is discussed in Appendix I. The topography of the sea floor at each location was taken into account to determine a nominal radius of influence for each location. The spacing of locations was arranged to avoid overlap of the areas of influence. This methodology is based on the assumption that deep-ocean water is stationary. However, it would also be a valid approach for spacing of locations where there are deep ocean currents that move parallel to the coastline.
- The number of power plant sites for each state is limited to one per million of population. This corresponds to a maximum contribution of 500 Watts of base-load coal-fired power per head of population.

The application of these criteria resulted in 180 potential disposal sites being identified around the world, predominantly in the tropics. In view of the large number of suitable sites a further constraint was introduced, based on existing patterns of power generation.

- The number of 500 MW power plants for each state is also limited to one per 4 TWh/annum (500 MW at 90% load factor) of thermal power generated in 1991 and 1992 (IEA data), so that only replacement of fossil fuel power plants is considered. This criterion was introduced to recognise that there would be a limit to the number of potential base-load fossil fuel fired power plants that could be installed in countries that have a major hydroelectric power resource.

This latter criterion, based on historical power production data, eliminates many states that were included in the initial screening. States excluded or curtailed by this criterion are Brazil, Colombia, Costa Rica, Ecuador, Guatemala, Jamaica, Mauritius, Oman, Panama, Papua New Guinea, Peru, Puerto Rico and Sri Lanka. In addition, consideration of historical base-load fossil fuel power demand limits the number of potential sites in Chile, Cuba, Dominican Republic, Honduras, New Zealand, Nicaragua and The Philippines.

Future expansion of demand in these states, combined with limited opportunities for expansion of hydroelectric power generation, may result in opportunities for the application of seawater scrubbing on a base load coal-fired power plant.

After application of these additional criteria, 89 locations remained in 29 states where 500 MW coal-fired power plants with seawater scrubbing could potentially be located with a pipeline length less than 100 km. These potential locations are listed in Table F-2. Also shown in Table F-2 is an estimate of the maximum number of 500 MW power plants that might be accommodated at each location.

The technical and economic evaluations in this report are based around 380 MW for coal fired plant and around 820 MW for gas fired plant. These scales of operation are derived from PH3/14, where they are fixed according to specific equipment sizes. For more generic analyses the IEA GHG default size of 500 MW is used.

This coastline survey is based primarily on bathymetric data presented in the Times Atlas of the World. Most maps in this reference only show the 1000 m and the 2000 m contour.

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Therefore the location of the 1500 m contour has been estimated by interpolation. In addition, the 1000 m and 2000 m contours shown on the maps may not be strictly accurate. Some discrepancies between bathymetric contours on different maps have been observed. Accordingly the results of this broad survey are only indicative. A review of more detailed bathymetric data would be required to determine the exact pipeline requirements and feasibility for each case.

Table F-2 – Detailed results of World Coastline Survey

Country or state	Location	Latitude		Long.		Sea temp.	Pipe length	Max. no.
		deg.		deg.		C	km	of units
Cuba	Santiago de Cuba	20	N	75	W	25	3	1
Cuba	Portillo	20	N	77	W	25	4	1
Indonesia	Genteng	7	S	106	E	29	4	3
Indonesia	Malang	7	S	113	E	29	4	3
Cuba	Gibara	21	N	76	W	25	5	1
Haiti	Les Cayes	18	N	74	W	25	5	1
Dom. Republic	Barahona	18	N	71	W	25	6	1
Philippines	Casiguran	16	N	122	E	28	6	1
Mexico	Pochutla	16	N	96	W	29	6	2
Philippines	Mati	7	N	126	E	29	8	1
Philippines	Tacloban	11	N	125	E	28	10	1
Japan	Matsuzaki	35	N	139	E	18	11	6
Philippines	Lanuza	9	N	126	E	28	11	1
Indonesia	Yogyakarta	7	S	110	E	29	12	3
Mexico	Pta. S. Telmo	18	N	103	W	24	12	2
Hawaii	Honolulu	21	N	158	W	23	12	4
Japan	Shiono-misaki	33	N	136	E	16	13	6
Japan	Nojima-Zaki	35	N	140	E	18	13	6
Chile	Totalal	28	S	71	W	17	14	1
Mexico	Cape Coriontes	21	N	106	W	23	14	2
Mexico	Tututepec	16	N	97.4	W	29	15	2
Mexico	Acapulco	17	N	100	W	29	15	2

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Mexico	Los Mochis	25	N	109	W	21	16	2
Spain	Santander	43	N	3	W	13	16	6
Portugal	Sagres	37	N	9	W	16	17	6
New South Wales	Jervis bay	35	S	150	E	22	18	3
New Zealand	Matakaoa point	37.5	S	178	E	18	18	1
California	Monterey	37	N	122	W	12	19	4
New South Wales	South West Rocks	31	S	153	E	24	22	3
New South Wales	Sugar Loaf Point	33	S	152	E	24	22	3
Portugal	Peniche	39	N	9	W	15	24	6
California	Point Arena	38	N	124	W	11	26	4
South Africa	Gamalakhe	31	S	31	E	26	28	6
Honduras	Punta Cortes	16	N	87	W	27	30	1
Mexico	Zihuatanejo	18	N	101	W	24	30	2
Mexico	Chamela	19	N	105	W	24	30	2
India	Pondicherry	12	N	79	E	29	32	6
Victoria	Cape Howe	37	S	150	E	20	32	3
Spain	Cape Tourinan	43	N	9	W	13	34	6
Portugal	Sezimbra	38	N	9	W	16	36	6
India	Muttukuru	14	N	80	E	29	36	6
South Africa	Umtata	32	S	28	E	25	36	6
New South Wales	Broadwater	29	S	153	E	24	36	3
Japan	Ochiisi-Misaki	43	N	145	E	6	38	6
California	Point Reyes	38	N	123	W	12	38	4
California	Cape Mendcino	40	N	124	W	11	40	4
South Africa	East London	33	S	27	E	25	42	6
Taiwan	Tai-Tung	23	N	121	E	25	43	6
Mexico	Mazatlan	23	N	106	W	22	44	2
Mexico	Pta. Delgada	20	N	96	W	24	44	2
Portugal	Barcalo	41	N	9	W	15	44	6
Mexico	Salina Cruz	16	N	95	W	29	46	2
California	Point Conception	35	N	121	W	12	46	4

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New South Wales	Sydney	34	S	151	E	23	46	3
Japan	Muroto Zaki	33	N	134	E	16	48	6
India	Mouths of Krishna	16	N	81	E	29	48	6
California	San Simeon	35	N	121	W	12	50	4
Burma	Bassein	17	N	94	E	28	50	6
India	Madras	13	N	80	E	29	50	6
Japan	Tone-g-Choshi	36	N	141	E	16	51	6
South Africa	Durban	30	S	31	E	26	51	6
Pakistan	Gwadar	25	N	62	E	28	52	6
Mexico	Aldama	23	N	98	W	24	55	2
Oregon	Coos Bay	43	N	124	W	10	55	4
Japan	Ashizuri-Misaki	32	N	133	E	16	56	6
Japan	Erimo-Misaki	42	N	143	E	6	58	6
Japan	Toi-Misaki	31	N	131	E	16	58	6
Nicaragua	San Juan del Norte	11	N	83	W	27	60	1
Pakistan	Ras Kochari	25	N	66	E	28	60	6
Pakistan	Ras Sakani	25	N	65	E	28	60	6
Queensland	Beenleigh	28	S	153	E	24	60	3
California	Crescent City	42	N	124	W	10	65	4
Victoria	Cape Conran	38	S	149	E	20	66	3
Taiwan	Hsueh Shan	24	N	122	E	24	67	6
Japan	Yamada-wan	39	N	142	E	11	68	6
El Salvador	San Salvador	13	N	89	W	28	70	1
South Australia	Millicent	38	S	140	E	18	70	3
India	Mattancheri	10	N	76	E	28	72	6
Queensland	Laguna Bay	26	S	153	E	25	72	3
Victoria	Portland	38	S	141	E	18	75	3
Oregon	Eugene	44	N	123	W	10	80	4
South Africa	Port Elisabeth	34	S	25	E	24	80	6
Washington	Centralia	45	N	124	W	11	88	4
North Carolina	Stacy	35	N	76	W	22	88	6

Appendix F – World Coastline Survey

Japan	Iwaki	37	N	141	E	18	90	6
India	Calicut	11	N	75	E	28	90	6
India	Mangalore	12	N	74	E	28	90	6
Victoria	Warnambool	38	S	142	E	18	98	3
Washington	Hoquiam	47	N	124	W	10	100	4

The number of locations and maximum number of 500 MW units identified for each of 29 states is summarised on Table F-3, where the states are arranged in order of the average of the pipeline lengths for the locations identified.

**Table F 3 World Coastline Survey
States with Potential Locations for 500 MW Power Plants with Seawater Scrubbing**

Country	Number of locations	Max no. of 500 MW units	Average pipe length – km	Minimum pipe length - km
Cuba	3	3	4	3
Haiti	1	1	5	5
Dominican Republic	1	1	6	6
Indonesia – Java	3	9	7	4
Philippines	4	4	9	6
USA – Hawaii	1	4	12	12
Chile	1	1	14	14
New Zealand	1	1	18	18
Spain	2	12	25	16
Mexico	12	24	27	6
Australia – NSW	5	15	29	18
Portugal	4	24	30	17
Honduras	1	1	30	30
USA – California	7	28	40	12
Japan	11	66	45	9
South Africa	5	30	47	28
Burma	1	6	50	50

Appendix F – World Coastline Survey

Taiwan	2	12	55	43
Pakistan	3	18	57	52
India	7	42	60	32
Nicaragua	1	1	60	60
Australia – Queensland	2	6	66	60
USA – Oregon	2	8	67	55
Australia – Victoria	4	12	68	32
South Australia	1	3	70	70
El Salvador	1	1	70	70
USA – North Carolina	1	6	88	88
USA – Washington state	2	8	94	88

Table F-3 also shows the approximate shortest distance to the 1500 m contour for each country subject to the criteria listed in Section F-1. The full listing shown in Table F-2 indicates that 11 potential opportunities for seawater scrubbing based on a pipe length of 10km or less have been identified. A further 20 potential opportunities would have a pipeline length between 10km and 25km. 28 potential opportunities have pipe length in the range 25km-50km and a further 30 are identified in the 50km-100km range

Also listed in Table F-2 is the latitude and longitude of each of the potential seawater scrubbing locations. It is noticeable that there is a significant link between latitude and distance to deep water, with most of the potential locations being in tropical regions. The maps in the atlas indicate that, as a general rule, the slope from the edge of the continental shelf to the deep ocean is steeper in the equatorial regions. This observation is significant for the assessment of ocean disposal CO₂ capture schemes because it implies that the technology is better suited to hot regions.

The average sea surface temperature for the 89 potential locations is 21°C. The 12 locations where the pipeline length would be 10 km or less have an average sea surface temperature of 26°C. Figure F-1 shows a comparison of the local sea surface temperature with the length of the disposal pipeline for the 89 locations that have been identified.

Figure F-1 Comparison of Sea Surface Temperature with minimum distance to 1500 m ocean depth contour

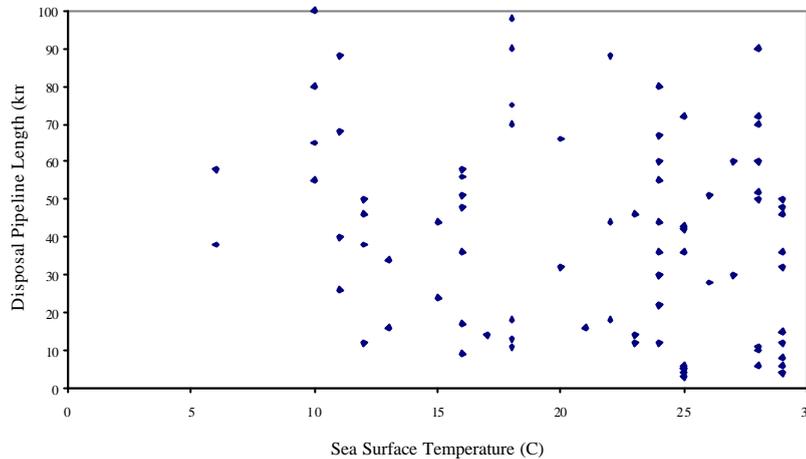


Figure F-1 shows that the majority of opportunities for seawater scrubbing lie in locations where the local sea surface temperature is in the range 20-30°C. The few opportunities for seawater scrubbing where the seawater is cooler (Japan, Spain and North America) generally correspond to longer disposal pipeline requirements.

From these considerations it is concluded that the technical evaluation of seawater scrubbing technology should be based on a local sea surface temperature of 25°C.

Figure F-2 shows a map of the world on which the 89 potential sea-water scrubbing locations are presented as white spots. The world map on which these locations are identified is a satellite image of sea surface temperatures¹.

¹ NOAA/NESDIS Satellite derived sea surface temperatures – April 1999.

Appendix G
Impact of CO₂ on pH of Seawater

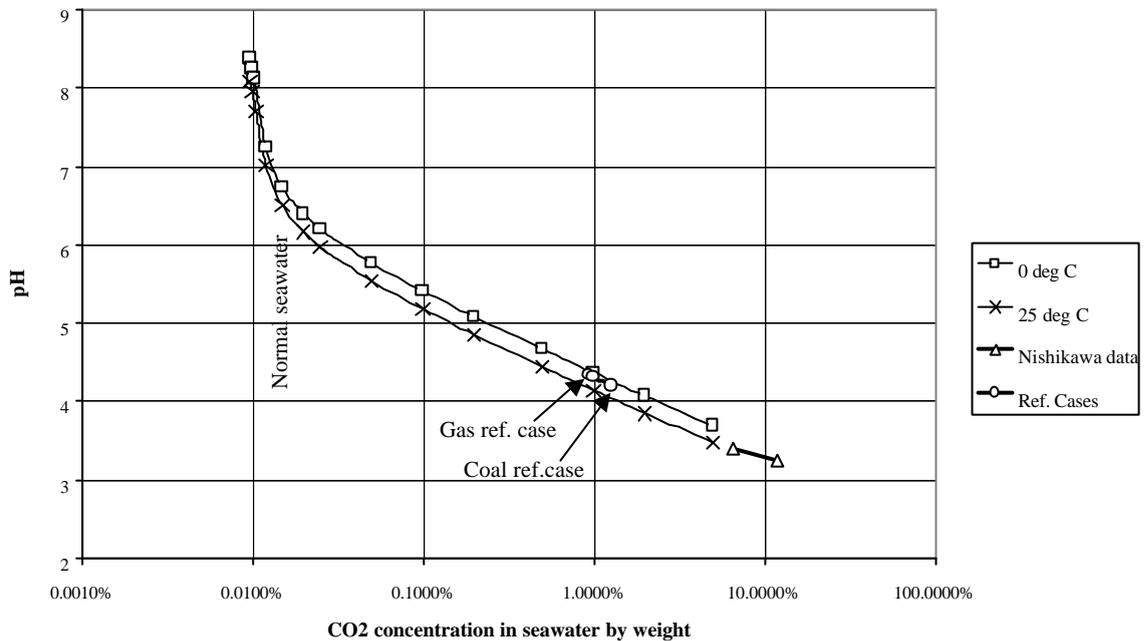
APPENDIX G

Impact of CO₂ on pH of Seawater

G.1 PH CURVES

Figure G.1 shows the results of a theoretical derivation of the dependence of pH on the extent of CO₂ dissolved in seawater at temperatures of 0°C, and 25°C.

Figure G-1 Dependence of pH on CO₂ concentration in seawater



This calculation takes account of the carbonic acid/bicarbonate/carbonate equilibria combined with activity coefficients for the bicarbonate and carbonate ions in seawater. The temperature dependence of the ionisation of water and the bicarbonate equilibria are also included.

G1.1 Derivation of Figure G-1

For the purpose of evaluating the distribution of dissolved carbon between carbonic acid, bicarbonate ions and carbonate ions, the normal practice is adopted of considering CO₂ in solution as if it is all in the form H₂CO₃, which is the weak carbonic acid.

The calculation of pH for Figure G-1 has been carried out by iterative solution of following relationships for five species in seawater; H₂CO₃, HCO₃⁻, CO₃⁻², H₃O⁺, OH⁻ {where [...] = Molar activity in gm moles per litre of H₂O}

- Ionisation of water

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-13.9965} \text{ (@ } 25^\circ\text{C)}, 10^{-14.9435} \text{ (@ } 0^\circ\text{C)}^1$$

Appendix G – Impact of CO₂ on pH of Seawater

- Carbonic acid decomposition

$$[\text{HCO}_3^-] * [\text{H}_3\text{O}^+] / [\text{H}_2\text{CO}_3] = 10^{-6.35} (@ 25^\circ\text{C}), 10^{-6.58} (@ 0^\circ\text{C})^1$$

- Bicarbonate decomposition

$$[[\text{CO}_3^{2-}] * [\text{H}_3\text{O}^+] / [\text{HCO}_3^-] = 10^{-10.33} (@ 25^\circ\text{C}), 10^{-10.62} (@ 0^\circ\text{C})$$

- Carbon balance

Total carbon content in H₂CO₃, HCO₃⁻ and CO₃²⁻ = total carbon in solution.

- Ionic charge balance (molar basis)

Total charge of H₃O⁺, OH⁻, HCO₃⁻ and CO₃²⁻, = 0.00247

This value corresponds to the net ionic charge of all the other elements in seawater and is used as a constant.

- Activity coefficients for H₂CO₃, H₃O⁺ and OH⁻ are taken to be 1. However, significant non-ideality is reported in the literature for bicarbonate and carbonate ions in seawater. Values of activity coefficients for HCO₃⁻ and CO₃²⁻ in seawater are taken to be 0.55 and 0.021 respectively¹

G.1.2 Comparison of pH curve with published data

This calculation method gives values for the pH of typical seawater of 7.8-8.1 at 25°C and 8.1-8.4 at 0°C. These values, which are strongly dependent on carbonate/bicarbonate buffering, are in line with typical data for seawater.

Nishikawa et al² reported the results of practical experiments involving the use of a high pressure pH meter with seawater and liquefied CO₂. Values of about pH 3.4 and pH 3.25 are reported for 1.5 and 2.8 molar solutions of CO₂ in seawater. Figure G-1 shows these two data points, which are in very good agreement with the theoretically determined curve.

G1.3 Discussion

Figure G-1 shows that there is a small effect of temperature on the reduction in pH that results from dissolution of CO₂. A minor pressure dependence of water ionisation is also reported³. The effect on water ionisation of an increase in pressure from atmospheric to 250 bar (2500 m depth) is minor and about the same as would result from increasing temperature by about 2 degrees C. The effect of pressure is therefore ignored.

The concentration of CO₂ in the seawater that is discharged from a seawater scrubbing system is 0.92% for the natural gas reference case and 1.27% for the coal/IGCC reference case. These cases, which are also shown on Figure G-1 correspond to pH value 4.3

¹ Horne R.A. 1969. Marine Chemistry; the structure of water and the chemistry of the hydrosphere. Wiley.

² CO₂ clathrate formation and its properties in the Simulated deep ocean. Nishikawa et al. Energy Conversion management Vol 33 page 651.

³ Handbook of Chemistry and Physics CRC. Page D 169/D.170.

Appendix G – Impact of CO₂ on pH of Seawater

For the step-off cases studied in this report, the CO₂ concentration ranges for 0.7% for the warm water natural gas case to 2.7% for the high pressure coal case. The corresponding pH of the effluent would therefore range from pH 3.9 to pH 4.5 on the logarithmic pH scale.

Figure G-1 shows that the discharged solution of CO₂ would have to be diluted 10 times to achieve pH 5 and 100 times to return to pH 6.

G.2 CALCIUM CARBONATE DISSOLUTION

The rate of discharge of CO₂-laden seawater from a scrubbing system would be high. Therefore a region of significantly acidic water would develop near to the discharge pipe. Acidity would reduce with distance from the discharge pipe. The pipe would be laid on the sea-floor and would therefore probably discharge acidic water directly onto the sea bed.

The calculations described in G.1.1 show that at elevated concentrations of CO₂ in seawater, the CO₂ reports principally as carbonic acid with very low concentrations of carbonate ions. As a consequence, the resulting solution is well under-saturated with calcium carbonate. Therefore, if calcium carbonate sediments are present in the vicinity of the discharge pipe, they will tend to dissolve in the acidic water. Dissolution of calcium carbonate sediments will consequently reduce acidity.

The extent that dissolution of calcium carbonate sediments would mitigate the acidity of the discharged water, in preference to dilution, would depend on reaction kinetics and local dispersion mechanisms. Evaluation of these mechanisms is site specific.

The solubility of calcium carbonate sediments in acidified seawater depends on the pH of the water. Figure G-2 shows the relationship between pH, dissolved CO₂ and the extent of additional calcium carbonate dissolution. Also shown on Figure G-2 is the calcium carbonate solubility line. If soluble calcium carbonate were present local to the discharge point it would tend to dissolve until the conditions of the solubility line are reached.

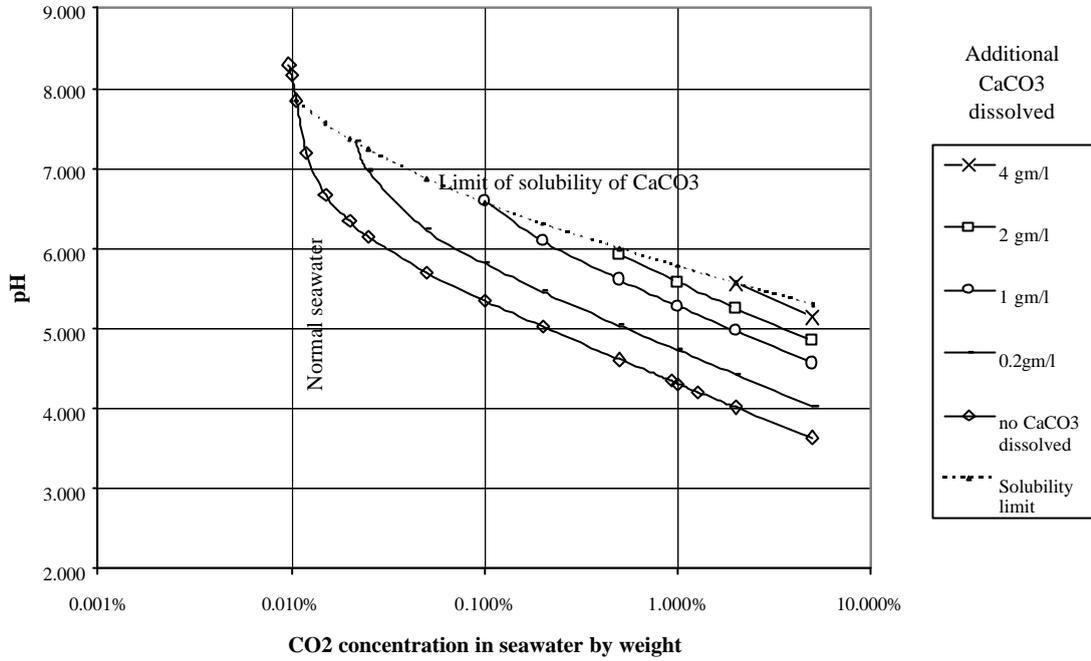
Figure G.2 shows that if no additional calcium carbonate is dissolved, the calcium carbonate solubility line meets the pH/CO₂ line at a pH of about 7.8 and at a CO₂ concentration about 10% greater than the natural CO₂ concentration in seawater. Thus, as progressive dilution of acidified seawater increases pH, the tendency for calcium carbonate to be dissolved by the acidified seawater would not be eliminated until the pH increases to about pH 7.8.

Figure G.2 also shows that normal seawater is a super-saturated solution of calcium carbonate. This observation is in accordance with common experience that surface seawater, particularly in warmer regions is super-saturated with calcium carbonate⁴.

⁴ R.A. Horne. Marine Chemistry. 1969.

Appendix G – Impact of CO₂ on pH of Seawater

Figure G-2 Dependence of pH on CaCO₃ dissolution at 5°C



Appendix H
Environmental Impact of Depression of pH

APPENDIX H

Environmental Impact of Depression of pH

H.1 PHYSICAL EFFECTS

It is identified in Appendix G that the acidic water from a seawater scrubbing process has the potential to dissolve calcium carbonate sediments local to the point of discharge. Other minerals may also be dissolved in an acidic environment. The rate at which dissolution of sediments would actually occur would depend on the nature of those sediments. Evaluation of the balance between acidity mitigation via dissolution of sediments and via dispersion would be a site-specific issue.

The coal and gas reference cases, evaluated in Appendix B, would result in discharges of CO₂ solutions of 1.27 and 0.92 weight percent CO₂ in water with pH values of 4.21 and 4.34 respectively. The step-off cases at high pressure or low temperature would result in more concentrated solution with lower pH values. (e.g. 3.24% CO₂ at pH 3.8 for the high pressure/cold water/ coal IGCC case). However, the acidification effect on the ocean environment would be proportional to the amount of CO₂ discharged and would be largely independent of the amount of water carrying that CO₂.

Figure G.2 in Appendix G shows that water discharged under from an IGCC/coal plant under the reference case condition, with a concentration of 1.27% CO₂ at pH 4.2, would have the potential to dissolve about 3.5 grams of calcium carbonate per litre, before the solution became saturated in calcium carbonate. The flowrate of this solution from a 500 MWe IGCC/coal fired power plant would be about 28,700 tonnes per hour. Undiluted, this body of acidic water would have the capacity to dissolve 100 tonnes per hour of calcium carbonate.

In the case of the reference gas-fired power plant with seawater scrubbing, the water discharge rate would be 19,800 tonnes per hour for a 500 MW installation, the pH would be 4.3 and the capacity to dissolve limestone would be about 3.3 grams per litre. Therefore, the acidic water from a 500 MW gas-fired plant could dissolve about 65 tonnes per hour of ocean floor limestone.

If the ocean floor were pure limestone, a rate of dissolution of 100 tonnes per hour would correspond to the development, over one year, of a hemispherical depression in a pure limestone ocean floor of about 144 m diameter, if there were no inhibiting influence. However, dissolution of soluble sediments would result in insoluble materials remaining on the surface, shielding underlying material. Therefore the extent of dissolution of sediments would probably be much less than this estimate.

Another site-specific physical effect with potential environmental consequences would be accelerated corrosion of man-made items, such as shipwrecks, or encased hazardous materials, on the ocean floor. For example, the trench off the northern coast of Puerto Rico, is the location of a US army dump for disused munitions, rendering it unsuitable for the disposal of acidified seawater.

Appendix H – Environmental Impact of Depression of pH

H.2 BIOLOGICAL EFFECTS

Seawater with a pH less than 6.5 is lethal to most coastal marine organisms. Oceanic species are likely to be more sensitive to environmental change due to the stability of their deep sea environment. Sub-lethal effects on reproduction, growth, metabolic rates and longevity would be experienced with smaller decreases in pH from the normal value of about pH 8. Limited knowledge of the physiological tolerance of inshore coastal species indicates that a pH of 7.5 would be the lower limit for many species¹. The impact of pH on marine biota is discussed further in section H.3. The natural concentration of total carbon (expressed as CO₂) in seawater is about 0.01%. Figure G-1 shows that a 20% increase in total carbon to 0.012% would cause the pH to reduce to about 7.5, at which the onset of adverse environmental effects can be expected. Figure G-2 shows that a reduction of the pH of seawater from a typical value of 8.3 (at 0.01% CO₂) to pH 7.8 (at 0.0106% CO₂) might result in elimination of the super saturation in calcium carbonate. Crustaceans, with a calcium carbonate shell in direct contact with the water, are obviously adapted to survive in water that is supersaturated in calcium carbonate. This is apparently due to the presence of inhibitors that prevent crystallisation of excess calcium carbonate onto their shells. However, it is possible that they would not be able to adapt to water that is under-saturated in calcium carbonate causing their shells to tend to dissolve. This view greatly simplifies the complex chemistry of the interaction of seawater with its inhabitants, but it indicates that the calcium carbonate saturation line might reasonably be taken as a practical limit beyond which adverse environmental effects could be expected.

The calculations presented in Appendix G indicate that, at 25°C, a 5% increase in the average CO₂ content of seawater, from 0.01% to 0.0105%, would result in a reduction in pH from 8.0 to 7.7 and would result in a reduction in super-saturation with calcium carbonate from 190% to 110%. This initial review indicates that such a change in the composition of seawater is likely to be free from significant adverse environmental effects.

The concentration of CO₂ in the effluent from a water scrubbing system is likely to be about 2% by weight and would therefore have a pH about 4. This level of acidity would certainly not be able to sustain marine life. Dilution by a factor of about 4000 with normal seawater at 0.01% CO₂ would be required to produce water with a concentration of 0.0105% CO₂, which would probably be environmentally satisfactory. This level of dilution is used as the basis for the estimates developed in Appendix I.

H-3 IMPACT OF pH ON MARINE BIOTA

H.3.1 Physiological Effects on Marine Animals

The solution of CO₂ in seawater leads to an increase in the H⁺ ion concentration (resulting in a decrease in the pH) and a higher partial pressure of CO₂. The tissues and body fluids

¹ Ormerod B., Angel M. (1996) Ocean Storage of Carbon Dioxide Workshop 2 – Environmental Impact. *IEA Greenhouse Gas R&D Programme*.

Appendix H – Environmental Impact of Depression of pH

of marine animals coming in contact with this seawater would consequently have higher concentrations of these chemicals due to the uptake of substrates via membrane exchange.

The sensitivity of marine animals to increased CO₂ concentrations in seawater is related to the characteristics of the animal in question, for example its energy requirements and its mode of life. Hence some species are more tolerant to the higher acidity and CO₂ concentrations than others.

A moderate rise in CO₂ concentration is likely to be lethal for the more active pelagic organisms whilst less active species appear to have a higher tolerance to a change in environmental conditions. However, even tolerant species would suffer, long term, sub-lethal effects at the population and species level if CO₂ enriched seawater is released in close proximity to their natural habitat.

H.3.2 Deep-Sea Fish

Fish can be grouped under two broad categories: -

- Pelagic fishes which inhabit the water column.
- Demersal fishes which, spend their lives close to the seabed.

The numerical abundance and overall biomass of both groups decline with increasing depth, with the biomass of demersal fish generally more than that of pelagic fish at comparable depths. The fish species living at greater depths tend to occupy larger bathymetric ranges than the shallow-living species. Some species of mammals regularly forage at depths >1000 m, for example the sperm whale, elephant seals and Weddell seals.

One of the main potential impacts of CO₂ enriched seawater release is interference with the reproductive processes of the deep-sea fish. Many demersal fish have restricted breeding grounds from where the spent adults and larvae disperse in different directions. As larval and juvenile stages are generally more vulnerable to environmental fluctuations than adults, the point of discharge would have to be located to ensure that it would not interfere with any of these restricted breeding grounds.

If oceanic release of CO₂ enriched seawater is to have minimal impact on fish and other large species, either directly, or indirectly via the food chains, then the CO₂ must be released in deep water, at depths of at least 1500 m. This is particularly relevant along continental slopes, as larval and juvenile fish densely populate these areas. The discharge should also be such that the discharge plume would disperse away from the continental margins, or any areas densely populated by fish.

The release point of CO₂ enriched seawater should also be located to avoid any deep-sea living fish stocks with any prospects of commercial exploitation.

H.3.3 Pelagic Ecology

There are five main zones in deep ocean ecosystems: the epipelagic (0-200 m), mesopelagic (200-1000 m), bathypelagic (1000-4000 m), abyssopelagic (4000-6000 m), and benthopelagic (in the benthic boundary layer which extends up to 100 m above the

Appendix H – Environmental Impact of Depression of pH

sea floor). An important consideration when assessing environmental impacts is the migration that occurs between the various pelagic zones. There are three important migrations to consider:

- Daily migrations, occurring on a 24-hour cycle, triggered by changing light intensity.
- Seasonal migration, undertaken by species at latitudes $>40^\circ$
- Ontogenetic migration involving eggs, larvae and sub-adult stages of the cycle occurring at different depths.

Pelagic biomass is highest in the epipelagic zone, with another maximum usually between 500-1000 m during the day as a result of the daily migrations. Otherwise the amount of biomass usually decreases to 10 % of that in the epipelagic at a depth of 1000 m and to 1% at 4000 m.¹ However the number of species increases to a maximum at depths of about 1000 m, below which there is a slow but steady decline. Both biomass and species richness increase again in the benthopelagic zone.¹

The main impact associated with CO₂ release to pelagic communities is interference with migratory processes as layers of low pH would be likely to act as a barrier to most types of migration.¹ If the layers were extensive and covered a large area of an ocean basin there could be a significant detrimental effect on the ecological processes within that basin. To minimise possible impacts CO₂ discharges should be at depths in excess of 1000 m, probably at depths of at least 1500 m.

CO₂ hydrate particles may have adverse effects on mesopelagic organisms. However, dissolution of the CO₂ in seawater prior to discharge would ensure that hydrate formation conditions are not encountered beyond the end of the discharge pipe.

H.3.4 Benthic Ecology

The sea floor at depths of less than 2000 m, is an active interface between the water column and the sediments. The benthic boundary layer is defined as a zone extending from the clear water minimum to the bioperturbed layer of the sediment, about 50cm into the sediment.¹ The benthic boundary layer is a zone of enhanced biogeochemical fluxes which transform and mineralise organic material, releasing the carbon and associated elements back into the water column - 90% of the organic carbon settling on the sea floor is returned to the active cycle by this process.¹

The severity of impact of a release of CO₂ on the benthic ecology would depend on the method of CO₂ release adopted. The worst case scenario would result from a release method that leads to the formation of a dense layer of CO₂-enriched water covering the sediment interface for an excessive period of time. Release methods designed to disperse the CO₂ in open water would have less direct impact, however potential interference with recycling and exchange processes affecting the benthic process is still a concern.

Marine bacteria, which are responsible for the remineralisation and re-cycling of organic carbon, show reduction in their metabolic and growth rates at pH 6.0.

Appendix H – Environmental Impact of Depression of pH

H.3.5 Slope Ecology

Slope regions are likely to be directly impacted by pipelines carrying and discharging CO₂ from onshore installations. Biologically the slopes are distinct from shelf seas and ‘blue water’, both ecologically and faunistically, forming regions of transition between these two environments.¹

The unique nature of the slope and shelf break, and the unique ecology associated with the area means that the potential impact of CO₂ discharge could be greater than in other parts of the water column. Slope regions sustain profuse biological activity mainly due to high nutrient concentrations as a result of enhanced vertical mixing. The extended depths at which biological activity is taking place means that pipelines may have to be taken to greater depths, to avoid impact on the slope communities. CO₂ discharges should be at depths deeper than 1000 m, preferably at least 1500 m.

Regions of high productivity, often associated with enhanced vertical mixing (coastal upwelling regions) should be avoided, as should areas where the CO₂ discharges could disrupt the migrations and/or spawning grounds of important species or regions where there are stocks of living resources.¹

The unique ecology associated with steep slopes and canyons may mean that their acceptability as CO₂ release sites is reduced.

H.3.6 Conclusions

These considerations indicate that discharge of seawater with a reduced pH would be likely to cause significant environmental impact on marine ecology at depths shallower than 1000 m. Accordingly for this study a minimum discharge depth of 1500 m is adopted as a system design criterion.

Even in excess of 1500 m depth, there is likely to be a small amount of biological activity. Free-ranging pelagic fish would be likely to migrate away from areas where the discharge of CO₂-laden seawater reduced the pH. Benthic organisms that inhabit specific areas of the sea floor would be unlikely to be able to migrate and would be unable to survive in close proximity to the outfall. The extent to which the uninhabitable region of the sea floor would spread around the discharge point would have to be assessed by site specific dispersion modeling.

H.4 ENVIRONMENTAL IMPACTS OF TRANSPORT SYSTEM

H.4.1 Offshore pipes

There is potential for environmental impact to occur during the installation of offshore pipes. The first few kilometers would be laid on the continental shelf, which is an ecologically sensitive zone. The issues would be the same as are faced by the oil and gas industry.

Appendix H – Environmental Impact of Depression of pH

In the case of CO₂ enriched seawater, the consequences of accidental rupture of a pipe would be less severe than for an oil, gas or liquid CO₂ pipeline. At shallow depths (less than 100m depth for the IGCC reference case, a small leak of liquid would “fizz” as CO₂ came out of solution. The released CO₂ would bubble up to the surface and re-enter the atmosphere. At greater depth, CO₂ would remain in solution and would cause acidification of the seawater in the vicinity of the ruptured pipe. This would be detrimental to marine communities in the surrounding area.

A seafloor pipe, or a pipe suspended in the water column, presents a new surface in the ecosystem. Any hardware fosters growth of attached organisms, these organisms tend to attract other larger organisms, which might graze on attached life, or prey on associated organisms. This raises the possibility of biofouling of important underwater devices².

H.4.2 On-shore facilities

The on-shore facilities associated with the ocean disposal of CO₂ would include a pumping station and storage tanks. The construction of such structures may result in the disruption of coastal habitat. There is also a remote risk of the accidental release of CO₂ enriched seawater, which is acidic as discussed in Section 3.

² Golomb D. 1993. Ocean Disposal of CO₂: Feasibility, Economics and Effects. *Energy Conversion and Management* **34**(9-11): 967 – 976.

Appendix I
Calculation of Capacity

APPENDIX I

Calculation of Capacity

I.1 ASSUMPTIONS

An objective of this study is to estimate the potential capacity for the concept of seawater scrubbing of CO₂ from fossil fuel fired power plants to contribute to the worldwide reduction in Greenhouse Gas emissions. This estimate is based on coal-fired power plants. The potential capacity to mitigate CO₂ from power plants would increase if some of those power plants were gas-fired.

There are many uncertainties associated with this concept, in particular the environmental consequences of the discharge of acidified water into the deep-ocean. Notwithstanding those issues, an approximate estimate of world-wide CO₂ emission mitigation capacity is made, based on the following assumptions:-

- Seawater scrubbing is applied to a single 500 MW coal-fired IGCC power plant at each of the 89 locations identified in Appendix F.
- The process conditions and plant configuration are those described for the reference case in Appendix B in which 85% of the CO₂ is captured.
- The power plant operates at base load with 90% availability
- The lifetime of the power plant is 40 years
- Environmental considerations limit the allowable average increase in the dissolved carbon concentration in seawater to 5% of the natural concentration of 0.01%, i.e. a maximum increase of 5 milligrams per litre of seawater.
- The deep-ocean water below the thermocline is considered as a stationary body of water in which the concentration of dispersed CO₂ would gradually increase with time

The following factors are calculated based on these assumptions: -

- CO₂ captured = 365 tonnes per hour = 2.9 million tonnes per year per power plant.
- Total CO₂ captured over 40-year lifetime of the power plant = 115 million tonnes.
- Allowable CO₂ absorption capacity of seawater = 5000 tonnes per cubic kilometer
- Volume of ocean required per installation for injected CO₂ over 40 years
= 23,000 cubic kilometers

In order to avoid compounding of environmental effects from adjacent seawater scrubbing installations, a spacing between installations has been adopted which allows each installation exclusive access to 25 cubic kilometers of deep-ocean water. The corresponding radius of influence for each case has been calculated with reference to the local ocean bathymetry. The minimum spacing of the installations along coastlines ranges from 100 to 200 km.

Appendix I – Calculation of Capacity

According to the criteria described in Appendix F, 89 potential locations for seawater scrubbing installations have been identified. On this basis, seawater scrubbing has the worldwide potential to remove about 260 million tonnes of CO₂ per year from coastal coal fired power plants. Table I-1 shows the dependence of this CO₂ disposal capacity on the CO₂ discharge pipeline length.

Table I-1 CO₂ capture potential of seawater scrubbing

Discharge pipeline lengths	Number of locations	Million tonnes per year CO₂ potentially captured
Up to 10 km	11	32
11 km to 25 km	20	58
26km-50km	28	82
51 km to 100 km	30	87
Total <100km	89	260

IEA projections in the World Coal Outlook¹ indicate that, under a business-as-usual scenario, coal-fired electric power generation in 2020 might emit about 9000 million tonnes of CO₂ per year. Therefore, subject to the criteria adopted for the development of this estimate, the use of seawater scrubbing could have the potential to mitigate about 3% of the world CO₂ emissions from coal-fired power generation in 2020.

I.2 ADDITIONAL CAPACITY

Several of the assumptions contributing to the estimate presented in Section 5.1 are conservative. The following considerations indicate that additional capacity might be available if the principle of seawater scrubbing for CO₂ abatement were found to be technically and economically feasible and environmentally acceptable, and if the demand for electricity in small countries with suitable coastline increases significantly.

I.2.1 Multiple units on a site

In some states the scope for the application of seawater scrubbing for CO₂ abatement is not limited by demand, but by the number of potential locations of separate 500 MW power plants along suitable coastline. In these cases, multiple 500 MW units on the same site would increase the capacity for CO₂ abatement by seawater scrubbing. There would also be economies of scale to be realised by the installation of multiple 500 MW units on a common site. Appendix F identifies states where multiple units could be installed on the same site without exceeding the local electricity demands.

If the criterion of separate 500 MW power plants were to be relaxed in favour of allowing up to 3 GW of generation capacity per site, then the total number of potential 500 MW

¹ Ecoal, World Coal Institute 30th June 1999

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units with seawater scrubbing would be increased nearly four times from 89 to 347 units. Countries where there is potential to increase capacity by the use of multiple 500 MW units on a site include; Australia, Burma, India, Indonesia, Japan, Mexico, Pakistan, Portugal, Spain, South Africa, Taiwan and USA.

I.2.2 Disposal into enclosed seas

One of the criteria on which the assessment of carried out is that the injected CO₂ solution must be able to ultimately disperse into the deep-oceans. Therefore disposal into seas which are not connected to the ocean by deep water has been excluded. If this criterion were to be relaxed then some addition capacity would be available. Table I.2 shows the states with coastline meeting the criteria detailed in Appendix F which could potentially host seawater scrubbing installations discharging into the Black Sea, the Mediterranean Sea, the Sea of Japan and the South China Sea. The other enclosed seas are not suitable because of inadequate depth close to well-populated land.

Table I-2 Opportunities for Seawater Scrubbing via Enclosed Seas

Sea	States	Number of locations	Average pipe length - km	Minimum pipe length - km
Black Sea	Turkey	3	30	12
	Bulgaria	1	70	70
	Ukraine	1	25	25
	Russia	1	250	25
Mediterranean	Lebanon	1	60	60
	Turkey	2	40	20
	Greece	2	20	15
	Italy	8	50	25
	Egypt	2	80	50
	Libya	2	80	40
	Spain	2	45	25
	Algeria	4	40	20
	France	2	25	25
Sea of Japan	Japan	5	25	10
	Russia	1	30	30
	North Korea	4	25	10
	South Korea	2	50	40
South China Sea	Taiwan	2	40	30

Table I.2 shows there could be addition seawater scrubbing locations comprising 6 into the Black Sea, 25 into the Mediterranean Sea, 12 into the Sea of Japan and 2 into the South China Sea. These opportunities are unlikely to be constrained by the demand for

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thermal electricity. These 45 enclosed sea locations correspond to a 50% increase in the world seawater scrubbing capacity.

The enclosed seas do not present the same potential for ultimate dispersion of CO₂ into deep-ocean water as is afforded by oceans. The total volume of waters of the Black Sea which are deeper than 1500 metres is approximately 150,000 cubic kilometres. On the basis, derived in Appendix H, that an allowance of 25,000 cubic kilometers of deep water per 500 MW power plant is unlikely to result in adverse environmental effect, six seawater scrubbing installations around the Black Sea is about the maximum which that body of water could accommodate.

The bodies of water deeper than 1500 m in the Mediterranean Sea, the Sea of Japan and the South China Sea are approximately 1.7, 0.7 and 1.5 million cubic kilometers respectively. Therefore the number of installations listed in Table 5-1 would account for about 35%, 45% and 3% of the ultimate capacity of those enclosed seas.

Following the arguments presented in Section I.2.1, the locations bordering the Mediterranean Sea, the Sea of Japan and the South China Sea could have the potential for multiple units at each location. If the maximum capacity of the Mediterranean Sea and the Sea of Japan were to be utilised for seawater scrubbing then an additional 72 units might be accommodated.

It is noted that consideration of enclosed seas for CO₂ disposal differs significantly from the use of the open ocean, because the enclosed seas do not have the same potential to regenerate absorptive capacity in the long term.

I.2.3 Impact of deep sea currents

This assessment has been based on the simple conservative assumption that deep-ocean water is effectively a stationary body of water into which the CO₂ disperses. However there are major currents in the deep-ocean. A principal mechanism causing deep-ocean currents is a sinking of cold water at the poles and a corresponding upwelling at the equator. Local impacts of deep-water movements in coastal regions will depend on site-specific factors, such as local topography.

The diameter of the mass of water influenced by diluted CO₂ from a power plant over 40 years of operation is typically estimated to be about 100 km. Therefore a deep water current in excess of about 0.3 metres per hour could have the effect of sweeping way the CO₂-laden water into an unaffected region, thus extending the capacity of a site to accommodate seawater scrubbing indefinitely.

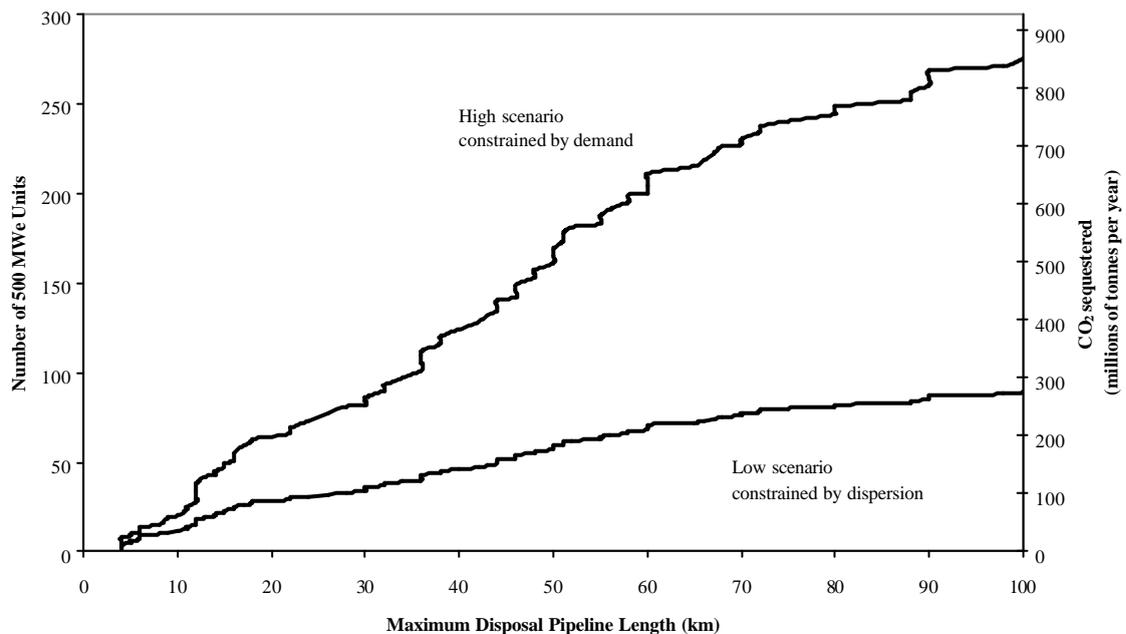
A simple one dimensional model of the effect of a slow current parallel to a steeply shelving coastline with a series of seawater scrubbing installations, would predict that the impact of the injected CO₂ would be displaced along the coast with no significant increase in capacity. However, faster currents in the whole deep-ocean environment have the potential to eliminate the dispersion constraint on the frequency or multiplicity of seawater scrubbing installations. Further study of deep-ocean currents would be required to quantify this issue.

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If deep-ocean dispersion is not a constraint on the number of seawater scrubbing installations, then the capacity for seawater scrubbing to contribute to CO₂ emission reduction in suitable locations is constrained primarily by the demand for electricity from the corresponding coal fired power plants. As identified in Appendix F, in the absence of other constraints, many developed states currently have a large demand for thermal electricity.

On this basis, Figure I-1 shows the dependence of the worldwide capacity for seawater scrubbing on disposal pipe length for two scenarios. The low scenario is dispersion-limited and is based on conservative assumptions to avoid compounding environmental effects. The high scenario is demand limited and is based on generic assumptions about the potential market for coal-fired base-load electricity.

Figure I-1 Worldwide Capacity for Seawater Scrubbing Installations



An important caveat which must be considered with regard to the estimates presented in Figure I-1 is that they are dependent on the environmental acceptability of the discharge of acidified seawater into a stationary body of deep-ocean water. If environmental concerns dictate that deep-ocean discharge can only take place where there are strong deep water currents to aid dispersion, then these capacity estimates may be greatly reduced.

Appendix J
Bibliography

APPENDIX J

Bibliography

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