The Commissioners,
Essential Services Commission,
Melbourne.

We refer to the application by Alcoa of Australia Limited re the Anglesea Power Station.

Our belief is that emphasis should be placed on the following, having regard to the siting of the power station.

1. Emissions: The power station is ideally located to operate with nil emissions as shown in the attachment "pulse combustion gasifiers 2.4.13". It can do so with nil increase in generating costs.
2. Cost of Power: This should be reduced in line with the above attachment claims. It does require modification to the power station which modifications will be self financing.
3. By Products: The fly ash is in demand and can be usefully used in cements. We can help in that regard if called upon. The sand supply is excellent and is required by industry, again we could help. An associated company (Westbury's) did extract sand.
4. Methane can be produced from the deposit as discussed below. Prices are attractive.

Docklands Science Park (DSP) has a patented and proven system being pulse combustion powered thermoacoustic refrigeration of greenhouse gases (PUTAR) which system produces 5.19 MWh of electrical power from one tonne of brown or black coal, versus 1.6 MWh which is the national average in Australia.
This can be done with **nil** emissions of greenhouse gases as they can be sequestrated, as liquids, in the subsea silts under 3,000 metres of seawater.
The cost of the electricity can be reduced by 10% even after sequestrating forever the liquefied greenhouse gases. See "Nat Academy CO2 storage", attachment.

An essential part of the process is the gasification of coal at the front end. It is a proven technology for many years, here and in USA. The technology, in Australia, has recently been improved by the use of acoustic resonance. Hence a production cost from brown coal and household rubbish at less than $1.00 per GJ.

We, Docklands Science Park, can provide the gas, extremely cheaply (see attachment) and transport it from the Latrobe Valley (as an example) to Melbourne or the Sydney area, using our armoured flexible, 30 inch pipeline we are developing with CSIRO. We can do it in the fast vanishing time to provide Sydney with gas! Hopefully we can use the existing easement. If not this pipeline allows the easy laying of the pipeline out to sea and back into Sydney or Melbourne and that might be the quickest route.

We are working on producing methane from our low grade coals (works better than with high grade which are more expensive) to which we add putrescible rubbish.

The production cost of the gas will be under $1.00 per gigajoule (GJ). Origin, a major gas supplier in Australia, want $10 per GJ which is outrageous when we have so much coal and plenty of household rubbish.

The gasifier shown in Section "A3 Gasifier", in the attached "pulse combustion gasifiers" is the one which was built for Wollongong Council and which was engineered to produce methane (CH4).
EDL did the construction, a person named Wall Hammonds was an engineer on site, contactable on Int'l 61-417061198. He can verify the performance of the unit. It has since been demolished to make

way for a council car park, or similar, unfortunately. The technology has advanced since then, hence we will build a small pilot plant.

Dr. David Proctor, consultant to Docklands Science Park (DSP) was the principal designer and he is here, with us in Melbourne.
CO2 emissions, or greenhouse gases in total, can be captured, as described in the attachment, using the PUTAR process. They are liquefied and can be pumped out to 3,000 metres depth and entombed forever in the silts. See the description of the process by Harvard University, "Nat.Academy CO2 Storage", attached. This has been endorsed by Stanford University and experiments carried out off Long Beach California.

We, holding the relevant patents, can action this matter immediately and would be able to produce large quantities of methane for requirements. Scaling up and multiple units are not problems of note.

Happy to talk to any interested group. Having had a family beach house at Anglesea for many years we are quite familiar with the mine and the local worries. Compatibility can be arranged.

All the best,

John Martin,
Docklands Science Park,
Phone, Int'tl 61 3 96141234
Mobile phone, Int'l 61 425 858 567,
New Office address:
North Building, Level 5,
333 Collins Street, Melbourne. 3000.
Website "www.docscipark.com.au"

PULSE COMBUSTION GASIFIERS

Summary

The use of pulse combustion technologies allows for the convertion of various cabon based materials to be converted into suitable fuels or electricity.

The cost of gases produced from black coal is \$0.40 GJ^{-1}

The cost of producing electricity using similar technologies is \$25.8/MW-h.

The bulk of the document (PART A) explains how and why pulse combustion has been chosen. PART B describes the new gasifier. Two case studies (PART C) are presented how the plant schematics might look. One is to produce $100MW_{thermal}$ equivalent of a gaseous fuel from black coal. The second is to produce $100MW_{elect}$ from black coal.

PART A PULSE COMBUSTION

1. Pulsed Combustion Technology and Its Benefits

Introduction

Much effort has gone into research on improving the emissions from combustion processes. These have addressed the reduction of the NO_x and SO_x, the elimination of unburnt hydrocarbons and CO. In some cases this has led to minor improvement in the ability to recover more heat from the exhaust gases, but these effect are at the best conditions only minimal. The conditions under which this occurs are attained through fan forced combustion processes. In terms of greenhouse gas production from a combustion process, this adds typically 3% to the effective CO_2 emission total. In the current global warming climate this is undesirable.

Combustion Basics

It would appear from combustion research community (Glassman (2000)), that purpose of combustion has been forgotten. The main purpose of burning fuel is to drive a desired process to produce a product by getting the released energy into the process as efficiently as possible. Most combustion engineers have concentrated on the combustion process itself. They have ignored what happens to the released energy.

Firstly, if we look at what happens to fuel, F, in a process, some of the energy ends up in the reactants and products, Q, and the rest as losses, L. The losses are determined in part by:

1. Unburnt fuel,
2. The process temperature,
3. The size of the plant, and
4. The exhaust temperature.

Unburnt fuel can be addressed by improving the combustion process itself. The unburnt fuel normally consists of some hydrocarbons and carbon monoxide. The item (2) is fixed and only the last two, (3) and (4), can be changed to lower the losses from the process. For both these items, the plant size and the exhaust temperature have to be lowered. The flip side of decreasing the plant size is that other factors driving the process of getting the liberated combustion energy into the process have to increase. What determines how much of the liberated combustion energy gets used in the process is determined by:

1. The heat transfer coefficients, U,
2. The heat transfer area , A, (which in turn controls the plant size), and
3. The difference between the combustion/flue gas temperature and the process temperature, ΔT.

In summary:

$$F = Q + L$$

i.e.

$$F = U.A.\,\Delta T + L$$

If A is increased, L will also increase. Thus to maximise Q and minimise L only U and ΔT can be increased, whilst the physical size of the plant has to be reduced. Increasing the flame temperature can increase ΔT, but for most combustion processes this only increases the NO_X in the exhaust. This is undesirable. If the heat transfer area is decreased not only has U to be increased to compensate, but U also has to be increased to transfer more heat into the process. This brings us to the second point - how is U to be increased?

There have been efforts to improve the heat transfer from fluids by flow pulsation (West & Taylor (1952); Linke & Hufschmidt (1958); Darling (1959); Lemilich & Armour (1965); Jackson & Purdy (1965); Baird (1967); Milburn (1969); Milburn & Baird (1970); Keil & Baird (1971). The mechanism to enhance the heat transfer has been through solenoid switching of the flow direction or pulsing the flow via a piston or set of pistons. The increase in the heat transfer coefficients obtain in these tests was of the order of 70%. Similar work has been done on enhancing mass transfer coefficients. Chandhok *et al* (1990) showed that under the correct conditions the mass transfer coefficient could be increased by 2 orders of magnitude. The main influencing factor is not the frequency of the pulsations, but the amplitude. The higher the amplitude the higher the increase in the transfer coefficient.

The work described here explores another method of enhancing the heat transfer coefficients through the use of self driven oscillation provided by the combustion process itself, namely pulse combustion.

Pulse Combustion

What is it?

Pulse combustion has been around since 1777, when Dr Higgins demonstrated his “singing flame”. During the WW2 it was used successfully by the Germans as the propulsion unit for the V-1 “buzz bombs”.

Pulse combustion is the consequence of a combustion instability that is driven into resonance by the geometry of the burner. Normally combustion engineers avoid combustion-generated instabilities at all costs, since they can very quickly lead to catastrophes. Here we actively utilise the instability to gain a number of advantages. This resonant driving locks the combustion instability into a very stable repetitive pattern at the resonant frequency, which can be anywhere between 1Hz to 20000Hz, but more frequently lies in 20Hz and 1000Hz range. The burner can become self-aspirating and there is no need for a fan to continuously supply the combustion air to overcome the acoustic pressure waves. The flame is not continuous but a series of discrete flamelets, that are ignited on the hot remnant gases of prior flamelets. Here we actively utilises the combustion instability to gain a number of advantages.

As a result, overall heat transfer and mass transfer coefficients are two orders of magnitude higher than conventional systems. The implications of this are that the size of the equipment can be reduced, i.e. the heat transfer area can be more than halved to carry out the same duty as a forced convection conventional combustion system supplying heat to an industrial/agricultural processes.

The acoustic pressure waves cause the gases (fuel, air and combustion products) and material in the combustion chamber and exhaust to oscillate rapidly. This has at least three known effects that cause an increase in the transfer rates:

- the boundary layer never gets a chance to establish itself and consequently it is always trying to develop,
- the temperature and concentration gradients at right angles to the mean flow are periodically extremely large, and
- thirdly, the heat transfer surfaces experience micro-vibrations that increase the heat transfer (Bergles 1969).

These effects are more than additive and as a result the transfer coefficients are at least two orders of magnitude greater than in conventional systems. We have seen evidence of a fourth effect increasing the heat transfer rate in which there is a thermal wave travelling into the material being heated. This has also been theoretically postulated by Merkin & Pop (2000), whose theoretical work indicates that there should be thermal waves assisting the heat transfer into the bulk of the material being heated.

2. Why use pulse combustion and what gains does it give?

1. Overall heat transfer and mass transfer coefficients that are two orders of magnitude higher than conventional systems. The implications of this are that the size of the equipment can be reduced for industrial process.
2. Exhaust gas emissions from pulse combustion are amongst the lowest available in the world, NO_X levels about a quarter of those proposed for the latest Californian emissions. Most people are only worried about the nitrogen dioxide (NO_2) emissions, but they should also be concerned about the nitric oxide (NO) emissions as they can rapidly turn into NO_2. Pulse combustion systems can deliver NO_X emission levels (i.e. NO plus NO_2) as low as 2 to 3ng/J of useful heat. Current mandated levels of total NO_X are at the 40ng/J of useful heat level. The proposed levels for California are 9ng/J of useful heat. Raising the inlet air temperature, to conserve energy, does not increase the NO_X levels, as would normally be expected with conventional systems.
3. Total hydrocarbon (THC) and carbon monoxide (CO) levels of zero attainable. In the best of conventional combustion systems there are usually small quantities of unburnt hydrocarbons and CO present in the exhaust gases.
4. SO_X emissions could possibly be reduced as well, for the same mechanism should also be present as in the NO_X formation chemistry. What the reductions might be is very hard to put a figure on it, as no measurements have been made with sulphur containing fuels.
5. Thermal efficiency of systems can be as high as 97%. This includes parasitic energy, which in the case of pulse combustors is minimal and only occurs at start-up. For other high efficiency combustion systems, forced convection, via fans, is used to increase the efficiency, but these consume about 3% of the energy supplies (9% if the primary energy is considered).
6. Greenhouse gas emissions per unit of desired duty can be dramatically reduced. There are many processes that can have their thermal input supplied by pulse combustion. They cover the following areas, which is by no means exhaustive:
    heating of gases, liquids and granular solids (10 to 25%)
    rotary kilns (10 to 50%)
    fluidised beds (20 to 60%)
    metal re-heat, annealing, etc. (10 to 35%)
    absorption refrigeration (40 to 75%)
    chemical reactor driving (20 to 40%)
    spray drying (10 to 35%)

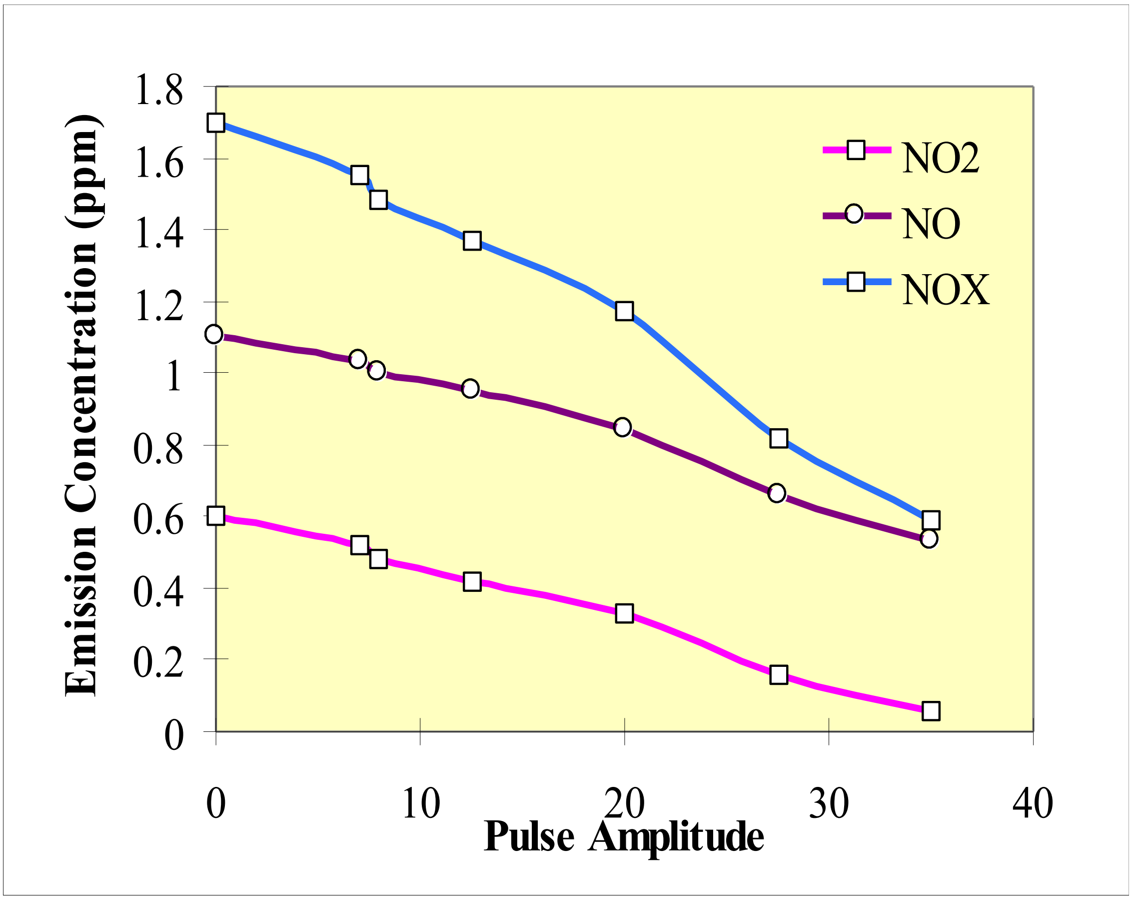
The figures in brackets are the potential fuel savings/greenhouse gas reductions that can be obtained. The particular process involved causes the range. The reasons for the reductions are several:

(a) Physical size of process equipment is smaller and hence energy losses are reduced. The corollary of this is that production can be increased for a given size of equipment when the thermal input is via pulse combustion.

(b) Throughput can be increased. In some situations the flow of product through a process is limited by the need to minimise the pick-up of material into the exhaust stream. As a result of the high heat transfer rates attainable with pulse combustion, the product stream can be separated from the combustion products and exhaust streams. This can result in the elimination of expensive dust removal facilities, such as electrostatic precipitators, and an increase in the throughput of product.

(c) Equipment tends to be self cleaning, i.e. as-new performance throughout the life of the plant. This effect results from the micro-vibrations that are generated. Even if the transfer equipment is fouled, in some instances it can be cleaned as soon as pulse combustion starts. In many process operations, fouling of equipment can represent an added cost as well as being a bottleneck in the process.

3 NO_x reductions as a function of the pulse combustion amplitude



The above figure shows what happens to the NO_X in a flame as the amplitude of the pulsing is increased. This causes two things to happen:

1. The flame gets stretched. As a consequence fuel fragments or radicals such as -CHO are no longer produced or their concentration is greatly reduced that their contributions to NO_X production chemistry is almost eliminated.
2. The resulting acoustic flow field also causes local exhaust gas recirculation. This suppresses NO_X formation by making it much harder for more NO_X to be produced.

It is because these two effects are occurring in pulse combustors, that it is possible to preheat the incoming combustion air without causing the NO_X levels to substantially increase.

The Rijke Tube Pulse Combustor

We propose using Rijke tubes for transferring the heat. Rijke tube pulse combustors are the simplest form from a construction and operating point of view. To date all who have used them have used them in a vertical arrangement, because it was thought they would not work in any other position. This has precluded their use for many applications. We have shown that it is possible to operate Rijke tube pulse combustors in the horizontal position or combinations of horizontal and vertical tubes, without loss of the advantages listed above. The drawback about using the Rijke tube in the purely horizontal position is that it requires a small constantly running fan to get the air and fuel into the tube.

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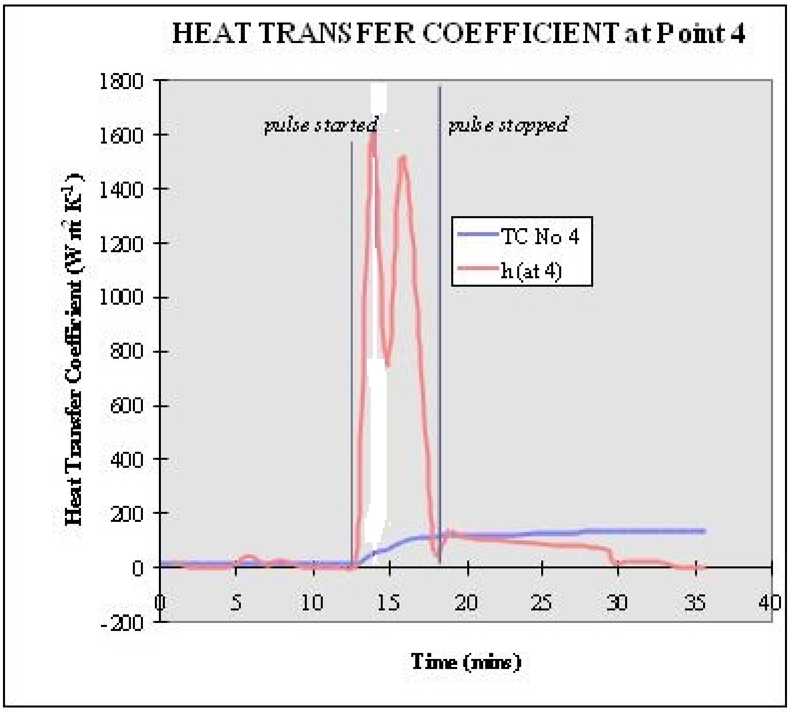
2. Deep bed heat transfer results

One of the experiments that we conducted involved running a special pulse combustor under varying rates of pulsing. The set up consisted of a deep bed of alumina with a pulse combustor embedded in the alumina with the option of having inert gas flowing through the bed, but not fluidising the bed.

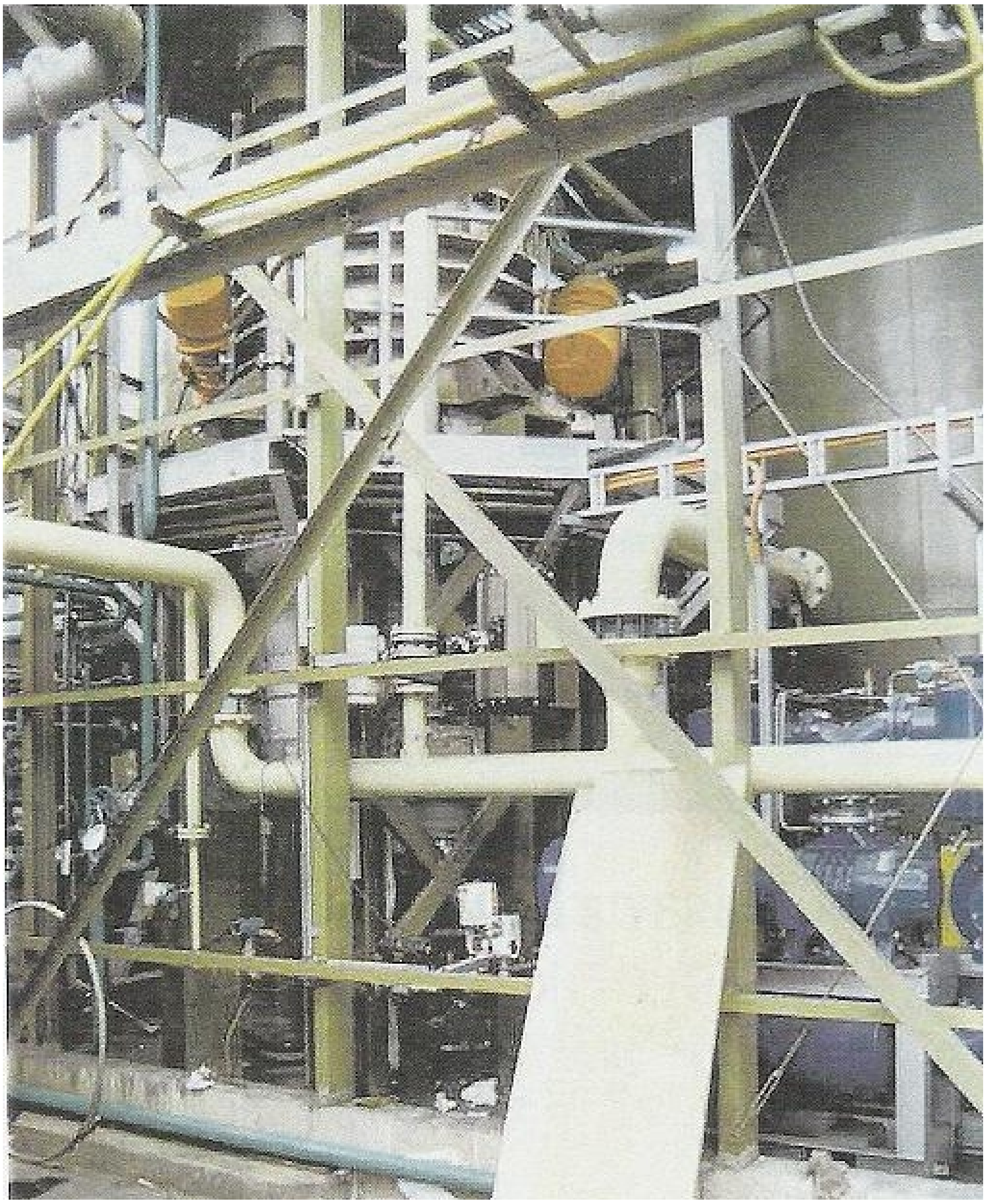


The above figure shows the temperature in the bed at one of the many locations in the alumina bed along with the derived heat transfer coefficient. Up to the 12.5 minute mark there is just conventional heating, then the pulsing is started then stopped at the 17.5 minute mark and the inert gas is left bubbling through the bed. When the pulse combustor was running, the bed appeared to be fluidised.

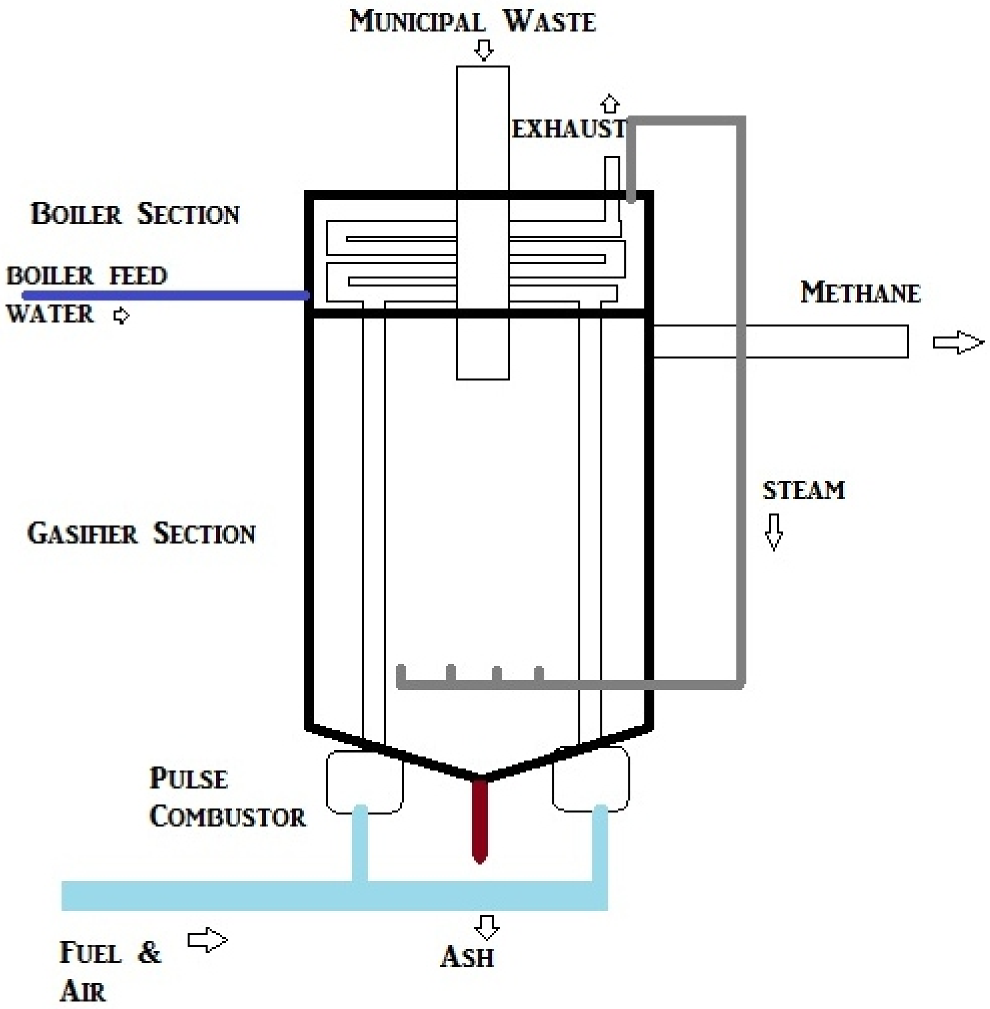
In another totally separate experiment involving the drying of a thick wet slab of plaster like material, rather than the surface next to the pulse combustor dry out first, the slab dried out as a whole. This, and what happened in the alumina bed corroberates what has been theoretically postulated by Merkin & Pop (2000), whose theoretical work indicates that there should be thermal waves assisting the heat transfer into the bulk of the material being heated.

3. Gasifier

The first commercial sized gasifier built was a twin 2.5MWt pulse combustion unit, processing prepared municipal waste to produce methane. This methane was used as the fuel in a modified diesel generating set linked to the NSW grid.



The above is a picture of this gasifier. Some idea of the size can be gained from the walkway around the gasifier where the orange cylinders are placed. Total oveall height is 5m. A block diagram of the unit is shown in the figure below. Although this unit met its performance criteria, we were not entirly satisfied and thought that it could be done better. Once we had developed the Delafield Pulse Steam Boiler, it became obvious to us how this could be achieved. A schematic diagram of the above unit is shown below:

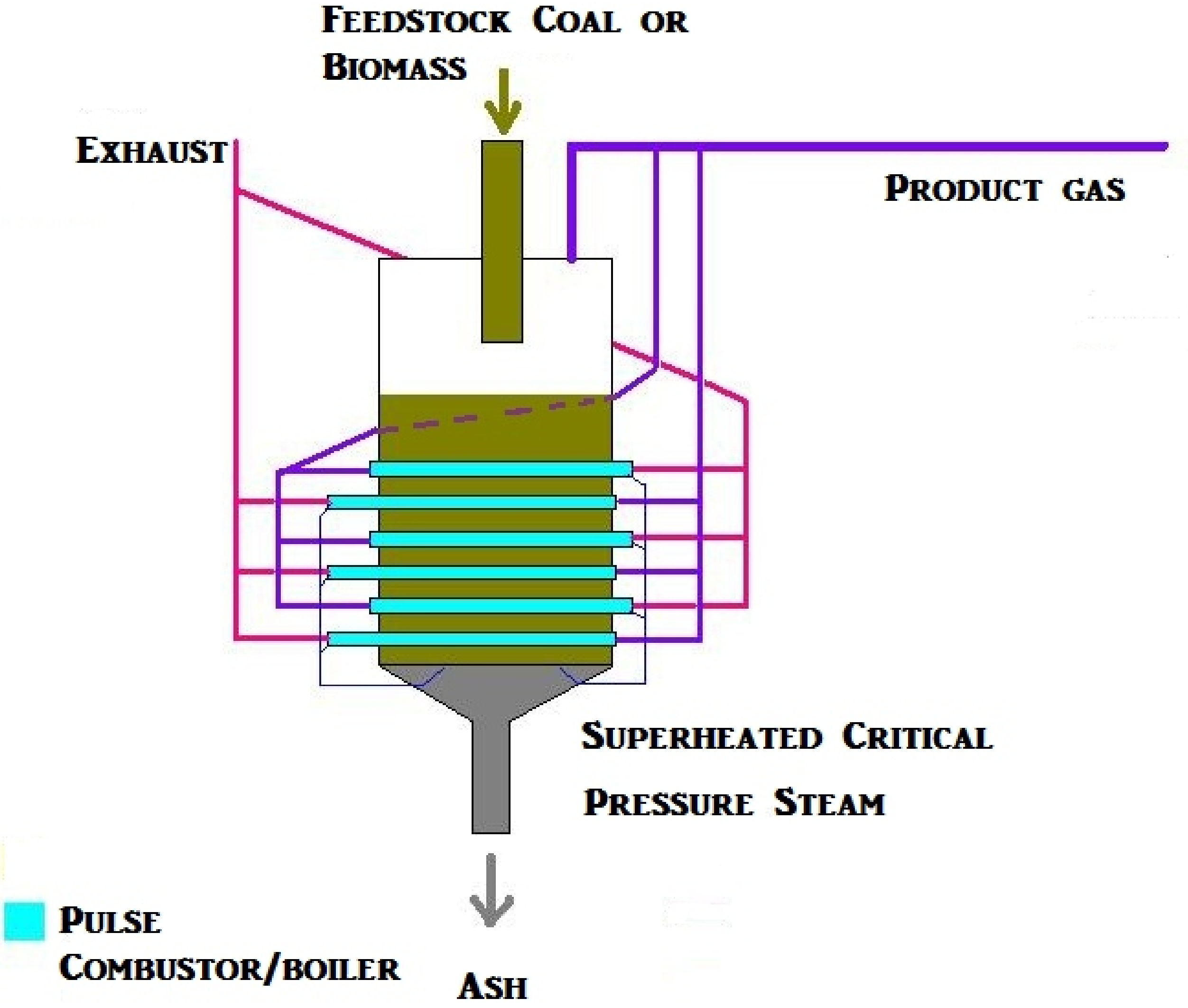


PART B NEW PULSE GASIFIER

The Delafield Pulse Steam Boiler was originally developed for steam sterilisation of soil. Its light weight and compactness opened up a whole range of new possibilities for pulse combustion applications. By combining the boiler section and the gasifier section into one, made the system more efficient, compact and cheaper to construct.

It is possible to add extra steam boilers into the gasifier to produce steam for other part of the plant close by, e.g. Steam turbine for power generation. The critical pressure steam injected into the gasifier will help stir the feedstock up along with the pulse combustor vibrations. The hot exhaust gases from the pulse combustors are used to pre-heat the incoming feed stock, which incidentally doesn't need to be dry. The ash that results from the process is suitable for soil conditioning or for geopolymer cement, depending on the what is used as a feedstock.

The gas that is produced depends on a number of factors such as feedstock, pressure and temperature inside the gasifier. Methane tends to be produced from biomass and brown coal at pressure and about 800°C temperature, whereas $H_2/CO/CO_2$ mix is produced from black coal at low pressure and 1000°C. In both cases the resultant gas can be improved by removing the CO_2 using another pulse combustion driven refigeration process that we have developed, viz. the PUTAR, which is also capable of liqifying methane. A schematic diagram of the gasifier is shown below:



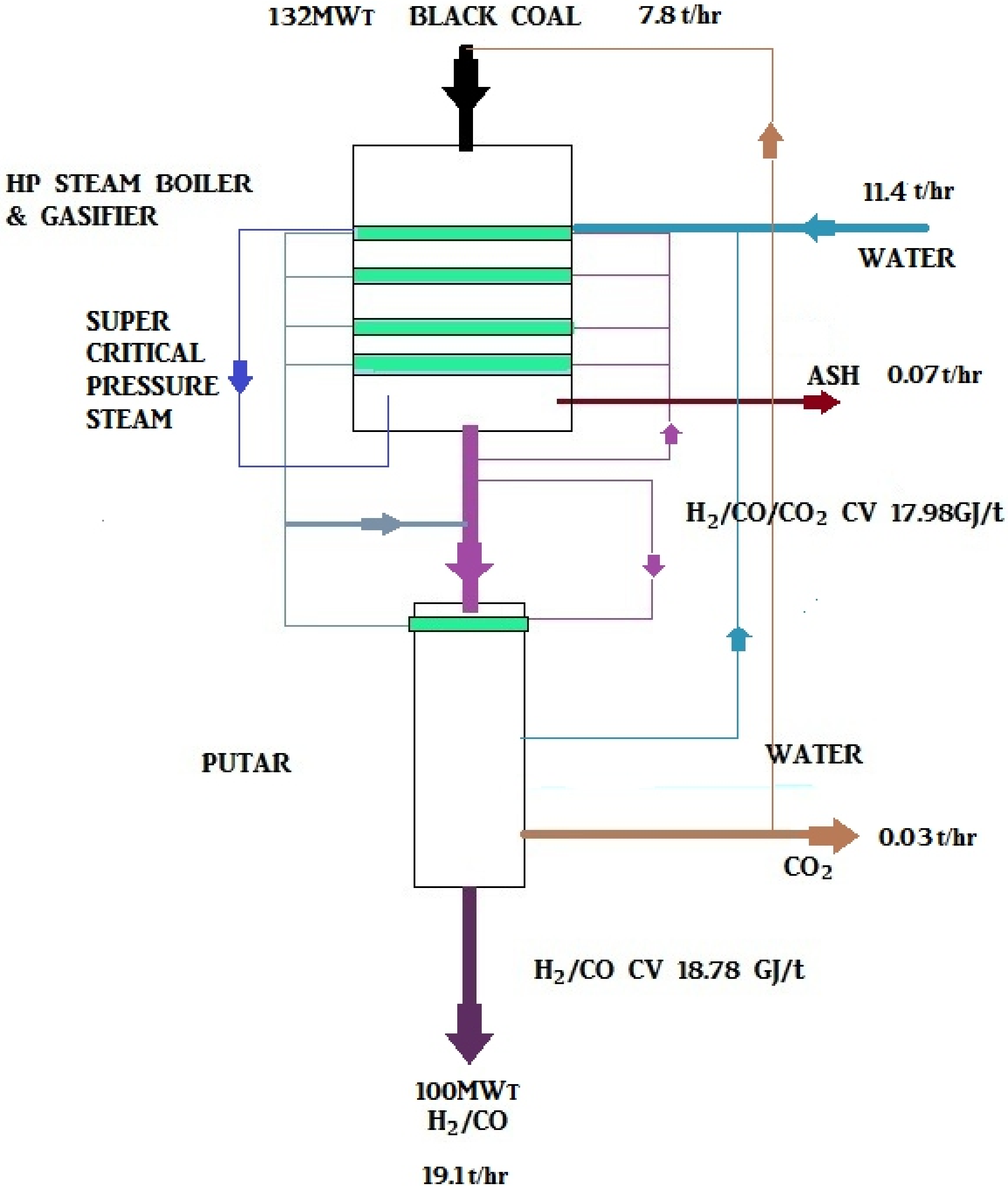
PART C CASE STUDIES

1. 100MWt Gasifier

This example is based on NSW black coal. The coal is fed into the gasifier in a CO_2 atmosphere. The CO_2 is present to suppress some of the reactions that could take place if it were absent. Temperature of the gasifier is 1000°C which results in a $H_2/CO/CO_2$ mixture with a CV of 17.98GJ/t. If we are not worried about the CO_2 in the mixture, the gas can be used as is, as we do in the pulse combustor boilers and heaters in this case.

This gas mixture can be enhanced by removing the CO_2 with the PUTAR. This device sequentially removes each gas according to their boiling points. It is a thermoacoustic refrigerator driven by pulse combustion heaters. The resultant CV of the H_2/CO mixture is 18.78GJ/t.

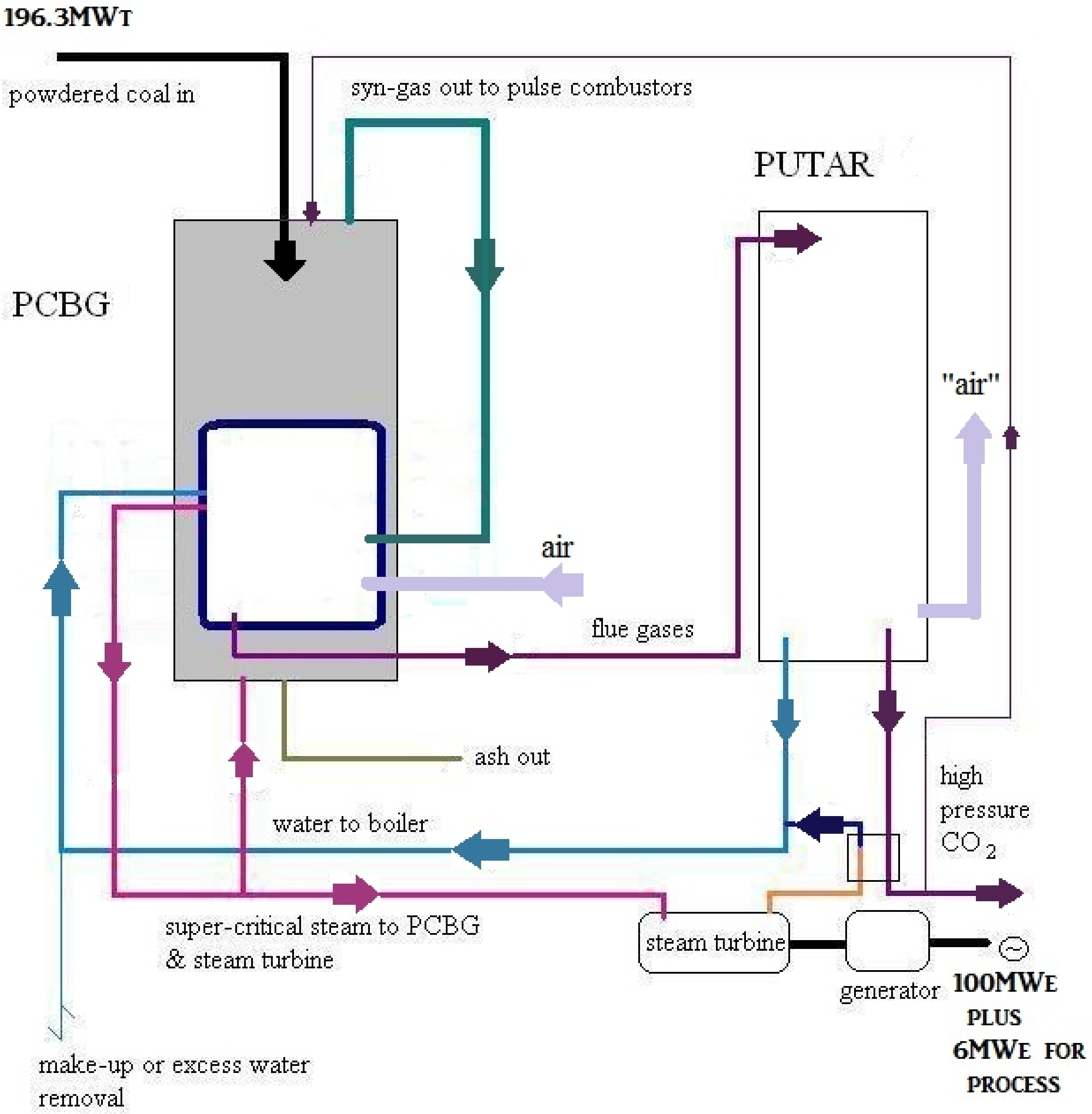
For simplicity a number of heat exhangers are not shown. These are plate heat exchangers with very low pressure drops and low temperature differences and are used to shuffle heat between varying streams. The CO_2 can be collected and converted into a variety of materials and fuels.



The cost of producing the H_2/CO mixture is \$0.40/GJ. Similar costs can be expected when methane is produced in the mixture of resulting gases. No account has been taken of the convertion of CO_2 to other fuels nor the selling of the ash as a soil conditioner or input to geopolymer production.

2. 100MWe of CO_2 free electricity

This process is slightly different from the above one, in that all the gas produced in the gasifier goes to raising super critical pressure steam for the steam turbine. No cooling towers are required since the cold CO_2 steam is used for the steam turbine condenser, which results in an additional 5 percentage point gain in the Carnot efficiency. The pulse combustion steam boilers have been measured at 98% efficiency (based on the higher heating value of the fuel), but in this example the boiler has been rated at 95% efficient. The PUTAR is used to strip all the moisture and CO_2 out of the exhaust steam and reject a nitrogen rich, CO_2 depleted air stream to the atmosphere.



The net cost of the electricity (again no account has been taken of the convertion of CO_2 to other fuels nor the selling of the ash as a soil conditioner or input to geopolymer production) delivered to the grid is $25.8/MW-h. This is similar to the cost of electricity production from newer systems with say IGCC plants without the CO_2 removal.

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Permanent carbon dioxide storage in deep-sea sediments

Kurt Zenz House, Daniel P. Schrag, Charles F. Harvey, and Klaus S. Lackner

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Permanent carbon dioxide storage in deep-sea sediments

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Communicated by John P. Holdren, Harvard University, Cambridge, MA, June 27, 2006 (received for review November 10, 2005)

Stabilizing the concentration of atmospheric CO_2 may require storing enormous quantities of captured anthropogenic CO_2 in near-permanent geologic reservoirs. Because of the subsurface temperature profile of terrestrial storage sites, CO_2 stored in these reservoirs is buoyant. As a result, a portion of the injected CO_2 can escape if the reservoir is not appropriately sealed. We show that injecting CO_2 into deep-sea sediments <3,000-m water depth and a few hundred meters of sediment provides permanent geologic storage even with large geomechanical perturbations. At the high pressures and low temperatures common in deep-sea sediments, CO_2 resides in its liquid phase and can be denser than the overlying pore fluid, causing the injected CO_2 to be gravitationally stable. Additionally, CO_2 hydrate formation will impede the flow of $CO_2(l)$ and serve as a second cap on the system. The evolution of the CO_2 plume is described qualitatively from the injection to the formation of CO_2 hydrates and finally to the dilution of the $CO_2(aq)$ solution by diffusion. If calcareous sediments are chosen, then the dissolution of carbonate host rock by the $CO_2(aq)$ solution will slightly increase porosity, which may cause large increases in permeability. Karst formation, however, is unlikely because total dissolution is limited to only a few percent of the rock volume. The total CO_2 storage capacity within the 200-mile economic zone of the U.S. coastline is enormous, capable of storing thousands of years of current U.S. CO_2 emissions.

climate change | CO_2 hydrates | energy | sequestration

Supplying the energy demanded by world economic growth without affecting the Earth's climate is one of the most pressing technical and economic challenges of our time. If fossil fuels, particularly coal, remain the dominant energy source of the 21st century, then stabilizing the concentration of atmospheric CO_2 will require developing the capability to capture CO_2 from the combustion of fossil fuels and store it safely away from the atmosphere (1).

Several ideas have been proposed for the long-term storage of captured anthropogenic CO_2. These proposals include: storing CO_2 in various geologic formations [e.g., oil and gas fields (2), coal beds (3), and saline aquifers (4)], injecting CO_2 into the deep ocean (5, 6), and chemically transforming CO_2 into thermodynamically stable minerals (1, 7) or bicarbonate brines (8, 9). We describe storing CO_2 in deep-sea sediments as a fourth storage option that combines beneficial elements of geologic storage, oceanic storage, and geochemical storage while addressing many of their drawbacks.

Storage of captured CO_2 in terrestrial geologic formations is a leading candidate for near-term storage. All terrestrial geologic formations, however, face a common challenge. Because of the geothermal gradient in the continental crust, the temperature at injection is always greater than the critical temperature of CO_2. Under the high pressures (10–30 MPa) and high temperatures (330–400 K) of terrestrial storage sites, supercritical CO_2 is 40–70% less dense than the surrounding pore fluid (10). This density contrast causes the buoyant CO_2 to migrate upward through any available conduit. As a result, all terrestrial storage reservoirs either must have impermeable layers (i.e., cap rocks) or all of the injected CO_2 must become immobile as residual saturation to prevent the release of buoyant fluids. Natural-gas reservoirs have existed for millions of years, demonstrating that geologic formations can store buoyant fluids for long time periods. Over the last century, however, millions of wells have been drilled in most of the basins being considered for geologic storage, and each of these wells is a potential conduit for buoyant CO_2 to escape (11). The concern over leakage will require geologic storage sites to be monitored for centuries, and it is unclear who will be responsible for verifying the storage integrity over these time scales.

Injecting CO_2 directly into the deep ocean, where most of it will dissolve as bicarbonate, is another option for CO_2 storage (12). Deep-ocean injection can be seen as accelerating the natural oceanic uptake of CO_2, which would occur over many centuries (13). Unfortunately, because of ocean currents and local supersaturation, a large fraction of the injected CO_2 will be released to the atmosphere after a few hundred years (14). Additionally, direct ocean storage is currently unpopular because of concerns about the effects of CO_2 on marine ecosystems.¶ Unless there is a change in the political climate, it is unlikely that direct ocean storage will be used on large scales.

Chemically transforming captured CO_2 into bicarbonate brines or thermodynamically stable minerals is a third storage option. Forming bicarbonate brines through the dissolution of calcium carbonate has been suggested as a way to neutralize carbonic acid before ocean injection (8, 9). Separately, it has been proposed that $CO_2(g)$ can be reacted with silicate minerals to form thermodynamically stable carbonate minerals (1). Mineralization, the most stable and permanent form of CO_2 storage, is an acceleration of the natural chemical weathering cycle (15). At surface temperatures, however, the reaction kinetics are very slow, and accelerating the kinetics to industrial rates with current technology costs 3 to 10 times more than terrestrial geologic storage (16).

Results

Gravitational Stability. Because of the high compressibility of $CO_2(l)$ relative to water, $CO_2(l)$ becomes denser than water at high pressures and low temperatures (Fig. 1). These temperature–pressure regimes do not exist in terrestrial settings; they are, however, common in the deep ocean. When $CO_2(l)$ is injected into the ocean at a depth of 3,000 m, it sinks, forming a lake of $CO_2(l)$ on the seafloor (17). As previously discussed, however, ocean currents will mix the injected $CO_2(l)$, causing a large fraction to eventually be released into the atmosphere (14). To ensure that deep ocean currents will not mix the CO_2 into shallower regions, CO_2 can be injected below the seafloor.

Conflict of interest statement: No conflicts declared.

Abbreviations: HFZ, hydrate formation zone; NBZ, negative buoyancy zone.

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¶Barry, J. P., Seibel, B. A. & Lovera, C., American Geophysical Union Fall Meeting, December 10–14, 2001, San Francisco, CA.

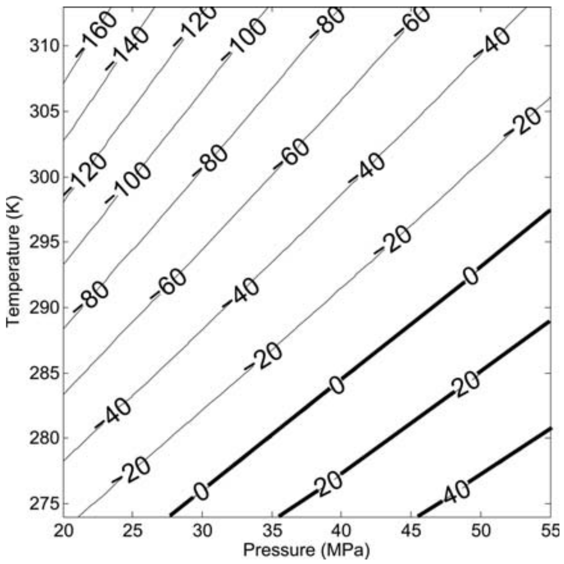

Fig. 1. Density (kg/m^3) difference between CO_2(l) and seawater (1,027 kg/m^3) as a function of temperature and pressure (10). The bold lines indicate the pressure–temperature space of the NBZ.

Furthermore, if the seafloor depth of injection is $>$3,000 m, then the injected CO_2 will be denser than the ambient pore fluid. The lower density pore fluid acts as a buoyancy cap on the system and ensures gravitational stability. The gravitational stability of the system in deep-sea sediments is in contrast with terrestrial geologic storage where the high pressures and high temperatures cause the injected supercritical CO_2 to be gravitationally unstable. The buoyancy cap, provided by the pore water, serves the same purpose in deep-sea sediments as a cap rock serves in terrestrial geologic formations. The buoyancy cap, however, is superior to a cap rock because conduits in a cap rock enable buoyant CO_2 to escape. In contrast, the gravitational stability provided by the buoyancy cap guarantees that fractures in the sediment column cannot serve as conduits for the CO_2, and even large geomechanical perturbations, such as earthquakes, cannot cause the CO_2(l) to be released.

Storing CO_2 in deep-sea sediments was first proposed by Koide *et al.* (18) who considered storing CO_2–clay–ash solutions and CO_2(l) below tens of meters of unconsolidated marine sediments. They identified three seafloor depth regimes for the storage of dissolved CO_2: "shallow subseabed" ($<$300 m), "deep subseabed" (300–3,700 m), and "super deep subseabed" ($>$3,700 m). In this study, we describe a different scenario than envisioned by Koide *et al.* Specifically, we consider injecting pure CO_2(l) below at least 3,000 m of ocean and several hundred meters of marine sediment. The key aspect of our study is to inject pure CO_2(l) below the sediment layer where CO_2 hydrates form and below the sediment layer of less dense pore fluid. As will be discussed, the relative location of these sediment layers and the injected CO_2(l) ensures permanent CO_2 storage.

The geothermal gradient, which varies from 0.02°C/m to 0.04°C/m, controls changes in the density of CO_2(l) injected into deep-sea sediments by expanding and contracting the mobile CO_2(l) until its density equals the density of the surrounding pore fluid. Given a seafloor depth of 3,500 m and a geothermal gradient of 0.03°C/m, the injected CO_2(l) becomes neutrally buoyant at $\approx$200 m below the seafloor (10). Above the sediment depth of neutral buoyancy, the CO_2(l) is denser than the ambient pore fluid. We refer to this range between the seafloor and the sediment depth of neutral buoyancy as the negative buoyancy zone (NBZ) (Fig. 2).

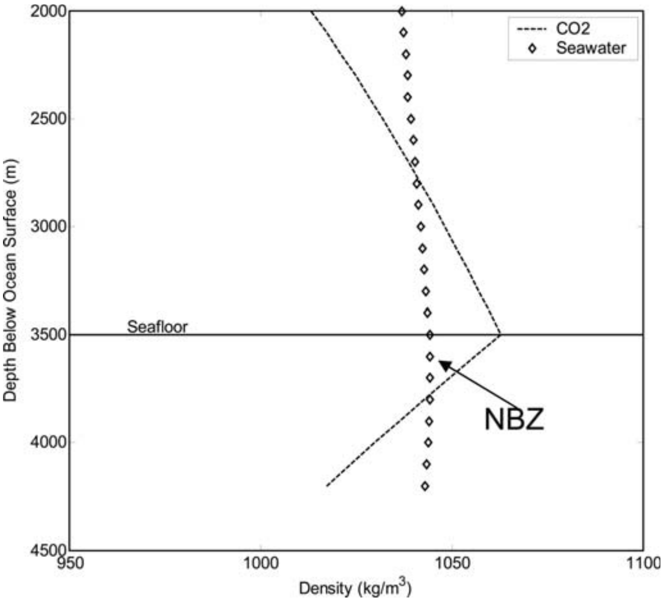

Fig. 2. Because CO_2(l) is more compressible than seawater, it becomes denser than seawater at $\approx$3,000 m (10). Once below the seafloor, however, the geothermal gradient causes the CO_2(l) to expand more rapidly than seawater. Eventually, the ambient temperature becomes hot enough that CO_2(l) becomes less dense than the pore fluid. (Note: A linear geothermal gradient of 0.03°C/m was assumed.)

Postinjection Chemistry and Sediment Composition. To fully describe the fate of CO_2 injected below the seafloor, the chemical reactions between CO_2, seawater, and sediments must be considered. CO_2 that has been injected into deep-sea sediments will slowly dissolve, forming a CO_2(aq) solution that is denser than the surrounding pore fluid (19). At 30 MPa and 3°C, the solution becomes saturated at a CO_2(aq) mole fraction of $\approx 5\%$ (20). The solubility of CO_2 indicates that a given quantity of CO_2(l) must interact with 20 times as much pore fluid to fully dissolve. Therefore, during the injection, CO_2(l) is the dominant phase.

The composition of the marine sediments near the injection site will determine how the injected CO_2 interacts with the host rock. Calcareous sediments might be an attractive repository because of their relatively high permeability (21) and their tendency to react with carbonic acid. If CO_2 were injected into calcareous sediments at high pressure, then the relatively low pH of the CO_2(aq) solution is expected to dissolve carbonate minerals and add alkalinity to the pore fluid. The addition of alkalinity to the pore fluid will decrease the concentration of CO_2(aq) by shifting the carbonate equilibrium toward bicarbonate. Bicarbonate is a more permanent storage state than CO_2(aq) because bicarbonate cannot directly degas from solution.

The total dissolution of carbonate minerals, however, is expected be relatively small; for a cubic meter of limestone of 50% porosity filled with CO_2-saturated pore water in equilibrium with 30 MPa pCO_2, $\approx$7.5 kg or 0.5% of the rock will dissolve before the pore fluid is saturated. It is important to note that the saturation calculation assumes the CO_2-saturated pore fluid is not flowing. As described in *Long-Term Fate of CO_2 in Deep-Sea Sediments* below, both the pure CO_2(l) phase and the CO_2-saturated pore fluid are expected to flow by buoyancy-driven advection. As result of that flow, certain regions in the porous media may become undersaturated in Ca^{2+}, enabling additional dissolution of the host rock.

Because CO_2 would be injected as a separate liquid phase, the host rock will not experience large fluxes of CO_2(aq) near the injection well. Nevertheless, host-rock dissolution may be im-

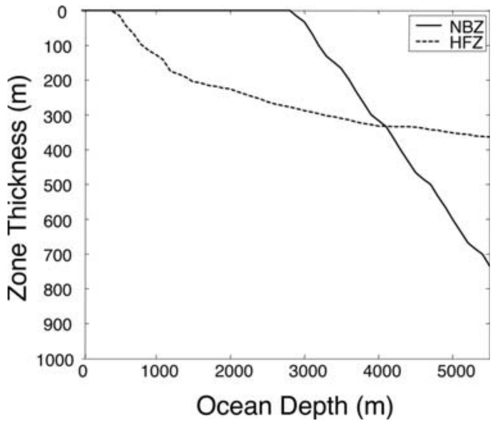

Fig. 3. The thicknesses of the HFZ and the NBZ as a function of the seafloor depth of injection. (Note: A linear geothermal gradient of 0.03°C/m was assumed.)

portant because minor increases in porosity have been shown to generate large increases in permeability (22–24). The exact relationship between porosity and permeability in carbonate sediment is highly variable (25), and further work is required to quantify whether carbonate dissolution will have a significant effect.

CO_2 Hydrate Formation. The high pressures and low temperatures necessary to compress CO_2(l) to greater density than the pore fluid are similar to the conditions necessary for CO_2 hydrates to form. CO_2 hydrates (5.75 $H_2O{\cdot}CO_2$) are nonstoichiometric crystalline compounds that form at high pressures and low temperatures by trapping CO_2 molecules in hydrogen-bonded cages of H_2O (26). These compounds occur in a three-phase metastable equilibrium between CO_2(l), CO_2(aq), and hydrate (20).

We refer to the subseafloor region with low enough temperatures and high enough pressures for hydrate formation as the hydrate formation zone (HFZ). The HFZ extends from the seafloor downward into the sediment until the temperature rises above the boundary of the hydrate stability field. A comparison of the stability conditions for CO_2 hydrates (27) with the CO_2 buoyancy-depth relationship reveals that the HFZ overlaps to a great extent with the NBZ. Although the HFZ exists in submarine sediment at seafloor depths of ≈400 m, CO_2(l) does not become denser than seawater until a seafloor depth of ≈2,900 m. Below ≈2,900 m of ocean, however, the thickness of the NBZ grows more rapidly then the thickness of the HFZ, and at seafloor depths >4,000 m, the NBZ is thicker than the HFZ (Fig. 3).

The overlap of the HFZ and the NBZ presents both implementation difficulties and storage opportunities. Hydrates are immobile crystals that clog pore spaces and impede flow. As a result, hydrate formation is expected to generate a self-forming cap that limits the migration of CO_2 and enhances storage stability. On the other hand, if the injection point is within the HFZ, then hydrate formation will decrease permeability near the injection point and may increase the energy required for injection. The optimal sediment depth of injection will depend on the relationship between depth and intrinsic permeability and on the degree to which hydrate formation affects the relative permeability of CO_2. The composition of the injection site below the HFZ may be either chalk or limestone. The intrinsic permeability of chalk and limestone ranges from 0.1 to 1,000 mD (28). If the intrinsic permeability below the HFZ is lower than the relative permeability of CO_2(l) to CO_2 hydrates, then no benefit is gained from injecting below the HFZ. Further work is needed to establish the effect of hydrate formation on permeability. We expect, however, that hydrate formation will cause sharp reductions in the relative permeability of CO_2(l), and that locating the injection point below the HFZ will be energetically favorable to locating it within the HFZ.

When the seafloor depth is shallower than 4,000 m, the HFZ is thicker than the NBZ, and avoiding hydrate formation near the injection point requires that the CO_2(l) be injected below both the HFZ and the NBZ. CO_2(l) injected below the NBZ is buoyant at the point of injection and will rise until it reaches the bottom of the HFZ. As the CO_2(l) flows into the HFZ, it will form CO_2 hydrates, which will clog the pore space and form a cap that limits the upward migration of the remaining CO_2(l) (29). If the hydrate cap does not form an impermeable seal, then some CO_2(l) may flow within the HFZ to the bottom of the NBZ. Once that CO_2 reaches the bottom of the NBZ, it becomes neutrally buoyant and gravitationally stable. Injecting below both the HFZ and the NBZ takes advantage of both the buoyancy cap provided by the NBZ and the self-forming hydrate cap provided by the HFZ.

If CO_2 were injected into sediment below a seafloor depth of 4,000 m, where the NBZ is thicker than the HFZ, then the CO_2 would be injected below the HFZ and directly into the NBZ. In such a configuration, hydrates are unlikely to form because the CO_2(l) is expected to percolate away from the HFZ to the bottom of the NBZ where it will reside beneath both the buoyancy cap and the hydrate cap.

Discussion

Thermal Evolution of the Injected CO_2. As the CO_2 is pumped from the surface to the seafloor, heat will be transferred from the relatively warm CO_2 to the relatively cold ocean water. The temperature of the CO_2 in the pipeline as a function of depth below the ocean surface is given by the solution to the radial heat equation:

$$T(z) = T_{\text{ocean}} + (T_1 - T_{\text{ocean}})e^{-\frac{2K}{u z \Delta r r_1 \rho C_p} z}, \qquad [1]$$

where k is the thermal conductivity of the pipe, ρ is the density of the fluid, r_1 is the inner radius of the pipe, Δr is the pipe thickness, T is the temperature of the CO_2 in the pipe, u_z is the velocity in the vertical direction, T_{ocean} is ocean temperature, and z is the water depth below the ocean surface. For reasonable values [$K = 50$ W/(m·K), $r_1 = 0.25$ m, $\Delta r = 0.1$ m, $Cp = 2{,}000$ J/(kg·K), $\rho = 1{,}000$ kg^3/m^3, and $u_z = 1$ m/s] the exponential coefficient becomes about -0.002 at $z = 3{,}000$ m. Therefore, unless the pipeline is insulated, the CO_2 in the pipeline will thermally equilibrate with the ocean by the time it reaches the seafloor.

Beneath the seafloor, the sediment temperature increases by 0.02 to 0.04°C/m, but the relatively short period it takes CO_2(l) to flow through the pipeline from the seafloor to the injection point is not long enough for the CO_2(l) in the pipeline to thermally equilibrate with the sediment. Furthermore, thermal boundary layers are expected to form in the sediment around the pipe, further insulating the CO_2 once it passes beneath the seafloor. As a result, if the temperature inside the pipe is not carefully controlled, then the CO_2(l) temperature at the injection point will be several degrees colder than the pore fluid and cold enough to form CO_2 hydrates. The primary reason to inject CO_2(l) below the HFZ is to avoid hydrate formation near the injection point. Therefore, it will be necessary to carefully control the CO_2(l) temperature at the injection point by either heating the CO_2(l) in the pipeline or insulating the ocean pipeline to keep the CO_2(l) at higher temperatures.

During injection, the CO_2(l) may be colder than the surrounding pore fluid and host rock. Depending on the injection temperature, the CO_2(l) may be positively, negatively, or neutrally buoyant near the injection point. Over time, however, the CO_2(l) plume will spread, and the regions of the plume farthest

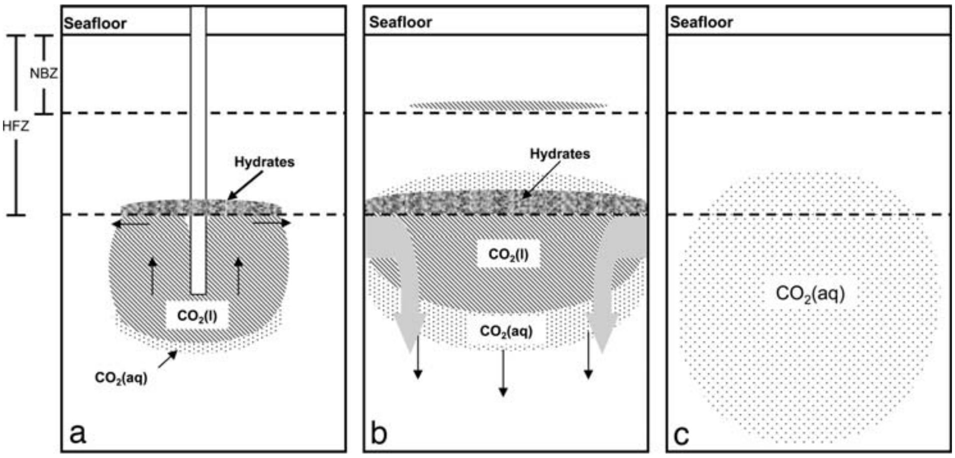

Fig. 4. The long-term evolution of the injected CO_2. (*a*) On the injection time scale (≈1 yr), small amounts of hydrate form as the top of the plume enters the HFZ. The hydrate that forms is expected to impede the upward migration of CO_2(l) and force the CO_2(l) to flow laterally. (*b*) After $\approx 10^2$ years, most of the CO_2 will have reached the bottom of the HFZ, and we expect the self-forming hydrate cap will have expanded laterally and trapped substantial quantities of CO_2(l) below it. Simultaneously, the CO_2-saturated pore fluid will sink away from the HFZ by buoyancy-driven advection. (*c*) Eventually the CO_2(l) and CO_2 hydrates will have dissolved and formed a CO_2(aq) solution. The solution will percolate through the porous matrix until it has mixed with a large enough quantity of water to become neutrally buoyant. Once the solution is neutrally buoyant, further solute migration will only occur by diffusion.

from the injection point will reach thermal equilibrium with the pore fluid. As heat is transferred from the pore fluid and the host rock to the CO_2(l), the CO_2(l) will expand and rise to the bottom of the HFZ where CO_2 hydrates begin to form.

An interesting feature of this system is that the coefficient of thermal expansion for CO_2(l) is high enough that, given a high enough intrinsic permeability, a typical geothermal gradient may drive some convection within the fully saturated CO_2(l) plume (30). The criterion for the onset of convection in a saturated porous layer subject to a vertical temperature gradient is given by the Rayleigh-Darcy number (30, 31). For the system of interest (i.e., liquid CO_2 at ≈30 MPa and ≈8°C subject to a geothermal gradient of ≈0.03°C/m) the stability condition indicates that the saturated CO_2(l) plume is convectively unstable when the effective permeability is greater than $\approx 10^{-15}$ m^2. This stability threshold indicates that we should expect some convection within the saturated CO_2(l) plume because the reservoirs of interest have permeabilities in the range of 10^{-15} m^2 to 10^{-12} m^2. The onset of convection may be important in entraining additional water into the CO_2(l) plume, which will cause the CO_2(l) to dissolve more rapidly.

Long-Term Fate of CO_2 in Deep-Sea Sediments. We expect the CO_2(l) injected below the seafloor to evolve in a way that ensures permanent storage (Fig. 4). Initially, the CO_2(l) injected below the HFZ and the NBZ will flow upward until it reaches the bottom the HFZ. Multiphase flow in porous media is partially described by Darcy's law with the additional relative permeability parameter (K_i):

$$u_i = -\frac{\kappa K_i}{\mu_i}\left(\nabla P_i + \rho_i g\right), \qquad [2]$$

where κ is the intrinsic permeability, K_i is the relative permeability of phase i, P_i is the pressure of phase i, ρ_i is the density of phase i, μ_i is the viscosity of fluid i, and g is gravity. As an order of magnitude calculation for the instantaneous flow rate of the CO_2(l) phase at a particular point in space and time, the driving force of the flow is the difference in density between CO_2(l) and seawater:

$$u_{\mathrm{CO_2}} \approx -\frac{\kappa K_{\mathrm{CO_2}} g}{\mu_{\mathrm{CO_2}}}\left(\rho_{\mathrm{CO_2}} - \rho_{\mathrm{H_2O}}\right). \qquad [3]$$

For reasonable values (e.g., $\kappa \approx 10^{-13}$ m^2, $K_{\mathrm{CO_2}} \approx 1$, $g \approx 10$ m/s^2, $\mu_{\mathrm{CO_2}} \approx 10^{-4}$ kg/(ms), and $\rho_{\mathrm{H_2O}} - \rho_{\mathrm{CO_2}} \approx 10^2$ kg/(m^3)], $u_{\mathrm{CO_2}}$ is on the order of 10^{-6} m/s (≈10 m/yr). All of the parameters described are well constrained except for the intrinsic permeability (κ), which can vary from 10^{-12} m^2 to $\approx 10^{-15}$ m^2, resulting in a range of velocities from 10^2 m/yr to $\approx 10^{-1}$ m/yr.

Once the CO_2(l) reaches the bottom of the HFZ, then CO_2 hydrates will form, clogging pore channels and creating a cap of limited permeability. We expect the additional CO_2 flowing up from the injection point to become physically trapped beneath the hydrate cap and be forced to spread laterally. As the CO_2(l) flows laterally, the hydrate cap will grow, resulting in a larger storage area.

The hydrates that compose the self-forming cap are stable as long as they are in contact with pore fluid saturated with CO_2(aq). Assuming the CO_2(l) to CO_2(aq) dissolution kinetics are rapid, then the pore fluid in contact with pure CO_2(l) plume will be saturated in CO_2(aq) until the entire plume of CO_2(l) dissolves. Therefore, the CO_2 hydrate cap will not dissolve until the CO_2(l) plume has fully dissolved.

The CO_2(l) plume will dissolve more rapidly than expected by diffusion alone because buoyancy-driven advection will mix the CO_2(l) with the pore fluid. Pore fluid that becomes saturated in CO_2(aq) will sink because it is denser than both the CO_2(l) and the pristine pore fluid (19). We expect the sinking of the saturated pore fluid to entrain additional pore fluid from outside the CO_2(l) plume and accelerate the dissolution of CO_2(l) and CO_2 hydrates. Assuming a diffusion constant of $\approx 10^{-9}$ m^2/s and a tortuosity of $\approx 10^{-1}$, diffusion sets the upper-bound on the time scale of hydrate dissolution at $\approx 10^6$ years.

It is clear, however, that buoyancy-driven advection and convection will accelerate the dissolution of the CO_2 hydrate and the downward transport of CO_2. Once the CO_2 hydrates fully dissolve, the CO_2(aq)-saturated pore fluid is expected to percolate downward through the sediment column, and the CO_2(aq) concentration is expected to decline as the solution mixes with greater and greater volumes of water. Eventually, the buoyancy-driven advection will cease as the density difference between the

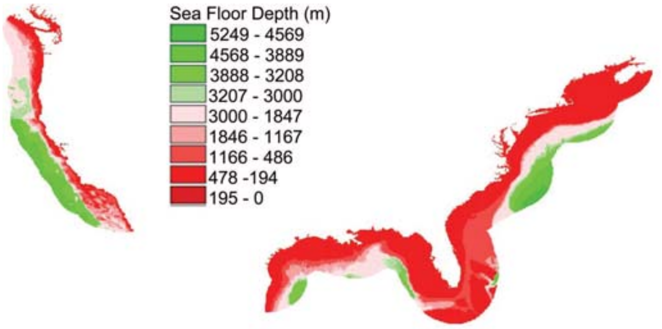

Fig. 5. More than 22% of the seafloor within the 200-mile economic zone of the U.S. coast is $<3{,}000$ m deep, which represents $>1.3 \times 10^6$ km^2 of potential CO_2 storage area.

$CO_2(aq)$ solution and the pore fluid vanishes. Once that occurs, further CO_2 transport can only be accomplished by diffusion of the aqueous phase. We hope that further modeling work will determine to what degree buoyancy-driven advection and convection accelerate the hydrate dissolution and the downward transport of CO_2.

Storage Capacity. If the CO_2 storage site is 300 m thick with 50% porosity and 50% residual water, then the total annual U.S. CO_2 emissions [$\approx$6 Gt of $CO_2(l)$] could be stored in a $\approx$80-km^2 area. Fig. 5 indicates that over $\approx$22% (1.3×10^6 km^2) of the seafloor within the economic zone of the continental U.S. is $>3{,}000$ m deep (32), which represents $>10^4$ Gt of permanent $CO_2(l)$ storage. Outside the economic zone of the United States, the total CO_2 storage capacity in deep-sea sediments is essentially unlimited.

Not all regions below 3,000 m of ocean are appropriate for CO_2 storage. Three factors will further limit the potential storage volume. First, the sediments must be thicker than the HFZ. Second, the sediments must be permeable enough to inject large quantities of liquid CO_2 at high flow rates. Third, $CO_2(l)$ should not be injected beneath very steep slopes as landslides may expose the $CO_2(l)$. The thickness of the sediment is not very limiting because the majority of deep-sea sediments on the North American continental margins are thicker than the HFZ. There may, however, be mechanical difficulties associated with injecting large quantities of CO_2 into deep-sea sediments that will be discovered after further study and experimentation. Finally, a volume of pore water roughly equal to the volume of injected CO_2 will be forced up into the ocean from the sediments. The implications of forcing the pore water into the ocean must be considered.

Summary

Deep-sea sediments at high pressure and low temperature provide a virtually unlimited and permanent reservoir for carbon dioxide captured from fossil fuel combustion. When injected below the ocean floor at an ocean depth $>3{,}000$ m, CO_2 will remain below a layer of more buoyant pore fluid. Hydrate formation will also impede the upward flow of CO_2 as it cools along a geothermal gradient. Carbonate dissolution will play a minor role in the system and may affect permeability within the reservoir. Over time scales of thousands of years, the CO_2 will dissolve into the pore fluid, and the $CO_2(aq)$ solution will sink until it becomes sufficiently dilute such that its density equals the density of the surrounding pore fluid. Further transport can only be accomplished by molecular diffusion over millions of years. If field experiments confirm that the system behaves as described, then the permanence guaranteed by the double cap of buoyancy and CO_2 hydrates will enable $CO_2(l)$ to be stored without any investment in monitoring or verification technology. For these reasons, we propose that CO_2 storage in deep-sea sediments at high pressures and low temperatures be considered along with other options.

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