

CO₂ Capture from Coal-Fired Utility Generation Plant Exhausts, and Sequestration by a Biomimetic Route Based on Enzymatic Catalysis - Current Status

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Introduction

A range of carbon management strategies will have to be implemented if meaningful reductions in CO₂ emissions are to be achieved in response to concerns about global climate change. It is becoming increasingly clear that some form or forms of carbon sequestration will have to be among these strategies, particularly if reductions are to be effected in the short to medium term. The easiest type of source to address is electric power generation, because this represents a relatively small number of very large stationary sources. A representative 300 MW coal-fired power plant, for example, operating at 35% net efficiency (from the coal in, to the electricity delivered to the system busbar) emits ~80 kg of CO₂ per second into the atmosphere. This “typical” plant (based on a hypothetical new 300 MW(e) plant in a Kenosha, Wisconsin, location, burning an Appalachian coal) produces 2.32 tonnes of CO₂ per tonne of coal, or 290 tonnes of CO₂ per hour. The U.S. utility industry as a whole is producing 2.1 billion tonnes of CO₂ per year from coal alone. Furthermore, the percentage of global energy consumption that comes from electricity has been increasing over the last 50 years, and is projected to increase still further over the next 50 years, while world population continues to grow rapidly. Since some of the most densely populated developing countries, such as China and India, have large coal reserves, it is unrealistic to think that these will not be exploited. Putting these factors together, it is clear that neither more efficient electricity generating plant, nor a move away from carbon-rich fuel, or even from fossil fuels in general, is likely to be sufficient to cap atmospheric CO₂ levels in the next 50 years. Thus there will be a need for local CO₂ capture and sequestration in the interim. Hence the focus of this work is on sequestration in the context of emissions from large fixed sources, such as those associated with electricity generation.

Most studies on local CO₂ capture and sequestration have been based on the assumption that CO₂ would first have to be concentrated from the exhaust gases from fossil-fuel combustion, and, in general, that it would then have to be transported to a suitable location for disposal. (The initial flue-gas composition contains only 10 to 15% CO₂. Technology for concentration and transportation of CO₂ already exists.) The techniques most immediately applicable to the case of a fossil-fuel power-plant exhaust would be chemical absorption (typically in alkanolamines such as monoethanolamine), followed by hot steam stripping to produce a concentrated gas stream, and then compression of the gas to form a liquid that can be pumped through pipelines to a sequestration site. There is likely, however, to be a significant economic penalty associated with these processes. The next issue that arises is where to sequester the CO₂. Various possible sequestration sites have been discussed in the last few years. In general, these sites can be divided into two categories: geological sites and marine sites. Geological and ocean sequestration options are presented, for example, in the Carbon Management Plan (1). Geological sequestration is seen as the technology that can most rapidly be developed to make significant inroads into the amounts of CO₂ released from fixed sources such as power plants (1), and in fact limited geological sequestration is already being implemented. The feasibility and expected advantages of geological sequestration have been widely published during recent years (2, 3). There are, however, aspects of this type of sequestration, as well as marine sequestration, which need further study, particularly in regard to safety. There is also the possibility that long-term, perhaps permanent, monitoring would be required for safety reasons, and this could increase costs significantly.

Sequestration of CO₂ in the form of a stable, environmentally friendly solid would have obvious appeal for safe long-term storage. Indeed, carbonate minerals, such as calcite, aragonite, dolomite and dolomitic limestone, constitute the earth's largest CO₂ reservoir, estimated to contain an amount of carbon equivalent to 150,000 X 10¹² tonnes of CO₂ (4). Thus the geological record demonstrates that large amounts of CO₂ can be stored indefinitely in carbonate form. If anthropogenic CO₂ can be fixed into solid carbonate form, such as calcium carbonate, then we have a stable and environmentally friendly product. The problem, of course, is one of rate. CO₂ fixation is needed on a commercial, not a geological, timeframe. The 300-megawatt thermal power plant described above, for example, would release about 290 tonnes of CO₂ per hour.

Objective

The overall objective of the present research is to develop a system resembling a CO₂ scrubber that can be used to reduce CO₂ emissions from, for example, fossil-fuel-burning power plants. In the system envisaged, an enzyme serves to catalyze the rate of CO₂ hydration for subsequent fixation into stable mineral carbonates, the counterions for which may be supplied from such sources as brines from saline aquifers, waste brines from desalination operations, or seawater. The enzyme, carbonic anhydrase, is the biological catalyst responsible for the interconversion of carbon dioxide and bicarbonate

in living organisms. The resulting biomimetic sequestration system would offer several advantages, including:

- No costly CO₂ concentration and transportation steps.
- A safe, stable, environmentally benign product.
- An environmentally friendly process, performed in aqueous solution at near-ambient temperatures.
- A site-specific solution to CO₂ sequestration.

Proof of principle has already been demonstrated (5-7). This presentation will provide an overview of the current status of the project, with particular emphasis on the performance of the enzyme in the presence of other chemical species likely to be present in the industrial situation. It is necessary first, however, to summarize the biomimetic approach, in order to put these results in context.

Approach

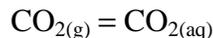
In order to address the problem of rate of carbonate formation, we adopted a biomimetic approach. It is useful to keep in mind here that we are defining a biomimetic approach as one in which a particular aspect of a biological process or structure is identified and applied to solve a specific non-biological problem (5). In other words, it is an approach in which:

- We have a specific engineering problem to solve.
- We identify a biological system in which an analogous engineering problem has been solved.
- We use the enabling part of that system, whether a structural design, a processing route, or a biochemical component, to solve our engineering problem.

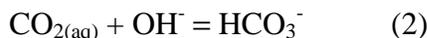
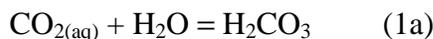
In the present instance, we studied the chemistry of CO₂ fixation into calcium carbonate in aqueous solution, examined the rate-limiting step, and then considered what lessons could be learned from biological systems in order to accelerate that step.

Calcium carbonate precipitates readily from aqueous solution given a suitable supersaturation of calcium and carbonate ions. The issue, in relation to CO₂ fixation, is then how to produce carbonate ions rapidly from H₂O and CO₂ (8). pH is an important factor in this regard, since it has a strong effect on the proportions of the carbonic species present (9), and, at low pH, there will be a tendency to dissolve rather than precipitate solid carbonates. Strongly caustic conditions would favor rapid carbonate formation, but would raise other concerns, both economic and environmental. Thus an environmentally friendly process for CO₂ fixation into carbonate would operate at very mildly basic pH values.

Gaseous CO₂ dissolves rapidly in water to produce a loosely hydrated aqueous form (10, 11).



This reaction is rapid. The aqueous CO₂ may then react either with water or, at high pH, with hydroxyl ions:



At pH < 8, reaction 2 is negligible due to the absence of OH⁻ ions. At 8 < pH < 10, both reaction sequence 1 and reaction 2 occur, while, at pH > 10, reaction 2 predominates. Except in high-pH situations (such as the absorption of CO₂ into lime), calcium carbonate precipitation involves reaction sequence 1.

Once bicarbonate ions are present in solution, carbonate ions can be produced by the following reaction:



The rate-controlling step in the fixation of gaseous CO₂ into carbonate ions is the hydration (reaction 1a) of CO₂ (except at high pH). The rate constant of the forward reaction 1a is 6.2 x 10⁻² s⁻¹ at 25°C and zero ionic strength, whereas reaction 1b is very rapid, the rate being virtually diffusion controlled (11). Reaction 3, though slower than 1b, is much faster than reaction 1a. Thus, if a viable means to accelerate the hydration of CO₂ (reaction 1a) could be found, it should be feasible to fix large quantities of CO₂ into calcium carbonate (without recourse to caustic conditions). This is where we can learn an important lesson from biological systems. A catalyst for the reversible hydration of CO₂ in fact already exists in biological systems: carbonic anhydrase.

The carbonic anhydrases (CAs) are a broad group of zinc metalloenzymes that are ubiquitous in nature (12-14). They are among the fastest enzymes known, and they catalyze the reversible hydration of CO₂. The fastest CA isozyme known is the human isozyme HCA II, each molecule of which can hydrate at least 1.4 x 10⁶ molecules of CO₂ per second (15); the catalyzed hydration occurs at or near the diffusion-controlled limit for the encounter rate of enzyme and CO₂. [Another group has, in fact, been looking at CA as a catalyst for short-term aqueous sequestration of CO₂ for use in completely closed systems, such as a space station (M. Trachtenberg, personal communication).]

Project Description

Initial feasibility of our biomimetic approach was demonstrated (5, 6), based on two types of experiment. One was designed to show acceleration of the overall process of forming a solid product (calcium carbonate) in the presence of CA. This involves a series of steps beyond the hydration of CO₂, but is vital to show potential industrial applicability. The other was designed to demonstrate the accelerated hydration of CO₂ in the presence of CA. This shows catalysis of a single reaction, and hence is applicable also to comparisons of enzyme performance for different isozymes, and under different conditions. Initial experiments were performed with bovine carbonic anhydrase (BCA), which is available in purified form from Sigma Chemical Corporation. Since an economical source of the enzyme would be essential for commercial application, tests were also performed on crude (dilute) extracts from plant sources (spinach and parsley) and yeast (*Saccaromyces cerevisiae*) (5). Very large accelerations of both CO₂ hydration and precipitation of calcium carbonate were seen with the purified BCA, but significant accelerations were also obtained even with very crude, dilute plant extracts. The simplest and cheapest means of obtaining large amounts of CA will be by means of overexpression by a genetically modified bacterial system. Hence we then turned our attention to HCA II obtained by bacterial overexpression, following the generous donation of the phage vector by Drs David Silverman and Peter Laipis at the University of Florida. Excellent results have been obtained (6), again with rather crude (though in this case less dilute) extracts; this is important because enzyme purification is expensive.

Experiments either have been performed or are under way in relation to the following general topic areas:

1. Catalyst identification, and demonstration of its applicability for CO₂ sequestration
2. Optimization of catalyst and catalyst source
3. Immobilization of catalyst
4. Effectiveness of catalyst under different process conditions
5. Precipitation of carbonate

Feasibility and Issues

Following the successful proof of principle, several topics were identified as needing further study, and some of these are discussed in references 5-7. Among these topics are optimization and robust immobilization of the catalyst, and source of the cations. Our isozyme of choice will be HCA II, provided that it proves robust enough for use in a realistic range of service conditions, because it is the fastest isozyme known, and because it can already be successfully produced by bacterial overexpression. So far, we have obtained excellent results with overexpressed HCA II. Furthermore, we have already immobilized CA successfully in an environmentally friendly matrix, based on porous alginate beads with a relatively hard chitosan coating (16,17).

We are currently considering three possible sources of cations, (particularly calcium ions), each of which could serve a dual function as both aqueous process stream, and

cation source. These are seawater, waste brines from desalination operations, and brines from saline aquifers. Selection of the source is anticipated to be site specific, depending on the location of the particular power plant.

In any approach to CO₂ sequestration, the huge quantities involved cannot be ignored, and the proposed biomimetic approach is no exception. These issues of scale are, however, by no means unique to the biomimetic approach; furthermore, they should be considered in the context of the already substantial quantities of both solids and liquid that are handled at a power plant. Consider, for example, a coastal power plant, cooled by the pumping of seawater. If the CO₂ were to be sequestered by the pumping of seawater through a separation vessel at the utility site, with a calcium ion concentration in the seawater of 400 grams per tonne, 100% removal from a unit of the size of the model Kenosha plant would require a flow of 18 million tonnes of seawater per day. This is a very large number indeed. It is, however, less than an order of magnitude higher than the cooling water flow through such a unit, which would be of the order of 2.4 million tonnes per day (based on a typical requirement of 800 tonnes of cooling water per tonne of coal burned). If the cooling water were subsequently pumped through the separation vessel, it would potentially be possible to remove 13.3% of the CO₂ with *no* increase in water flow. Removal of 20% of the CO₂ would require an increase of only 50% over present water flow for such a plant. It should be noted also that seawater is the most dilute of the brines being considered as possible cation sources, and so it is by no means certain that such a large flow through the plant would be necessary.

The amount of solid product would also be very large. For example, if 100% of the CO₂ produced by the model Kenosha plant were to be sequestered as calcium carbonate, CaCO₃, this would correspond to 666 tonnes of product per hour, or close to 16,000 tonnes per day. The masses involved are a factor of over fifty times that involved in flue-gas desulfurization (FGD). A more useful comparison in terms of solid handling, however, is with the amount of coal consumed, which is approximately 3,000 tonnes per day, from which the scale-up would be by a factor of a little over five (for 100% sequestration of the CO₂ produced). On this basis, it would be possible to remove 18.75% of the CO₂ without any increase in the solids handling requirement beyond the level already required for the coal.

One of the issues that arise in relation to sequestration products is their potential marketability, although it should always be remembered that it is dangerous to try to justify remediation processes on the basis of product marketability. For example, the product of FGD is gypsum, and this can be sold, but the amount produced by FGD has quickly exceeded the market. This is a well-known fact. Nevertheless, potential markets are definitely of interest. At first thought, there may appear to be little potential market for a solid carbonate, because carbonates are such common minerals. In most commercial applications, however, the requirement of a fine particle size would make the (powder) product of our proposed process likely to compete very well with mined and crushed carbonate.

Because of the novelty of this approach to CO₂ sequestration, there were many questions to be addressed. Considerable progress has been made since the inception of the project, but there is still much work to be done, as discussed below under Future Activities.

Results

Results of the early phases of the project include:

- 1) *Identify catalyst and demonstrate its applicability for CO₂ sequestration*
 - Substantial acceleration of both CO₂ hydration and carbonate formation in presence of CA demonstrated. Initial experiments performed with BCA (bovine CA, available from Sigma Chemical Corporation).
 - More than two orders of magnitude acceleration of carbonate formation shown in deionized-water-based systems. (Precipitation essentially instantaneous.)
 - Feasibility of use of different CA isozymes demonstrated.
 - Feasibility of principle demonstrated
 - Value of examination of different isozymes shown

- 2) *Optimize catalyst and catalyst source*
 - Bacterial overexpression selected as most cost-effective production route for CA production.
 - HCA II successfully overexpressed (with phage vector kindly donated by D. Silverman and P. Laipis)
 - Growth and harvesting procedure for the HCA II production being optimized
 - Excellent activity obtained from relatively crude HCA II extracts after initial growth and harvesting optimization
 - More than two orders of magnitude acceleration of carbonate formation shown with bacterially overexpressed HCA II in deionized-water-based systems (precipitation essentially instantaneous)
 - Bacterial overexpression is the method of choice for large-scale CA production
 - HCA II (the fastest known CA isozyme) successfully overexpressed and used for accelerated carbonate formation
 - Other isozymes short-listed for possible overexpression and comparison with HCA II re robustness in typical service conditions

3) *Immobilize catalyst*

- CA successfully immobilized in three different matrices: acrylamide, alginate, and chitosan-alginate
- Alginate and chitosan-alginate matrices shown to give better enzyme activity than acrylamide
- Alginate and chitosan-alginate matrices desirable because they are cheap and easy to produce, non-toxic, biodegradable, environmentally friendly
- Feasibility of use of cations from seawater to crosslink alginate gels demonstrated: more environmentally friendly than the conventional use of CaCl_2
- Useful levels of enzyme activity obtained with immobilization in alginate and chitosan-alginate matrices
- Chitosan-alginate matrices highly resistant to enzyme leakage
- CA stability at elevated temperature improved by immobilization
- Good levels of enzyme activity also shown in artificial seawater for CA immobilized in alginate and chitosan-alginate matrices
 - Alginate, and particularly chitosan-alginate, matrices shown to provide potentially suitable immobilization media for CA for use in CO_2 sequestration
 - Environmentally friendly immobilization system
 - Optimization well underway

4) *Discover range of conditions under which catalyst is effective*

- CA shown to have excellent robustness under mechanical agitation
- Both BCA and bacterially overexpressed HCA II shown to retain their activity in artificial-seawater-based solutions
- Good retention of enzyme activity shown in variety of solutions containing higher concentrations (than seawater) of salts used in artificial seawater
- Enzyme shown to be effective down to low concentrations
 - CA shown to have the necessary mechanical robustness
 - CA shown to perform well in likely aqueous streams, whether freshwater or seawater. (Data needed for stronger brines)
 - CA shown to perform well at low concentrations

5) *Extract carbonate*

- Precipitation of calcium carbonate shown to be almost instantaneous at mildly basic pH in CA-catalyzed deionized-water-based systems
- Modest heating (to $\sim 50^\circ\text{C}$) shown to overcome inhibition of precipitation in artificial seawater

- Yields (percent calcium ions present) from artificial seawater on modest heating shown to be high
 - Calcium carbonate shown to precipitate out either spontaneously or on modest heating, depending on the chemical composition of the aqueous solution
 - Calcium in seawater shown to be potentially usable source of counterions
 - Other potential sources of counterions identified

An issue of prime importance in relation to the catalyst is its ability to perform in likely service environments. As indicated above, CA has been shown to have excellent robustness under mechanical agitation, and is thus expected to withstand high fluid flow rates. Furthermore, it has been successfully immobilized in chitosan-alginate matrices, which are highly resistant to enzyme leakage. This will not only provide additional mechanical protection, but is also expected to enhance the chemical stability of the enzyme; it has already been shown that CA stability at elevated temperature is improved by immobilization, a good indicator of generally enhanced robustness. BCA and bacterially overexpressed HCA II have both been shown to retain their activity in artificial-seawater-based solutions. Good levels of enzyme activity have also been shown in artificial seawater for CA immobilized in alginate and chitosan-alginate matrices, and in a variety of solutions containing higher concentrations (than seawater) of salts used in artificial seawater.

Some inhibition of CA activity by various anions has been reported previously (see, e.g., references 18 and 19). By far the most potent of the inorganic anionic inhibitors of CA, however, is CN^- , which is not expected to be an issue for the proposed application. Very small amounts (unlikely to exceed 100 ppm) of SO_x (20) and NO_x may be present in the flue gases. Higher concentrations of anions are to be expected in the process water used, particularly, of course, if it is brine or seawater. There are other contaminants besides SO_x and NO_x , the effects of which will need to be determined. It is our belief that a carbon-scrubbing device based on the proposed method would follow an FGD system at an actual power plant, and hence relatively few other contaminants in the flue gas would reach it. Nevertheless their effects should be investigated, and work on this is already in progress. Flue gas that had passed through an FGD system would have been in contact with a relatively basic (calcium hydroxide) environment, and so other acid gases would have been removed. The only issue in relation to pH would then be the acidity of the CO_2 itself. We know that a buffering system may well be necessary, and we are looking at possible buffering systems.

Our results indicate that inhibition by SO_x and NO_x is unlikely to present any problem. Data on CA-catalyzed hydration of CO_2 were obtained in deionized-water-based solutions containing different SO_4^{2-} and NO_3^- concentrations, ranging from 5 mM to 200 mM. [5 mM corresponds to 480 ppm for SO_4^{2-} , and 310 ppm for NO_3^- .] There was little indication of inhibition at concentrations below 100-200 mM. Experiments have also been performed in solutions based on ASW (artificial seawater), since it is expected that

the actual process stream would be based either on seawater, or on some other brine, as discussed above. Data were obtained for different SO_4^{2-} and NO_3^- concentrations, ranging from 0.5 mM to 100 mM. Again the enzyme was found to perform well. Noticeable inhibition did not occur until 100 mM.

The possibility of inhibition by cationic species must also be investigated. For example, coal combustion liberates very small amounts of mercury, which is mostly in elemental form from lower-sulfur coal, and mostly in divalent form from higher-sulfur coal. The concentrations in the exhaust from a power plant are only 1 to 10 $\mu\text{g per m}^3$ (21), i.e. on the order of parts per trillion, but nevertheless cannot be ignored. Data on CA-catalyzed hydration of CO_2 were obtained in deionized-water-based solutions containing different Hg^{++} concentrations, ranging up to 2.9 ppm. There was little sign of inhibition for concentrations less than 1-2 ppm, which is a much higher concentration than would be likely to arise in the aqueous process stream from the 1 to 10 $\mu\text{g per m}^3$ present in the exhaust. The effects of Pb^{++} were also investigated for concentrations ranging up to 2.9 ppm. Limited inhibition began to appear only when the concentration reached 1-2 ppm.

Application

Application of the biomimetic process to which the proposed research relates would:

1. Allow for long-term sequestration of CO_2 in the form of carbonate minerals. This form of sequestration has been geologically proven to be safe over millions of years.
2. Avoid the need for long-term monitoring of the sequestered product.
3. Produce the carbonate product without recourse to high temperatures and pressures, or geological timescales.
4. Be used in an on-site scrubber to provide a plant-by-plant solution to reducing CO_2 emissions.
5. Avoid the need for concentration of CO_2 from flue gases.
6. Avoid pressurization or, it is expected, significant heating or cooling of the process stream.
7. Provide an environmentally benign process with an environmentally benign product.

One of the major attractions of the biomimetic approach is that it is geared to the development of an environmentally friendly system.

- The catalyst, CA, is a ubiquitous enzyme, present in (and indeed necessary for) all types of living organism, including animals, plants, algae and bacteria.
- The immobilization system that has been developed for the enzyme is based on alginate and chitosan, materials that are both of biological origin, and biodegradable.

- The product, calcium (and possibly magnesium) carbonate, is safe, stable, and environmentally benign.
- The process takes place in aqueous solution, without necessitating extremes of pH, temperature or pressure.

Future Activities

(a) Cation sources

We are currently considering three possible sources of cations, (particularly calcium ions), each of which could serve a dual function as both aqueous process stream, and cation source. These are seawater, waste brines from desalination operations, and brines from saline aquifers.

The most appropriate source may well prove to be site-specific, depending on the location of, for example, the specific power plant. For each type of source, the following topics will be researched:

- Representative ranges of chemical compositions will be selected for subsequent experiments. Of the three sources of counterions being considered, the greatest compositional variability will be for brines from different saline aquifers, for which the greatest possible difficulty in finding a broad base of data might also be expected. In this regard, however, the proposed work will be greatly facilitated by the recent DOE-funded development of a GIS database of attributes, including water chemistry, for 21 saline formations in the United States (Hovorka et al., (22)).
- Solubility of CO₂ in solutions of these compositions, (essential information for estimation of water flow required).
- Solubility of carbonates in solutions of these compositions.

Another very important opportunity is the use of magnesium as the cation. Magnesium carbonates are also widespread, and are highly stable and environmentally neutral. We were originally led in the direction of calcium carbonate as the desired product because, in the marine environment, this is the case. It is interesting to note that shell-forming marine organisms produce calcium carbonate and not magnesium carbonate, even though the concentration of magnesium ions in seawater is around five times that of calcium ions. The ability to precipitate magnesium carbonate would greatly reduce the flow of seawater required. We have looked into this issue, and believe that we understand why magnesium carbonate is inhibited. Not only does magnesium carbonate have a somewhat higher solubility than calcium carbonate, but also magnesium ions are more strongly hydrated than calcium ions, which inhibits crystal growth (22, 23). It is our intention to

study methods to overcome this inhibition, though not necessarily with seawater as the cation source.

(b) Catalyst optimization

The following issues will be addressed in relation to catalyst optimization:

- Enzyme performance in the different aqueous solutions will be assessed, to determine the effects of different ionic species in solution, and salinity and ionic strength of the solutions. Particular emphasis will be placed on possible inhibitory effects of the various chemical species that are likely to be present, not only from the aqueous stream (counterion source) itself, but also by dissolution from the flue gases (including, for example, small traces of ammonia and mercury). Of course, the actual impurities that will reach a potential CO₂ scrubber will depend on where the scrubber is located relative to the other flue-gas cleanup systems.
- Comparison of relatively crude extracts of bacterially overexpressed human CA II (or HCA II), with purified enzyme. HCA II offers the advantage of being the fastest known isozyme, while the relatively crude extract would be much cheaper to supply on an industrial scale.
- Assessment as to whether the HCA II isozyme is robust enough for the anticipated service conditions, or whether, for example, Methanosarcina CA, which is slower but likely to be much more salt-tolerant (since Methanosarcina is an organism that inhabits marine sediments), should be investigated as an alternative. Should this latter situation arise, Dr J. Greg Ferry (Pennsylvania State University), with whom we are already communicating, is producing bacterially overexpressed Methanosarcina CA.
- Assessment as to whether directed-evolution studies would be worthwhile, to enhance enzyme performance in the types of solution in question. We are currently not intending to perform genetic engineering to improve catalyst performance. However, directed-evolution studies might be worthwhile. In the event that this appears to be necessary, Dr Frances H. Arnold of the California Institute of Technology is already working on the directed evolution of new biocatalysts (F.H. Arnold et al., www.che.caltech.edu/faculty/fha, 2000).

(c) Accelerated precipitation of carbonate

Precipitation of calcium carbonate from supersaturated seawater-based solutions is relatively slow, but can be accelerated to a usable timeframe by modest heating. The extent to which such an approach would be necessary, following enzymatically accelerated increase in bicarbonate ion concentrations, will be established also for

solutions corresponding to each of the other two types of counterion source proposed. The process will be optimized in relation to the following parameters, within the ranges consistent with the proposed use of the method in an actual power plant:

- Solution chemistry
- pH
- Temperature
- Pressure

Based on these results, in the case of brines from saline aquifers, comparison will be made of:

- On-site precipitation of carbonate at the utility site for subsequent disposal.
- Injection of carbonate/bicarbonate-enriched brine back into saline aquifers, for in-situ mineralization.

Once again, the amounts of product are very large with both of these methods. This is, of course, also true of other methods of sequestration: the weight of CO₂ generated in the coal-combustion process itself is 2.3 times the weight of the coal fired (for the Appalachian coal used in the Kenosha model plant), and the volume of the reservoir required is greater, for example, than the volume of the (unrelaxed) mine from which the coal was removed.

However, the eventual aboveground storage of the carbonate product from our proposed process is not a major issue, because of its stability and environmental neutrality.

(d) Mechanism of pH control.

The importance of pH control has been recognized from the inception of the idea of biomimetic sequestration of CO₂ in carbonate form, in relation both to CO₂ hydration to produce bicarbonate ions, and to carbonate formation. In the experiments to date, pH has been controlled by chemical means. On an industrial scale, however, it is anticipated that the pH will be controlled electrochemically. This technique for pH control should be developed, but is seen as a topic for future research.

(e) Possible geometries of commercial system

We are actively looking at possible geometries of a commercial system based on our proposed biomimetic sequestration method. At this time, there is still too much research remaining to be done, for us to describe a potential scrubber in detail. The different types that have been used or proposed for FGD will probably not be directly scalable to the requisite size, but the gas/liquid contacting systems are likely to be the same in general principle.

Although, in the case of the use of seawater, brines from saline aquifers, or waste brines from desalination operations, the uncontrolled release of the product liquors following

carbonate separation could result in local damage to sensitive ecosystems, the return of these liquors to the source of the brines should present few problems. It is recognized, however, that this will need to be assessed in each case.

Acknowledgments

The authors gratefully acknowledge support from EPRI under contract number WO9000-26, as well as the generous donation of the phage vector for bacterial overexpression of HCA II by Drs David Silverman and Peter Laipis at the University of Florida.

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