Biomimetic and geologic mineralization approaches to carbon sequestration

G.M. Bond,[1] B.J. McPherson,[1] A. Abel,[1] P. Lichtner,[2] R. Grigg,[1] N. Liu[1] and J. Stringer[3]

[1]New Mexico Tech

[2]Los Alamos National Laboratory

[3]EPRI

Introduction and Overview

CO_2 mineralization is a novel concept for binding carbon dioxide in a solid form, which eliminates the need for long-term monitoring, avoids the licensing problems that may arise with other sequestration options, and removes any concerns over the long-term fate of the carbon dioxide. CO_2 mineralization is an ongoing natural process, occurring in both the subsurface geologic system and the terrestrial system. It is of interest because carbonate minerals offer a geologically proven safe long-term repository for CO_2. The drop in atmospheric CO_2 levels from Cretaceous to post-Cretaceous times is attributed in large part to two natural processes: weathering of silicates to carbonates, and deposition of CO_2 into calcium carbonate (limestone and chalk), much of which is of biogenic origin (Wright et al., 1995). Carbonate minerals, including calcite, aragonite, dolomite and dolomitic limestone, constitute a massive CO_2 reservoir, estimated to contain an amount of carbon equivalent to 150,000 x 10^{12} tonnes of CO_2.

Our biomimetic process uses a biological catalyst, carbonic anhydrase, to accelerate the hydration of CO_2 to form bicarbonate ions, preparatory to the formation of solid carbonate in the presence of a suitable source of cations such as produced water from oil and gas production, or brines from deep saline aquifers. The aim is to develop a system resembling a CO_2 scrubber for direct (at plant) removal of CO_2 from the flue gas into the aqueous phase. Suitable pH control would then allow either for carbonate formation and removal above ground, or for slower underground carbonate formation following reinjection of bicarbonate-enriched brines. Feasibility of the process has been demonstrated at the bench scale (Bond et al., 2001a, 2002), and now also at the laboratory scale.

One of the major attractions of the biomimetic approach is that it is geared to the development of an environmentally friendly system, and has no costly CO_2 concentration and compression steps. The catalyst, carbonic anhydrase, is a ubiquitous enzyme, present in (and indeed necessary for) all types of living organism, including animals, plants, algae and bacteria. The immobilization system for the enzyme is based on alginate and chitosan, materials that are both of biological origin, and biodegradable (Simsek-Ege et al., 2002a, b). The carbonate product is safe, stable, and environmentally benign. The process takes place in aqueous solution, without necessitating extremes of pH, temperature or pressure. The uncontrolled release of brines could result in local damage to sensitive ecosystems but the oil and gas industry already has expertise in brine handling.

CO_2 mineralization with brines will require an on-site scrubber at the power plant. However, if the equipment is combined with a unit which also has a wet sulfur scrubber, the capital expense associated with the CO_2 removal system will be relatively modest: the particle removal steps and the reheating prior to the stack are not affected at all, and it seems likely that, since the volumetric flow is essentially the same, the fan capacity needed should not be all that much greater. Beyond this, some of the infrastructure for producing, transporting, and reinjecting the brines will already exist in an area such as the Permian Basin, but additional infrastructure of this type would be needed. A closer study of these needs will have to be to be performed. Given the need for potable water in this region, the possibility of desalination of produced waters coupled with use of the resulting more concentrated brines for CO_2 sequestration should also be considered. The focus in the present paper is on the possible use of brines, particularly produced waters, in the Permian and San Juan Basins.

For mineralization with brines, the principal challenges are the determination of the relative merits of reinjecting bicarbonate-enriched brines versus carbonate precipitation above ground, and development of the pH control system. These issues are the current focus areas in our ongoing research. There are a number of questions that have to be answered concerning the robustness of the chemistry, and the design and economics of the system, but none of these introduce radical new concepts, and the equipment needed for any of the possible systems in which the concept proposed here will be applied is essentially similar to that used in a number of mature large-scale industrial chemical applications.

In any approach to CO_2 sequestration, the huge quantities involved cannot be ignored, and the proposed biomimetic approach is no exception. The very large scale of the materials handling equipment that may be required must be considered. The Kenosha plant (a hypothetical new 300 MW(e) plant in a Kenosha, Wisconsin, location, burning an Appalachian coal) will be taken as a reasonable basis to start an economic estimation for the removal of CO_2. The corresponding coal burn rate is approximately 125 tonnes per hour, producing 290 tonnes of CO_2 per hour. If the CO_2 from the Kenosha plant was to be sequestered by the pumping of brine through a separation vessel at the utility site, with a calcium ion concentration in the brine of 600 g/tonne, 100% removal from a unit the size of the model Kenosha plant would require a flow of 12 million tonnes of brine per day. This is a very large number indeed. It is, however, less than five times higher than the cooling water flow through such a unit, which would be on 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), and this does not take into account the magnesium ions in the brine.

Biomimetic Mineralization Option 1: Surface Mineralization

Surface mineralization offers the benefits of known risks (minimal) and predictable costs. At first thought, one might expect that biomimetic catalysts would be expensive. HCA II (human carbonic anhydrase II), however, has been successfully produced by bacterial overexpression, which affords the possibility of economic production (Bond et al., 2001b). [HCA II is the fastest known isozyme of carbonic anhydrase, and tests to date suggest that it will perform well in actual service conditions.] A variety of other enzymes are now produced on an industrial scale at modest cost. The enzymes used in certain detergents, for example, range in price from a little under $1 to around $3 per kg.

Analysis of data from OSE (New Mexico) and the Railroad Commission of Texas reveals that the waters produced and reinjected annually in New Mexico and the Permian Basin region of Texas contain on the order of 2.07 Mt (millions of metric tons) of calcium ions (Figure 1) and 0.67 Mt of magnesium ions.

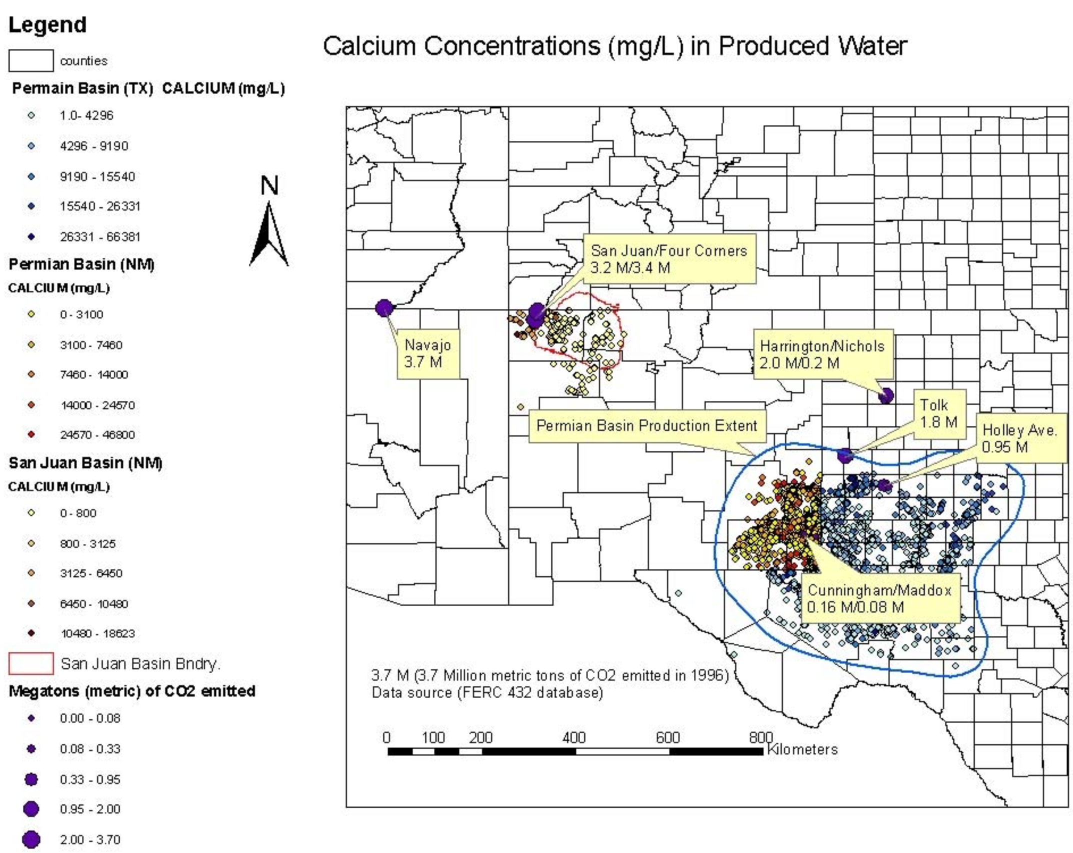

Figure 1. Measured calcium concentrations in produced water in NM and the Permian Basin region of Texas.

If all these ions were used to produce carbonates (obviously an upper-bound scenario, but if mineralization operations are carried out at the surface, this may be possible), they would sequester approximately 3.49 Mt CO_2 per year, based on aboveground carbonate formation and separation. Produced waters from the Permian Basin alone would sequester 2.97 Mt CO_2 per year, on this basis. This is a substantial quantity, particularly when it is remembered that these waters are already being produced and reinjected, for the most part as a waste product. To put it in context, the total annual production from Harrington, Nichols, Tolk, Holley Ave., Cunningham and Maddox power plants is ~ 5.19 Mt CO_2. Thus these produced waters could be used to sequester a substantial part of the CO_2 emitted by the power plants in the area of the Permian Basin.

Injection of bicarbonate-enriched brines offers an alternative route to CO_2 sequestration via this produced water. The produced water in southeast New Mexico alone is taken as a small-scale case study for comparison of the amounts of CO_2 that could be sequestered by each route. Obviously very much larger amounts of brine exist in the saline aquifers of this region, which could, in turn, sequester very much larger quantities of CO_2 if additional brine was produced.

Biomimetic Mineralization Option 2: Subsurface Mineralization

Subsurface mineralization with brines requires the production, piping, and reinjection of brines that have been subjected to the biomimetic catalyst to produce bicarbonate-enriched brines. In areas such as the Permian Basin, however, a substantial quantity of brine is already being produced, transported, and reinjected by the oil and gas industry. Some of these produced waters are presently used in water flooding for secondary production, but most of the produced waters constitute a waste product requiring disposal. In the Permian Basin, approximately 90% of these waters are reinjected for disposal. It would offer obvious environmental advantages if sequestration of a substantial quantity of CO_2 could be "piggy-backed" onto this process.

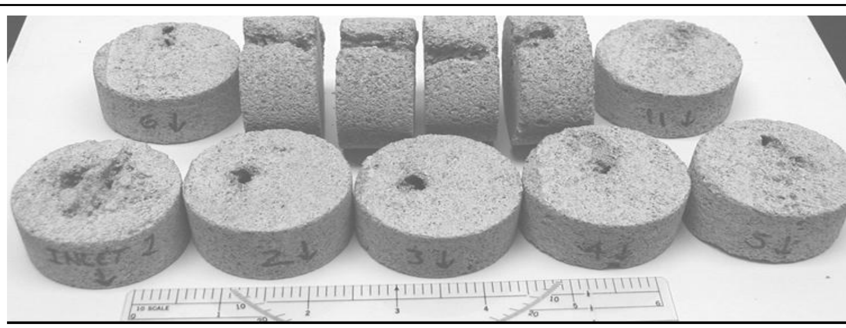

Figure 2. Post-flow test core (limestone). Note "wormhole" development.

Estimating capacities for subsurface mineralization is difficult, and a detailed risk-assessment framework and monitoring/verification program must be established for each potential injection site. However, preliminary calculations suggest that potential capacities are relatively large, and the use of flue-gas CO_2 in lieu of natural CO_2 in enhanced petroleum recovery operations may offset most costs of this disposal option.

At present, we are using reservoir/basin-scale numerical models of reactive transport to assess capacities and costs, and to assist in developing a general risk assessment framework. These models are being calibrated with results of multiphase CO_2/brine core-flooding experiments on various rock types, in collaboration with Grigg et al. (described by Grigg et al., this volume). Preliminary results of the experimental work (Figure 2) indicate that "wormhole" development is common, suggesting implications for injectivity as well as mechanical and chemical integrity of reservoirs and adjacent sealing formations. Experimental permeability changes are a function of time, space, rock type, pH and brine composition; the reactive transport simulation models are being developed to assess these aspects, with both a general sensitivity analysis and specific case studies in: the San Juan Basin, New Mexico; the Permian Basin, New Mexico and Texas; and the Powder River Basin, Wyoming.

Summary

A biomimetic system would offer the advantages of an environmentally friendly process, performed in aqueous solution at near-ambient temperatures and pressures, and modest pH, with no costly CO_2 concentration and compression steps. There would be obvious additional economic advantages if sequestration of a substantial quantity of CO_2 could be "piggy-backed" onto the disposal of produced water. Also, if brine-based sequestration were to be combined with desalination operations, then a freshwater byproduct would be produced. This freshwater could be a particularly important value-added product in the semi-arid southwest.

Acknowledgment

We gratefully acknowledge support from EPRI through contract number WO9000-26.

References

Bond, G.M., J. Stringer, D.K. Brandvold, F.A. Simsek, M-G. Medina and G. Egeland (2001a). Development of integrated system for biomimetic CO_2 sequestration using the enzyme carbonic anhydrase. *Energy and Fuels* **15**, 309-316.

Bond, G.M., M-G. Medina, and J. Stringer (2001b). A biomimetic CO_2 scrubber for safe and permanent CO_2 sequestration. *Eighteenth Annual International Pittsburgh Coal Conference Proceedings* (December 3-7, 2001, Newcastle, NSW, Australia).

Bond, G.M., M-G. Medina, B. McPherson, J. Stringer, A. Abel, and N. Liu (2002). Capturing and sequestering CO_2 nature's way: Biomimetic approaches. *Future Energy Systems and Technology for CO_2 Abatement Proceedings,* (November 18-19, 2002, Antwerp, Belgium), 269-276.

Simsek-Ege, F.A., G.M. Bond, and J. Stringer (2002a). Polyelectrolyte complex cages for a novel biomimetic CO_2 sequestration system, *Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century,* edited by Maroto-Valer et al., Kluwer Academic Publishers, 133-146.

Simsek-Ege, F.A., G.M. Bond, and J. Stringer (2002b). Matrix molecular weight cut-off for encapsulation of carbonic anhydrase in polyelectrolyte beads. *J. Biomater. Sci. Polymer Edn.* **13,** 1175-1187.

Wright, J., A. Colling, and Open University Course Team, *Seawater: Its Composition, Properties and Behaviour,* 2nd Edition, Pergamon-Elsevier, Oxford, (1995).