Biomimetic Sequestration of CO$_2$ in Carbonate Form: Role of Produced Waters and Other Brines

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Introduction

The overall purpose of this research from its inception has been to establish the feasibility of essentially permanent sequestration of CO$_2$ in mineral form, and particularly to examine the possibility of achieving this end by the mimicry of natural processes. A biomimetic approach has been devised, which uses a biological catalyst, carbonic anhydrase. Thus the objective is to develop a system resembling a CO$_2$ scrubber, in which carbonic anhydrase serves to catalyze the rate of CO$_2$ hydration for subsequent fixation into stable mineral carbonates. Feasibility of the approach has been demonstrated, and the emphasis is now on development of the approach into a chemical engineering reality. The present focus is on the use of produced waters and other brines as sources of cations for carbonate formation.

Mineralization routes to sequestration

Sequestration of CO$_2$ in the form of a stable, environmentally friendly solid offers obvious appeal for long-term storage of CO$_2$ with low risks and minimal monitoring requirements, and would be unlikely to encounter licensing problems. Carbonate minerals, such as calcite, aragonite, dolomite and dolomitic limestone, constitute the earth’s largest CO$_2$ sink, and are selected as representative cation sources, corresponding to two very different brine types. Total dissolved solids (TDS) are much lower in brines from the San Juan than in those from the West Pearl Queen Reservoir. Ca$^{2+}$ and Mg$^{2+}$ concentrations in produced waters are, respectively, 0.0871 M and 0.1468 M for the West Pearl Queen Reservoir, and 0.1743 M and 0.0692 M for the San Juan Basin.

Experiments with synthetic produced waters

Bench-scale experiments were first performed with synthetic produced waters as follows, prior to larger laboratory-scale experiments. 200μl 0.1mg/ml bovine carbonic anhydrase (BCA) were added to 10.0ml CO$_2$-saturated deionized (DI) water and mixed well. 10.0ml synthetic produced water and 1.0ml 1M Tris. buffer were added immediately. pH value and precipitation time (time to onset of precipitation) were measured, both in the presence of BCA and in control solutions without BCA. Calcium carbonate precipitated much more quickly in the presence of BCA than from control solution; for example, the precipitation time was 15 sec. (pH=8.54) in the presence of BCA, but 86 sec. (pH=8.53) in the control solution for the synthetic San Juan Basin produced water. For synthetic West Pearl Queen Reservoir produced water, the precipitation times were longer: for example, 254 sec. (pH=8.43) in the presence of BCA and 326 sec. (pH=8.51) in the control solution. This is attributed to the difference in the ratios of Ca$^{2+}$ to Mg$^{2+}$ for the two brines. Magnesium ions are well known to be potent inhibitors of CaCO$_3$ precipitation.

A laboratory-scale reactor has been built and used for subsequent tests on the synthetic brines. In these experiments, the enzyme was immobilized in chitosan-alginate beads. 0.0010 g per ml BCA powders were dissolved in 2% (w/v) sodium alginate solution. Chitosan solution was prepared by dissolution of the reagent in 3% (v/v) acetic acid solution (pH=2.5) to give 2% (w/v) of chitosan solution. In order to produce beads, the enzyme-containing alginate solution was dripped with a syringe into a crosslinker solution (comprising 1:1:1 (v/v/v) 0.2M CaCl$_2$; 2% (w/v) chitosan solution; DI water) at room temperature. The pH of the solution was adjusted with 0.1M NaOH or 0.1M HCl to 5. The solution was placed on a magnetic stirrer. Beads were stirred in the solution for 2 hrs, washed with de-ionized water, and refrigerated at 4°C until use.

CO$_2$-saturated DI-water was pumped with buffer solution into the reaction chamber of the laboratory-scale reactor, where it flowed across enzyme-loaded beads. As the solution left the reaction chamber, synthetic brine was pumped from the brine supply barrel to mix with the H$_2$CO$_3$-buffer solution, and then passed through a heating vessel. In the secondary settling pan, CaCO$_3$ precipitated, and the remainder of the solution was re-injected into the H$_2$CO$_3$ supply barrel. Inflow rates of the CO$_2$-saturated DI-water, synthetic brine,
and Tris. buffer were adjusted to give proportions equivalent to those used in the bench-scale tests. The results are listed in table 1.

**Table 1. The Results of Laboratory-Scale Experiments with Simulated Produced Water**

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Precipitation Time (sec.)</th>
<th>pH Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Pearl Queen</td>
<td>With BCA 252</td>
<td>8.63</td>
</tr>
<tr>
<td>Queen Reservoir</td>
<td>No BCA 303</td>
<td>8.71</td>
</tr>
<tr>
<td>San Juan Basin</td>
<td>With BCA 7</td>
<td>8.58</td>
</tr>
<tr>
<td></td>
<td>No BCA 122</td>
<td>8.65</td>
</tr>
</tbody>
</table>

**Injection Capacity Analyses**

Another approach to carbon sequestration that utilizes the carbonic anhydrase reactor is the injection of bicarbonate-rich water into subsurface reservoirs. In this process, produced water or other brine pumped from the reservoir to the surface is then enriched with bicarbonate ions by means of the carbonic anhydrase reactor. The resulting solution would then be injected into subsurface reservoirs, for example the West Pearl Queen (depleted oil and gas reservoir) and the Frio Sand (deep saline aquifer, Southeast Texas).

Injection or production capacity is a major consideration when evaluating the disposal of fluids by subsurface injection or optimizing production rate. The term injection (production) capacity can be defined as the maximum injection (production) rate possible for a given reservoir. Reservoir permeability, geometry (thickness), and reservoir conditions (temperature and pressure) influence injection (production) capacity tremendously.

A simple relationship can be applied to a certain set of field-scale parameters to determine the injection (production) capacity of a given reservoir. This can be used to give a reasonable estimation of the amount of CO$_2$ that could be stored within the reservoir within a given year. L.P. Dake, L.P. first explored injection (production) capacity in the context of oil and gas reservoir engineering, but we can apply his relationship both to the injection of bicarbonate-rich brine into a reservoir, and to the production of brine as a cation source for surface mineralization. This relationship states that the injection (production) capacity is proportional to the reservoir thickness, reservoir permeability, and the pressure difference between the point of injection (production) and the reservoir.

The main field parameters that enhance injection (production) capacity are permeability and reservoir thickness. The change in pressure applied to the injection (production) of fluids is limited to the maximum overpressure that can be applied to a specific reservoir before reservoir failure. Reservoir engineers have said that this pressure difference must be limited to between 9 and 18 % of the original reservoir pressure to prevent reservoir failure. The West Pearl Queen reservoir permeability has been measured to be approximately 6.91 x 10$^{-14}$ m$^2$ and the thickness of the reservoir is approximately 6 meters. These field parameters correspond to an injection (production) capacity of ~0.164 m$^3$/day. The Frio Sand reservoir permeability of 8.88 x 10$^{-14}$ m$^2$ and reservoir thickness of 30 meters correspond to an injection (production) capacity of ~6.80 m$^3$/day.

The main factor that inhibits injection (production) capacity is the product of permeability and reservoir thickness, as can be noted from the comparison between the capacities of the Frio Sand reservoir and the West Pearl Queen reservoir. The predicted possible cumulative mass injection (production) of brine injected over 365 working days is approximately 65,500 kg (West Pearl Queen reservoir) and 2.7 million kg (Frio Sand reservoir). Throughout certain oil and gas basins there are thousands to hundreds of thousands of wells that inject and produce brine for disposal purposes, and it can be seen that the cumulative capacity for carbon storage within these basins is significant.

It is also important to note that the ability to produce brine as a source of cations is extremely important when evaluating surface mineralization options. Cation (Ca$^{2+}$ and Mg$^{2+}$) fluxes can be calculated on the basis of chemical analyses of brine compositions and production rate. Cation fluxes for two field sites (West Pearl Queen and Frio Sand) were calculated given their respective brine compositions. The corresponding estimates were approximately 459 kg of divalent cations per year for the West Pearl Queen site and 5,962 kg of divalent cations per year for the Frio Sand site. These cation fluxes correspond to carbon sequestration potentials via surface mineralization of 502 kg CO$_2$ stored (West Pearl Queen) and approximately 6,550 kg of CO$_2$ (Frio Sand).

**Conclusions**

Demonstrations of the bench-scale and laboratory-scale carbonic anhydrase reactor have been accomplished. Carbonic anhydrase has shown promising results for use as an enzyme to increase the rate of precipitation of carbonate mineral, with produced waters as a cation source. Synthetic produced waters have been used to demonstrate the feasibility of the system. The possibility of overcoming the inhibition of CaCO$_3$ precipitation when the ratio of magnesium ions to calcium ions is higher, by, for example, modest heating of the solution, will be investigated.

Injection (production) capacity analyses performed on several well-scale pilot sites (West Pearl Queen Reservoir and the Frio Sands aquifer) have shown a definitive carbon sink in terms of the possibility of surface mineralization utilizing cations from brines, or the injection of bicarbonate-rich waters at depth.

**Acknowledgement**

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**References**