

# Enzyme Based Membrane Reactor for CO<sub>2</sub> Capture

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## ABSTRACT

Control of carbon dioxide (CO<sub>2</sub>) is crucial for all crew inhabited space-flight missions. Air revitalization requires safe and reliable CO<sub>2</sub> extraction systems characterized by small volume, low mass, low rate of energy use, minimal use of consumables, and little or no crew time for operation and maintenance. Current designs are relatively costly to operate due to consumable usage rates (e.g., LiOH), high mass and/or volume (solid amines), and/or high energy costs associated with regeneration of CO<sub>2</sub> adsorption capacity (e.g., metal oxide).

Our work focuses on the development of a highly efficient enzyme catalyzed, Carbonic Anhydrase based liquid membrane biomimetic reactor. We report here on the use of aqueous chemistry modeling to guide the design of new liquid membrane compositions. We examine the effects of these new solutions on enzyme activity and on the solubility of other gases in the mix. We also discuss our initial efforts to enhance reactor performance through localized pH control.

## INTRODUCTION

NASA is in need of a next generation air revitalization system (ARS) that will have an even lower equivalent system mass (ESM) than is currently the case. ESM is a metric developed by NASA management that attempts to unitize such discrete parameters as mass, volume, power requirements, consumable usage, and maintenance time to facilitate comparative evaluation. It is analogous to monetization in economics.

One or more ARS designs are needed for the spacesuit (Extravehicular Mobility Unit – EMU) for use during extravehicular activities (EVA). Another is needed for long duration space missions, e.g., to Mars. The cost factor for a Mars mission is about 10 times that for

launch to low Earth orbit (LEO) making the concern for ESM obvious.

Historically three physicochemical approaches have been used to extract the very low concentration CO<sub>2</sub> present in the astronaut expiratory gas. The apparatus used for this purpose has been referred to by the acronym CDRA – carbon dioxide removal assembly. The physicochemical approaches include adsorption, physical absorption and chemical absorption. The last encompasses all of the chemical reaction mechanisms whether they are readily reversible or not. In general these reactions result in the formation of carbonates, bicarbonates or carbamates from oxides, hydroxides or amines. Typically, the adsorption or absorption step is readily accomplished. The desorption step, in most cases, is energy dependent and tends to limit both the rate of production and the quality of the product.

The design must address issues of chemistry and reactor chemical engineering to satisfy the interdependent issues of the rate and magnitude of the process, the energy requirements, the mass and volume, possible toxicity, stability and reliability, and the service related labor requirement. Chemistry largely deals with the rate and magnitude of the process, the energy requirements, possible toxicity, stability and reliability while chemical engineering focuses on issues of mass, volume, mass transfer and the service related labor requirement.

With regard to the chemistry we have been seeking ways to maximize the operation of the enzyme carbonic anhydrase (CA – E.C.4.2.1.1) to catalyze the conversion of CO<sub>2</sub> to bicarbonate and the converse. By arranging the enzyme such that it operates at two gas-liquid interfaces, the first the feed side exposed to gas rich in CO<sub>2</sub>, the second the sweep side, exposed to gas lean in CO<sub>2</sub>, we can cause the CO<sub>2</sub> to leave the rich stream and be delivered to the lean stream. This is common to all

reversible chemical facilitation approaches. The benefits of the enzyme are the very high rate, the high sensitivity to very low  $p\text{CO}_2$ , the ability to run at ambient or body temperature, and the low toxicity.

With regard to the chemical engineering we have examined a variety of designs utilizing microporous hydrophobic polymer membranes to separate the gas and liquid phases. We have experimented with flat sheet and hollow fiber designs. The latter can be arrayed as flat sheets and as spiral winds using both parallel or orthogonal fiber alignments.

The focus of this paper is on the chemistry as we explore ways of increasing performance, i.e., increasing permeance for  $\text{CO}_2$  and decreasing permeance for other gases, specifically nitrogen ( $\text{N}_2$ ) and oxygen ( $\text{O}_2$ ) (1-4). Towards this end, in this work we consider ways of altering the salt and buffer makeup of the contained liquid membrane (CLM). We also consider the relative merits of diffusion vs. convection dependent designs. Finally, we consider ways to alter the local pH to optimize the desorption rate.

## AQUATIC CHEMISTRY

The liquid membrane is an aqueous film containing various salts, buffers and the enzyme CA. The role of the enzyme in the liquid film is to catalyze the conversion of  $\text{CO}_2$  to bicarbonate, at the feed side, and to catalyze the reverse reaction at the sweep or permeate side. The buffer controls the release and supply of protons, as they are an integral part of this reaction. The role of the salts is: (1) that they are at a minimum an integral part of the buffer; and (2) that additional salt (ion) will serve to reduce the solution capacity of other gases in the feed to enhance the selectivity, i.e., the ratio of  $\text{CO}_2$  to non- $\text{CO}_2$  gases in the permeate. The salt-buffer system also controls the capacity of the liquid membrane for bicarbonate. While it is critical that the liquid membrane capacity for bicarbonate not limit the rate of substrate delivery, it is possible, under certain conditions, that the amount of bicarbonate available at the sweep gas side may be excessive. Then, by virtue of end-product inhibition the absorption rate will be reduced, possibly even to the extent that it will be below the desorption rate.

In order to characterize the effects of altering the ionic makeup of the liquid membrane solution we began construction of a 1-Dimensional Reactive Transport (1-DRT) model. The first part of this effort was development of the aquatic chemistry section. Eventually the 1-DRT will define the salt, buffer and enzyme concentrations that provide the best trade-off for selectivity and permeance, i.e., promoting the flux of  $\text{CO}_2$  while minimizing the flux of  $\text{N}_2$  or  $\text{O}_2$ .

The benefit of this approach is that the higher the permeance the smaller the apparatus. The higher the selectivity the more likely that a one-pass device will

perform satisfactorily, i.e., that minimal amounts of  $\text{N}_2$  or  $\text{O}_2$  will be lost to space (AEVA). Our target for spacesuit (EVA) application is a selectivity of  $\text{CO}_2:\text{O}_2$  of 3000:1. This consideration is far less important for advanced life support (ALS) applications on a spaceship (SS) or space station. High selectivity in ALS will result in a higher purity  $\text{CO}_2$  stream. If we can achieve >95% then the permeate can be fed directly to the Sabatier.

In the SS and EVA situations the driving force for removing  $\text{CO}_2$  from respiratory gas is low (<0.5% vs. 0.79% arterio-venous difference). Two factors stand out when examining our past data as well as the new 1-DRT information. The first is that, given the very low  $\text{CO}_2$  driving force, the optimal design window is narrow. Second, interfacial availability of catalyst, here CA, is a major factor.

Development of a 1-DRT model can be broken into three parts – steady state thermodynamics, i.e., aquatic chemistry, addition of diffusion equations and, finally, addition of kinetics equations. The first goal of this work was to begin to characterize the concentration profiles across the thickness of the liquid membrane for any given feed  $p\text{CO}_2$ . Thermodynamic considerations are adequate for this task. This is central to determining if we are facing reaction limitations that decrease effective enzyme activity or if we are facing diffusion limitations that could be addressed by use of convective flow for the CLM film. Another goal was to determine if modifying the salt solution could contribute to decreasing the solubility of the non-reactive gases by salting out.

We selected the StreamAnalyzer<sup>®</sup> software from OLI Systems, Inc. (Morris Plains, NJ) as the engine to perform these calculations. We were particularly concerned about the ability to alter gas solubility by increasing ionic strength, i.e., salting out, while making certain that the higher ionic strength would not negatively impact enzyme activity. Further the selection of auxiliary ions is critical as certain ions increase water binding efficiency and could aid in stabilizing the enzyme. These are known as kosmotropes. Their opposite, chaotropes, promote denaturation in proteins. The ionic strength of the fluid can be increased in two ways. In one the concentration of phosphate buffer is elevated. In the other another salt is added that does not affect enzyme activity. In this case we used cesium sulfate ( $\text{Cs}_2\text{SO}_4$ ). Cesium is a weak chaotrope while the sulfate ion is a strong kosmotrope. We therefore examined the effect of increasing the concentration of  $\text{Cs}_2\text{SO}_4$  on gas solubility and enzyme activity.

Over 150 sets of calculation have been performed using the StreamAnalyzer<sup>™</sup> software. These have included calculations related to design of cesium based liquid membrane solutions and further investigation of the behavior of phosphate based liquid membrane solutions.

The results of some of these calculations are given in Figure 1. The calculation was performed at 30°C for a 1

ATM vapor phase having a dry gas composition of 0.1% CO<sub>2</sub>, 79% N<sub>2</sub>, and 20.9% O<sub>2</sub>. The decreasing solubility of N<sub>2</sub> and O<sub>2</sub> with the increasing Cs<sub>2</sub>CO<sub>3</sub> addition is apparent. Note that the Cs<sub>2</sub>CO<sub>3</sub> values shown illustrate how the amount of Cs<sub>2</sub>SO<sub>4</sub> present changes the amount of Cs<sub>2</sub>CO<sub>3</sub> needed to obtain the pH 7 conditions for this partial pressure of CO<sub>2</sub> (~0.001atm).

Figure 2 further illustrates what is occurring in the solution. In this plot the N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> concentrations in solution are plotted on a log scale versus the ionic strength. From this plot it is apparent that the percent change in solubility of each gas is the same. These data are re-plotted on a linear scale and as a function of temperature in Figure 3. It is clear that salting out is a significant effect for non-reactive gases.

The question then becomes how this can lead to an increased selectivity for CO<sub>2</sub>. The answer lies in the fact that dissolved CO<sub>2</sub> is not the dominant transport species for CO<sub>2</sub>, the bicarbonate ion is. This calls for a look at the effect of ionic strength on the bicarbonate concentration in equilibrium with 0.1% CO<sub>2</sub> at pH 7 as is shown in Figure 4. From Figure 4 we get a result we could not anticipate or know without use of these sophisticated aquatic chemistry models. Figure 4 shows that increase in ionic strength from 0 to ~1.5 M increases the bicarbonate ion concentration. Further increases in ionic strength cause the bicarbonate concentration capacity to decrease until, for ionic strengths above ~7.5 M, the bicarbonate concentration is lower than it was at ~0.001M. Surprisingly, these data suggest that the optimum selectivity for CO<sub>2</sub> will be found at moderate ionic strengths rather than at high ionic strengths.

We have explored two different buffer systems. The first was a phosphate design, the second a CsHCO<sub>3</sub> / Cs<sub>2</sub>CO<sub>3</sub> design often supplemented with glycine. The former has more flexibility while the latter can give better performance, under the correct circumstances. The lower flexibility of the CsHCO<sub>3</sub> / Cs<sub>2</sub>CO<sub>3</sub> design means that for any given pCO<sub>2</sub> the buffer concentration is fixed. For this buffer system there is no opportunity to change buffer strength without changing pH. Figure 5 illustrates this situation. This plot shows the Cs ion concentration (added as CsHCO<sub>3</sub> or Cs<sub>2</sub>CO<sub>3</sub>) needed to obtain a given pH versus a 1 ATM vapor phase containing 0.1% CO<sub>2</sub> and 0.5% CO<sub>2</sub>, respectively.

The data illustrate the limitation mentioned above, and the fact that the pH at the feed side of the membrane reactor would be very sensitive to the partial pressure of CO<sub>2</sub> when using this type of buffer system. To further illustrate this point let us take a situation where liquid membrane is designed to give a pH of 7.0 versus 0.1% CO<sub>2</sub> in 0.1 ATM air. If the CO<sub>2</sub> concentration in the air increased to 0.5% the pH would decrease to 6.3. If the CO<sub>2</sub> concentration changed to 0.05% the pH would increase to 7.3. Similarly for a pH of 8.0 versus 0.1%

CO<sub>2</sub> the pH versus 0.5% would be 7.3 and that versus 0.05% would be 8.3.

A situation wherein pH changes greatly over the expected range of reactor operation is unfavorable. Due to this we have begun efforts to again look at the use of phosphate buffered systems. However, the CsHCO<sub>3</sub> / Cs<sub>2</sub>CO<sub>3</sub> system is inherently of high molarity while the phosphate design needs supplementation by cesium sulfate to change the ionic strength.

Figure 6 illustrates the ionic profiles for a variety of solutions based on either a phosphate or a phosphate-cesium sulfate composition. All of the solutions subscripted with an "o" indicate the absence of Cs<sub>2</sub>SO<sub>4</sub> while those subscripted "i" include this salt. Table 1 (upper right) lists the solution salt makeup. Solutions I, II, III and IV describe solutions of increasing ionic strength. The graphs show that the most stable pH profiles are achieved with solutions IIIo and IVo. As expected the selectivity of IVo will be greater due to decrease in solubility of N<sub>2</sub> and O<sub>2</sub>.

## DIFFUSION VS. CONVECTION

At the feed gas interface the CO<sub>2</sub> is converted to bicarbonate. The bicarbonate then must cross the liquid membrane to access the sweep side where it is converted to CO<sub>2</sub> and released to the sweep gas. The liquid membrane thickness can range from 80μm to 600μm (2,4). Diffusion presents a fixed transport limitation as only so many molecules can cross the thickness of the membrane per unit time. However, it may be that a convection model will be more effective in distributing the dissolved species, particularly if we are using a hollow fiber based design where recruitment of all of the available surface area is critical (1,2).

We therefore examined the effect of altering the circulation rate of the CLM. We created a number of hollow fiber reactors for this purpose. They were organized in both spiral wound and flat sheet array. The fluid was arranged to flow either parallel or perpendicular to the fiber organization. We examined CLM flow rates from 0 cm<sup>3</sup> hr<sup>-1</sup> to 2000 cm<sup>3</sup> hr<sup>-1</sup>. The data reveal that for a longitudinal flow pattern an 87% improvement is reacted by 600 cm<sup>3</sup> hr<sup>-1</sup> and a 95% by 1000 cm<sup>3</sup> hr<sup>-1</sup>.

## LOCALIZED pH

Another issue of concern is that the reaction of CO<sub>2</sub> with water, particularly when facilitated by CA, releases a proton at the feed side and consumes a proton at the permeate side of the liquid membrane. This process acidifies at the feed side and causes an alkalization at the sweep side. Using the 1-DRT we determined that the magnitude of the pH gradient is on the order of 0.24 pH units for a pCO<sub>2</sub> of 0.1% and a buffer of 20 mM phosphate. This pH shift is in the direction opposite that desired. The absorption of CO<sub>2</sub>, i.e., the hydration to bicarbonate, occurs most rapidly and completely under

more alkaline conditions. In contrast desorption (dehydration) of bicarbonate to CO<sub>2</sub>, occurs best under acid conditions. The significance of this effect can be seen in Figure 7.

The data show that the maximum CA catalyzed dehydration rate (occurs at low pH) is 22.4% of the maximum CA catalyzed hydration rate (occurs at high pH). At pH 7.0 the CA catalyzed hydration rate is 50% of its maximum with the CA catalyzed dehydration rate also being 50% of its maximum or 11.2% of the maximum hydration rate. Thus under the condition where the CLM is well buffered at pH 7.0 the dehydration rate will be limiting with the hydration rate being 4.46 times the dehydration rate. Providing a weaker buffer system only makes the situation worse because the feed side (where hydration occurs) will tend toward lower pH (lower hydration rate) and the sweep side (where dehydration occurs) will tend toward a higher pH (lower dehydration rate). The expected benefit of controlling the local pH at the gas-liquid interface is to help maximize the dehydration rate at minimum cost to the hydration rate.

To address this event we examined the ability to induce surface fixed charges in order to drive the feed gas interface more alkaline and the sweep gas interface more acid. We began developing two different methods for activation and functionalization of the polypropylene membranes. Polypropylene is very stable and unreactive. The first step in activation it is to expose it to an environment that will increase the surface energy and introduce polar functional groups to the surface. Either oxidizing radiation or wet chemistry oxidation can activate the polypropylene. Radiation options include UV activation, plasma CVD (controlled vapor deposition) and <sup>60</sup>Co radiation. Plasma activation is far preferred because it is more readily controlled and does less damage to the polymer. This technique will allow the addition of acrylic acid, carboxylic acid or sulfonyl acidic groups as well as amino alkaline groups to the membrane.

We generated a wet chemistry protocol in anticipation of access to the plasma devices. Wet chemistry is less desirable for two reasons. First, it is highly aggressive and can easily damage the polypropylene. At short duration exposure the nanopores can be blocked while at long duration exposure the treatment can induce microtears. Using a shorter reaction time and milder conditions to avoid the degradation of the polymer also means that fewer sites are activated, limiting the ability to add large numbers of reactive groups.

We have treated polypropylene membranes using sulfur trioxide as an oxidizing agent in conjunction with sulfuric acid. This treatment functionalized the membrane surface with acidic sulfonyl groups. Such membranes exhibit a pH of ~4.3 when covered with water and a pH of ~5.6 when covered with a 20mM phosphate buffer solution having a bulk fluid pH of 7.0. The buffer

neutralizes some of the acid sites on the membrane. If this membrane pH can be maintained at the sweep side against a pH of 7.0 at the feed side the relative rates of the hydration and dehydration reactions to the maximum CA hydration rate would be 50% and 21.5%, respectively. This is almost a 2x improvement in the dehydration rate from the pH 7.0 condition discussed earlier, and while the dehydration rate would still be limiting the ratio of the hydration to dehydration rate is only 2.33 rather than 4.46.

## CONCLUSION

These data indicate that a rational, modeled design approach can be used to understand this complicated system. The 1-DRT showed an unexpected increase in bicarbonate solubility that may be beneficial in later operations. The ability to use a flowing fluid for solute distribution allowed us to recruit a far larger fraction of the available hollow fiber membrane surface.

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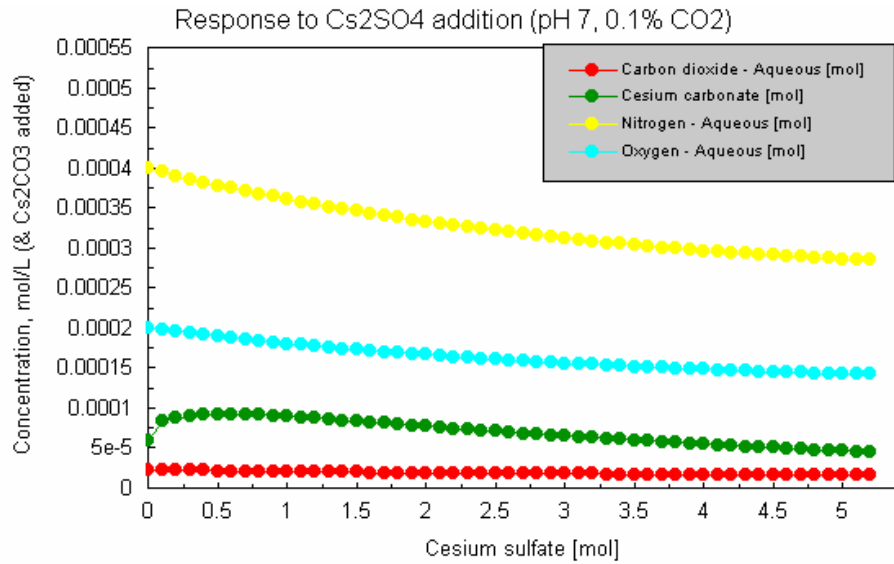


Figure 1. Solubility of CO<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> in the presence of cesium sulfate.

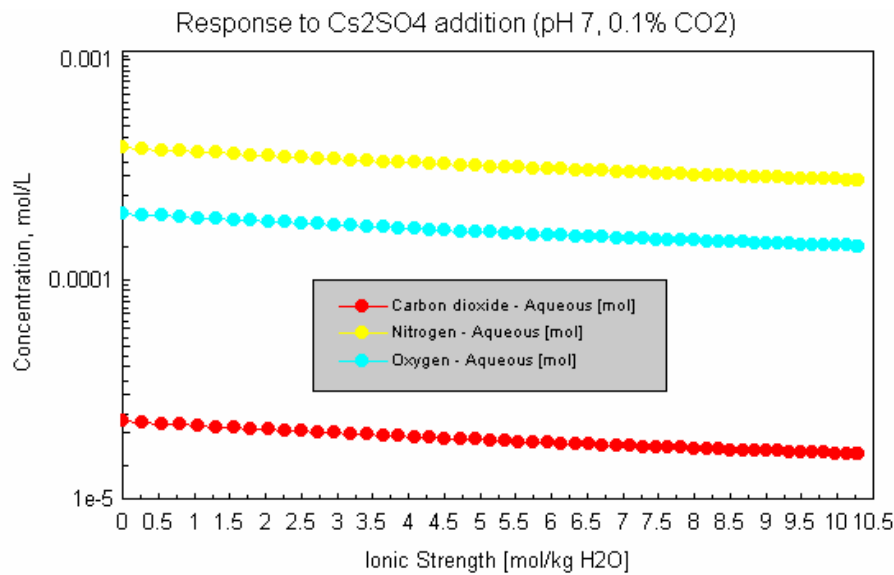


Figure 2. Solubility of CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub> as a function of total ionic strength.

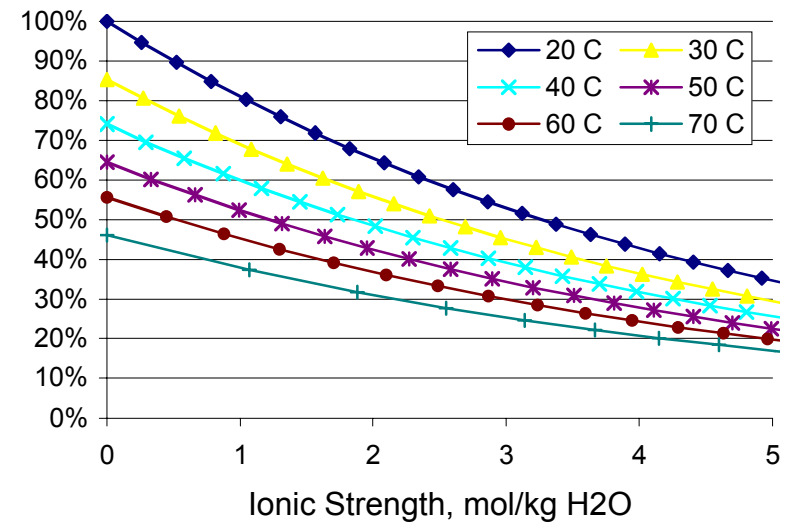


Figure 3. Gas solubility in an aqueous medium as a function of ionic strength.

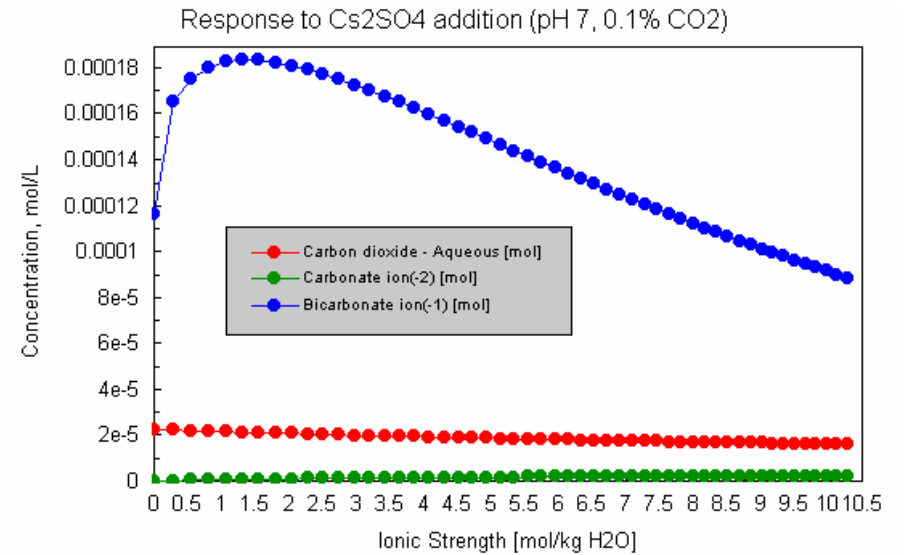


Fig. 4. Solubility of carbonate, bicarbonate and CO<sub>2</sub>, as a function of ionic strength.

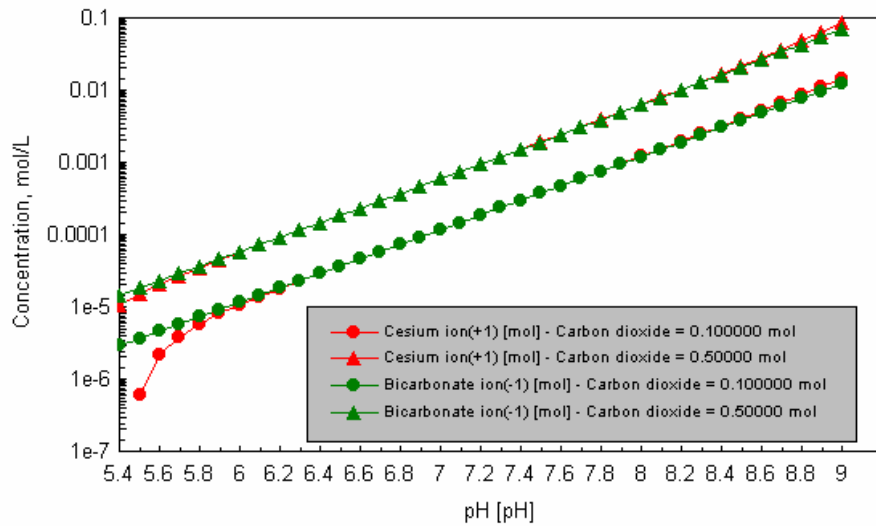


Figure 5. Concentration of cesium and bicarbonate in the presence of 0.1 % or 0.5 % CO<sub>2</sub> (total gas phase = 100 mol).

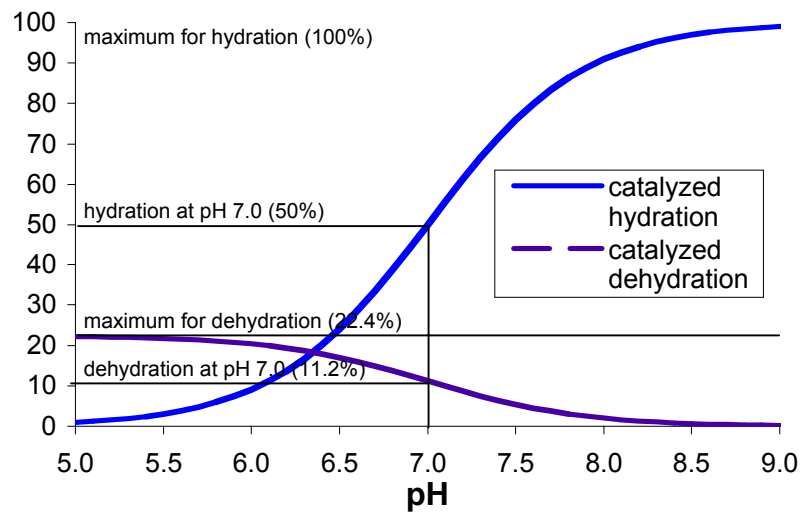
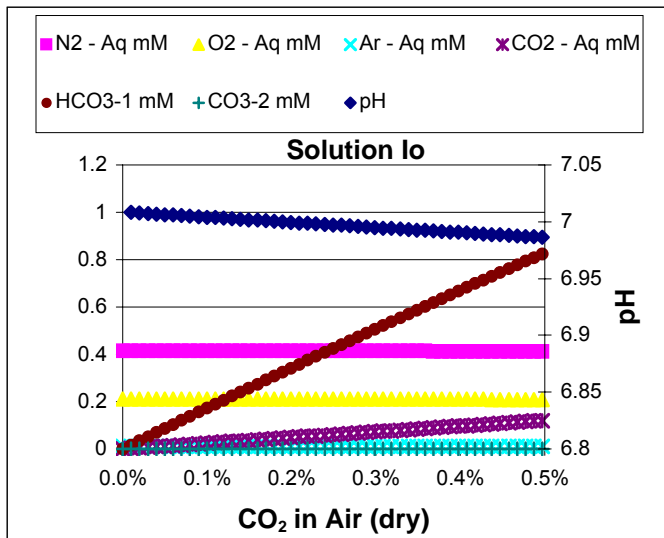


Figure 7. Rates of CA catalyzed hydration and dehydration reactions normalized to the maximum CA catalyzed hydration rate as a function of pH.



**Table 1.** A map of seven different CLM solutions set to pH 7.0. Solutions subscripted with  $\text{N}_2\text{O}$  contain no  $\text{Cs}_2\text{SO}_4$ . Their ionic strength is controlled by the amount of phosphate. Solutions subscripted with  $\text{NiO}$  increase ionic strength by the addition of  $\text{Cs}_2\text{SO}_4$ .

Solution ID	Ionic strength mol/kg H <sub>2</sub> O	with 10 mM bicarbonate		
		K <sub>2</sub> HPO <sub>4</sub> mM	KH <sub>2</sub> PO <sub>4</sub> mM	Cs <sub>2</sub> SO <sub>4</sub> mM
Io	0.16	41.5	24.7	0.0
Ilo	0.64	175.3	67.9	0.0
IIlo	1.61	397.1	115.8	0.0
IVo	4.01	727.9	183.0	0.0
Ii	0.65	49.2	16.2	179.8
Iii	1.59	92.1	19.0	496.8
IIii	4.01	140.5	15.0	1346.4

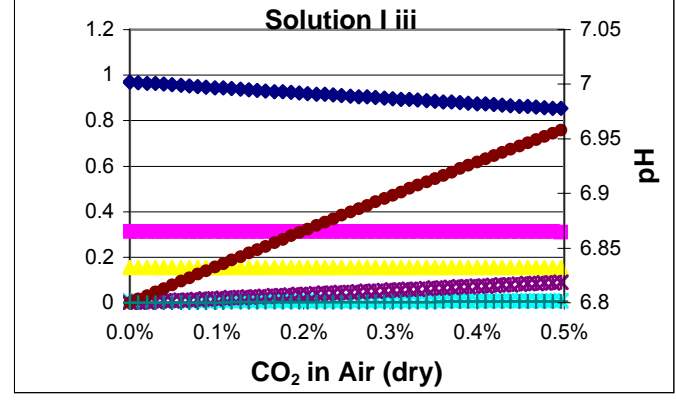
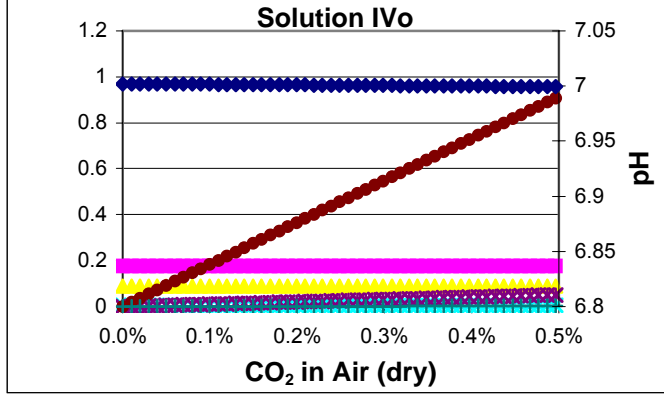
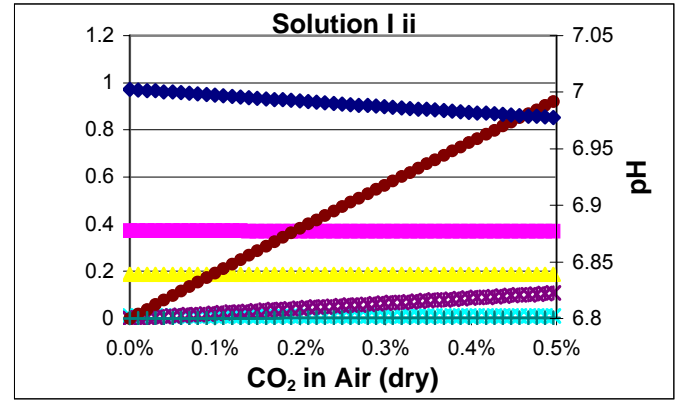
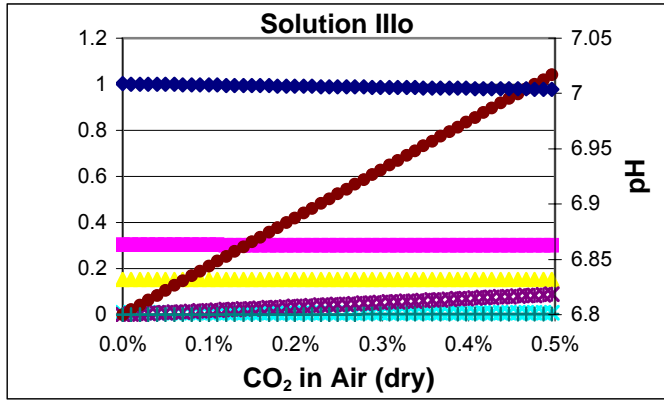
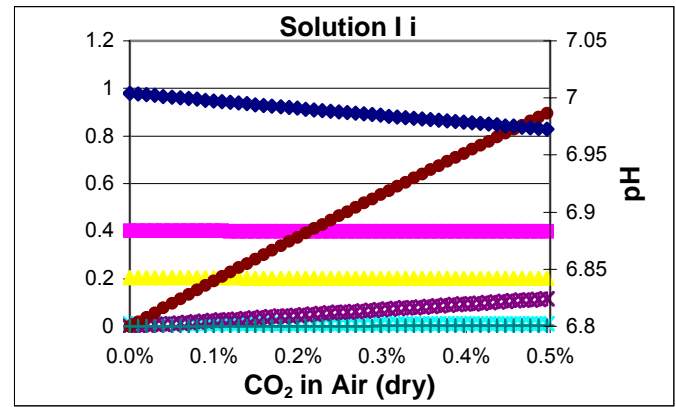
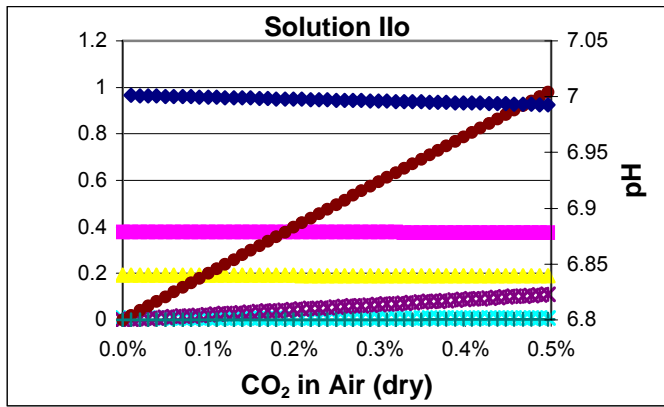


Figure 6. Calculated values for pH, and concentrations of oxygen, argon, CO<sub>2</sub>, bicarbonate and carbonate in the CLM for buffer conditions described in Table 1.