

Greenhouse Gas Emission Reductions: Development of Energy Efficient Catalysts for Post Combustion Capture of CO₂.

Raymond Davy, Robert Shanks, Philip Marriott, Matthew Gustafson and Brodie Zamberg.

School of Applied Sciences, RMIT University, Melbourne, Victoria, 3001 Australia.

ABSTRACT

There is a large energy penalty in the proven technology of chemical absorption/stripping of CO₂ using amine solvents. The aim in this study is to develop fast catalytic absorption/desorption of CO₂ at low temperatures using water as solvent. The naturally occurring zinc metallo-enzyme carbonic anhydrase (CA) can concentrate CO₂ using a reversible hydration/dehydration cycle at neutral pH and at ambient temperatures. Some tripodal complexes of zinc (II), and other metals mimic the CA catalytic process, which proceeds by hydration of CO₂ to bicarbonate followed by the reverse dehydration of the bicarbonate to regenerate CO₂. This initial study is of the fast catalysis of the reverse reaction (the dehydration of the bicarbonate ion back to CO₂) at temperatures in the range 20–55 °C. The turnover rate constants for the catalytic desorption have been measured for the zinc tripodal complexes: zinc-nitrilo-tris(2-benzimidazolyl-methyl-6-sulfonic acid - (zinc-L1S), and zinc-tris(2-benzimidazolylmethyl)-amine - (zinc-LI). The measured kinetic parameters show that the catalytic cycle may be rapid enough to allow its utilization in a new capture process, hence avoiding the energy intensive steam stripping steps necessary with amine solvents.

Keywords: Bicarbonate dehydration; carbonic anhydrase; CO₂ capture; catalysts; catalytic absorption; catalytic desorption; CO₂ hydration; post combustion capture; zinc complexes; Monoethanolamine - MEA.

1. Introduction

Anthropogenic CO₂ production is a major contributor to atmospheric CO₂ levels that have increased from around 250 ppm at the start of the industrial revolution to around 380 ppm currently. Projections by the International Panel on Climate Change predict that a business as usual (BAU) scenario will produce a level of 850 ppm by 2050 and will result in serious climate extremes (melting polar ice, sea level increases, and disruption of ocean currents). Reductions from this projected level, could be achieved from efficiencies, by switching to generation of energy from renewable or non-carbon sources, (solar, wind, hydro or nuclear generation), however fossil fuels will still be essential to maintain future energy demands. To achieve the emission reductions desired, carbon capture and storage will be required as the major technology that must be implemented. While new power plants may use the newer technologies that facilitate CO₂ capture (decarbonisation with pre-combustion capture, oxy-fuels), retrofitting of existing conventional power generating plants is more problematical.

The flue gases from conventional industrial plants using carbon-based fuels typically contain 4 - 14% carbon dioxide, which must be concentrated by capture to allow compression for storage. At present, the best method for capture - used in the purification of natural gas - is the chemical absorption–stripping cycle of CO₂ with an amine solvent -

usually monoethanolamine (MEA). This mature technology is expensive on the large scale (around \$40-\$80US /tonne of CO₂ captured) and retrofitting to existing coal burning plants is uneconomic, reducing efficiencies to as low as 10%. Disadvantages of MEA include its corrosive properties, requirements to replenish evaporative losses, chemical and thermal degradation (particularly by SO_x, NO_x and unburnt oxygen) occurring in the absorption-stripping cycle. A further major disadvantage of MEA is the energy cost in the stripping procedure requiring steam at temperatures of around 120 °C.

Carbonic anhydrases, (CA), are widely occurring zinc metallo-proteins (enzymes) that catalyse reversibly the hydration and dehydration of CO₂ at ambient temperatures in living organisms. Several authors have suggested using CA in a new carbon capture system, but the enzyme is costly to produce, has a high molecular weight of 30,000 g/mol (limiting molar concentration) and it is only stable below 85 °C. Nevertheless, Trachtenberg and Bao [4] proposed a system, using CA in conjunction with a thin liquid membrane, with a projected cost reduction to \$26US /tonne.

Some tripodal zinc complexes that mimic CA but are much more stable than the enzyme, have been identified and are suggested for development as a capture system.

2. Theory:

2.1 Amine solvents

Davidson [1] and Rochelle [2] have reviewed the alkanolamine solvents, (amine solvents).

CO₂ is a weak acidic gas that is absorbed into a solvent containing the amine, (a weak base), where RNHCOO⁻ is carbamate ion which is formed with both primary and secondary amines, but tertiary amines (and hindered amines) form the bicarbonate ion in a reaction with water as shown below from Rochelle et.al. [3], and Davidson [1]. (Equations 1 and 2).



The absorption capacity of tertiary amines is twice that of primary or secondary amines, (from equations 1 and 2 above), however the rate of absorption is lower Davidson [1], Trachtenberg and Bao [4].

2.2 Carbonic anhydrase.

Carbonic anhydrase (CA) is an enzyme found in virtually every animal and plant with catalytic function (equation 3) of converting CO₂ to bicarbonate (hydration) and the reverse (bicarbonate dehydration). The protein has a molecular weight around 30,000g/mol.



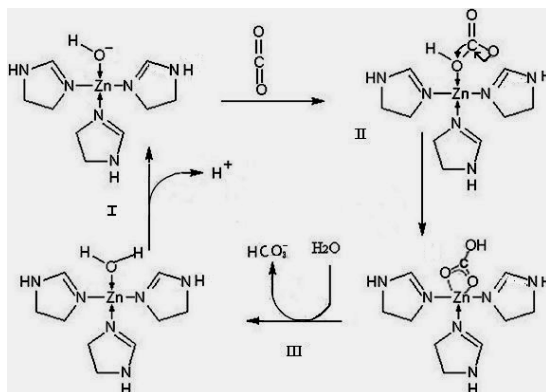
The active site of CA, features tetrahedrally coordinated zinc that is attached to the protein backbone by three histidine amino acid residues with the fourth site occupied by a water molecule. As discussed by Parkin [24], the tetrahedral geometry enhances the Lewis acidity of the zinc center (ie. zinc accepts ligand electrons for strong coordination) and also the Bronsted acidity of the coordinated water. This water ligand exhibits a pKa around 7 and therefore alternates between the H₂O and OH⁻ form depending on pH. Carbonic anhydrase

is one of the fastest enzymes known with one molecule able to turnover a million molecules of bicarbonate per second, Lindskog and Liljas [5], and according to Trachtenberg et.al. [20], the CA turnover rate is more than 4,000 times faster than MEA. The mechanism of the catalysis by CA (Figure 1) has been summarized concisely by Nakata et. al. [6] and by Bräuer et. al. [7], as follows:

- I. Deprotonation of the liganded water $(\text{His})_3\text{-Zn}^{2+}\text{-H}_2\text{O} \rightleftharpoons (\text{His})_3\text{-Zn}^{2+}\text{-OH}^- + \text{H}^+$
- II. Nucleophilic attack of $(\text{His})_3\text{-Zn}^{2+}\text{-OH}^-$ on CO_2 to form $(\text{His})_3\text{-Zn}^{2+}\text{-HCO}_3^-$
- III. Ligand exchange – the zinc bound HCO_3^- ligand is replaced by H_2O and the $(\text{His})_3\text{-Zn}^{2+}\text{-OH}_2$ is reformed. $(\text{His})_3\text{-Zn}^{2+}\text{-HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons (\text{His})_3\text{-Zn}^{2+}\text{-H}_2\text{O} + \text{HCO}_3^-$

Figure 1. Mechanism of catalysis of CA.

Zinc is the metallic ion at the active site of CA; several model compounds of zinc, (Table 1), also show activity for hydration of carbon dioxide and the reverse dehydration reaction. Again the zinc atom is the active catalytic centre of the reactions. Christianson and Fierke [13] in their review, have suggested that CA uses a proton shuttle of amino acids to achieve the fast deprotonation of the liganded water to the active liganded hydroxide form for the next hydration cycle, and that the process is also enhanced by a hydrophobic pocket which is an integral part of the CA metallo-protein. Nakata et. al. [6] have determined that the mechanistic step facilitated by the zinc is the same in both the enzyme and the mimicking complexes which lack the proton shuttle enhancement, therefore CA is a considerably faster catalyst than these smaller zinc (II) complexes. Further, diffraction studies by these authors have shown that the hydrophobic pocket of CA is similar but smaller in the zinc-L1S complex.



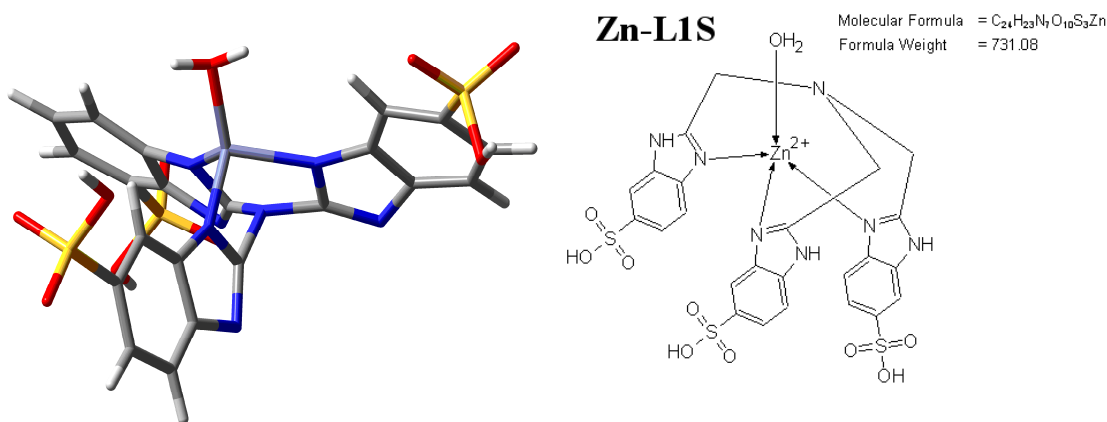
According to Vahrenkamp [12], the zinc metal ion is apparently ideal for catalytic purposes due to redox inertness, high kinetic lability and low thermodynamic stability. For an acid, the pKa is the pH at which the acid is 50% deprotonated. The pH of the chemical environment together with the pKa of the water/ hydroxide ligand attached to the zinc metal entity in the CA enzyme catalyst (or the metal complex catalyst) is the determinant of the form of the catalyst and hence the direction of the catalysis. Since the liganded water in CA has its pKa around 6.8, Kimura [15], the predominant form of CA above pH 6.8 will be the $\text{L}_3\text{Zn-OH}^-$ form. This OH^- form catalyses the hydration of carbon dioxide to bicarbonate ion, while below pH 6.8 the $\text{L}_3\text{Zn-OH}_2$ is the predominant form which catalyses the reverse reaction, the dehydration of the bicarbonate ion. Zinc (II) has a high affinity for bicarbonate ion as a monodentate ligand, and Koike and Kimura [8] postulate that if the zinc were more acidic, the bicarbonate may become deprotonated to carbonate ion and act as a bidentate ligand. The pKa of unbound water is around 15.5 so as discussed by Vahrenkamp [12], the zinc metal has reduced the pKa of the bound water by around 7-8 pKa units in CA (and also in the mimetic zinc complexes) making hydroxide available to react with CO_2 at near neutral pH.

2.3 Inorganic Zinc Complexes that mimic Carbonic Anhydrase

We have identified a class of inorganic metal complexes structurally resembling the active site of CA that mimic the enzyme. The catalytic process in both CA and the biomimetic

metal complexes proceeds by the same mechanism as previously described. These inorganic catalysts are stable at high temperatures, operate over a wide pH range, and show fast rates of catalysis that are comparable with CA on a weight basis, and promise affordable technology that will allow CCS retrofitting to existing power stations - (Figure 2).

Figure 2: Zinc-L1 tripod: Zinc-tris-(2-benzimidazolmethyl)-amine; and zinc-L1S tripod: (Zn-Nitrilo-tris(2-benzimidazol) methyl-6-sulfonic acid)



A number of zinc(II) complexes and several examples of complexes of divalent cobalt, copper and nickel and manganese ions have been prepared as models for carbonic anhydrase II, Ge et.al. [9], Koike and Kimura [8], Nakata et.al.[6], Zhang et.al. [10, 11], Vahrenkamp [12], Christian and Cox [19].

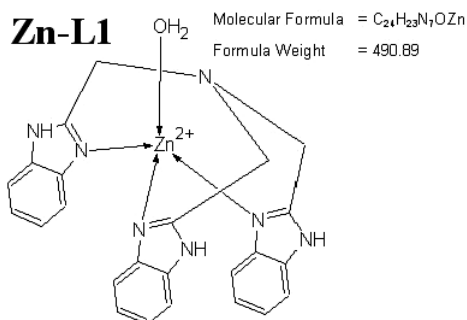
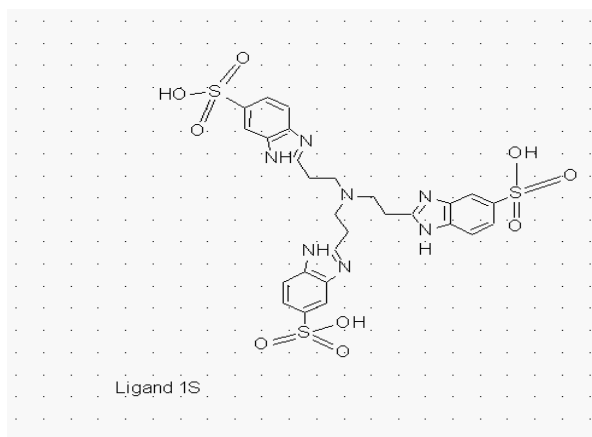


Figure 3. Ligand 1S: Nitrilo-tris(2-benzimidazolmethyl-6-sulfonic acid)



Nakata et.al. [6] and Koike and Kimura [8] have published studies of the water-soluble macro cyclic zinc(II) complex, the Tripod Zn-L1S – Zn-Nitrilo-tris(2-benzimidazolmethyl-6-sulfonic acid), see Figure 2; in addition, a sparingly water soluble tripod without sulfonate groups – Zn-L1, Zn-Tris-(2-benzimidazolmethyl)-amine. Both of these complexes mimic the catalytic effect of carbonic anhydrase and have high activity for carbon dioxide absorption. Zinc (II) complexed with ligand L1S (figure 3), was able to catalyse the capture of CO₂ at a rate extrapolated almost to within an order of

magnitude of that of carbonic anhydrase. A number of other simple zinc complexes prepared by researchers previously, modelled on carbonic anhydrase, have been shown to activate the bound ligand water molecule for nucleophilic attack towards CO₂.

2.4. In this initial study we report the preparation, characterization and stability testing using thermogravimetry, of the zinc tripodal complexes: zinc-L1 - zinc-tris(2-benzimidazolyl-methyl)-amine and zinc-L1S - zinc-nitrilo- tris(2-benz-imidazolyl-methyl-6-sulfonic acid). Further studies are in progress to immobilize the complexes onto polymer surfaces and within polymer membranes or gels, to form heterogeneous catalysts with improved stability and longevity in industrial plant operations. Water is the solvent for CO₂ capture, using CA mimetic complexes as catalysts. The aim of this research is to develop processes for CO₂ capture that have reduced energy requirements, and are less susceptible to degradation as experienced with the amine absorbents. Several authors, - Trachtenberg and Bao [4], Bond et.al. [14], Rochelle [2], Rochelle et. al. [3], [16] have proposed the use of water with promoters as the solvent for CO₂ capture. The enzyme carbonic anhydrase, (CA), is a protein - one of the fastest biological catalysts known - that has been studied because of its fast hydration and dehydration of CO₂ in water. Both Trachtenberg and Bao [4], and Bond et. al. [14] have proposed the use of carbonic anhydrase as the catalyst for an energy efficient capture procedure; however a carbonic anhydrase catalyst system is subject to the limiting factors associated with all proteins (temperatures below 60° - 80° C are required, there is a considerable cost of production by over-expression, a limited pH stability range, and solubility versus ionic strength etc. being some of the disadvantages).

3. Experimental:

3.1 Ligands.

3.1.1 Tripod L1 Tris-(2-benzimidazolylmethyl)-amine was synthesized from o-phenylene diamine and nitrilotriacetic acid by the method described by Thompson et.al. [17]. Nitrilotriacetic acid (15.3 g, 0.08 mol) and o-phenylene diamine (27 g, 0.25 mol) were finely ground and heated together at 200 °C in an oven. The reaction mixture was cooled, crushed then dissolved in methanol, decolorized by boiling with charcoal, filtered hot and then the volume was reduced with the product crystallizing out in 50% yield.

3.1.2 Tripod L1S, Nitrilo-tris(2-benzimidazolylmethyl-6-sulfonic acid), was prepared by the method as described by Nakata et.al. [6].

3.2 Complexes.

3.2.1 Bovine Carbonic anhydrase from erythrocytes was purchased from the Sigma Company and used without further purification.

3.2.2 Zinc-L1 tripod: Zinc-tris-(2-benzimidazolylmethyl)-amine was prepared by the method of Thompson et.al. [17]. Stoichiometric amounts of Zn(ClO₄).6H₂O and L1 were dissolved separately in hot ethanol and the hot solutions mixed with stirring. Reduction of volume and cooling produced a solid product. Yield 35%.

3.2.3 Zinc-L1S tripod: The zinc-L1S tripod, (Zn-Nitrilo-tris(2-benzimidazolyl) methyl-6-sulfonic acid) was prepared by the method of Nakata et. al. [6]. An aqueous solution of L1S

and $\text{Zn}(\text{ClO}_4)_6 \cdot 6\text{H}_2\text{O}$ was adjusted to pH 7 with NaOH solution. Addition of ethanol produced a blue-white solid compound. Yield 25%.

3.3 Kinetic measurements were performed by following the loss in weight using a loosely stoppered conical flask on an analytical balance with 2-5 mL of 1M sodium bicarbonate solutions added to buffer and enzyme. Blank measurements were also performed to take account of evaporative losses and spontaneous dehydration of the bicarbonate solutions at the acidic pH 6. A typical experiment was performed as follows: Into a conical flask with a stopper was measured 25 mL of a 0.1M acetate buffer pH 6, one drop of Dow Corning antifoam, and 0.5 mL of catalyst at a concentration of 3-10 mg/mL. In a separate flask was mixed 2.5 mL of 1.0M NaHCO_3 solution and 42 mL of water. At zero time the solutions were mixed and the weight recorded on an analytical balance accurate to 0.0005 g. The weight was recorded every 30 seconds to obtain an estimate of the initial rate of reaction (loss of CO_2).

3.4 Thermogravimetric Studies on Zn-L1 and Zn-L1S were made over a temperature range of 20 – 800 °C. (See Figure 4 below).

4. Results and Discussion.

The second order rate constants $k_{\text{cat}}^{\text{h}}(\text{M}^{-1}\text{s}^{-1})$ and $k_{\text{cat}}^{\text{d}}(\text{M}^{-1}\text{s}^{-1})$ for the hydration or dehydration reactions respectively as reported in the literature and / or measured in this study are summarized in Table 1.

Table 1. The kinetic data for carbonic anhydrase and some model metal (zinc) complexes that show reversible hydration of CO_2 to bicarbonate ion and the dehydration of bicarbonate back to CO_2 .

Complex/ Enzyme	pKa of H_2O ligand	Temperature °C	pH	$k_{\text{cat}}^{\text{h}}$ $\text{M}^{-1}\text{s}^{-1}$	$k_{\text{cat}}^{\text{d}}$ $\text{M}^{-1}\text{s}^{-1}$	Reference
HCAII	ca. 7	25	7	1,100,000	220,000	[11]
Co(II)HCA	ca. 6.6	25	7	305,000	-	[11]
Bovine CA	ca. 7	25	6		35,000	This study
Bovine CA	ca. 7	55	6		95,000	This study
Cu-cyclen- H_2O	8.1	55	6		121	This study
Tripod ZnL1S	8.3	15	9.5	3,300		[6]
Tripod ZnL1S	8.3	25	9.5	10,000* (*extrapolated)		[6]
Tripod ZnL1S	8.3	25	6		363	This study
Tripod ZnL1S	ca 8.3	55	6		797	This study
Tripod ZnL1	ca 8.3	25	6		235	This study
Tripod ZnL1	ca 8.3	55	6		684	This study

The catalysts studied in this work, (Table 1), carbonic anhydrase (CA) which is a zinc(II) metallo-enzyme, model zinc(II) tripodal complexes with L1 and L1S, are suggested as suitable catalysts to be used in the CO₂ absorption/desorption process, using water as solvent in place of high concentrations of amine solvents. The zinc (II) complexes mimic the activity and the mechanism as shown by CA for the CO₂/HCO₃⁻ reaction cycle. In this study, the second order rate constants k_{cat}^d , for the dehydration reaction at 25 °C and 55 °C have been calculated for comparison with the fast CA enzyme.

The basis of the catalysis is the lowering of the pKa of the liganded water molecule attached to the zinc metal from the pKa of around 15.5 for the free water molecule, to around pKa = 7 in CA and in the range of pKa = 6 – 9 in the mimetic complexes. Catalysis of the forward reaction (hydration of CO₂ to HCO₃⁻) proceeds at the high end of the pH range (around pH 9) with the concurrent release of a proton, when the active catalyst is in the [L-Zn-OH] form. The reverse reaction (dehydration of HCO₃⁻) proceeds at the lower pH (around pH 6), with the active form of the catalyst as [L-Zn-OH₂].

Simsek and Bond [14], and Bond et. al. [21], have investigated the use of the enzyme CA to catalyze CO₂ hydration, (the absorption step), and proposed that the subsequent sequestration should be done by precipitation using sources of cations, (particularly calcium ions); the sources proposed included seawater, waste brines from desalination operations, or from saline aquifers. In this proposal, Simsek and Bond [14] note that the amounts of solids produced and the amounts of brines required would be very large – a 300 MW plant would produce around 290 tonne of CO₂ per hour and require around 750,000 tonne of seawater per hour and produce 666 tonne of calcium carbonate per hour. Trachtenberg and Bao [4] suggested the use of CA in a contained liquid membrane (CLM) utilizing CA as catalyst with a pressure differential between the feed (hydration) side and the sweep (dehydration/stripping) side of the membrane. This approach is a novel means of reducing the stripping penalty, and is fast enough to be feasible for further development. (The pressure differential aspect may also enhance a catalytic process of the type that is proposed in this study).

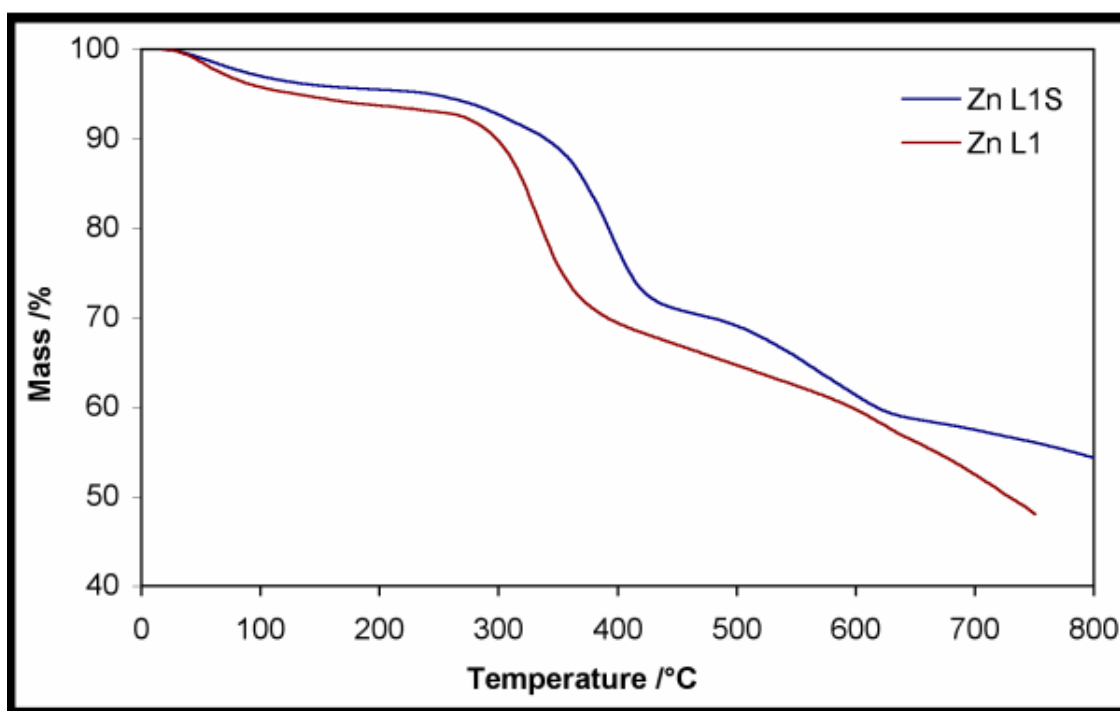
Both of these proposed methodologies could be used as an alternative to MEA absorption and stripping, particularly if the enzyme could be made more robust by stabilization. Simsek and Bond [18] have suggested the CA enzyme may be immobilized in chitosan/alginate beads, and Bao and Trachtenberg [4] have reported a lifetime of up to six months without immobilization would apply to CA in the contained liquid membrane. In practical terms, Bao and Trachtenberg [4] have defined CA as a family of enzymes, each with a different temperature range, and catalysis of the reaction rate is only modestly temperature sensitive, and have suggested that for a thermophilic form of the enzyme CA the upper temperature limit is around 85 °C.

The approach suggested in this study is the use of bulk liquid and catalyst to capture CO₂ from flue gases (at up to 15% of CO₂) as bicarbonate at high pH, around 9, and then strip the CO₂ using the same catalyst with lowered pH around 6. The zinc mimetic catalyst is to be used for both the forward and the back reaction, as it is switched from the ligated (OH⁻/dehydrogenated) active hydration catalytic form to the water ligated (dehydration active form) by passive and active (perhaps electrochemical) control of the pH. The optimum pH for the absorption (hydration) process is at least one pH unit above the pKa of the liganded H₂O/OH⁻ in the catalyst where 90% of the catalyst is in the deprotonated (OH⁻) active form. For the stripping (dehydration reaction) the pH needs to be at least one pH unit below the pKa of the water ligand in the protonated (H₂O) form. Lindskog and A. Liljas [5] give the

pKa values that apply; for CA the pKa of the liganded water is around 6.9 and for the zinc complexes the pKa's have values between 7 – 8.5, so at pH 9 or above the hydration catalyst function of CA is favoured, while at pH 6 or below the dehydration function of the CA catalyst is the active reaction.

The dehydration (stripping) reaction is the energy intensive step so the initial studies have been made of the rates of dehydration, but all the catalysts considered have been shown to catalyze reversibly. It should be noted however that there is an apparent general trend for the dehydration rate to be one or two orders of magnitude smaller than for the hydration reaction. This is apparent from Table 1; for CAII, for the hydration k_{cat}^h is $10^6 \text{ M}^{-1}\text{s}^{-1}$ – with the corresponding dehydration k_{cat}^d around $10^5 \text{ M}^{-1}\text{s}^{-1}$, Zhang and van Eldik [11,]. For the tripod Zn-L1S, k_{cat}^h is around $10000 \text{ M}^{-1}\text{s}^{-1}$ as extrapolated (to 25 °C) by Nakata et. al., and k_{cat}^d (for dehydration) values of 363/ 797 $\text{M}^{-1}\text{s}^{-1}$ have been measured at 25 °C / 55 °C in this study (Table 1).

Figure 4.
Thermogravimetric Studies: Zn-L1 and Zn-L1S over a temperature range of 20 – 800 °C.



The mass loss from about 50-200 °C is due to loss of water/solvent adsorbed on the complex or included as water of hydration. Degradation of the complex begins at 270 °C with mass loss of about 22 %·w/w, and Zn L1S is more stable by about 50 °C for this step. A second degradation step occurs to 600 °C with a further 10 %·w/w mass loss. The mass then declines to 50-55 %·w/w at 800 °C. The final product is expected to be zinc oxide or zinc carbonate.

The zinc tripod complexes examined are more stable than CA at the increased temperatures, and increased rates of catalysis at higher temperatures. The utilization of waste heat alone from power generation may be sufficient to provide a high enough temperature for fast catalysis in the stripping step.

The pH in the experiments of this study have been controlled by buffer solutions and/ or adjusted by acid or base additions. The hydration reaction releases hydrogen ions automatically as the CO₂ is absorbed, and the dehydration reaction releases hydroxide ions in the reverse reaction. Thus the pH is automatically adjusted in the correct direction ready for a new catalytic absorption or desorption cycle; to maintain optimum velocity in scaled up industrial systems however the pH may need to be further adjusted perhaps electrochemically, to ensure that the catalyst is optimally converted to the form required for the forward or reverse reaction required. The additional electrical power for electrochemical control could also allow production of hydrogen gas which could be offset against the additional energy requirement. Aines et.al. [22] have proposed that ion pumping of bicarbonate, that is reverse osmosis, could be used to effect an increase in the concentration of bicarbonate, and this process alone could be used to capture and then strip CO₂. If ion pumping was included, the catalytic effect of the mimetic zinc complexes would assist in increasing the bicarbonate concentration at the higher pH.

A recent report from Mani et. al. [23], reported the absorption of CO₂ into potassium carbonate solutions at temperatures in the range of 10 – 60 °C followed by addition of zinc(II) salts resulting in a partial stripping of CO₂ (accompanied by the production of basic zinc carbonate precipitates). This process is of interest because of the fast rates of absorption and desorption of CO₂ - again associated with zinc at low (ambient) temperatures - although it is not the reversible capture/stripping catalysis using the zinc complexes (such as Zn-L1S) that has been proposed in this study.

5. Conclusion

These initial studies of several zinc complexes which mimic the catalytic function of carbonic anhydrase, demonstrate that a CO₂ capture system in water may be feasible to reduce the energy penalty and other disadvantages inherent in the current technology using amine solvents. The initial rates of dehydration that can be achieved by using the zinc catalysts are less than those of the fast CA enzyme, but can be achieved at moderate temperatures and around neutral pH, at a rate that is comparable with that of amine systems. Additional research is to be undertaken to examine further complexes and to develop the laboratory studies for an improved process and up-scaling. Future directions of investigations: the zinc catalysts may be able to be immobilized in polymeric matrices in a similar way to the immobilization as reported by Bond et al [21], or alternatively finely divided heterogeneous catalysts instead of the homogeneous systems discussed here may be viable.

6. References.

1. R.M. Davidson (ed.), IEA Greenhouse Gas R & D Programme (IEA GHG), “Post Combustion Carbon Capture from Coal Fired Plants – Solvent Scrubbing”, 2007/15 July 2007.
2. G. Rochelle, Research needs for CO₂ capture by aqueous absorption/stripping, International Test Network for CO₂ Capture: report on a workshop, Gaithersburg, MD, USA, 11-12 Oct 2000, Report PH3/33, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 4 p. (Dec 2000).
3. G. Rochelle, S. Bishnoi, S. Chi, H. Dang and J. Santos, Research needs for CO₂ capture from flue gas by aqueous absorption/stripping. DE-AF23-99FT01029, Pittsburgh, PA, USA, Federal Energy Centre 154pp. (17 Jan 2001).
4. M.C. Trachtenberg and L. Bao, Facilitated transport of CO₂ across a liquid membrane: Comparing enzyme, amine and alkaline, *Journal of Membrane Science* 280 (2006) 330 -334.
5. S. Lindskog and A. Liljas, Carbonic anhydrase and the role of orientation in catalysis, *Current Opinion in Structural Biology* 3 (1993), 915-920.

6. K. Nakata, N. Shimouura, N. Shiina, M. Izumi, K. Ichikawa, and M. Shiro, Kinetic study of catalytic CO₂ hydration by water-soluble model compound of carbonic anhydrase and anion inhibition effect on CO₂ hydration. *Journal of Inorganic Biochemistry* 89 (2002) 255-266.
7. M. Bräuer, J.L. Pérez-Lustres, J. Weston and E. Anders, Quantitative Reactivity Model of Carbon Dioxide by Biomimetic Zinc Complexes, *Inorg. Chem.* 41 (2002) 1454-1463.
8. T. Koike and E. Kimura, Carbonic Anhydrase Models in *Encyclopedia of Supramolecular Chemistry*, Pub. Dekker C.H.I.P.S., USA., J.L. Atwood and J.W. Steed (eds.) (2004) 178-182.
9. O. Ge, Y. Guo, H. Lin and S. Zhu, *Internat. Journal of Chemical Kinetics* 36 (3) (2004) 197-203.
10. X. Zhang, R. van Eldik, T. Koike and E. Kimura, *Inorg.Chem.* 32 (1993) 5749-5755.
11. X. Zhang and R. van Eldik, *Inorg.Chem.* 34 (1995) 5606-5614.
12. H. Vahrenkamp, *Acc.Chem. Res.* 32 (1999) 598-596.
13. D.W. Christianson and C.A. Fierke, *Acc. Chem. Res.* 29, (1996) 331-339.
14. G.M. Bond, N. Liu, A. Abel, B. J. McPherson, and J. Stringer, Biomimetic Sequestration of CO₂ in Produced Waters and other Brines, *Fuel Processing Technology* 86 (14) (2005) 1615-1625.
15. E. Kimura, Macrocyclic Polyamine Zinc(II) Complexes as Advanced Models for Zinc (II) Enzymes, *Progress in Inorganic Chemistry*, 41 (1994) 443-491.
16. G.T. Rochelle, G.S. Goff, J.T. Cukllinane, and S. Freguia, (2002) Research results for CO₂ capture by aqueous absorption/stripping. Paper presented to: Laurance Reid gas conditioning conference, Oklahoma City OK, USA 25-27 Feb 2002. 21p.
17. L.K. Thompson, S. Ramaswamy, and E. A. Seymour, *Can. J. Chem.* 55 (1977) 878-888.
18. F.A. Simsek, and G.M. Bond, Immobilisation of Carbonic Anhydrase for Biomimetic CO₂ Sequestration. *World Resources Review Vol 13 (1)* (2001) 74 – 90.
19. D.W. Christianson, and J.D. Cox, Catalysis by Metal Activated Hydroxide in Zinc and Manganese Metalloenzymes, *Annu. Rev. Biochem.* 68 (1999) 33-57.
20. M.C. Trachtenberg, L. Bao, S.L. Goldman, D.A. Smith and X. Wu, Flue Gas capture by a Green Liquid Membrane , in *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies* (Eds. M. Wilson, T. Morris, J. Gale, and K. Thambimuthu) (2004) 1751-1754.
21. G.M. Bond, N. Liu, A. Abel, B.J. McPherson, and J. Stringer, in *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies* (Eds. M Wilson, T. Morris, J. Gale, and K Thambimuthu) (2004) 2359-2362.
22. R. Aines, W. Bourcier, M. Johnson, Separation of carbon dioxide from flue gases using ion pumping, in *Proceedings from GHGT8 – 8th International Conference on Greenhouse Gas Control Technologies Trondheim Norway* (2006).
23. F. Mani, M. Peruzzini, P. Stoppioni, Combined Process of CO₂ Capture by Potassium Carbonate and Production of Basic Zinc(II) Carbonates: CO₂ Release from Bicarbonate Solutions at Room Temperature and Pressure, *Energy and fuels* 22 (2008), 1714 –1719.
24. G. Parkin, *The Bioinorganic Chemistry of Zinc: Synthetic Analogues of Zinc Enzymes that Feature Tripod Ligands*, *Chem. Commun.* (2000) 1971-1985.