

# 12th Greenhouse Gas Control Technologies Conference

## Advances in carbon capture and storage research

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### Introduction

The International Conference on Greenhouse Gas Control Technology is a biennial meeting now in its twelfth incarnation and is a highlight for carbon dioxide sequestration researchers around the globe. The conference was held between 4th–9th October 2014 at the Austin Convention Center, Texas, USA. Over four days the conference encompassed all aspects of the carbon capture value chain. Approximately 30% of the sessions focused on CO<sub>2</sub> capture technology and 30% on CO<sub>2</sub> storage, with the remaining sessions covering case studies, CO<sub>2</sub> utilisation, commercial issues, CO<sub>2</sub> transport, policy and social science. The conference was attended by 1166 delegates comprising of an almost even distribution of students, academics, industrial representatives, research institutes and government agencies. There was a high level of participation with 874 contributions presented throughout the seven parallel sessions and well-planned poster sessions. Furthermore a small selection of exhibitors complimented the technical programme providing details of commercial ventures and institutional programmes.

This selective review highlights interesting advances presented at the conference. For a more comprehensive overview of the area the reader is directed to a number of encompassing reviews on the topic (1–3).

### Plenary Speakers

Julio Friedmann (US Government, USA)	From Vision to Inheritance – The Technical Foundation for the Next Decade of CCS Projects
David G. Victor (University of California, San Diego, USA)	Global Climate Policy and the Future of CCS
Juho Lipponen (International Energy Agency, France)	Gas-Fired Power Generation With CCS – A Competitive Option
Michael J. Monea (SaskPower, Canada)	Boundary Dam – The Future is Here
Suk Yee Lam (Department for Energy and Climate Change, UK)	The UK’s CCS Programme: Policy and Delivery
Gary T. Rochelle (The University of Texas at Austin, USA)	From Lubbock TX to Thompsons, TX: Amine Scrubbing for Commercial CO <sub>2</sub> Capture From Power Plants
Xu Shishen (Huaneng Clean Energy Research Institute, China)	Greengen and CO <sub>2</sub> Capture Projects in China
Emma ter Mors (Leiden University, Netherlands)	The Value of Social Science Research for CCS Deployment
Greg Schnacke (Denbury Resources Inc, USA)	CO <sub>2</sub> EOR: U.S. Opportunities and Challenges

## Status of Carbon Capture and Storage

Carbon capture and storage is at a pivotal stage. SaskPower's Boundary Dam power station has started to operate the first large scale carbon capture unit on a commercial power plant. The next two years will see the commissioning of two larger power generation projects: Kemper County in 2016 and Petra Nova, Texas in 2016. There are over twenty large scale projects in operation or under construction across the globe (4). These developments are built upon the lessons of hundreds of pilot plants around the globe and thousands of research hours. In the past ten years the energy consumption of amine scrubbing has been reduced from 300–350 kWh per tonne CO<sub>2</sub> to 200–250 kWh per tonne CO<sub>2</sub>. Although promising, this approach to capture is limited by the large energies required to regenerate the solvent, and by long term solvent durability. Cost reduction is the motivation of much of the ongoing research with advances that increase the rate of adsorption or reduce the regeneration energy highly sought after. It was a core theme of the conference that carbon capture and storage has the potential to mitigate emissions from power generation and industrial processes for which there are no substitutes.

## New Capture Technologies

Owing to differences in their adsorption mechanism, tertiary amines are promising candidates for CO<sub>2</sub> adsorption with the potential to offer higher amine efficiency and lower desorption requirements compared to simple primary and secondary amines. The main limitation of tertiary amines in liquid scrubber systems is the sluggish formation of carbonic acid. Cameron Lippert (University of Kentucky, USA) took inspiration from the enzyme carbonic anhydrase which readily catalyses the hydration of CO<sub>2</sub> in the majority of plants and animals. The mechanism of carbonic anhydrase is well understood, beginning with the deprotonation of the ligated water coordinated to the zinc centre (Figure 1) (5). This is followed by the nucleophilic attack of the enzyme on CO<sub>2</sub>. Finally ligand exchange occurs with the Zn bound HCO<sub>3</sub><sup>-</sup> replaced by water regenerating the starting species. Previous studies have shown that this enzyme denatures under conditions akin to industrial capture units (6, 7). Much prior research has focused on mimics, however these are retarded by the coordination of anions blocking the active site. To circumvent this issue Lippert investigated ligands with

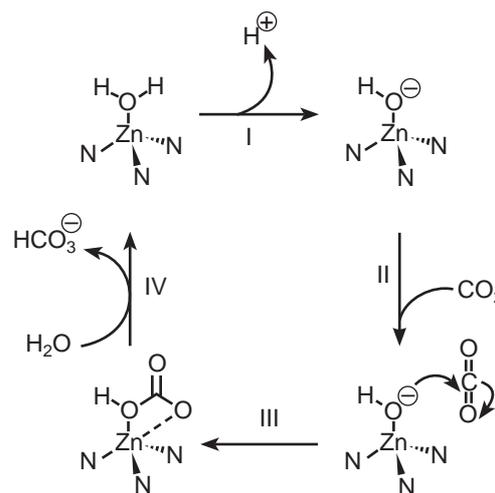


Fig. 1. Carbonic anhydrase cycle

strongly electron donating groups thereby facilitating bicarbonate dissociation and retarding inhibition. The work used Zn salen (N,N'-bis(salicylidene) ethylenediamine) hexafluorophosphate complexes as catalysts for liquid amine systems (Figure 2). The incorporation of such catalysts led to a significant increase in the rates of CO<sub>2</sub> hydration. The catalytic cycle is thought to mimic that of the enzyme. If scalable the addition of these catalysts could vastly improve the CO<sub>2</sub> adsorption kinetics leading to more efficient adsorption systems.

Carbonic anhydrase also provided inspiration for Richard Blom *et al.* (SINTEF, Norway) who built upon the work by Murthy *et al.* presenting the Zn complex [Zn{N[CH<sub>2</sub>(2-py)]<sub>3</sub>}(μ-OH)]<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (8). As well as catalysing the hydration of CO<sub>2</sub> such complexes can directly react with CO<sub>2</sub> to form a metastable complex. The complex was found to absorb CO<sub>2</sub> in the presence of water forming a trimeric Zn species bridged by a carbonate species (Figure 3) (9). The absorption could be completed at 40°C with purely thermal regeneration possible at 80°C; a temperature at which liquid amines show very little desorption. Such low desorption

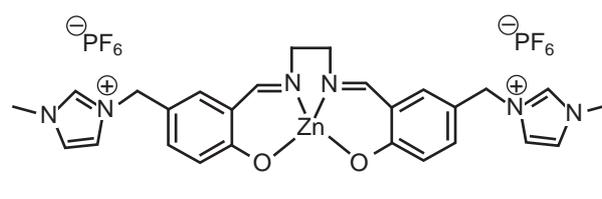


Fig. 2. Carbonic anhydrase mimic

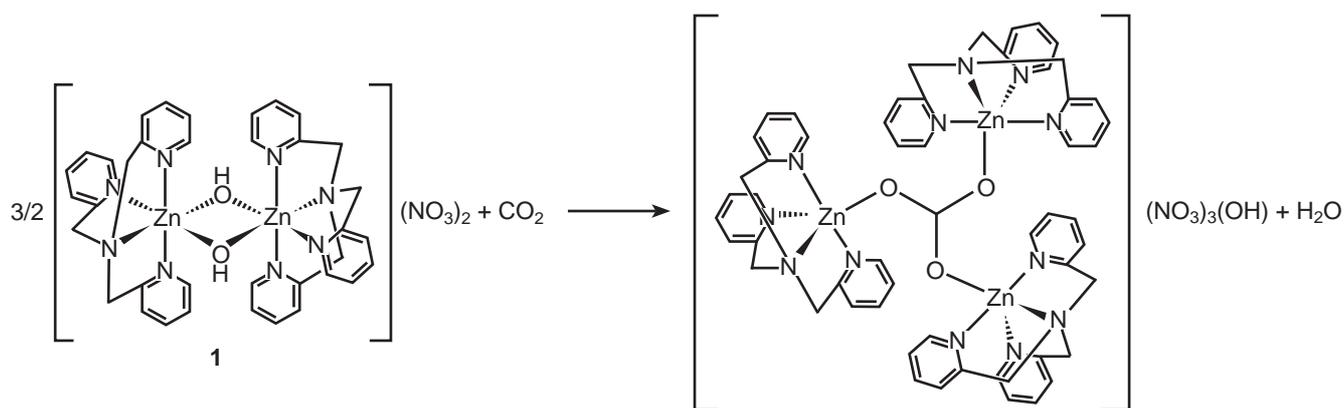


Fig. 3. Trimeric zinc complex, adapted from (9)

temperatures are promising, offering significant reductions in regeneration requirements. Furthermore this complex was found to readily remove  $\text{CO}_2$  from air at low temperatures opening up a series of niche applications for this technology. The behaviour of the complex is also being investigated under different solvents to avoid the additional heating requirements brought about by the high heat capacity of water and to overcome issues relating to solubility.

There were a number of talks highlighting new  $\text{CO}_2$  capture technologies for post combustion capture. Joshua Stolaroff (Lawrence Livermore National Laboratory, USA) gave a talk on microencapsulated sorbents. These double emulsion materials feature an active liquid phase constrained within a porous polymer shell. They are produced using a microfluidic device in a linear process at a rate of 50 Hz (Figure 4). In such a process mixtures of monoethanolamine (MEA) and water are passed through the inner capillary with a silicone polymer pumped through the middle tube

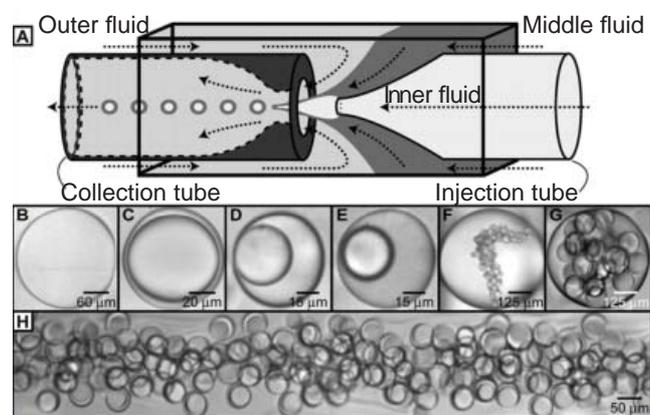


Fig. 4. Microfluidic device (Reproduced with permission from (10))

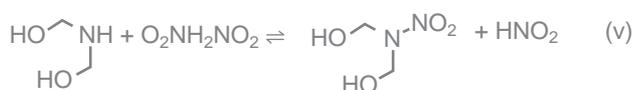
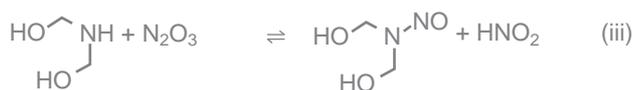
to yield a coaxial flow. A poly(vinyl alcohol) (PVA) stabiliser is pumped in a counter current manner to achieve hydrodynamic focusing with the three streams passing through a single exit where they form spheres. By using a silicone polymer and additives the outer PVA and silicone shells can be cured under ultraviolet (UV) light to yield aqueous monoethanolamine solutions encapsulated in a porous polymer shell.

Microfluidic devices enable monodisperse spheres to be easily produced with particle sizes controlled by the dimensions of the device. The team began encapsulating simple amines such as aqueous solutions of MEA and piperazine which yielded rapid absorption of  $\text{CO}_2$ . Their recent work in this area highlighted that the rate determining step was not mass transit through the polymer shell with encapsulated absorbents having a rate twelve times that of their liquid counterparts (11). They found that the working fluid was stable over numerous absorption-desorption cycles. Furthermore the capsules have soft gelatinous physical characteristics negating the issue of attrition prevalent in solid adsorbents and catalysts. Encapsulated sodium carbonate slurries mitigate the issue of precipitates and offer significantly better rates of absorption. Currently such double emulsions are made in a serial fashion and Stolaroff and his team are working to improve the production capacity of such systems by combining parallel arrays of the microfluidic devices.

## Amine Degradation

Liquid amine based  $\text{CO}_2$  absorption is the most developed capture technology and the most likely candidate for initial full scale deployment. A typical liquid amine absorber includes a water wash at the

end of the absorption process to remove the amine and other water soluble products from the exhaust gases. With liquid amine columns appearing to be the first generation of carbon capture technology the issue of amine slip and degradation products needs to be thoroughly investigated. There is much discussion surrounding the potential release of nitrosamines and nitroamines formed by the reaction of nitrogen oxides and amines (12–14). Various nitrosamine structures are believed to be carcinogenic and could present a significantly increased hazard compared to the parent amine. Nitrosamines have been detected in laboratory experiments, photochemical experiments, numerous pilot plant studies and are formed by the reaction between an amine and a suitable nitrosating agent (15, 16). In the flue gas, nitrogen oxide can react with nitrogen dioxide forming dinitrogen trioxide (Equation (i)). Nitrogen dioxide can also dimerise to form dinitrogen tetraoxide ( $N_2O_4$ ) (Equation (ii)). These species can then react with various amines to yield nitrosamines (Equations (iii) and (iv)) or nitroamines (Equation (v)) depending on the reacting isomer. Furthermore nitrate can be generated in solution by the decomposition of either  $N_2O_3$  or  $N_2O_4$  which can directly react with amines.



These species and their tautomers can react with amines to form nitrosamines or nitroamines either in the absorber column or desorber and recirculating wash water. There is potential for these pollutants to volatilise and contaminate local air or water resources. Studies suggest that  $NO_x$  concentrations down to around 25 ppm lead to the formation of nitrosamines (17). For reference a typical flue gas from a coal fired power station contains 50–100 ppm  $NO_x$ . After flue gas desulfurisation and de $NO_x$  this drops to 5 ppm. Traditionally the performance of de $NO_x$  systems is

driven by changing legislation and as such systems to reduce these emissions further are still under development.

The extent of solvent loss, nitrosamine formation and potential release is highly dependent on the flue gas and exact nature of the process used. A number of solutions were presented at the conference. Nathan Fine (The University of Texas at Austin) investigated the rates of thermal decomposition of MEA and piperazine nitrosamines. For fresh solutions of MEA they found minimal conversion to nitrosamine. In cases where 1% of the MEA had degraded to N-(2-hydroxyethyl)glycine a build-up of nitroso-2-hydroxyglycine was apparent. MEA is regenerated at 120°C to preserve the structure of the amine and at this temperature the nitrosamines were not sufficiently thermally degraded. It was found that 15% of the  $NO_2$  absorbed by piperazine was converted to nitropiperazine. Piperazine systems could be regenerated at 150°C leading to appreciable thermal decomposition of the nitropiperazine.

A forward thinking presentation by Jesse Thompson (University of Kentucky) explored the possibility of nitrosamine destruction as an end of pipe treatment. The benefit of nitrosamine reduction is twofold; mitigating the release of nitrosamine and regenerating degraded solvent. Using nitrosopyrrolidine as a probe molecule and a circulating up-flow reactor Thompson *et al.* demonstrated that a commercial palladium catalyst cleanly regenerated pyrrolidine at typical desorption temperatures. Given the low fraction of nitrosamine in the solution, selectivity between the nitrosamine and the parent amine is crucial. Silica based Pd, Ni and Fe catalysts were investigated but found to have limited stability over successive cycling. This limited stability was attributed to the highly alkaline environment slowly degrading the silica surface leading to metal leaching. In a move to combat this, 2x2 manganese octahedral molecular sieves (OMS-2) (Figure 5) co-impregnated with Fe, Pd and Ni were prepared.

In such structures the guest metal ion resides in the centre of the cage with catalytic activity believed to be maintained by electron transfer from the vacant states of the OMS-2 structure. The Pd OMS-2 showed enhanced activity compared to Ni and Fe–OMS-2 however nitrosamine destruction was limited to 60%. Although possessing a lower activity than Pd, iron(II) oxide (FeO) was also investigated as a catalyst owing to its ready availability in fly ash. Fly ash containing 5.37 wt% FeO yielded fair nitrosamine destruction

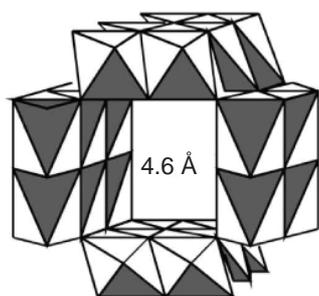


Fig. 5. Structure of OMS-2 (Reprinted with permission from (18). Copyright (2012) American Chemical Society)

behaviour under hydrogenation conditions. Successive cycling of the fly ash catalyst exhibited a decrease in performance attributed to active phase leaching into the amine solution. Given the conditions, flow rates and competitor species this is a challenging hydrogenation however this work shows that hydrogenation has potential to limit nitrosamine formation and regenerate the solvent. Thompson and his team demonstrated that supported Pd, Ni and Fe catalysts show promise for the hydrogenation of nitrosamines back into their parent amines in the solvent native to the process (Figure 6).

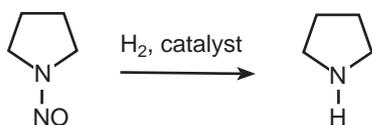


Fig. 6. The nitrosamine reduction concept put forward by Thompson *et al.*

## Conclusion

This review presents only a fragment of the presentations and posters disclosed. The popularity of the conference, combined with the large number of key stakeholders present highlights the importance of carbon capture and storage. A significant number of the talks and posters discussed pilot plant experiences of both capture and storage technologies. Carbon capture and storage is at a crucial stage in development with first generation systems becoming a commercial reality. The large variety of novel concepts and technologies indicate the potential for further advances in second and third generation systems. These technologies look to address the core issues of regeneration requirements, material stability and the possible behaviour of

nitrosamines. The closing session presented the clear message that as a technology carbon capture and storage is ready, with the greatest challenge being policy support to incentivise deployment.

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## The Reviewer



Christopher Starkie graduated with a MSci in Chemistry from the University of Nottingham, UK. He is currently undertaking postgraduate study at the Engineering Doctorate Centre in Efficient Fossil Energy Technologies under the supervision of Professor Ed Lester, Professor Sean Rigby and Professor Trevor Drage. Working in collaboration with Johnson Matthey he is investigating novel functionalised materials for CO<sub>2</sub> separation. His research interests include adsorbents, surface functionalisation of porous materials and novel material synthesis.

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