

Post-Combustion CO₂ Capture Workshop

11 - 13 July 2010
Tufts European Center
Talloires, France

PROCEEDINGS

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Sponsored by
| MIT Carbon Sequestration Initiative |
| Global CCS Institute |
| Clean Air Task Force |
| Asia Clean Energy Innovation Initiative |



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11 - 13 July 2010

Talloires, France

OVERALL MEETING SUMMARY

On July 11-13, 2010, approximately 30 scientists and engineers from academia, industry, and government agencies gathered at Tufts University's European Center in Talloires, France to assess advanced technologies for Post-Combustion Carbon Dioxide Capture. The organizers, Howard Herzog of MIT and Jerry Meldon of Tufts, arranged presentations by internationally recognized authorities on state-of-the-art and emerging technologies, and the challenges to be met prior to full-scale implementation. Other stakeholders in this very active field of scientific research and policy development were also invited to attend and participate.

To that end, the organizers invited three internationally renowned experts to organize and chair sessions on CO₂ capture via (1) absorption : Professor Hallvard Svendsen of the Norwegian University of Science and Technology (NTNU), (2) adsorption : Professor Abdelhamid Sayari of the University of Ottawa, and (3) membranes and ionic liquids: Professor Eric Favre of the University of Nancy. The chairs recommended as speakers investigators at the forefront of the respective research areas.

In addition to the above sessions, an opening session included presentations by David Luebke on the U.S. Department of Energy's research activities and Mark Hartney on the DOE's ARPA-E program, as well as a keynote address by Olav Bolland of NTNU on the "Outlook for Advanced Capture Technology." Two additional presentations were given by Professor Meldon on "Modeling of amine-based post-combustion CO₂ capture," and by Professor Alan Hatton of MIT on "Electrochemically mediated separations for CO₂ capture." The meeting ended with a wrap-up discussion chaired by Professor Meldon.

Nine papers based on the presentations will comprise a forthcoming special issue of Chemical Engineering Journal.

The meeting was sponsored by the MIT Carbon Sequestration Initiative, Global CCS Institute, Clean Air Task Force and Asia Clean Energy Innovation Initiative.

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OPENING SESSION

Howard Herzog, MIT

Howard J. Herzog is a senior research engineer in the MIT Energy Initiative. He received his undergraduate and graduate education in chemical engineering at MIT. He has industrial experience with Eastman Kodak (1972-1974), Stone & Webster (1975-1978), Aspen Technology (1981-1986), and Spectra Physics (1986-1988). Since 1989, he has been on the MIT research staff, where he works on sponsored research involving energy and the environment, with an emphasis on greenhouse gas mitigation technologies. He was a Coordinating Lead Author for the IPCC Special Report on Carbon Dioxide Capture and Storage (released September, 2005), a co-author on the MIT Future of Coal Study (released March 2007), and a US delegate to the Carbon Sequestration Leadership Forum's Technical Group (June 2003-September 2007).

David Luebke, US DOE

Dr. David Luebke is a member of the technical staff of the U.S. Department of Energy's National Energy Technology Laboratory (NETL) in Pittsburgh, PA. He joined NETL in 2002 and now serves as the Research Group Leader for the Advance Carbon Dioxide Capture Group which is responsible for conceiving and developing capture technologies. Dr. Luebke received his B.S. in Chemical Engineering at the University of Arkansas, Fayetteville in 1998. He did his graduate work in Chemical Engineering at the University of Pittsburgh, earning his Ph.D. in 2002. His research expertise is primarily in the field of membrane science.

Opportunities and Challenges for Post-Combustion Capture: U.S. D.O.E. Research Activities

The U.S. Energy Information Administration predicts that in 2030 80 percent of CO₂ emissions from coal-fired power generation will come from pulverized coal combustions plants in existence today. If emissions are to be mitigated through capture/sequestration in a timely fashion, capture techniques far more efficient than existing amine scrubber systems, which could raise the cost of energy services from these plants by as much as 80 percent, must be developed. The capture of CO₂ from dilute flue gas streams is challenging in its own right and becomes much more so when it must be integrated into plants with limited space and restricted water resources. To address these issues, NETL supports a research program including development of solvent, sorbent, and membrane capture technologies as well as process integration and efficiency improvement. The talk will describe major challenges in post-combustion capture and NETL's approach to overcoming those challenges through its research program.

| [Link to PDF of Presentation](#) |

Mark Hartney, US DOE

Dr. Mark Hartney joined ARPA-E in July, 2009 as one of the founding program directors. As a program director, he is responsible for selecting and managing technical projects, defining new research program opportunities, and facilitating activities in support of the ARPA-E missions of reducing greenhouse gas emissions, enhancing energy security, and improving energy efficiency.

Prior to joining ARPA-E, Mark served the past two years as the Chief Technical Officer for FlexTech, an industry-government partnership focused on research and development for flexible electronics including displays, photovoltaics and OLED lighting. While at FlexTech, he also founded and served as the managing director for the 3D@Home Consortium. Mark previously worked at Silicon Image, a semiconductor manufacturer in a variety of technical, marketing and business development roles, and at dpiX, a display and sensor manufacturing company in similar roles.

An Overview of ARPA-E Programs in Carbon Capture

In the first two rounds of project selections, ARPA-E has selected 20 projects focusing on carbon capture technology. An overview of these project selections and a description of the role ARPA-E plays relative to the Fossil Energy program will be provided. Technology approaches include membranes, sorbents, electrochemical and phase change approaches as well as catalytic solvent processes.

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Olav Bolland, NTNU

Olav Bolland is Professor of Thermal Power Engineering at the Norwegian University of Science and Technology (NTNU). He is Head of the Department of Energy and Process Engineering. Bolland obtained a PhD in Thermal Engineering in 1990, and has since then worked at NTNU. Since 1989, Bolland has worked with CO₂ capture, and is widely published in the areas of various power cycle analyses, integration of CO₂ capture in power cycles, and dynamic performance. Olav Bolland was one of the lead authors for the 2005 IPCC Special Report on Carbon Dioxide Capture and Storage. In 2007 Bolland was among the IPCC scientists researching climate change issues to receive the Nobel Peace Prize. Bolland organized the 2006 GHGT-8 conference in Trondheim Norway with almost 1000 participants.

Outlook for Advanced Capture Technology

The Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report states that it is very likely (>90% probability) that human emissions of greenhouse gases are warming the planet surface. In order to reduce the man-made warming, concerted action to mitigate

emissions of greenhouse gases is now needed. The main greenhouse gas generated by human activities is carbon dioxide (CO₂). CO₂ is produced mainly by the combustion of fossil fuels in the power sector, manufacturing industry and in the transport sector, but also in the production of energy carriers and services. Projections by the International Energy Agency indicate that fossil fuels will be the dominant source of energy until 2030 and most likely beyond then. It is, therefore, becoming increasingly important that we develop and deploy mitigation technologies that can make significant reductions in CO₂ emissions in all sectors.

It is generally agreed that the capture cost, and also to some extent the energy consumption, depend on the size (tonnes/day) of the capture process. When looking at the man-made sources of CO₂ above a certain rate, for example 0.1 Mt CO₂/year, it is evident that power generation is by far the most important emitter, followed by the cement industry, refineries and iron/steel industry. The current trend of increasing demand for power globally, indicates that power plants will be the primary targets for implementation of CO₂ capture. Other large-scale sources of CO₂ and in particular those with high partial pressure of CO₂, are also of primary interest in this respect.

CO₂ has been captured from industrial process streams for over 80 years, although most of the CO₂ that is captured is vented to the atmosphere because there is no incentive or requirement to store it away from the atmosphere. Current examples of CO₂ capture from process streams are purification of natural gas and production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels.

So what is the problem? Why can't we just capture a sufficient amount of CO₂ and store it underground? There are issues related to added cost of power, availability of technology, additional fuel consumption, safety of transport and storage, and a general uncertainty whether carbon dioxide capture and storage can actually make a difference.

There is an underlying basis given by the thermodynamics related to the formation of CO₂ and to the separation of CO₂ from gas mixtures, which dictates the size of components and the energy required. The presentation will focus on the theoretical basis of CO₂ capture, as well as present a status for various technologies for the capture of CO₂ in power plants.

When CO₂ is generated by oxidation of carbonaceous fuels, it typically ends up diluted by other gases, so the fraction and partial pressure in the gas mixture of CO₂ are reduced. The purpose of CO₂ capture is to produce a concentrated stream that can be readily transported to a CO₂ storage site. The requirements for the condition of CO₂ for transport and storage are typically >100 bar pressure and a low temperature ensuring it is in a dense/liquid state. The content of non-CO₂ gases is normally expected to be restricted to less than 5%.

The dilution of CO₂ in the oxidation products causes two disadvantages:

- A larger volume of non-CO₂ gases per unit of CO₂ that requires larger and more expensive equipment to handle the gas volume
- A lower partial pressure of CO₂ in the gas mixture necessitates more energy to be spent in bringing it up to the transportation pressure

In the above processes the CO₂ may be diluted with substances from the following sources:

- The oxidant
 - non-reactive components in air (mainly N₂, Ar)
 - non-reactive components (N₂, Ar) along with oxygen from an air separation plant
 - excess H₂O
- In the case of combustion, oxygen from use of excess air (ordinary combustion) or excess oxygen (oxy-combustion)
- Substances present in the fuel like nitrogen and sulfur, where the latter is converted to H₂S, COS, SO₂, and SO₃, depending upon the extent of oxidation. Mercury (Hg) and other metals; As, B, Cd, Mo, Pb, Se, Cr, Cu, Ni, V and Zn, are to various extent present in solid and liquid fuels. Some of these may be released and transported with the oxidation products on particles or as vapours. Ash particles may be entrained by the oxidation products.
- The oxidation process is also a source of gas components like NO, NO₂, N₂O, as well as soot, depending upon fuel composition, extent of oxidation, presence of steam, and for full oxidation; the combustion process itself with respect to temperature, mixing, and residence time.
- Un-oxidised fuel (mainly CH₄, CO, H₂) caused by too low temperature, insufficient residence time or lack of oxidant for complete oxidation. Note here that hydrogen (H₂) may be a desired oxidation product with respect to capturing CO₂ (pre-combustion capture of CO₂).

Depending upon which method is used for the oxidation for the carbonaceous fuel in a power cycle, the volumetric fraction of CO₂ in the resulting gas mixture may vary from about 0.03 to over 0.9.

There are a number of separation processes that can be used to separate CO₂ from a gas mixture. In general, separation can be accomplished by phase-change; where CO₂ in a gas mixture is solidified by crossing the sublimation line, or it can be liquefied by crossing the boiling/condensation line. Otherwise the CO₂ has to be separated from a gas mixture by a gas/gas separation process.

Another approach is to minimise or to avoid the dilution of the CO₂ resulting from an oxidation process. The dilution with nitrogen can be avoided by using pure oxygen rather than air for the

combustion. This requires the use of an air separation process upstream the oxidation process or air separation integrated in the oxidation process. The use of a nitrogen-containing oxidant can be reduced by partial oxidation with oxygen or air, and then use steam to complete the oxidation in a water gas-shift process. The nitrogen-dilution can also be reduced by recycling the oxidation products, in order to reduce the excess air in a combustion process; which may be applicable in a gas turbine cycle.

There are three basic principles for capturing CO₂ from fossil fuelled power plants:

- Post-combustion CO₂ capture
- Pre-combustion CO₂ capture
- Oxy-combustion CO₂ capture

Post-combustion CO₂ capture: Capture of CO₂ from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO₂.

Pre-combustion CO₂ capture: The fuel molecule is split by partial oxidation resulting in a syngas consisting of hydrogen (H₂) and carbon monoxide (CO). In presence of steam (H₂O) the equilibrium can be shifted towards H₂ and CO₂, which are subsequently separated. The idea is to form CO₂ while converting as much as possible of the fuel heating value into heating value of molecular hydrogen. The hydrogen can then be used as fuel in a power plant.

In **oxy-combustion CO₂ capture** pure oxygen is used for combustion instead of air, resulting in a flue gas that, in the ideal case, consists of only CO₂ and steam (H₂O). An ideal case would be that: 1) the fuel consists of hydrogen, carbon and eventually oxygen, 2) combustion is complete with no excess of oxygen, and 3) the oxygen is 100% pure. If the fuel is burnt in high-purity oxygen, the flame temperature would be excessively high, so that either a non-adiabatic combustion process (heat removal) or recirculation of cooled combustion products is needed. Removing H₂O from the CO₂ is considered an easy task because its condensing temperature is higher than the ambient temperature, unless for a very small partial pressure. In a real process the CO₂ is diluted also with other substances, not only H₂O, which, to various extents, are allowed or desirable to be present in the mixture with the CO₂ during transport and in the storage site. Oxy-combustion is about to have the major gas separation process (oxygen from air) upstream the combustion process, but in practice also a downstream separation is necessary in order to remove substances, present in small fractions, except for H₂O in some schemes, from a bulk stream of CO₂.

[| Link to PDF of Presentation |](#)

ABSORPTION SESSION

Session Summary

Chair Hallvard Svendsen opened the absorption session by reviewing the challenges remaining to be overcome before reactive absorption for post combustion CO₂ capture can be practically implemented on a large scale. Dr. Svendsen concentrated on three aspects: energy requirements, capital cost and size, and environmental concerns.

His discussion of process heat requirements focused on the impacts of solvent selection and process modification, and stressed the sensitivity of equilibrium temperature to choice of solvent. In conventional temperature-swing absorption/desorption, high temperature sensitivity increases the possibility for obtaining high CO₂ partial pressures at the top of the stripper, which translates into reduced stripping steam requirements. Temperature sensitivity generally reflects a high heat of absorption. However, despite relatively small differences among the heats of reaction of amines of the same type (primary, secondary, etc.), their temperature sensitivity may vary substantially, which suggests the need to identify amines with atypical and/or non-ideal behaviour.

Svendsen also emphasized the importance of close approach to equilibrium at the bottom of the absorber, the effect of which will be similar to that of employing an amine with high equilibrium temperature sensitivity. This should be kept in mind when comparing mixed and single amine systems, since mixed amines typically include one fast and one slow reacting component. The latter systems will exhibit low absorption rates at high loadings and, therefore, be less likely to approach equilibrium closely.

As regards energy requirements, Svendsen believes that the development of so-called first-generation solvents like MEA and KS1 have achieved reached a lower limit in conventional process flowsheets with energy requirements in the range of 3.3-3.5 GJ/ton CO₂ captured.

Process improvements that have been suggested and implemented include intercooling in the absorber, interheating in the stripper, lean vapor recompression and, needless to say, optimization of lean/rich solvent heat exchange. The effects of these modifications depend on the choice of solvent. Intercooling generally has its greatest effect when the solvents have a high heat of absorption and interphase transport is equilibrium-controlled. That typically means primary amines or mixtures of primary amines with amines that have lower heats of absorption; the best location for applying intercooling is 1/4 to 1/3 of the column height above the bottom. When mass transfer is equilibrium-controlled, intercooling tends to increase rich solvent loading. In stripper interheating, the lean solution is used to heat the liquid in the middle and upper sections of the stripper. This raises the temperature throughout most of the stripper and normally reduces energy requirements. Lean vapor recompression reduces steam

demand and appears to be most effective when stripping steam requirements are high, e.g., with MEA as the solvent. The positive effect must be weighed against the additional, recompression energy requirement, whether steam or electricity.

On the environmental side, Svendsen stressed the need for ecologically acceptable solvents, and noted that many solvents in use today exhibit too low biodegradability. Deploying them on a large scale will require design for near-zero emissions. A possible means to achieve that is to combine chilled water and acidic washes. If there is a large temperature difference between the absorber and the water wash, significant condensation will occur in the latter, which will have the beneficial effect of promoting recovery of the solvent from the gas – subject, of course, to process water balance. Volatile degradation products may be captured by an acidic last wash stage. It will be necessary to include a bleed stream to recover volatiles and/or a biological sewage treatment plant.

During the discussion period, a question was raised concerning the low off-gas temperature and possible problems associated with exhaust dispersion above the stack. This may indeed pose a problem and will have to be examined on a case by case basis.

The second presentation, “Aqueous Piperazine as a New Standard for Amine Scrubbing Technology,” was from Prof. Gary Rochelle’s group at U. of Texas. Austin and was delivered by Eric Chen. Dr. Chen pointed to the fact that while 30 wt% MEA has been the industry standard for decades, there is as yet no standard second generation solvent and most information about solvent blends is proprietary. He proposed 40 wt% piperazine as a new standard second generation solvent. Although unloaded piperazine exhibits limited solubility in water, loading with CO₂ increases its solubility, creating a window for possible industrial utilization, even at a concentration of 40 wt% , with a loading swing between 0.31 and 0.41 mol CO₂/ mol amine. It was also noted that when it is paired with other amines, piperazine solubility is normally not a major issue. To its advantage, piperazine reacts with CO₂ twice as fast as MEA, and has higher cyclic capacity, lower volatility, greater thermal and oxidative stability and somewhat lower energy requirement for regeneration. However, exploiting that reduction in energy need requires stripping at 150°C.

Chen also presented a novel stripper concept, namely a two-stage flash, and the associated advantages, including recovery of pure CO₂ at pressures of up to 17 bar. He also discussed irreversibilities and associated exergy losses in the various stages of the process. He predicted lower heat requirements with piperazine than with 30 wt% MEA, whereas the total equivalent work would be about the same with either amine because of piperazine’s higher regeneration temperature. Finally, Chen presented data showing good stability, low volatility, and ease of reclaiming piperazine.

In the discussion period, the question of piperazine's disadvantages was raised. Chen mentioned its cost, 2-3 times that of MEA, and the relatively narrow solubility window that restricts the allowable operating conditions, which must be kept in mind, especially during transient periods like startup and shutdown. In addition, the process has yet to be substantially scaled up. Concerns about the ecological aspects of using piperazine were also raised. Biodegradability is low, while ecotoxicity is not a problem. In response to a question about process economics, Chen stated that with a high-pressure stripper and two flashes, the capital costs may become high, though the footprint will be relatively small. Finally, the issue of corrosivity was raised. The speaker Chen responded that it was less of a problem than with MEA.

Dr. Ludovic Raynal from IFP next discussed two processes, one based on MEA and the other on "demixing" solvents. IFP has developed the MEA-based HiCapt+ process, which uses 40 wt% MEA (compared with the conventional 30 wt%), and compensates for potentially increased amine degradation and corrosiveness by including additives. Over 130 additives were screened and the results were reportedly very good. The process is undergoing testing at the ENEL Brindisi power plant at a capacity of 2.25 t/h of captured CO₂.

The demixing process was offered as a new concept involving what might be termed third generation solvents. It involves a solvent that forms two liquid phases in the absorber at sufficiently high CO₂ loadings. Because only a fraction of the total liquid is sent to the stripper, capital cost reductions of about 30% are envisaged, primarily by virtue of the smaller desorber and fewer stages in the compressor. However, the most significant savings would be on the energy side. The CO₂-carrying capacity of the CO₂-rich liquid phase will be high and, therefore, different stripping characteristics will be exhibited compared to MEA. Furthermore, the desorber pressure may be relatively high, which will reduce stripping steam requirements while reducing electrical power consumption in the compressor. According to IFP, the "DMX" process under development shows great promise. Extensive testing has demonstrated rapid absorption, high capacity, attractive desorption characteristics, and good stability.

In response to a question about phase separation, Dr. Raynal noted that physical separation of the two phases is done at relatively high temperature, which lowers viscosity and facilitates separation. Although one might expect poorer CO₂ distribution between phases at elevated temperatures, Raynal indicated that it could go either way. With tripping at 7 bar, and 160°C, the system exhibited good stability. In addition, heat requirements were as low as 2.3 GJ/ton CO₂ captured, and the total reduction in power consumption, including reduced compression costs, are estimated at 25%. Another question was raised about possible effects of suspended particles on separation. Raynal acknowledged a potential effect on the phase interface. In the next stage of testing, which will be in a pilot plant, effects of contaminants including particulates, SO_x, and NO_x etc. will be evaluated. A final question was raised about the nature

of the test gas (the answer was syngas) and the effects of particulates in the 40 wt% MEA pilot tests (they were not tested).

The final presentation in this session was delivered by Dr. S.S. Bandyopadhyay from the Separation Science laboratory in IIT Kharagpur, India. He described an experimental and theoretical investigation of CO₂ absorption in piperazine (Pz)-activated MDEA. The speaker traced the development of a thermodynamic model to predict speciation and CO₂ partial pressure, and presented details of the computational method. The solvent's physical properties including viscosity, density and CO₂ solubility (by N₂O analogy) were measured. In addition, kinetic experiments were undertaken and the results were inserted in theoretical expressions for the interphase transport "enhancement factor." The speaker reported the effects on the enhancement factor of varying the piperazine content between 2 and 8 wt%. A rate-based mass transfer model was developed and its predictions agreed well with experimental results. He also presented species concentration profiles within the liquid film during interphase transfer.

A question was raised as to whether the speaker's model accounted for reaction between protonated piperazine and CO₂. Dr. Bandyopadhyay responded that it was not, because the kinetic tests were all undertaken at early stages of reaction with initially unloaded solutions. However, he also was noted that the MDEA is important for proton transfer. The speaker pointed out, contrary to the earlier presentation by Dr. Chen of the Rochelle group, piperazine was found to be corrosive.

The speaker had reported that pilot tests with both MDEA/Pz and AMP/Pz were planned. It was pointed out by a member of the audience that high Pz concentration might be necessary in order derive a significant advantage. The speaker replied there is a dramatic increase in enhancement factor is dramatic even with small Pz concentrations (at zero loading). In response to another question, the speaker stated that the kinetic tests will be expanded to included loaded solutions. A final question was raised about whether direct reaction with Pz had been accounted for in enhancement factor calculations. The answer was affirmative, and the speaker added that Pz alone had also been tested, and that there is a synergetic effect between MDEA and Pz.

Hallvard Svendsen, NTNU (chair)

Hallvard F. Svendsen, PhD NTNU 1976, 2 years in Tanzania starting Chemical Eng. education there, 6 years in SINTEF Applied chemistry, since 1984 associate/full professor at Department of Chemical Eng. NTNU. Research areas: Solvent extraction/hydrometallurgy, chemical reactor technology, multiphase reactors, absorption with chemical reaction, and since around 1990 working with CO₂ absorption from natural gas and exhaust gases(post combustion capture).

CO₂ Capture by Solvents; Possibilities and Challenges

The presentation will give an overview of solvent based post combustion CO₂ capture processes. Further, the problem areas of the existing processes such as size, energy requirement, and environmental issues will be discussed. Finally, the potentials for new solvents, e.g. phase change solvents will be discussed in a process context.

| [Link to PDF of Presentation](#) |

Eric Chen, University of Texas at Austin

Dr. Eric Chen is a Research Engineer in the Department of Chemical Engineering at the University of Texas at Austin. Dr. Chen managed the modification of the pilot plant at the Separations Research Program at the University of Texas at Austin into an absorber/stripper system for CO₂ capture. Dr. Chen also led the development and oversaw construction of pilot algae harvesting equipment as part of an algae biofuels effort. He is currently responsible for the design and construction of the high temperature 2-stage flash pilot skid for CO₂ capture using concentrated piperazine. Dr. Chen also has extensive process modeling experience in Aspen Plus and RateSep.

Concentrated Piperazine: A Case Study of Advanced Amine Scrubbing

CO₂ capture by concentrated piperazine with a 2-stage flash regeneration has all the desirable properties of an advanced system for amine scrubbing. Piperazine can be used with a reasonable viscosity at 40 wt% (8 m) and offers a reversible CO₂ capacity of 0.8 mole/kg amine+water, as compared to 0.4 for 30 wt% MEA or 1.2 for concentrated hindered amines. It provides a rate of CO₂ absorption that is twice as fast as 7 m MEA. Piperazine has a moderately high heat of absorption (70 kJ/mole) that combines with exceptional thermal stability to provide 10 to 20% better energy performance with thermal swing regeneration at 150OC and 7 to 15 bar. With careful integration into an existing coal-fired power plant the energy requirement should approach 0.2 MWH/tonne CO₂ removed.

The capital cost of CO₂ capture by concentrated piperazine will be about \$100-yr/tonne CO₂. This system will include an intercooled absorber to maximize reversibility and solvent regeneration will be simplified by a two-stage flash heated at 150oC. The captured CO₂ will be

compressed to 150 bar in a multistage intercooled compressor. The use of a high T flash regeneration will reduce the compression requirement. Steam will be extracted from at variable working pressure before the existing low pressure turbines.

Secondary environmental impacts and costs of solvent makeup will be minimized with the advanced process. Even in the presence of dissolved CO₂, piperazine is stable up 150oC. Oxidation of piperazine is slow and will be further reduced by a proprietary oxidation inhibitor. Piperazine volatility at lean conditions is less than 20 ppm and an effective water wash will further reduce emissions to 1 ppm or lower as required to mitigate any significant effects on atmospheric air pollution. Reclaiming by sulfate crystallization and advanced thermal distillation will remove sulfate, flyash, and other impurities from the flue gas and carryover from limestone slurry scrubbing. Piperazine is a commercial available amine that has been heavily used in acid gas treating. World-scale production of piperazine can be achieved in new plants by the hydrodimerization of monoethanolamine.

[| Link to PDF of Presentation |](#)

Ludovic Raynal, IFP Process Division

Ludovic Raynal is project manager at IFP; he is in charge of research and development on new processes for post-combustion carbon capture. He joined IFP in 1998 in the process development division at IFP-Lyon. He has been working on gas treatment for the last 9 years, and started to work on CO₂ capture when participating to the Castor project proposal in 2003. He graduated from the Institut National Polytechnique de Grenoble in 1993, he holds a PhD in Mechanical Engineering (1997) and spent one year at the University of California, San Diego.

From MEA to Demixing Solvents and Future Steps, the IFP Solutions for Lowering the Cost of Post-combustion Carbon Capture

Following the recommendations of the IEA, Carbon Capture and Storage is one important answer to develop for reducing CO₂ emissions. So far, the MEA based processes are the only technologies whose performances have been proven on industrial pilots. However, it is well known that the standard MEA process requires high energy consumption and face oxidative degradation issues. IFP has developed HiCapt+™, a process based on a high concentration MEA solvent with high performance oxydative inhibitors. This could be the first step towards CCS deployment.

However, if one expects significant cost reductions, it is believed that one should also develop breakthrough solutions. To do so, it is of great importance to fully characterize the costs repartition of the MEA process and thus identify the drivers that would enable important costs reductions. In most studies, people focus on the energy loss at reboiler, expressed in GJ/tCO₂.

Despite this item actually corresponds to the main part of the capture costs, it is far from being the only one to focus on. Indeed, it represents about 50% of the operating costs, the latter representing about 2/3 of the total capture cost (CAPEX included) which makes a total of only 30%. This paper aims at showing in details where all costs are in order to further support original developments.

Breakthrough solutions could come from phase change systems, the latter phase changes corresponding to high CO₂ concentration in solvents inducing low circulation rates and low energy penalty. Phase change systems may correspond to the formation of solids in liquid solvents at absorption step as it occurs in the chilled ammonia process or in the capture process via hydrates formation, it may also corresponds to the original solution of the demixing solvents. The DMX™ process, involving the generation of two liquid phases one having a very high concentration of CO₂, has been developed by IFP in the last few years. The data obtained on this system in terms of thermodynamic properties, kinetics, degradation, corrosion, L/L separation... but also process simulations data and corresponding cost estimations is shown in regards to the cost evaluation made for the MEA process. Such systems could be the second step towards CCS deployment.

Last, a quick overview of other original approaches, such as new efficient solvents, ionic liquids, original chemistry, adsorption is also presented, each time with a discussion on the economics of the process.

[| Link to PDF of Presentation |](#)

S.S. Bandyopadhyay, IIT Kharagpur

Dr. S.S. Bandyopadhyay, Professor. Cryogenic Engineering Centre, IIT Kharagpur, obtained the B Tech. and M.Tech degrees in Chemical Engineering from the University of Calcutta, India, and Ph.D in Chemical Engineering from the Indian Institute of Technology Kharagpur (IIT Kharagpur), where he has been on the faculty for the last twenty five years. His major research activities include gas treating for removal of CO₂ and H₂S from sour natural gas, synthesis gas and refinery off-gas streams, and CO₂ capture from power plant flue gas streams by chemical absorption in single, blended, and activated amine solvents. He has published some thirty papers in international peer reviewed journals and co-edited a book, *Advances in Separation Processes* (Allied publishers, New Delhi, 2005) His current research interests also include hydrogen energy and air-breathing propulsion. At IIT Kharagpur he has served as Chair of the Cryogenic Engineering Centre (1986-87, 1997-2000) and Chair of the Central Library (2004-2007). He is on the Editorial Board of the journal *Indian Chemical Engineer* and served as its editor in 2008. Dr. Bandyopadhyay has been a visiting faculty at the University of California, Davis (1987-88), University of Waterloo, Canada (1994-95), and recently at Tufts University, Massachusetts (June 2009).

Absorption of Carbon Dioxide into Piperazine Activated Aqueous N-Methyldiethanolamine

Carbon dioxide capture from the flue gas streams of thermal power plants is very important today in order to mitigate the problem of global warming. The United Nations' Intergovernmental Panel on Climate Change (IPCC) identified CO₂ capture and storage as one of the several approaches to address the problem of global warming and climate change. Hence, efficient and less energy intensive capture of CO₂ from flue gases with subsequent geological storage is increasingly being viewed as a mid-term option for reducing CO₂ emission. In view of this, extensive research activities are in progress globally to develop efficient and economic processes for CO₂ capture from the flue gas streams of coal based power plants.

This work presents a theoretical and experimental investigation on the absorption of CO₂ into piperazine (PZ) activated aqueous N-methyldiethanolamine (MDEA) solvent. A comprehensive numerical model based on Higbie's penetration theory has been developed to analyze the experimental data. The model involving coupled mass transfer–reaction kinetics–chemical equilibrium incorporates all important reversible reactions in the liquid phase. The model is validated with the experimental results of steady state absorption measurements of CO₂ in a 2.81×10⁻² m o.d. stainless steel wetted wall contractor. The rates of absorption of CO₂ into this solvent have been measured over the CO₂ partial pressure range of 2–14 kPa and temperature range of 298 – 313 K. Absorption experiments are performed over the MDEA concentration range of 1.89 - 2.41 kmol.m⁻³ along with PZ concentrations of 0.24, 0.60 and 0.95 kmol.m⁻³. Steady state absorption measurements of this work have shown that the CO₂ absorption rates into aqueous MDEA increase significantly with the addition of small amounts of PZ in the solvent. This establishes the potential of the PZ activated aqueous MDEA solvent for absorption of CO₂. Good agreement between the model results and experimental results indicates that the combined mass transfer-reaction kinetics-equilibrium model can effectively represent CO₂ mass transfer rates in PZ activated aqueous MDEA for wide range of operating conditions. This paper also presents a comparison of the performance of PZ activated aqueous MDEA with that of the other activated solvents for the absorption of CO₂.

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ADSORPTION SESSION

Session Summary

This session was devoted to recent development in the area of low temperature, low pressure CO₂ capture via adsorption. Adsorbents included 13 zeolite, amine modified-nanoporous materials and metal-organic frameworks (MOFs).

Session chair Abdel Sayari presented an overview on “CO₂ capture by amine-modified materials”, with particular emphasis on proprietary triamine-functionalized pore-expanded MCM-41 silica. He demonstrated the beneficial effect of using materials with larger pore diameter and pore volume than typical MCM-41 silica. To do so, he used so-called pore-expanded mesoporous MCM-41, with typically 10-12 nm pores, large surface area (ca. 1000 m²/g) and pore volume (ca. 2.5 cm³/g). He stressed the importance of amine-grafting conditions. Under optimal conditions, the latter materials exhibit high CO₂ adsorption capacity, high CO₂ selectivity, fast adsorption and desorption kinetics, low regeneration energy requirements, and high tolerance for the presence of water vapor in the gas feed. Sayari also noted that the same material exhibits long-term stability through extensive recycling.

In a presentation entitled “CO₂ capture by adsorption processes: from materials to process development to practical implementation”, Paul Webley described Monash University’s R&D program for CO₂ capture from flue gas via pressure swing adsorption (PSA) using 13X zeolite. The research activities span fundamental adsorbent studies to process development and implementation.

In conjunction with the screening of 100 CO₂ adsorbents, Webley developed a “Capture Figure of Merit” based on adiabatic adsorbent working capacity, selectivity of CO₂/N₂ selectivity and the energy required to recover the CO₂ under vacuum conditions. Using 13X zeolite protected from moisture by a layer of Sorbead, they developed a nine-step cycle incorporating product purge and pressure equalization steps to enrich CO₂ up to 95% at 80% recovery with relatively low power requirements. Based on data from a 1 ton/day test unit, Webley reported preliminary results with actual flue gas demonstrating recovery of 70% CO₂ via a simple 6-step cycle without product purge.

Sunho Choi (Georgia Institute of Technology) described a family of CO₂ adsorbents based on a hyperbranched amine that is covalently tethered to the internal surface of mesoporous silica, including SBA-15 and mesocellular foam. The latter hybrid materials, which were synthesized via in situ polymerization of aziridine, exhibited high loading when exposed to CO₂ at concentrations as low as 400 ppm in simulated air. These amine-based solid adsorbents exhibited high stability during repeated adsorption/desorption cycles, indicating that they are promising materials for efficient carbon control.

Randal Snurr (Northwestern University) discussed “molecular modeling and design of metal-organic frameworks (MOFs) for CO₂ capture”. Given the large numbers of possible MOF topologies, linkers and metal nodes, and consequently huge variety of potential materials, the elucidation of fundamental structure/function relationships is an essential step toward the development of effective new MOF-based adsorption processes. Focussing on a diverse collection of 14 MOFs for CO₂ capture from simulated flue gas, Snurr described a fully predictive, generalized strategy for molecular modeling of CO₂ adsorption on MOFs.

Abdelhamid Sayari, University of Ottawa (chair)

Professor Abdel Sayari is the Canada Research Chair in *Nanostructured Materials for Catalysis and Separation* at the University of Ottawa. He received his PhD in Heterogeneous Catalysis in Lyon (France) in 1980 while pursuing an academic career in his native Tunisia. After a postdoctoral stay at the University of Pittsburg, he joined the National Research Council of Canada in 1986, then the Department of Chemical Engineering at Laval University (Québec) in 1990. In 2001, he moved to the University of Ottawa as Professor of Chemistry and Founding Director of the Centre for Catalysis Research and Innovation. There, he built a state-of-the-art facility fully dedicated to the discovery and understanding of novel catalysts and catalytic processes. Prof. Sayari has made several important contributions in the development of microporous and mesoporous materials and their applications in separation and catalysis. In particular, he discovered a series of surface modified, large pore materials with unprecedented attributes for CO₂ adsorption. Dr. Sayari published over 240 refereed papers including several authoritative reviews. He also edited four books, and published six book chapters and four patents. He is currently Editor of the *Journal of Molecular Catalysis A: Chemical*, and member of the Editorial Board of *Catalysis Communications*. He is also Member of the International Commission on Mesoporous Materials and several other organizations.

Carbon Dioxide Capture by Amine-modified Materials

Pore-expanded MCM-41 (PE-MCM-41) silica is obtained via a two-step strategy consisting of synthesis of MCM-41 followed by hydrothermal treatment in the presence of an aqueous suspension of dimethyldecylamine (DMDA). The extent of the pore expansion process depends on the synthesis temperature of the starting MCM-41 material as well as the conditions (temperature, time and DMDA to MCM-41 ratio) of the hydrothermal treatment. After calcination, the material exhibits a unique combination of high specific surface area (> 1000 m²/g), pore size (up to 20 nm) and pore volume (up to 3.5 cm³/g). Optimization of surface grafting of PE-MCM-41 using triaminesilane led to novel CO₂ adsorbents (TRI-PE-MCM-41) with excellent attributes. These materials exhibit high CO₂ adsorption capacity, infinitely high selectivity for CO₂ vs. N₂, O₂, CH₄, H₂, etc. Moreover, although these adsorbents capture moisture, the occurrence of water vapor has a positive effect on CO₂ adsorption. The effect of pore expansion and grafting conditions on CO₂ adsorption will be described. The stability of TRI-PE-MCM-41 was investigated in depth using extensive adsorption-regeneration cycling. The mechanism of deactivation was delineated and a corrective strategy was established to use such adsorbents over thousands of cycles without any capacity loss. This presentation will be focused on the potential use of TRI-MCM-41 and similar amine-containing adsorbents for the treatment of flue gas.

The most important and versatile material is D, which offers unlimited opportunities for surface modification. Incorporation of mono-, di- and tri-amine functionalities gave rise to outstanding

adsorbents for acid gases, particularly CO₂. In this talk the following issues will be addressed: (i) optimization of grafting conditions, (ii) CO₂ adsorption capacity and rate, (iii) tolerance to moisture in the feed, (iv) selectivity toward CO₂ vs. other adsorbates such as N₂, O₂, H₂, CH₂, H₂S, and (v) cycling.

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Sunho Choi, Georgia Institute of Technology

Sunho Choi is currently a Dreyfus foundation postdoctoral fellow in the department of Chemical & Biomolecular Engineering at the Georgia Institute of Technology, where he has investigated amine-based solid adsorbents for post-combustion and air capture of CO₂ in the laboratory of Prof. Christopher Jones. He received his Ph. D. from the University of Minnesota, where he worked under the supervision of Prof. Michael Tsapatsis on hydrogen-selective nanocomposite membranes for pre-combustion gas processing. He recently co-authored a critical review of solid adsorbent materials targeting post-combustion CO₂ capture, which appeared in ChemSusChem.

Designing Inorganic-organic Hybrid Solid Adsorbents for CO₂ Capture Applications from the Ambient Air

Growing concerns about the 35% rise in atmospheric CO₂ concentration to 390 ppm since the industrial revolution, and the effect of anthropogenic CO₂ generation on global climate, have motivated interest in renewable, carbon-neutral wind, solar and biomass-based energy. Yet even in the face of significant growth of renewable energy usage, it is expected that the atmospheric CO₂ concentration will continue to rise over the next decades. Because of this, capture of CO₂ from large point sources, such as fossil-fuel-burning power plants, has been proposed. However, this approach can be at best carbon neutral and, as such, it does not offer the possibility to reduce atmospheric CO₂ levels below where they are today. Furthermore, capture of CO₂ from distributed sources such as cars, planes and ships is unlikely to be economically feasible.

In contrast, CO₂ capture from ambient air can be carbon negative. This approach has been largely overlooked due to the perceived technical difficulty and cost of capturing CO₂ from such a low concentration source. In this talk, a new technique will be presented, which is capable of removing CO₂ from the ambient air via CO₂ fixation on solid adsorbent materials. Different types of solid sorbents have been prepared and evaluated for adsorption of CO₂ at a concentration of 400 ppm. The experimental data strongly suggest that this approach to CO₂ capture from ambient air is a promising strategy for reducing the level of CO₂ in the atmosphere.

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Paul A. Webley, Monash University

Paul Webley is currently Professor & Director of the Adsorption Engineering Laboratory at Monash University and Head of the Department of Chemical Engineering. He has a PhD in Chemical Engineering from MIT and spent several years at Air Products & Chemicals Inc, as a senior research engineering specializing in adsorption systems. After joining Monash University in 1996 he established the Adsorption Engineering Laboratory where he now runs a large group of PhD students and postdoctoral fellows working on many aspects of adsorption engineering. The group has produced over 120 publications and several patents on many different aspects of adsorption engineering. The recent focus has been on development and testing of materials and processes for capture of CO₂ from a range of pre- and post combustion gases.

CO₂ Capture by Adsorption Processes: From Materials to Process Development to Practical Implementation

Over the last decade there has been an explosion of research interest in development of advanced adsorbent materials for CO₂ capture. New materials are reported weekly usually accompanied by adsorption isotherms and often heats of adsorption. Less frequently reported are adsorption process developments in which new or existing materials are evaluated for their ability to capture CO₂ from a variety of gas streams with a variety of process cycles. In this work we cover the spectrum from materials to field installations and show how the synergy between materials development, process development and realities of field operation are essential in providing a complete adsorption solution to this difficult technology. We will cover our work in materials development, show how the potential of new adsorbents depends on more than just adsorption capacity and discuss practical problems encountered in field operation. In addition we should how screening of adsorbents can be handled through an appropriate capture figure of merit (CFM).

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Randall Snurr, Northwestern University

Randy Snurr is a Professor of Chemical and Biological Engineering at Northwestern University. He holds BSE and PhD degrees in chemical engineering from the University of Pennsylvania and the University of California, Berkeley, respectively. From 1994-95, he performed post-doctoral research at the University of Leipzig in Germany supported by a fellowship from the Alexander von Humboldt Foundation. Other honors include a CAREER award from the National Science Foundation and the Leibniz professorship at the University of Leipzig in 2009. He is a Senior Editor of the Journal of Physical Chemistry and serves on the editorial boards of the Journal of Molecular Catalysis A and Current Nanoscience. His research interests include

development of new materials for energy and environmental applications, molecular simulation, adsorption separations, diffusion in nanoporous materials, and catalysis.

Molecular Modeling and Design of Metal-Organic Frameworks for CO₂ Capture

One of the biggest challenges in capturing CO₂ by adsorption is the design of new adsorbents with improved properties. Metal-organic frameworks (MOFs) are a new class of nanoporous materials synthesized in a “building-block” approach that may open new options for understanding and designing sorbent properties. MOFs are synthesized by the self-assembly of metal or metal-oxide vertices interconnected by rigid organic linker molecules. The rational synthesis approach opens up the possibility of incorporating a wide variety of functional groups into the materials. Because of the predictability of the synthetic routes and the nearly infinite number of variations possible, molecular modeling is an attractive tool for screening new structures before they are synthesized. Modeling can also provide insight into the molecular-level details that lead to observed macroscopic properties. This talk will focus on molecular modeling of adsorption of CO₂, N₂, and water in MOFs. We will show that atomistic Monte Carlo simulations can predict adsorption of simple gases in a range of MOFs in good agreement with experiment. This paves the way for using simulation to screen existing and hypothetical MOFs for adsorption separations. In addition, some post-synthesis strategies for modifying MOFs will be presented.

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MEMBRANES AND IONIC LIQUIDS SESSION

Session Summary

In his opening presentation, session chair Eric Favre noted that membrane processes have attracted considerably less attention for potential application to post-combustion carbon dioxide capture, than absorption and adsorption processes. He attributed this to the widely held view that membrane processes have high energy requirements and capital costs, with no economy of scale, and that available membranes are insufficiently selective. Similarly, while there is growing interest in potential applications for ionic liquids in a variety of chemical processes, their utility in carbon dioxide capture remains to be explored.

R. W. Baker of Membrane Technology and Research (MTR) described his company's pilot membrane separation process, the first of its kind to treat real flue gas, in this case from a natural gas power plant. Dr. Baker discussed the performance of novel polymeric membranes for CO₂/N₂ separation in terms of the solution-diffusion mechanism. He noted that purity and capture ratio constraints require a two-stage process, for which MTR which has designed a novel retentate recycle loop. He explained the trade-off between membrane area (which impacts capital costs) and compression and/or vacuum energy requirements (which impact operating costs). He stressed the importance of using very highly permeable (versus highly selective) membrane materials.

By comparison, cost-effective post-combustion CO₂ capture in a single-stage process requires a membrane CO₂/N₂ selectivity on the order of 150. That precludes essentially all polymeric membranes with acceptable permeabilities. However, this limitation of membrane materials in which permeation is via simple solution and diffusion, may be overcome with chemically reactive materials. Success with the latter alternative approach was discussed by R. W. Noble of the University of Colorado, whose co-workers impregnated polymeric membranes with a variety of novel chemically reactive, non volatile ionic liquids.

David Heldebrant of the U.S. Department of Energy's Pacific Northwest Laboratory presented an overview of the range of structures offered by ionic liquids as dedicated CO₂ solvents. Using a wide variety of chemical building blocks and synthesis pathways Dr. Heldebrant's group synthesized a family of physical and chemical solvents which range in volatility, chemical and thermal stability, CO₂ capacity and regeneration energy requirements. The most promising molecules will soon be tested in either conventional absorbers or hybrid systems processes involving liquid membranes, and impregnated solids or particles.

Membrane contactors offer the potential to intensify absorption processes, including post-combustion CO₂ capture. The high selectivity of a chemical solvent is paired with a non-selective but highly permeable membrane material that separates gas and liquid phases. The

high degree intensification that is achievable has the potential to substantially decrease installation volume, footprint and possibly total cost as well. Ryan Lively of Georgia Tech discussed an alternative hybrid concept that combines membrane and adsorption for efficient CO₂ capture. Novel adsorbent-filled porous polymeric materials cast as composite hollow fibers enable both process intensification and effective heat integration for steam-driven desorption.

Eric Favre, University of Nancy (chair)

Eric Favre is a chemical engineering professor and member of the executive committee at the Ecole Nationale Supérieure des Industries Chimiques (ENSIC) at Nancy Université, France. He holds a PhD in chemical engineering from INPL as well as graduate degrees from Dijon University (France) and EPFL (Switzerland). His research activities on separation processes started first at EPFL and at the Department of Chemical Engineering and Materials Science at the University of Minnesota (USA), where he was a visiting scientist in 1989. Since 1998, he is based at the Laboratoire Réactions et Génie des Procédés, CNRS, Nancy. His current research activities are mainly concerned with chemical engineering studies of gas separation processes, mostly by membranes. Eric Favre is the author of more than 70 publications in scientific journals, and he is a member of the editorial board of the *Journal of Membrane Science* since 2005. He received the French Society of Chemical Engineering award in 1994, the Montgolfier Prize in 1998 and a national teaching award (*Palmes Académiques*) in 2006.

Membranes & Post Combustion Carbon Dioxide Capture: State of the Art & Challenges

This presentation intends to give an overview of the different strategies which can be proposed in order to use membrane processes for post combustion carbon capture. Scientific and technological challenges will be addressed, with a particular emphasis on the industrial context and the associated constraints. In a first step, intensified gas-liquid absorption through membrane contactors will be briefly discussed. Material challenges and technological bottlenecks in a real flue gas environment will be more specifically detailed.

The state of the art of gas separation membranes, mostly based on polymeric materials, will next be exposed. The major targets of the capture process in terms of selectivity, energy requirement and productivity will be reviewed and compared to membrane performances (selectivity / permeance). At this stage, two basic strategies can be identified in order to achieve the targets:

- A single stage approach, which most often requires a high CO₂/N₂ selectivity material (typically 100 or more),
- A multistage approach based on membrane materials which show a moderate CO₂/N₂ selectivity (classically 50 to 70)

Different flowsheets based on these two major approaches will be presented and discussed. Additionally, a brief review of the various polymeric materials which can be proposed will be achieved in order to evaluate the real possibilities of membrane processes.

In the last part, unexplored issues such as the sensitivity to particles or the fate of "minor" flue gas components (such as oxygen, water, NO_x, SO_x ..) will be discussed. Alternative process

strategies will finally be exposed: reverse selective materials, hybrid processes with membrane separations and liquid membrane approaches.

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Richard W. Baker, Membrane Technology and Research

Richard Baker received his doctorate in physical chemistry in 1966 at Imperial College, London, where he studied under Professor R. M. Barrer, one of the pioneers of membrane science. Subsequently, he joined Amicon Corporation, Lexington, MA, and helped develop a series of ultrafiltration membranes now sold under the name Diaflow®. While at Alza Corporation (Palo Alto, CA) from 1971 to 1974, he collaborated in the development of the Ocusert® ocular delivery system. In 1974, he co-founded Bend Research, Inc. (Bend, OR), where he was the Director of Research until 1981. Dr. Baker founded Membrane Technology and Research, Inc. (MTR) in 1982. He served as president until 2007 and is currently a member of MTR's Board of Directors. He is leading a new development program for MTR's membrane-based biomass/biofuel separations technology. His work in membrane science has been recognized by several awards, including: an IR 100 Award in 1984 for work on facilitated transport gas separation membranes; The Controlled Release Founders' Award in 1985; an R&D 100 Award for MTR's membrane vapor recovery systems (1990); The *Chemical Engineering Magazine* Kirkpatrick award for monomer recovery in polyolefin plants (1997); MTR was the first small business to ever receive this award; The first Alan S. Michaels Award for Innovation in Membrane Science and Technology, presented by the North American Membrane Society (2002).

Carbon Dioxide Separation & Sequestration from Flue Gas with Membranes

Carbon dioxide capture from power plant flue gas and subsequent sequestration is expected to play a key role in mitigating global climate change. Conventional amine technologies being considered for separating CO₂ from flue gas are costly, energy intensive, and if implemented, would result in large increases in the cost of producing electricity. Membranes offer potential as an energy-efficient, low-cost CO₂ capture option. Recently, working with the U.S. Department of Energy (DOE), MTR has developed membranes with CO₂ permeances of greater than 1,000 gpu and a CO₂/N₂ selectivity of 50 at 30°C. These membranes, in combination with a novel process design that uses incoming combustion air as a sweep gas to generate driving force, could meet DOE CO₂ capture cost targets. The membranes have been packaged into 4-inch and 8-inch membrane modules and are being evaluated on flue gas slip streams at the Red Hawk power station operated by Arizona Public Services (APS). A larger 1 ton/day test system has just started up at the APS Cholla power station. Initial results of these tests will be described.

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Richard W. Noble, University of Colorado

Professor Richard Noble is the Alfred T. and Betty E. Look Professor of Chemical Engineering at the University of Colorado. Prof. Noble has over 20 years of experience in the modeling and analysis of membrane and other thin film systems that include diffusive transport and chemical reaction. His 275 papers have been cited close to 5500 times (h factor = 40). He is the leading researcher in the US in the modeling and experimental implementation of facilitated transport membranes. He has 3 book chapters, 76 publications and 7 patents in this area. His expertise includes the modeling and use of pH, electrical and photon fields to obtain solute separation and concentration. Prof. Noble is an internationally recognized leader in the use of novel membrane and thin film materials, including zeolites and ionic liquids, for chemical separations. His research in each area has been separately highlighted in *Chemical & Engineering News* recently. He has over 50 publications, 4 patents and 7 patent applications in these areas.

His recent work on ionic liquids includes 25 publications and 4 patents and patent applications. His initial five papers in this area have been cited 194 times. His research is the basis for a new company ION Engineering, that was recently formed. He is on the editorial board of three separations related technical journals and co-director of the NSF Membrane Applied Science and Technology (MAST) Center at the University of Colorado. He has been chair of the AIChE Separations Division, ACS Separations Science and Technology subdivision, as well as the Gordon Research Conferences on Separation and Purification, and Membranes: Materials & Processes.

CO₂ Separations in Imidazolium-based Room-temperature Ionic Liquids & Polymers

Room-temperature ionic liquids (RTILs) are organic salts that are liquid at room temperature. They have several properties that make them excellent candidates for highly selective gas separations. They are stable over a wide temperature range, have negligible vapor pressure, and have a huge range of structural variations including polymeric versions. Strong electrostatic interactions constrain the ions to remain in the liquid phase.

The use of RTILs as media for CO₂ separations appears especially promising, with imidazolium-based salts as the focus of much of this research effort. The incorporation of amines into RTILs has been shown to be a promising alternative to aqueous-based amine scrubber technology. The kinetics of CO₂-amine reactions are very rapid in this solvent. The salt formed has a very low solubility in the RTIL and forms a two-phase system. This two-phase system can be decanted so that only the phase containing the salt needs to be heated to release the gas and recover the solvent. In addition, the heat capacity of RTILs is one-half to one-third that of water, thereby providing a substantial energy savings.

Polymeric versions of RTILs have been synthesized and have excellent permeation and selectivity for CO₂/N₂ separations. Modifications to the imidazolium cation by the addition of ether or nitrile groups improve the selectivity for CO₂.

Composite structures can also be formed that provide additional benefits. An RTIL can be incorporated into the polymeric version with a similar chemical structure. The resulting composite maintains the selectivity while enhancing the permeability by an order of magnitude. Gelled RTIL membranes can be formed with the addition of a few percent gelator. These gelled membranes have the permeability and selectivity of a liquid membrane but improved mechanical properties. The gelled membranes have permeabilities above 1000 barrers and selectivities for CO₂/N₂ exceeding 30.

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David J. Heldebrant, Pacific Northwest National Laboratory

Dr. David Heldebrant is currently a Senior Research Scientist in the Materials Chemistry and Surface Research Group in the Energy and Efficiency Division at Pacific Northwest National Laboratory in Richland, Washington. David received his PhD in 2005 under the supervision of Professor Philip Jessop at the University of California at Davis. David's current research interests include the design and development of switchable ionic liquids that chemically capture acid gases such as carbon dioxide and sulfur dioxide from power plant gas emissions. His new materials are known as CO₂-Binding Organic Liquids (CO₂BOLs), and they have potential to capture CO₂ and SO₂ using up to 50% less energy compared to existing gas capture technologies.

Characterization and Performance of Single-Component CO₂-Binding Organic Liquids (CO₂BOL) for Post Combustion CO₂ Capture

We report the synthesis, characterization and system performance of multiple third generation CO₂ binding organic liquids (CO₂BOLs) as a solvent system for post combustion gas capture. Alkanolguanidines and alkanolamidines are single component CO₂BOLs that reversibly bind CO₂ chemically as liquid zwitterionic amidinium / guanidinium alkylcarbonates. Three different alkanolguanidines and alkanolamidines were synthesized and studied for CO₂ capacity and binding energetics. Solvent performance of these three CO₂BOLs was assessed by batch-wise CO₂ uptake and release over multiple cycles. We report each CO₂BOLs activity and selectivity towards CO₂ as well as solvent durability with and without the presence of water.

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Ryan Lively, Georgia Institute of Technology

Ryan Lively received his Bachelors of Science in Chemical and Biomolecular Engineering at Georgia Tech in 2006, where he first became interested in developing composite spinnerets for spinning hollow fiber membranes. His research interests developed from this starting point to consider ways to spin high loaded mixed-matrix fibers for use in adsorption systems. His research has since focused on exploring the potential to use these fiber sorbents as a low-cost CO₂ capture platform. He has been an invited speaker in Washington D.C., has published a paper and filed a patent pertaining to his research.

Hollow-Fiber-Based Adsorbent System for CO₂ Capture from Flue Gas

We describe a rapid temperature swing adsorption (RTSA) system based on hollow polymer fibers impregnated with CO₂ sorbents and designed for the capture of CO₂ from flue gas streams of coal-fired power generation facilities. This post-combustion capture system relies on a four-bed configuration, each bed being composed of hollow fibers with sorbent particles dispersed in the porous polymer matrix. The system takes advantage of the hollow fiber morphology by passing cooling water through the bores during sorption to maximize sorption capacities and steam or hot water through the bores during desorption to release CO₂ to the collection system. The thin walled hollow fibers offer the advantage of rapid heat and mass transport. To ensure that the heating and cooling agent only thermally interacts with the fiber walls, a dense barrier layer is required on the interior of the fiber wall. This layer offers significant resistance to molecular transport between the fiber sheath and the core. One of the key advantages of fiber sorbents lies in the fact that the hollow fiber beds act as a structured sorbent system. Pressure drops through these beds will be correspondingly lower than those of packed or fluidized solid sorbent beds, which drives down draft fan costs. When heat integration strategies are considered, such as utilizing feedwater preheating heat flows (without disrupting plant operation) and utilizing heats generated during CO₂ compression, the overall parasitic load decreases dramatically. Namely, zeolite MFI-based fiber sorbents consume approximately 0.13 GJ per tonne of CO₂ captured.

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CROSS-CUTTING PRESENTATIONS

Modeling Talk

Jerry Meldon, Tufts University

Jerry H. Meldon is Associate Professor of Chemical and Biological Engineering at Tufts University. He received his chemical engineering education from the Cooper Union (B.E.) and Massachusetts Institute of Technology (Ph.D). His pre-and post-doctoral research focused on transport and reaction of oxygen and carbon dioxide in aqueous media. While a postdoctoral fellow in the Physiology Department at the University of Odense, Denmark, he co-authored with Dr. Lars Garby, MD, the monograph, *The Respiratory Functions of Blood*. His major research interests are in the mathematical modeling of transport processes, especially mass transfer with simultaneous chemical reaction.

Modeling of Amine-based Post-combustion Carbon Dioxide Capture

The considerable energy penalty of flue gas CO₂ capture via absorption in monoethanolamine (MEA) solutions has motivated extensive research worldwide aimed at identifying more cost-effective scrubbing media, adsorbents and membranes. A key component of such R&D programs is computer-based modeling. Mathematical modeling facilitates the interpretation of experimental data - e.g., the testing of proposed kinetic mechanisms, and the inference of rate constants from mass transfer rates measured in bench-scale absorption equipment. It also guides the selection of experimental conditions, and enables both scale-up and process simulation. This paper reviews the mathematical modeling of CO₂/amine reaction equilibria and kinetics, vapor/liquid equilibria, and interphase mass transfer, for purposes of assessing the potential utility of novel amine-based scrubbing media, adsorbents and membranes in post-combustion CO₂ capture.

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Novel Approaches to CO₂ Capture

Alan Hatton, MIT

T. Alan Hatton is the Ralph Landau Professor of Chemical Engineering Practice and Director of the David H. Koch School of Chemical Engineering Practice at the Massachusetts Institute of Technology. He obtained his BSc and MSc degrees at the University of Natal, Durban, South Africa, and worked at the Council for Scientific and Industrial Research in Pretoria for three years before obtaining his PhD degree at the University of Wisconsin, Madison. His research interests encompass self-assembly of surfactants and block copolymers, synthesis and functionalization of magnetic nanoparticles for chemical, biological and environmental

separations and catalysis, and the exploitation of stimuli-responsive materials for chemical processing applications

Electrochemically-Mediated Separations for CO₂ Capture

Carbon capture and sequestration (CCS) has been proposed as an effective approach for the mitigation of the contribution of anthropogenic CO₂ emissions to climate change.

Implementing this technology is a challenging task due to the scale at which CO₂ is produced and the energy requirement to drive the separation process. Thermal-swing separation processes based on chemical sorbents show potential for facilitating large-scale CO₂ capture; however, the energy efficiency in the current thermal-swing processes is unacceptable for their implementation. New approaches to gas separation have may overcome this problem.

Electrochemically mediated processes to facilitate CO₂ capture from a dilute gas mixture will be discussed, in which the significant changes in molecular affinity of certain sorbents for CO₂ molecules when they undergo a redox cycle may be exploited. Such processes have the potential for reducing the parasitic energy of the current solvent-based absorption processes since they do not require significant temperature swings to regenerate the sorbents. Molecular optimization of the redox sorbents is required to enhance their chemical stability, and implementation requires efficient electron transfer operations for rapid redox switching.

The general concepts and the advances needed in both the chemistry and the technology for successful implementation will be outlined.

| [Link to PDF of Presentation](#) |

APPENDIX

Agenda

Sunday, July 11	
3:00pm	Registration Opens at the Tufts European Center
4:00pm	Opening Session Howard Herzog, MIT <i>Welcome Remarks</i> David Luebke, US DOE <i>Opportunities & Challenges for Post-Combustion Capture: US DOE Research Activities</i> Mark Hartney, US DOE <i>An Overview of ARPA-E Programs in Carbon Capture</i> Olav Bolland, NTNU <i>Outlook for Advanced Capture Technology</i>
7:00pm	Reception and Dinner (guests invited) at the Hôtel L'Abbaye
Monday, July 12	
9:00am	Absorption Session Hallvard Svendsen, NTNU (chair) <i>CO₂ Capture by Solvents; Possibilities and Challenges</i> Eric Chen, University of Texas at Austin <i>Concentrated Piperazine: A Case Study of Advanced Amine Scrubbing</i> Ludovic Raynal, IFP Process Division <i>From MEA to Demixing Solvents and Future Steps, the IFP Solutions for Lowering the Cost of Post-combustion Carbon Capture</i> S.S. Bandyopadhyay, IIT Kharagpur <i>Absorption of Carbon Dioxide into Piperazine Activated Aqueous N-Methyldiethanolamine</i>
11:15am	Break

Monday, July 12	
11:45am	<p>Modeling Talk</p> <p>Jerry Meldon, Tufts University</p> <p><i>Modeling of Amine-based Post-combustion Carbon Dioxide Capture</i></p>
12:30pm	Lunch
2:00pm	<p>Adsorption Session</p> <p>Abdelhamid Sayari, University of Ottawa (chair)</p> <p><i>Carbon Dioxide Capture by Amine-modified Materials</i></p> <p>Sunho Choi, Georgia Institute of Technology</p> <p><i>Designing inorganic-organic hybrid solid adsorbents for CO₂ capture applications from the ambient air</i></p> <p>Paul A. Webley, Monash University</p> <p><i>CO₂ Capture by Adsorption Processes: From Materials to Process Development to Practical Implementation</i></p> <p>Randall Snurr, Northwestern University</p> <p><i>Molecular Modeling and Design of Metal-Organic Frameworks for CO₂ Capture</i></p>
4:15pm	Free time
7:15pm	Bus leaves from the Hôtel Le Lac for the dinner cruise
8:00pm	Dinner cruise on lake (guests invited)
11:15pm	Bus leaves Annecy and returns to the Hôtel Le Lac

Tuesday, July 13	
8:30am	<p>Novel Approaches to CO₂ Capture Alan Hatton, MIT <i>Electrochemically-Mediated Separations for CO₂ Capture</i></p>
9:00am	<p>Membranes and Ionic Liquids Session Eric Favre, University of Nancy (chair) <i>Membranes & Post Combustion Carbon Dioxide Capture: State of the Art & Challenges</i> Richard W. Baker, Membrane Technology and Research <i>Carbon Dioxide Separation & Sequestration from Flue Gas with Membranes</i> Richard W. Noble, University of Colorado <i>CO₂ Separations in Imidazolium-based Room-temperature Ionic Liquids & Polymers</i> David J. Heldebrant, Pacific Northwest National Laboratory <i>Characterization and Performance of Single-Component CO₂-Binding Organic Liquids (CO₂BOL) for Post Combustion CO₂ Capture</i> Ryan Lively, Georgia Institute of Technology <i>Hollow-Fiber-Based Adsorbent System for CO₂ Capture from Flue Gas</i></p>
11:45am	Break
12:00pm	<p>Wrap-up Discussion Jerry Meldon, Tufts University (moderator)</p>
1:30pm	Lunch
3:00pm	Meeting Adjourns

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