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Meeting report

Alternatives to amine-based capture & new technologies

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PRESENTATION

Ionic liquids as novel materials for energy efficient CO_2 separations

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Large improvements in separations technology will require novel materials with enhanced properties and performance. The fundamental interlinks for success in merging synthesis and process incorporation are the structure, relevant physical/chemical properties, and performance of new materials. Specific materials with these interlinks are room-temperature ionic liquids (RTILs) and their polymers and composites. As a chemical platform, RTILs have an enormous range of structural variation that can provide the ability to "tune" their properties and morphology for a given application. Introduction of chemical specificity into the structure of RTIL-based materials is an additional key component.

Membrane separation is the focus as a process for implementation. There have not been new materials successfully developed for this process in thirty years. For CO_2 capture, the target improvement in productivity is two orders of magnitude or more compared to commercial materials currently available.

PRESENTATION

Metal-organic frameworks and porous polymer networks for carbon capture

Julian Patrick Sculley, Jian-Rong Li, Jinhee Park, Weigang Lu, Hong-Cai Joe Zhou

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The ability to rationally design materials for specific applications and synthesize materials to these exact specifications at the molecular level makes it possible to make a huge impact in carbon dioxide capture applications. Recently, advanced porous materials, in particular metal-organic frameworks (MOFs) and porous polymer networks (PPNs) have shown tremendous potential for this and related applications because they have high adsorption selectivities and record breaking gas uptake capacities. By appending chemical functional groups to the surface of these materials it is possible to tune gas molecule specific interactions. The results presented herein are a summary of the fundamentals of synthesizing several MOF and PPN series through applying structure property relationships.

PRESENTATION

Introduction to market challenges in developing second generationcarbon capture materials

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Absent an economic or social cataclysm, there is no plausible way to meet what will be the world's unavoidable energy demands without utilizing its vast supply of fossil fuels. One important technology being contemplated to mitigate the negative impact of anthropogenic carbon dioxide loading of the atmosphere is Carbon Capture and Storage (CCS). CCS will play a vital role in least-cost efforts to limit global warming[1]. To achieve future least-cost solutions, second generation or '2.0' carbon capture materials are being developed with government support to improve efficiencies over the current applied solution that is "a very expensive proposition"[1] for the installed energy generation base. One 2.0 material, Metal Organic Frameworks (MOFs), is "capable of increasing (carbon dioxide) selectivity, improving energy efficiency, and reducing the costs of separation processes"[1] in CCS. Such materials can address CCS utilization outcomes in addition to lowering the carbon capture cost. To support further 2.0 carbon capture material development while CCS faces economic challenges, framergy™ is leveraging alternative usages for MOFs and other 2.0 materials developed for carbon capture.

PRESENTATION

CCS from industrial sources

Paul S. Fennell[1]*, Nick Florin[1], Tamaryn Napp[2], Thomas Hills[1,2].

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The literature concerning the application of CCS to industry is reviewed. Costs are presented for different sectors including "High Purity" (processes which inherently produce a high concentration of CO_2), Cement, Iron and Steel, Refinery and Biomass. The application of CCS to industry is a field which has had much less attention than its application to the electricity production sector. Costs range from less than $\$_{2011}$ 10/tCO_2 up to above $\$_{2011}$ 100/tCO_2. In the words of a synthesis report from the United Nations Industrial Development Organisation (Unido) "This area has so far not been the focus of discussions and therefore much attention needs to be paid to the application of CCS to industrial sources if the full potential of CCS is to be unlocked".

DISCUSSION

Editor's note. Ornstein gave his presentation slightly later in the program but, since it follows closely the work discussed by Zhou, it is included here.

This segment first covered three papers and presentations on carbon capture using techniques that could replace the well-established procedures of amine scrubbing. A motivation is that these alternative techniques, or their variants, will have to be considered commercially. **Ornstein** put this forcibly. He quotes Herzog[1]:

> *"Today, the only proven CCS capture technology is amine scrubbing. In some ways it works very well – it is highly selective for CO_2 and has recovery rates above 90%...It makes retro-fitting older, less efficient plants very difficult. For example, an existing plant with 35% efficiency when retrofitted with CCS will have its efficiency reduced to 20–25%. This is a very expensive proposition."*

Hanley, however, submitted this observation: **Zhou** and **Ornstein** have made the point that the energy penalty to regenerate MEA solutions could account for 35% of a power plant's energy output. An argument in favour of using an alternative is that this loss could be reduced. It would be fairer, however, if the efficiency of an amine alternative was assessed in comparison with that of many of the commercial amine solutions. (But, of course this latter information is usually confidential.) Along these lines, do the authors have any comments on how – with respect to energy consumption – their alternative capture techniques might compare with the traditional amines? **Ornstein** responded with the statement that the materials licensed from Dr. Zhou's group would have a significant energy

[1] http://sequestration.mit.edu/pdf/Research_Program_for_Promising_Retrofit_Technologies.pdf.

savings due to their lower regeneration heats, corresponding to a potential approximate 40% reduction in the parasitic energy.

Noble started the session with his presentation on ionic liquid solvents and membranes. **Hanley** raised the point that the possible environmental hazards of ionic liquids have been questioned, but **Noble** rebutted by stating that the chemicals he is discussing are not toxic and, furthermore, are safe enough to be ingredients in cosmetics.

Palmer asked what would be the physical size of the ionic liquid capture unit in a power plant and **Noble** responded: "the unit would be the same size as an amine scrubber for a liquid. For a membrane configuration, with the membranes stacked vertically, the volume would be in the order of a few thousand square meters." **Ornstein** added the cautionary comment that replacing solvent scrubbing with a membrane could be challenging commercially because of the volume of flue gas that would need to be processed.

Kira Schipper (*TNO*) asked how the ionic systems would react for flue gas with significant amounts of water vapour. **Noble** answered by stating that there is some vapour in the system (bound water), but water vapour does not affect the membrane which, for example which we have confirmed does not swell. In fact, a hydrophobic membranes can be formed specifically to remove any water present. **Moene** followed this up: "building on the previous point on water: from past experience we know amine and water react. Is this important in this case?" Noble replied that the chemistry/reaction conditions are different for his systems because the ionic liquid is a different solvent than water. Thus, the amine reactions do not follow the same stoichiometry and, in some cases, do not include water in the reaction mechanism.

In his talk **Noble** quoted that an approximate cost of CO_2 capture was $10/tn. **Fennell** picked up on this and asked if that estimate could be explained. **Noble** stated that the economic analysis was carried out by third parties and he could not give a precise answer. He did, however, note that a membrane only has a small ionic liquid content, which would keep the costs down. Following up on the membrane format, **Fennell** asked how many cycles do the membranes last. **Noble** answered that he had not explicitly tested for this but he has yet to see any effect of membrane degradation.

Maitland speculated what would happen if you added the ionic liquid/amine phase to the polymer membrane, instead of only the ionic liquid. **Noble** acknowledged this was a good point and his group was looking into it; he would expect improved performance.

After the technical presentations of **Noble** and **Zhou**, the audience was interested in the presentation of **Ornstein** who discussed the promotion of alternative capture technologies, particularly that of his colleague, Dr. Zhou. Unfortunately, as is often the case with discussions on problems of industrial concern, we cannot give a published summary of the questions and answers because much of the material is privileged.

There was, however, a lively debate following **Ornstein's** remarks on projected storage difficulties. He offered the opinion that the Carbon Capture Storage picture might have changed. Accordingly:

> *"Without a storage option, the concept of 'utilization' for captured carbon dioxide from CCS has gained popularity. Several key organizations have relabeled CCS by adding "utilization" to the acronym, thus CCUS, or sometimes – as in the UK – even removing the word storage altogether, thus CCU."*

That utilization rather than storage might be a path to follow lead to the following comment from **Fennell**:

> *"If the UK is actually diverting into carbon capture and utilisation (CCU), I disavow my countrymen. Carbon dioxide utilisation is a dangerous distraction from CCS. Roughly 30Gtn of* CO_2 *are emitted per year worldwide. The total utilisation of* CO_2*, excluding EOR is of the order of 100 Mtn/year—orders of magnitude less. Moreover, most processes capturing* CO_2 *(particularly urea production, at 65–146 Mtn/ year, release the* CO_2 *immediately after production). The other main processes of methanol, polyurethanes, technological and food and drink production, use around 10 Mt/yr each. Utilisation is nothing compared to total* CO_2 *emissions and it is nonsense to suggest that they are part of the solution to global warming."*

Ornstein countered:

> *"I am not saying that there is a policy towards CCU in the UK at the moment, but certainly it's something that's been looked at. It may not be a permanent solution, or solution on its own, but certainly a step change towards a more broad approach. In addition, this approach may help to mobilise capital in this area towards CCS."*

Fennell submitted this response:

> *"I was an expert reviewer for the CCU report produced by the centre for low carbon futures in the UK, to which I presume you refer. There were many aspects which I found highly troubling—many changes suggested were not made (this is reflected in the introduction). You have suggested that mobilisation of capital into the area of CCS may be predicated in the US on CCU applications. Again, this is potentially a worrisome area because if technologies have a niche CCU application, sub-optimal technologies for full-chain CCS may be developed and promoted. At the end of the day, CCU will do almost nothing for climate change, owing to the tiny amounts of* CO_2 *used."*

"From a private capital perspective, pointing out to governments that CCU could be a good investment is important for moving things forward financially," replied **Ornstein.**

Contributing to this debate, **Zhou** made the observation that storage, in contrast to CCU, is going to be very difficult to push forward without any accepted national and international policy: a problem that has been alluded to by previous speakers and will be taken up again.

Part of **Fennell's** lecture followed up the comments made on the first day in that he reminded the attendees that carbon capture issues are not only fossil fuel related—which tends to be the public's perception. He discussed, for example, the significant amount of carbon produced by cement production and the iron and steel industry with possible ways to reduce and/or capture it. The technique of Calcium Looping was promoted as a realistic viable procedure.

Hanley submitted a comment and question. Shown is **Fennel's** slide (Fig. 1) indicating a possible interaction between cement processing and the production of electricity. The observation is consistent with a theme discussed at the onset of the Workshop: namely, that the necessary carbon emission reduction will be impossible unless there are substantial improvements in energy efficiency, together with process integration. He asked **Fennell** if this potential linkage in the cement production process is being researched, or was even at a proof-of-concept stage.

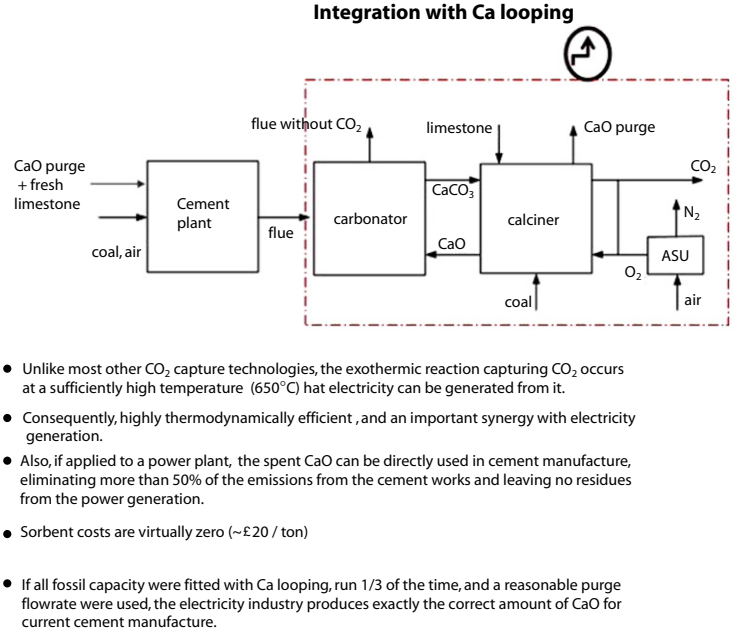

Figure 1. Integration with Ca looping.

Fennell replied that there is indeed some research ongoing around the world into this synergy [1–3], with research at Imperial College [4] being the first to demonstrate experimentally that the spent material from the calcium looping technology described is actually suitable for use in cement manufacture. This was done by demonstrating that the cement produced has similar properties to that produced from fresh limestone. The research is supported by Cemex, the world's third largest cement manufacturer. Indeed, Alstom and Heidelberg Cement [5] have also recently announced that they will trial the technology, with a view to potential scale-up.

NOTES

All presentations and related materials referred to in this article are available as 'Supplementary Material' online at http://www.qscience.com/toc/stsp//CCS+Workshop.

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