Conference report

Dr Thomas Hills, Imperial College London

On 18th July 2016, around 60 people descended upon Endcliffe Student Village in Sheffield, UK, for a three-day Faraday Discussion about Carbon Capture and Storage. Faraday Discussions have existed for many years and have a distinctive format. Attendees are asked to read the papers in advance, and papers are presented in groups of three or four for five minutes each. A discussion on each paper of at least ten minutes followed, and then a general discussion across all those papers was conducted for at least half an hour. The reason for this format is that the meeting acts as a form of peer review for the papers, so extensive time for questioning and discussion is necessary.

This meeting, in collaboration with the Institution of Chemical Engineers (IChemE) focussed upon Carbon Capture and Storage (CCS). That said, there were no papers on CO_2 transport, only one paper on CO_2 storage and one on CO_2 utilisation compared with twenty-one for CO_2 capture. The papers covered a wide range of topics, from experimental techniques and results to thermodynamic modelling and life-cycle analysis.

The meeting commenced with an opening speech from Professor Berend Smit (University of California, Berkeley) who framed the meeting by explaining why CCS is required, and how it has progressed over the last few years. He summarised some of the themes of the meeting, and explained how each presentation would fit into the topic. He highlighted that the bottlenecks for CCS are the high cost of capture and the lack of public acceptance for CO_2 storage. However, CCS used as a negative emissions technology will probably be required to offset emissions from existing infrastructure.

The first session was entitled "CCS: a technology for now" and contained six papers split into two groups of three. The first group was started by Professor Jon Gibbins (UK CCS Research Centre) who discussed the costs of CCS in the electricity generation industry and how they could be lowered; building *n*th of a kind (NOAK) plants is likely to be cheaper than first of a kind (FOAK) plants due to the reduction of risk (and therefore cheaper financing) as well as reductions in capital cost. He emphasised the need to work on a 'commercial readiness' scale as well as the traditional 'technology readiness' scale in order to understand the barriers to wide-scale adoption of CCS. He was followed by Professor Gary Rochelle of the University of Texas at Austin, USA, who showed the results of an advanced flash stripper system using piperazine as the amine solvent. The system uses a two-stage flash and can save 25% of the heat duty of the system simply by rearranging the process with little extra capital-intensive equipment required. Exergy analysis showed that the process is now approximately 50% thermodynamically efficient. The session's presentations were rounded off by Daniel Sutter from ETH Zurich, Switzerland, who showed a process innovation for the chilled ammonia capture process. An issue with most chilled amine systems is the crystallisation of ammonium bicarbonate on equipment including the CO_2 absorption column. He proposed the control

of the crystallisation by including a crystalliser in the process where the solids could be removed. This would allow for better conditions in the rest of the process, reducing specific primary energy consumption for CO_2 avoided) by 17%. The group discussions touched on several topics, including load factors of CCS plants which run to balance grids with large penetrations of intermittent renewables, and the opinion that CCS R&D is not time-constrained because there is little demand for the processes.

The second part of Session 1 started with a presentation by Felix Donat who presented work by his colleagues at ETH Zurich, Switzerland. In this work, the authors had produced sorbents for the calcium looping process. Calcium looping typically involves two fluidised beds. CaO reacts reversibly with CO_2 in the carbonator, and the reaction is reversed in the calciner where a stream of concentrated CO_2 is released. The CaO sorbent must be porous in order to allow fast and relatively complete carbonation, and one way to make such a sorbent is to use a sacrificial template. Pure CaO sorbents, as well as CaO supported on several metal oxides, were produced using a carbon gel which was then burned off in a furnace. This method produced very porous sorbents, and the CaO sorbents stabilised with yttrium and alumina were the most promising. María Erans from Cranfield University, UK produced CaO sorbents using calcium aluminate cement as a support and wheat flour as the sacrificial template instead. She and her co-workers studied the effect of SO_2 and steam on the performance of the sorbent. SO_2 reacts with CaO to form calcium sulphate, which does not decompose under calcium looping conditions. Steam, on the other hand, plays an important role in increasing the rate of carbonation. These materials out-performed plain limestone sorbent in thermogravimetric analysis (TGA) but the templated sorbents suffered from severe attrition in the bubbling fluidised bed (BFB) tests, questioning their suitability. Those bound with calcium aluminate performed better in the BFB, but under TGA conditions captured less CO_2 per unit mass of sorbent due to the inert cement. Results like this highlight the importance of using a range of tests to characterise capture materials, and in fact discussions about the materials made via sacrificial templating in Zurich revealed that they are not suitable for use in fluidised or bubbling beds due to their fragility. The final presentation of the session was from Liya Zheng of Imperial College London, UK. She showed results of her tests of cement made under oxy-fuel conditions. This is another capture technology which involves combusting fuel in a CO_2/O_2 atmosphere, reducing the complexity of gas separation later on due to the low N_2 concentration. The proposal is to change all of the gas streams at a cement plant to oxy-fuel streams, thus changing the properties of gas and potentially the product which formed when in contact with these gases. Her tests showed that there is little difference between cements made in traditional conditions and in oxy-fuel conditions, which suggests that there should be no problem with the products coming from an oxy-fuel plant. There was also discussion about the cost of applying CCS to cement plants per unit product, and whether there will be isolated sources of waste O_2 which could be used by cement plants.

After this session there was a drinks reception and time to view the posters. They covered a range of topics and the prize for best poster was given to Yoan Delavoux, Queen's University Belfast, UK.

The second session, held on Tuesday morning, was entitled "CCS: A technology for the future" and like the first session was broken into two groups. Lisa Joss from ETH Zurich, Switzerland (now at Imperial College London) started this session with a presentation of the results of modelling the performance of five metal-organic frameworks (MOFs) in a temperature swing adsorption (TSA) process. MOFs are promising capture materials and these new versions are significantly better than the existing commercial MOF 'zeolite 13X' because they require a smaller temperature swing to effect capture and release. Nevertheless, MOFs still require significant research to determine how to produce them on a large scale and to discover versions which have lower energy penalties than competing technologies such as amine scrubbing. The discussion highlighted how *in silico* testing of MOFs can help us determine the limitations of this material type when it comes to performance in carbon capture processes. MOFs also degrade, something that was studied in the paper presented by Professor Stefano Brandani of the University of Edinburgh, UK. He showed the results of tests performed upon MOFs in the zero-length column (ZLC) in the presence of water and humid flue gas containing SO_2. This work is important because completely drying the flue gas coming from a power station is likely to be costly and energy-intensive. The MOFs degraded on contact with flue gas containing water, with Mg-CPO-27 completely deactivating. Longer tests on Ni-CPO-27 showed that, although there was some loss in performance over the first few cycles, the capture capacity then stabilised. Unfortunately a paper by Li, Liang & Cai from Tsinghua University, China was not presented but questions were welcomed. A rate equation theory to describe vacancy production and their coagulation into pores was developed and integrated into a shrinking core model. They compared their model to experimental results and found good agreement. This understanding of how materials act can then be integrated into process simulations and experiments. The next paper, presented by Dr Matthew Dunstan of the University of Cambridge, UK, also looked at the behaviour of CaO sorbents but concentrated on experimental observations rather than modelling. The paper described the use of in-situ x-ray tomography, x-ray and neutron diffraction and pair distribution function analysis to watch the surface reactions happening during carbonation and calcination of CaO sorbents. The effect of steam, whose exact mechanism is not understood, was also explored. It appears $Ca(OH)_2$ forms outside of its thermodynamically stable region, something which perhaps poses more questions than it answers.

After morning tea Dr Niall Mac Dowell (Imperial College London, UK) discussed the improvement of energy efficiency at carbon-negative biomass-to-energy CCS (BECCS) plants. He noted that less efficient capture plants can lead to more carbon negative electricity per MWh produced. Therefore in a system where sequestration of CO_2 rather than electricity is the main product, using t CO_2/MW_e as the metric, which is used across most electricity generation technologies, can lead to perverse results. He also highlighted how the moisture content of biomass is also influential in determining the efficiency of the plant; condensing this and harnessing the medium-grade energy for district heating or other processes could reduce overall exergy destruction. Dr Rahul Anantharaman (SINTEF Energy Research, Norway) presented work on the potential of

membranes for CO_2 separation. Dual-sweep systems are not as energy efficient as amine scrubbing systems for post-combustion capture systems, but for pre-combustion capture systems, where CO_2 is separated from H_2, they may be more promising. Part of the benefit is the higher pressures that pre-combustion capture systems run at. Next, Joshuah Stolaroff (Lawrence Livermore National Laboratory, USA) discussed his paper on microencapsulated ionic liquids (ILs). Ionic liquids are salts which are liquid at room temperature. They are not volatile, and the anions and cations can be tuned to provide different properties. The paper explained how encapsulating the ILs can improve the surface area through which CO_2 can be absorbed compared with conventional scrubbing processes in liquid films. The concept is compelling but there are still challenges, such as improving the rate of CO_2 absorption, to overcome. The final presentation was that of Dr Rosa Cuellar-Franca (University of Manchester, UK) who has performed lifecycle analyses on ILs. The synthesis of ILs for CO_2 capture has not been scaled up but this paper showed how the life cycle impacts of ILs can be predicted and LCA can be incorporated into IL design. The example IL showed that the life cycle impacts are worse for most metrics. This is important and should be taken into account; Gary Rochelle suggested including the effectiveness of the IL and therefore the environmental benefit of its use as well.

After lunch, the third session, "Modelling: Molecules to mega-scale" commenced with a presentation by Professor George Jackson (Imperial College London, UK) which described an approach to modelling CO_2 capture by amines. It involved the SAFT-VR (Statistical Associating Fluid Theory-Variable Range) model, which is a molecular equation of state. An absorber model was optimised using a diffusivity correcting factor, τ, which allowed for the SAFT-VR model to produce accurate temperature and composition profiles across the entire unit. Richard Graham (University of Nottingham, UK) also presented work based upon molecular simulations, but which concentrated on the effect of impurities on the behaviour of CO_2. This is of interest not only to CO_2 capture experts, but also those involved in transport and storage. Two different methods for acquiring the force-fields were presented: using semi-empirical method, and an *ab initio* one using quantum-chemical calculations. The latter method is yet to be fully-developed but could provide first-principles simulations of carbon capture processes. Lennart Joos (Ghent University, Belgium) presented a rather different model. This one relaxed the constraints of the quality of the CO_2 and looked at how this would affect the energy requirements of capture. This is of note for CO_2 users who do not need it to be delivered to the exacting standards of that normally specified. Joos and co-workers found that over half of the parasitic energy use of CCS is caused by compressing the CO_2 from 1 to 150 bara. If the purity requirement can be reduced and the CO_2 used at 1 bara, the parasitic energy requirement of capture via adsorbents can be reduced by almost 60%. As with other papers in this conference, this one highlights how widely-held assumptions about the CCS chain influence the final result.

Following afternoon tea Professor Rafaella Ocone (Heriot-Watt University, UK) presented her techno-economic investigation of chemical looping combustion (CLC) at a gas-fired power station. Chemical looping combustion is a form of oxy-fuel combustion that involves using metal 'oxygen carriers' in various oxidation states to carry oxygen

from an air reactor to a fuel reactor rather than injecting oxygen as a gas. Thus, fuel can be burned without the use of air and a more concentrated CO_2 stream is produced. Prof Ocone and her co-workers investigated the levelised cost of electricity (LCOE) when using a nickel oxygen carrier. To bring CLC to an LCOE similar to amine scrubbing with monoethanolamine (MEA), the oxygen carrier's lifetime would have to be 4000 hours, which is impractical for the particles which attrit over time. Next, Yue Zhang (University of Texas at Austin, USA) presented a hybrid membrane-amine capture system which should reduce capital costs by increasing the concentration of CO_2 in the flue gas before absorption. The direct contact cooler used in absorbers does not seem to be necessary in this set-up, and can be replaced with pump-around cooling; this saves even more capital. If these systems are to be built in fleets across the world, studies like this can avoid the spending of unnecessary millions of dollars each time, adding up to huge amounts of money. The final presentation of this session, by Robert Bell (University College London, UK) discussed computational approaches to investigating the mechanism of CO_2 capture in ionic liquids to try and aid the design of better ILs. The studies showed feasible mechanisms for carbamate formation using only one ionic liquid molecule. It also discussed the benefits and drawbacks of strong binding of between the IL and CO_2.

The conference dinner was held in The Edge in the student village on Tuesday evening. As well as good food and great company Eleanor Campbell, the President of the Faraday Division, introduced the Faraday Discussion's Loving Cup, a 300-year-old silver two-handled cup which is the centre of an ancient Anglo-Saxon tradition. Loving cups are a shared drinking vessel, and the ritual involves passing the cup from one to each other with a bow, reciting a memorial to three distinguished late members of the RSC and taking a sip of the port wine inside. The loving cup ceremony is thought to go back to the aftermath of the killing of King Edward the Martyr in 978. Nowadays, however, having a friend draw a sword to defend you from murder whilst drinking from the cup with two hands is generally omitted.

The final half-day contained three presentations in the session "End use and disposal of CO_2 – storage or utilisation?" and started with a presentation by Professor Peter Styring (University of Sheffield, UK) on solid ionic liquids (SoILs). Prof Styring and his co-workers have modelled several SoILs based on an acetate anion which capture CO_2 through physisorption in a pressure swing adsorption (PSA) system. The rate of capture was fast, and if this can be scaled up then far less of the SoIL would be required compared with ILs that are liquid at room temperature. This was followed by Ross Hubble (University of Cambridge, UK) who presented work on the methanation of CO_2 over a nickel-alumina catalyst in a packed bed reactor. The kinetics of the reaction seem to be rate-limited by the dissociation of CO_2 to CO and O on the catalyst. The final presentation was given by Professor Martin Trusler (Imperial College London, UK) whose paper looked at the dissolution of carbonate minerals in CO_2-acidified brines. This is important for CO_2 storage because the dissolution affects the resistance to diffusion and flow of CO_2 within saline aquifers. The results show that salinity does not affect the reactivity of pure calcite much, and calcite-rich carbonates tend to react at a similar rate. Dolomite (i.e. calcium magnesium carbonate) and magnesium carbonate

dissolve much more slowly and the rate is determined by pH. The experimental results are similar to the calculated values.

Closing remarks were given by Professor Geoffrey Maitland (Imperial College London, UK) who noted the focus on carbon capture rather than storage in this Faraday Discussion. He also mentioned that ionic liquids, which have been like fusion power in not seeming to progress despite much research, are finally getting closer to commercialisation. One benefit of ILs is that they can be designed, something that turned into a theme in this meeting that encompassed several different capture technologies: Professor Maitland suggested that this could be described as Materials-Process Integrated Design. He mentioned that there was little work presented outside of carbon capture on electricity generation; only one paper looked at BECCS and only one on capture at an industrial facility specifically, despite the need for progress, especially in the former, after COP 21 in Paris last year.

Prof Maitland also commented on the fact that several benchmarks remain the ones to beat: amine scrubbing is still efficient and getting more so due to the innovations shown in the meeting. Furthermore, although several new solid sorbents for calcium looping were presented they seemed to have issues that mean that limestone is still likely to be the sorbent of choice. However, this does not mean that we should not try to beat these technologies – there is always room for improvement! An example of how technologies can end up playing an important role is membranes for CO_2 concentration. Although they are not efficient enough for use on their own, using them alongside other technologies to intensify the overall process is a promising approach. Professor Maitland summarised the majority of papers presented at the meeting and then, to try and balance the meeting, concluded by showing some new simulations of CO_2 storage developed at Imperial College London.

I knew before the conference that I would be writing this review and, since it was my first time at a Faraday Discussion, decided to ask several other attendees about their views on the format. The general consensus was that the space for more discussion compared with a normal conference was very welcome. Not everyone had read all of the papers but most had read the ones which interested them. Although some of the discussions were dominated by a few delegates, no one felt that their views or opinions were not heard or were discarded. The intimate and personal nature of the meeting was compared favourably with some of the larger conferences where delegates can spend most of their time dashing between rooms, or even between venues! The general feeling was that the format should be more widely adopted.