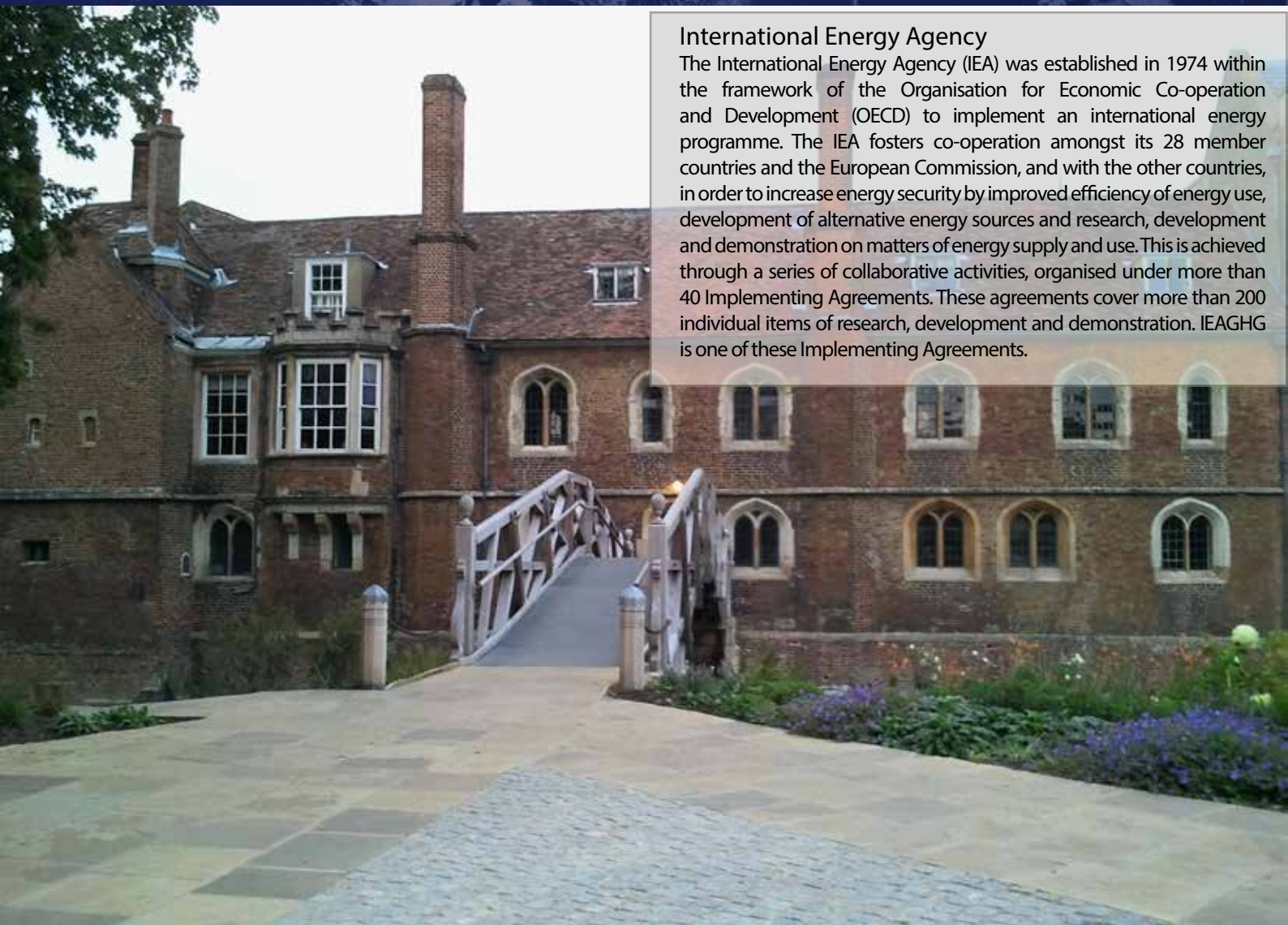




5th IEA High
Temperature Solid
Looping Cycles
Network Meeting





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IEAGHG supports and operates a number of international research networks. This report presents the results of a workshop held by one of these international research networks. The report was prepared by IEAGHG as a record of the events of that workshop.

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Front & back cover images: Walnut Tree Court with the College Chapel; Conference facilities at Cripps Court, Queens' College; Queens' Great Gate; River Cam;
Inside cover: The famous Mathematical Bridge, connecting the older and the newer half of Queens' College

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The President's Lodge at Cloister Court (the oldest buildings on the river, ca. 1460) / Delegates at the dinner in the Old Hall of Queens' College



Introduction

The IEAGHG High Temperature Solid Looping Cycles Network (HTSLCN) emerged from the preceding International Workshop on In-situ CO₂ Removal (ISCR) and aims at bringing together researchers and developers of CO₂ capture technologies that operate at high temperatures in cyclic processes using either circulating or fixed beds of solids.

The 5th HTSLCN Meeting was held from 2nd to 3rd September 2013 at Queens' College, University of Cambridge, UK. It was jointly organised by IEAGHG, University of Cambridge and Cranfield University and received support from the UKCCS Research Centre and Johnson Matthey. A number of 60 delegates attended the meeting, which offered 36 presentations organised in three sessions. The first session covered demonstrations and pilot scale trials. The second session was split in two parallel streams that discussed the fundamentals in calcium looping (CaL) and chemical looping combustion (CLC) respectively. The third session presented new process concepts and system modelling and evaluation. A subsequent panel discussion and a site visit to the facilities at Cranfield University rounded off the technical programme.

Thanks to the sponsorship by Johnson Matthey, the Scientific Committee had the ability to give away two awards for the best presentations to Markus Junk (Technische Universität Darmstadt) and Vincenzo Spallina (Eindhoven University of Technology).

The following report summarises some but not all of the presentations from the meeting.

The members of the Scientific Committee for this meeting are:

- Juan Carlos Abanades, CSIC-INCAR, Spain
- Edward J. Anthony, Cranfield University, UK
- Ningsheng Cai, Tsinghua University, China
- Paul Cobden, ECN, The Netherlands
- Bernd Epple, Technische Universität Darmstadt, Germany
- Adolfo Garza, Cemex, USA
- Jasmin Kemper, IEAGHG, UK
- Anders Lyngfelt, Chalmers University of Technology, Sweden
- Tobias Pröll, University of Natural Resources Vienna, Austria
- Andrés Sanchez, ENDESA, Spain
- Stuart Scott, University of Cambridge, UK



Welcome Address – John Dennis, University of Cambridge

John Dennis welcomed the delegates and provided a brief introduction to solid looping technologies and their current status. He then gave an overview of the upcoming programme and opened the technical part of the meeting by handing over to the chairs of the first session.

Session 1: Demonstrations, Systems and Pilot Trials

Chair: Paul Fennell, Imperial College London, and Bernd Epple, Technische Universität Darmstadt

Post-combustion capture with CaO: experimental results from the 1 MWth pilot facility of La Pereda – Carlos Abanades, CSIC-INCAR

A flexible experimental facility to validate the concept of continuous post-combustion CO₂ capture (PCC) CaL technology is in operation in “La Pereda”. The pilot plant consists of two interconnected circulating fluidised bed (CFB) reactors at 1.7 MWth scale and has more than 1800 h of operation in coal combustion mode, including more than 400 h in CO₂ capture mode. With standard CaO solids and operating conditions the pilot plant achieved CO₂ capture rates between 80-90% and SO₂ capture rates of over 95%. The good performance depends on the use of low-ash coal for combustion; however, natural limestones are sufficient for these coal-based systems. In addition, a high carbonate inventory (~1000 kg of limestone in the loop) is key to maintaining the high CO₂ capture rate despite sulphation. The successful operation of the pilot plant under a large range of conditions has proven the concept.

Continuous carbonate looping tests in a 1 MWth pilot plant – Bernd Epple, Technische Universität Darmstadt

The 1 MWth CaL pilot plant at TU Darmstadt, which is part of the COORETEC project, was commissioned in 2010. It has more than 2000 h of operation in coupled CFB mode under hot conditions and more than 300 h of operation in CO₂ capture mode. The pilot plant runs on a synthetic flue gas, consisting of CO₂ and air, with a calciner that is either propane- or coal-fired. The CaL plant will cause a ~6% drop in efficiency, including compression, while capturing ~87% of the CO₂ for a 1052 MWel power plant. The first estimate for the CO₂ avoidance cost is ~20 €/tCO₂. The campaigns undertaken in the pilot plant show stable operation is possible and that there is a strong dependence of CO₂ absorption in the carbonator on temperature. Further work includes optimisation of the operating conditions and investigation of process improvements.

Progress in calcium looping post combustion CO₂ capture: process investigations at 200 kWth pilot scale – Heiko Dieter, University of Stuttgart

The 200 kWth CaL pilot plant at IFK in Stuttgart is a highly flexible facility enabling process demonstration and characterization with realistic process conditions. The pilot plant is able to operate in two different carbonator set-ups: turbulent or CFB. The CFB set-up allows for high carbonator velocities, high flue gas throughput and high gas-solid contact, whereas the turbulent set-up allows for variable carbonator velocities and flue gas throughput, while still providing sufficient gas-solid contact and carbonator capture rates above 90%. The pilot plant completed over 800 h of operation with high hydrodynamics stability, stable sorbent circulation and high flexibility as it operated over a wide range of temperatures and looping rates. The sorbent calciner was operated with oxyfuel combustion of coal using hot recycled CO₂ enriched with oxygen up to a concentration of 50%. It could be demonstrated that humidity of the flue gas has a significant effect on the CO₂ capture efficiency, and so opens potential for further optimisation of process efficiency. Capture efficiencies of more than 90% are achievable for realistic flue gas containing 15% water vapour at temperatures below 640°C. Sorbent loss due to attrition was observed to be low and sulphur did not cause a significant decrease in capture or process efficiency.

CO₂ capture experiments from CanmetENERGY pilot-scale dual fluidised bed system – Dennis Lu and Scott Champagne, CanmetENERGY

CanmetENERGY's 100 kW dual fluidised bed pilot facility in Ottawa has more than 400 h of operating experience. Testing campaigns proved that more than 90% CO₂ capture efficiency can be achieved over a wide range of sorbent types and operating conditions. The experiments also showed that carbonation with steam enhances sorbent intake performance and helps with predicting behaviour under realistic wet flue gas conditions. Main issues of the process are sorbent attrition and elutriation but optimising sorbent make-up can help managing this. Biomass might be an ideal fuel in oxyfuel combustion mode, due to its low sulphur, low ash and high moisture content. Comparison of the results with a simple reactor model developed by Alonso et al. shows a good fit. Next steps will be investigating real combustion flue gas, process optimisation and integration of CaL in CO₂ capture, gasification and H₂ production.

Fluidised bed calcium looping: the effect of oxy-firing calcination conditions and SO₂ concentration on sorbent CO₂ capture capacity and attrition – Antonio Coppola, CNR

One of the main issues in CaL technology is the decay of CO₂ capture capacity of the sorbent due to sintering and/or presence of SO₂. It is the aim of the Cal-Mod project to model and experimentally validate the CaL CO₂ capture process for application in power plants. This includes a comparison of different sorbents under realistic conditions, i.e. presence of SO₂ under oxyfiring conditions. The experiments consisted of five calcination/carbonation cycles with different SO₂ concentrations (0/0 ppm, 750/75 ppm, 1500/1500 ppm). Dolomite showed a better CO₂ capture performance than the limestones investigated but also had higher attrition rates. Presence of SO₂ generally slightly reduced the extent of fragmentation.

Operation of a 100 kW chemical looping combustor for solid fuels – Anders Lyngfelt, Chalmers University of Technology

Chalmers' 100 kW CLC pilot plant was designed and built in the ECLAIR project and has been in operation for more than 66 h in stable conditions. The system is flexible and allows for variation of a number of parameters. Operational difficulties encountered during the tests were mostly related to external equipment, e.g. steam generator. CO₂ capture rate during the experiments was very high with 98% and gas conversion was up to 84% with bituminous coal and 94% with biochar. In this regard, the solids inventory in the fuel reactor strongly influences the gas conversion rate. The use of pulverised coal showed a large loss of unconverted char of ~40% and a high loss of ilmenite of more than 2%/h. However, this will not be relevant for large-scale plants because of different equipment, such as higher riser, better/additional cyclone and fines recycling. Generally, the test showed that CLC with solid fuels works and that ilmenite is deployable, low cost oxygen carrier. Next steps are now scale-up, optimisation and determination of which process designs would lead to cost reduction.

Pilot plant testing of Fe- and Mn-based oxygen carriers for chemical looping combustion – Karl Mayer, Vienna University of Technology

TUV operates a 120 kW test rig with natural gas as design fuel. The experiments included three different oxygen carriers, one Fe-based and two Mn-based CLOU (chemical looping with oxygen uncoupling) carriers. Total operation time of each carrier was at least 30 h. During the tests, the Fe-based carrier showed high losses at the beginning and a high solids circulation rate was required. The CLOU carriers showed attrition during either the beginning or over the whole time of the test but with these carriers full conversion was possible. In general, temperature has a large influence on the performance of all carriers, e.g. for the Fe-based carrier methane conversion, CO₂ yield and combustion efficiency increase up to a temperature up to 960°C.

Demonstration of packed bed CLC of syngas using ilmenite as oxygen carrier – Maria Ortiz Navarro, Eindhoven University of Technology

Packed bed reactors offer the advantage that they do not require transport of the solid and gas or particle separation, so they are the preferred option for high pressure operation. This work provides the first lab scale demonstration of packed bed CLC using ilmenite. It is important that the oxygen carrier is able to bear a high mechanical, thermal and chemical stress. The results show a delayed breakthrough of CO, so operation without fuel slip is possible. The experiments also reveal that a higher pressure increases the degree of reduction and the reaction rate. In addition, a numerical 1D model was developed that provides a good description of the H₂ breakthrough and the temperature profiles of the oxidation.

Two-stage CLC: a novel reactor configuration for packed bed CLC with syngas – Paul Hamers, Eindhoven University of Technology

The two-stage CLC process has the benefit of smaller temperature changes per reactor (T_{\max} 400°C). At the same time, the active weight content is lower and the melting point of the oxygen carrier is less an issue, so the process allows for a combination of different oxygen carriers. The main criteria for the selection of the carrier are that the first carrier has a high reactivity at the low temperature (e.g. Cu) and the second carrier is stable at the high temperature (e.g. Mn). This concept was demonstrated theoretically by a 1D packed bed reactor model. Criteria for operation of a two-stage CLC process are a pressure drop less than 5%, prevention of fuel slip and similar cycle times for oxidation and reduction. The simulation results show that the temperature changes at the outlet of the bed are less intense than for a standard process layout and the temperature of CO₂ and H₂O is higher. According to the energy balance, the airflow sent to the gas turbine is only 4% less. Next steps are the experimental demonstration of the process and the detailed comparison of the electrical efficiency with the single-stage process.

Session 2a: Chemical Looping Fundamentals

Chair: Anders Lyngfelt, Chalmers University of Technology, and Tobias Pröll, University of Natural Resources Vienna

Enhancement of gasification by chemical looping – Marco Saucedo, University of Cambridge

CLC with solid fuels usually involves initial gasification of the solid char, which is the rate-limiting step. Thus, it is important to investigate if and how the oxygen carrier affects the rate of gasification. Batch experiments were carried out in a quartz reactor to compare the gasification rate of lignite coal when using iron oxide carrier particles or inert sand. The gasification rates in presence of iron oxide carrier and sand both show a temperature dependence. At low temperatures, i.e. 800°C, the external mass transfer is negligible and the iron oxide carrier has only a small effect on the gasification rate. At higher temperatures, i.e. 850°C and 900°C, the rates become higher because the presence of the iron oxide carrier seems to eliminate the external mass transfer resistance. In addition, the gasification rate generally increases up to carbon conversions of 20%, where it has a maximum. This effect is even more distinct at higher temperatures. A numerical model was developed that shows excellent agreement between the predicted and the experimentally obtained gasification rates.

Chemical looping combustion of coal for CO₂ capture: process simulation and optimisation using Aspen Plus – Sanjay Mukherjee, University of Surrey

The aim of this work was to develop and optimise industrial scale flow sheet models of IGCC power plants with a CLC process and compare it with conventional CO₂ capture technologies, in this case Selexol and PSA, both for electricity and combined electricity and H₂ production. Selexol and PSA cases have net electrical efficiencies of 36.4% and 37.8%, compared to 42.5% for the base case, and CO₂ capture efficiency of 93.5% and 89.9%, respectively. The CLC case has a net electrical efficiency of 37.2% and CO₂ capture efficiencies of 100%, which clearly indicates the suitability of CLC for CO₂ capture in IGCC power plants. For CLC cases the net electrical efficiency increases by up to 3.03%, when N₂ from the air separation unit (ASU) is used in the air reactor. A sensitivity analysis performed on the CLC process shows that it is favourable to operate the air reactor at higher temperatures and to cool the air reactor by using excess air supply instead of water/steam for more power output. Future work will include the development of a kinetics-based model and a system level cost analysis.

Chemical looping combustion research at the University of Utah – JoAnn Lighty and Kevin Whitty, University of Utah

Current research at the University of Utah is addressing several issues related to the Cu-based CLOU process, including optimisation of the oxygen carrier, energy utilisation and design and operation of a 100-200 kWth process development unit (PDU). The approach covers lab scale experiments, such as oxygen carrier characterization and measurement of carrier oxidation and reduction kinetics, as well as process modelling with Aspen Plus. Analysis of CLOU combustion of Mexican petcoke was used to investigate the comparison of CLOU with CLC. Aspen Plus models for each process have been developed to envision material and energy balance scenarios for the PDU and ultimately larger-scale systems.

For a system feeding 100 kg/hr coal, the CLOU system (with fuel reactor at 950°C and air reactor at 935°C) generated approximately 510 kW of electric power, including 5 kW of compressor/pump work. Due to the volume of oxygen carrier needed, the CLC unit has a higher pressure drop, yielding less energy. The next steps are construction and analysis of a cold-flow unit and use of a commercial computational fluid dynamics (CFD) code for scale-up.

Development of promoted ilmenite for high temperature CLC and CuO oxygen carrier for low temperature CLC and continuous 100 h tests in dual fluidised beds – Hongmin Sun, Tsinghua University

Key requirements for oxygen carriers in direct solid fuel CLC are a high reducing reactivity and a low cost. The main issue with ilmenite for high temperature CLC is its low reactivity, which leads to incomplete gas conversion and a large bed inventory. One way to improve the reactivity is the impregnation with foreign ions, such as K⁺, Na⁺ or Ca₂⁺. Results from thermogravimetric analysis (TGA) experiments show that the reactivity of promoted ilmenite increases over 40 cycles and that this increase is more distinct than for raw ilmenite. K15-ilmenite (i.e. ilmenite promoted with 15% K⁺) is the best option, as its reactivity is 7 times faster than that of raw ilmenite. In addition, K15-ilmenite demonstrates stability over 100 cycles in a fluidised bed reactor, showing almost no attrition (below 1%) or agglomeration. For low temperature CLC, cement supported CuO shows good stability of reactivity over 20 cycles in TGA experiments and no agglomeration in fluidised bed tests. Attrition was 11.2% loss of the initial mass after 100 cycles. In general, the continuous operation tests demonstrated the feasibility of both carriers for CLC. Future work will include scale-up of the reactor to 50 kW and extended continuous tests with biomass and lignite

Reducing properties of model bio-oil compound acetic acid on NiO catalyst during chemical looping reforming – Feng Cheng, University of Leeds

Chemical looping reforming (CLR) can produce a highly pure H₂ stream. A benefit of the process is the avoidance of complex heat exchange because the coupling of endothermic and exothermic reactions leads to a low external heat demand. Challenges for CLR are the commercial scale-up, the availability of high performing and stable oxygen carriers with suitable reduction reactivity and catalytic properties for the reforming step. As most existing investigations focus on CH₄ as a fuel, this work wants to study the reducing properties of acetic acid (HAc) on NiO, which is the most suitable carrier/catalyst for CLR. In the experiments, NiO could be completely reduced by HAc in 360s at 650°C, with 550°C being the lowest temperature for reduction to proceed smoothly. Compared with a catalyst reduced by H₂, the catalyst auto-reduced by HAc exhibited a slightly decreased catalytic activity during the subsequent steam reforming. Possible reasons for this behaviour are denser carbon deposits and a larger Ni loss. The next step will be the investigation of the cyclic behaviour of the catalyst in alternating fuel and air feeds.

Bubbling fuel reactor modelling in in-situ gasification chemical looping combustion (iG-CLC) using CFD – Panneerselvam Ranganathan, Cranfield University

Multiphase CFD simulation is suitable a tool to develop validated computational models that describe physical and chemical phenomena in continuous CLC. With such a model, it is possible to determine the performance of the fuel reactor. The reactions between ilmenite and fuel gases, devolatilisation and char gasification of coal are described via kinetics models. The hydrodynamic CFD model was validated against literature data and the hot-flow model was compared with experimental data of ICB-CSIC-500W. However, the model predictions for continuous CLC process operations are not satisfactory yet. Future work will now focus on improving the model, e.g. inclusion of the more complex reactions, such as the water gas shift (WGS), consideration of the changes in coal particle density and rendering the devolatilisation and gasification models more precisely.

H₂ production via chemical looping: a thermodynamic and kinetic study – Claire Thompson, Newcastle University

As H₂ is essential now and will be even more in the future, it is important to find suitable oxygen carrier materials for CLR. Currently used iron oxide carriers are cheap and have a large oxygen capacity but are unstable over longer cycles and prone to thermal sintering. Perovskites are a potential replacement for iron oxide material as they allow for a more stable operation and regeneration. In this work, an equilibrium model was made for LSF731 (La_{0.7}Sr_{0.3}FeO_{3-δ}) in a packed bed and the bed behaviour was studied, showing infinitely fast kinetics. The agreement of the preliminary kinetic studies and the thermodynamic predictions encourages further research into these new materials, e.g. determination of the heat capacity.

Reactive spray synthesis of metal oxides for chemical looping combustion – Arnold Lambert, IFPEN

The reactive spray technology (RST) was used to produce NiO/NiAl₂O₄ and Cu_{0.95}Fe_{1.05}AlO₄ powders with high surface area (up to 100 m²/g), small particle size (<10 μm) and controlled porosity. After pelletizing, tests performed using a TGA apparatus showed that the RST produced Ni-based particles showed increased oxidation rates compared to particles with the same composition produced by granulation, while RST produced Cu/Fe-based particles showed higher reduction rates than particles with the same composition prepared by co-precipitation. The increased reactivity of RST-made compositions can probably be attributed to smaller particle size and higher surface area.

Iron oxide-MIEC hybrid materials for hydrogen production using chemical looping technologies – Cristina Dueso, Newcastle University

The steam-iron process traditionally uses iron oxide as the oxygen carrier material because of its favourable thermodynamics, low cost and environmental friendliness. However, the slow reaction kinetics with carbonaceous fuels and the low stability after several redox cycles require the development of alternative materials. Hybrid materials, in this case combining iron oxide, perovskite and a mixed ion-electron conducting (MIEC) membrane, can improve the stability and the reactivity for H₂ production in the steam-iron process. The results show an increase in reactivity during both the reduction with CO and the oxidation with CO₂ with respect to perovskite or iron oxide alone. The MIEC material facilitates the O²⁻ ion mobility and transport from the bulk to the fuel due to the presence of oxygen vacancies. Moreover, the amount of H₂ produced is higher.

CLC research & development at CERT – Kumar Patchigolla, Cranfield University

The test facilities at Cranfield University include a 25 kW bubbling/entrained fluidised bed reactor for CaL and a 50 kW dual CFB reactor for CLC, which is the first pilot scale demonstration of CLC in the UK. The latter pilot plant is flexible in configuration, either as twin CFB legs or as a single entrained flow riser with bubbling bed. It is possible to run the plant in either oxy-combustion or H₂ production mode, both with a large flexibility of operating parameters. The first trials were completed with natural gas and simulated syngas as fuels and included an extensive characterisation of a Fe-based oxygen carrier. The next campaigns will involve a single reactor phase testing, an assessment of the reactor in full looping configuration and the transition to the CLOU process.

Session 2b: Calcium Looping Fundamentals

Chair: Carlos Abanades, CSIC-INCAR, and John Dennis, University of Cambridge

Design, construction and commissioning of a pilot-scale dual fluidised bed system for CO₂ capture – Robert Symonds, CanmetENERGY

CanmetENERGY's objective has been to design a pilot-scale facility that is capable of operating over a wide range of conditions and configurations. CanmetENERGY's 0.1 MWth CaL facility was originally commissioned in 2006 and the first continuous CO₂ capture experiments took place in 2007. The plant underwent re-design to improve flexibility and overcome issues, such as the difficulty to control solids transfer between reactors, the gas bypass and the transfer from calciner to carbonator being possible via overflow only. Commissioning trials of the new plant were completed in August/September 2012. Current experiments with steam addition have shown considerable CO₂ capture and sorbent performance improvements as well as reduced sintering due to a lower calcination temperature. Future pilot-scale activities will include the investigation of CLC with several reactor configurations.

Coal combustion in oxygen-enriched atmosphere in regenerator of CaL process – Tadaaki Shimizu, Niigata University

Anticipated problems with the regenerator in a CaL process are the formation of NO_x and char. Coal combustion at high temperature and in high O₂ concentration results in NO_x formation, which can then lead to HNO₃ formation during compression. If char is formed in the regenerator and transported to the carbonator, this can result in the release of CO and CO₂ in the off-gas. Thus, the main objectives of this work are to evaluate the above-mentioned issues and the effect of fuel type on these emissions. Experiments in a bench-scale solid fluidized bed circulation system revealed that high-volatile fuels are favourable for CO and CO₂ control. However, these fuels may have a problem of uncontrollable volatile

matter combustion under O₂-enriched and high-temperature conditions. A solution to this problem might be the capture of volatile matter by porous CaO as demonstrated using a fixed bed reactor.

Understanding the enhancement effect of steam on the carbonation reaction of CaO with CO₂ – Zhenshan Li, Tsinghua University

Steam, which is always present in CaL flue gases, can enhance the carbonation, indirect and direct sulphation, and can decrease the oxidation of NH₃ on the CaO. The steam-enhanced carbonation reaction of CaO with CO₂ is a widely observed phenomenon, but its mechanism is still unclear. For this reason, research at Tsinghua University aims to apply the theories of defect chemistry and ion diffusion to analyse the steam enhancement and to discuss the effects of steam fraction and temperature on carbonation. Investigations revealed that OH⁻ formation caused by the dissociation of H₂O molecules might explain the enhanced carbonation. The relationship of oxygen vacancies with OH⁻ was established and integrated into a new carbonation model. This new model included a simplified rate equation model to describe product island formation and a multi-ion diffusion model to describe product layer diffusion. Experimental studies of carbonation and sorption-enhanced WGS reactions in a fluidized bed reactor validated the new model.

CO₂ recovery from CPU vent of CFB oxyfuel plants by Ca-looping process – Matteo Romano, Politecnico di Milano

Oxyfuel power plants produce concentrated CO₂ streams with some non-condensable gases that originate from several sources within the process. Typically, auto-refrigerated processes based on low temperature flash are proposed for their separation but some CO₂ will be inevitably vented with the non-condensable gases and the CO₂ capture efficiency drops from potentially 100% to 85-95%. This situation leads to the question, whether it is economical to recover this vented CO₂, which is available in a clean stream at relatively high concentrations (~30-45%vol.). In this regard, CaL can be a good alternative because >90% of the CO₂ can be recovered from the vent, thus leading to an overall CO₂ capture efficiency of ~99%. In case of a CFB boiler, the CaL purge can be reused in the main boiler for sulphur capture, so no additional solid material needs to be imported or displaced. As the coal burned in the calciner is converted with approximately the same efficiency as the coal burned in the main boiler, there would be no significant thermodynamic penalty. First simulations show that the energy per kg CO₂ captured is slightly reduced and the capture efficiency rises from ~92% for the oxy-CFB case to ~99% for the oxy-CFB-CaL case. To fully understand the potential of this process and optimize it, an economic analysis would be the next step.

High-purity hydrogen via the sorption-enhanced steam methane reforming reaction over a synthetic CaO-based sorbent and a Ni catalyst – Ben Anthony, Cranfield University

Sorbent enhanced steam methane reforming (SE-SMR) is an important technology able to produce H₂ from hydrocarbons with in-situ CO₂ capture. In this work, SE-SMR was studied by using a mixture containing a Ni-hydrotalcite-derived catalyst and a synthetic calcium aluminate supported sorbent for CO₂ capture. The catalyst produced a stream of high purity H₂ (99% pure on a H₂O and CO₂ free basis), and the CO₂ sorbent maintained almost double the CO₂ capture achieved by limestone alone after 10 cycles.

Reversible CO₂ absorption by the 6H perovskite Ba₄Sb₂O₉ – Matthew Dunstan, University of Cambridge

Desirable properties for CaL sorbents are high selectivity and absorption capacity for CO₂ at elevated temperatures, good absorption/desorption kinetics, good cyclability and good hydrothermal and mechanical properties. Problems with standard CaO or other alkaline metal oxides, e.g. Li- or Na-based, include either a capacity loss during cycling or poor kinetics. Perovskites like Ba₄Sb₂O₉ exhibit excellent thermal and mechanical stability and the ability to tune their physical properties through a range of chemical substitutions. However, they were thought to carbonate irreversibly or at too high a temperature, making their application in carbonate or chemical looping challenging. In TGA experiments, Ba₄Sb₂O₉ now showed reversible absorption of CO₂ to form BaCO₃ and BaSb₂O₆. The capacity over 100 cycles was stable and scanning electron microscopy (SEM) investigations revealed self-generated porosity upon cycling. Future research will explore use of perovskites as a framework material to alter the properties of conventional sorbents.

An internally circulating fluid bed for attrition testing of Ca looping sorbents – Vlatko Materic, Callaghan Innovation

As most CaL systems use fluidised beds, particle attrition is inevitable. Attrition has negative effects on fluidised bed operation, e.g. due to loss of fines and particle size reduction. To understand and minimize attrition in these systems, it is essential to quantify sorbent friability. Attrition occurs by a range of different mechanisms. At low velocity abrasion

dominates, which will result in small fragments, i.e. fines. At higher velocity fragmentation takes place, first by chipping and then by splitting. This causes larger fragments compared to abrasion. There is also a differentiation between primary attrition (initial particle rounding off, thermal shock, etc...) and secondary attrition (steady state characteristic of the particles). Ideally, an attrition testing method should measure friability over a range of velocities and during different phases in the CaL cycle. Tests in an internal CFB prototype showed that calcined sorbents are more friable than carbonated sorbents, mainly due to increased sintering. Although the CaCO_3 content changes with increasing cycle number, this does not affect carbonated sorbent friability. Sorbents reactivated by superheating are comparable to unreactivated sorbents and hydration-dehydration generated weak sorbents, which tend to fragment at low velocities. Future work will focus on improving and upgrading the test prototype.

HBr-enhanced sorbents, reactions with SO_2 – Mohamad Al-Jeboori, Imperial College London

This work focussed on testing different ways to improve long-term sorbent reactivity in the CaL cycle. The experiments were carried out in a small fluidised bed reactor at atmospheric pressure. Application of 0.167 mol% HBr dopant leads to an increase in carrying capacity compared to raw limestone. The combined presence of 10% steam and HBr dopant further improves the carrying capacity. Using seawater also increases the carrying capacity of the sorbent. However, the effect is less distinct compared to doping with HBr. Again, there is a synergistic effect between seawater doping and addition of 10% steam on the reactivation of the limestone.

The presence of SO_2 generally reduces the cyclic carrying capacity of the limestone. Even doping with the most effective HBr concentration of 0.167 mol% and 10% steam only slightly improve the carrying capacity of limestone. X-ray fluorescence (XRF) investigation show that no bromine moiety is left in the HBr-doped sorbent after 13 cycles in the presence of SO_2 . The effects of pelletisation and the presence of steam on the carrying capacity of the sorbent are additive too, as in the case of doping and steam. This underlines that pelletisation and steam addition are effective approaches to improve reactivation and long-term reactivity of the limestone.

Session 3: System Modelling, Design and Evaluation

Chair: JoAnn Lighty, University of Utah, and Fabrizio Scala, CNR

Implications of grid codes: challenges for CCS power plants utilising high temperature solid looping processes – Mike Haines, Cofree Technology

The ability of power plants to comply with electrical grid code in respect of short-term response to sudden frequency drops can vary greatly. The UK has rather strict requirements because of the small grid size, i.e. 80GW, and the few interconnections with other systems. A drop of 0.5Hz over 10 s must result in an immediate primary response of 10% power ramp up over 10 s, held until 30 s. By then the plant must provide the secondary response, which must be maintained for 30 min. After this time, a new response must be possible. General ways to provide this short-term frequency response are throttling steam to the turbine (but this reduces efficiency), condensate stop (which can only provide 2-3% of the 10% needed), auxiliary load-shedding and pre-pulverised coal storage. For CCS plants, there are several load-shedding possibilities: tripping the CO_2 compression, the entire post combustion capture unit or the ASU and stopping steam supply for regeneration. All of these options are potentially disruptive to the CCS process. Solid looping systems have several places, where there is significant energy available for short-term release, i.e. thermal energy in the hot circulating solids, chemical energy in the reduced form of oxygen carriers, and thermal or pressure energy in heat recovery steam generator (HRSG) systems. First calculations show that there is enough thermal energy present, i.e. ~5 MWth, to supply the power required by the UK code for just over 1 min. To extract this energy, the gas flow has to be temporarily increased and the most suitable option to realise this are a recycle of CO_2 in the calciner or increased airflow in the carbonator. Because generating more steam from an HRSG is a slow process, tube selection can have a considerable effect on the primary response capability of the plant. In CLC systems, heat release can be ramped up more rapidly by increasing

airflow than in CaL systems. However, both systems have unique attributes, which might help to enhance response to frequency drop disturbances. Further research needs to include the identification, verification and quantification of fast response capabilities in integrated power plant systems.

Development of three-towers CFB Ca looping biomass/coal gasification – Shiyong Lin, JCOAL

Fundamental experiments have shown that CaO is also a good catalyst for reforming of hydrocarbons. Based on these results, a three-tower CFB CaL gasification process is developed. The process layout includes a combustor, gasifier and a reformer. It is the aim of the process development activities to produce a low tar, low H₂S syngas to simplify the gas clean-up step and to recycle the off-gas in order to enhance syngas production. Analysis results from an Aspen simulation show that the three tower process can produce syngas with a H₂/CO ratio of about 2 and low concentrations of CO₂, CH₄, H₂S and tar. Subsequently, a 2 kW test facility was set up to evaluate the process further and to provide proof-of-concept. First experimental results show that presence of CaO reduces tar generation in biomass as well as coal gasification and thus CaO is a suitable catalyst for hydrocarbon reforming.

Design of a 300 kWth indirectly heated carbonate looping test facility – Markus Junk, Technische Universität Darmstadt

The CARINA project focusses on investigating a CaL process, where an external combustor supplies the heat for the calciner via heat pipes, so the ASU, which provides oxygen for firing the calciner, becomes redundant. Because the ASU in a standard CaL process accounts for a large amount of the energy penalty (2%-points out of the total of 3%-points, excl. CO₂ compression), the indirectly heated process will have a lower energy penalty of ~1 % point. As there is no coal present in the calciner, few additional impurities (e.g. sulfur, ash) enter the system, which reduces the flow of circulating solids and facilitates the further utilisation of deactivated sorbents. Retrofit of the indirectly heated carbonate looping process is generally possible but causes big plant sizes, therefore new-built construction with thermal integration is more applicable due to a reduced plant size and higher efficiency. Pressure characteristics of a cold-flow model confirmed the coupling concept of the planned test facility. In addition, solid flux investigations showed that the heat pipes do not significantly influence the particle flow through the calciner and the required solids mass flow through the reactor is achievable. A 300 kWth test rig is under construction and will start operation mid 2014 at TU Darmstadt. If the concept also works technically, this will be a significant thermodynamic improvement for new-builts.

Reactions of sulphur during chemical looping combustion using iron – Zili Zhang, Imperial College London

When sulphur, in the form of H₂S, enters the CLC system, the following two questions are of interest: (1) How is the sulphur products distribution in air and fuel reactor? and (2) What is the effect of sulphur on kinetics and long-term reactivity of iron oxide? To answer these questions, experiments were carried out in a closed-system fluidised bed reactor investigating the different fates of sulphur before and after completion of reduction of Fe₂O₃ to Fe₃O₄ at 823K, with 3 vol% CO and 300 ppm H₂S. Most of the H₂S was converted into SO₂ in the fuel reactor before complete reduction of Fe₂O₃, while after complete reduction most of the H₂S was converted into FeS. Because FeS was released as SO₂ later in the air reactor, this shows that sulphation is nearly reversible and Fe₂O₃ seems to be fully regenerable. Quantitative XRF analysis detected elemental sulphur in the downstream trap of the reactor. Increasing the residence time of H₂S only has a significant effect on the reduction rate if the increase occurs after complete reduction. Generally, increasing H₂S concentration has an adverse effect on the rate of reduction. Investigation of the reduction rate of Fe₂O₃ for various CO concentrations in the presence of H₂S confirms a first order dependency with respect to CO. In conclusion, a good process control could avoid the production of SO₂ in the air reactor in the first place.

Chemical looping combustion using Aspen Plus – Raffaella Ocone, Heriot Watt University

It was the aim of this work to develop a fluidised bed model for CLC in Aspen Plus without using a Gibbs reactor model, which is widespread in the literature of CLC. The analysis considers several related issues, such as an adequate contact time between fuel, air and solid oxygen carrier to achieve maximum conversion, the size of the two reactors, a suitable solids inventory and a sufficient molar flowrate ratio between air and fuel. NiO/Ni supported by bentonite is the oxygen carrier system, the fuel reactant is pure methane and the oxidising agent is air. The bubbling bed fuel reactor model is a combination of CSTR's (continuous stirred tank reactor) and PFR's (plug flow reactor); whereas the fast riser air reactor model consists of CSTR's. Results of the bubbling bed model show that conversion increases with the number of stages. Comparison with data from the literature confirms that the observed conversion corresponds to 5 stages. The conversion

in the new model is higher because the Gibbs reactor model does not consider gas by-pass in the bubble phase. A set of parameters to achieve a conversion of solids that allows the circulation of solid particles between air and fuel reactor in steady state conditions was obtained from the results of the riser model. Because the new model has a higher accuracy, takes into account hydrodynamics and kinetics and is able to estimate the main process variables, it will be a valuable tool for efficiency calculations, economic analysis and life cycle assessment (LCA). Future work will concentrate on the integration of Aspen Plus with CFD modelling to study the gas by-pass, the overall efficiency of the process and CLC process intensification.

Environmental evaluation of IGCC-based chemical looping processes – Letitia Petrescu, Babes-Bolyai University

An impact assessment or optimisation of a power plant usually includes technological and economical, but not environmental factors. However, the environmental factors are getting more and more attention, so there is a growing need for evaluation tools. One such tool for sustainability and environmental evaluation is the Process Sustainability Prediction (PSP) Framework by ICS-UNIDO. This programme uses 1D, 2D or 3D indicators, depending on the number of intersections between the three areas environment, economy and society. Examples for 3D indicators are material intensity, energy intensity, potential chemical risk and potential environmental impact, whereas 1D indicators relate to various impact outputs. The use of CAPE OPEN methodology in the approach results in a standard module that can be integrated in almost every process simulator software available on the market. Case studies were undertaken to identify the most environmental friendly and sustainable design from four different process alternatives: (1) IGCC without CCS, (2) IGCC with pre-combustion CaL, (3) IGCC with post-combustion CaL and (4) IGCC with pre-combustion Fe-based CLC. All cases have been modelled and simulated using process flow modelling software in order to generate mass and energy balances necessary for the technical and environmental evaluations. The technical evaluation, based on model data, is made according to key performance indicators, such as net power, energy efficiency, carbon capture rate, specific CO₂ emissions, etc. The environmental evaluation, based on the technical indicators, was performed using the PSP Framework. The analysis shows that IGCC with pre-combustion CaL is the best option regarding material intensity, with the other two 3D indicators being the same for all cases. IGCC with pre-combustion CaL and IGCC with post-combustion CaL have the best performance regarding the 1D indicators. In conclusion, the results confirm that PSP is a good tool for choosing the most environmental friendly design and that IGCC with CaL is a promising option for future sustainable power generation.

Plenary Discussion

Moderators: Ben Anthony, Cranfield University, and Tobias Pröll, University of Natural Resources Vienna

Panel: Carlos Abanades, Paul Cobden, Paul Fennel, Tadaaki Shimizu, Bernd Epple and Mike Haines

The meeting finished with a panel discussion that addressed the broader challenges and future developments of solid looping technologies. CaL with solid fuels seems to require severe calcination conditions to achieve a sufficient performance for industrial applications. As the meeting did not include any detailed discussion about the pressure in combustion in CaL processes, the next meeting would need to include this topic. The most pressing question concerning CaL at the moment is: when will the first large-scale demonstration go online? CLC development, still lying behind CaL, will have to improve the conversion of solid fuels to meet the requirements of industrial applications.

Carlos Abanades said that it was important to carefully design and control experiments to make sure all particles react as they should. In addition, under non-differential conditions a model would be needed for correct interpretation of the experiments. Paul Cobden commented that most fixed-bed CLC projects focussed on IGCC and were not looking for alternative fuels, such as CH₄. However, if the DemoCLOCK project could show that these systems work, then there was large hope. There was also no need to go for coal as a fuel and the cheapest oxygen carrier material only. According to Paul Fennell, post-combustion CaL for power generation was generally solved and just needed an appropriate scale-up. Industrial applications, like cement and iron & steel, still had to be explored and right conditions to be chosen.

Then a small debate broke out regarding the application of bubbling bed (BB) instead of more conventional CFB technology. Tadaaki Shimizu said we should try to employ BBs. The heat removal should not be forgotten over the reaction kinetics and a BB could improve this. Carlos Abanades replied that for post-combustion capture from a power plant only CFB could be used, as BB would be more complicated and costly. Bernd Eppele stated he agreed with Carlos Abanades because his own experience from industry indicated a limitation in scale-up for BBs. In addition, it was no problem to remove the heat from a CFB reactor.

Bernd Eppele then went on that in industry customers were used to certain standard applications. They could be convinced to use CFB quite easily but maybe not to apply unknown fixed-bed technology. The mechanical stability of the carrier in CaL needed to be proven in addition to the TGA tests. Natural limestone modification was an interesting option if it would not be too costly. Also, industry was asking for longer test runs, beyond 1000 h, before they would provide further funding for projects. CLC was a bit more complex to operate but also a bit more promising in terms of efficiency. The indirectly heated CaL process would be applicable for 100s MW size. Carlos Abanades commented that it was a challenge to mix the materials as quickly as possible and that the standard CaL configuration needed a lot more optimisation but was already doing well.

Mike Haines then shifted the topic to market conditions for CO₂ capture with solid looping technologies. He said there was no market for CO₂ storage at the moment, only one for use in enhanced oil recovery (EOR). Here, PCC and oxyfuel were the main competitors in the field, so it was important to answer what advantage CaL had over these. One advantage was the lower energy penalty but the niche for CaL in sectors like cement or steel still needed identification. Paul Fennel replied that we needed a sensible price for CCS in general to go forward with any CCS technology. Bernd Eppele said in the past there was a reservation towards CaL but now people were convinced by the first results, especially because amine-based PCC had so many different issues. Paul Cobden concluded that you needed to talk to industry in mol steam / mol CO₂. There would always be issues for power plant scale-up but there was a good outlook for application of solid looping in other sectors.

Meeting Conclusions

The 5th HTSLCN Meeting provided detailed information about the technical performance of CaL and CLC processes. The results from the pilot plants show that there is further improvement in CO₂ capture efficiencies and fuel conversion rates. The current scale of CaL pilots is up to 2 MW and 200 kW for CLC respectively, with the hours of operation steadily increasing. Certain impurities, such as SO₂ and H₂S, have an adverse effect on the sorbent carrying capacity in CaL and the reduction rate in CLC. However, other research showed that new hybrid materials, promoted/doped sorbents, pelletisation and steam addition are a way to enhance the performance. In addition, several new promising process concepts have been presented, including an indirectly heated CaL process, a two-stage CLC process and a packed bed design for coal-based CLC. First environmental evaluations demonstrate that, besides having a lower energy penalty, CaL processes can be more environmental friendly than conventional or competing CO₂ capture technologies. A key statement from the meeting is that CaL for post-combustion CO₂ capture is generally proven and now just needs the scale-up to demonstration or commercial scale. On the other hand, there are a number of challenges and next steps lying ahead. For both CaL and CLC only rough cost estimates are available, so it will be necessary to establish and validate techno-economic performance figures. Similar to any other CCS technology, CaL and CLC both need a sensible price for CO₂ to go forward. At the moment, the main market driver is the use of CO₂ in EOR operations but here CaL and CLC would compete with the other CCS technologies. It will be important for the future development of solid looping that CaL and CLC clearly demonstrate their advantages and identify their commercial opportunities.



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