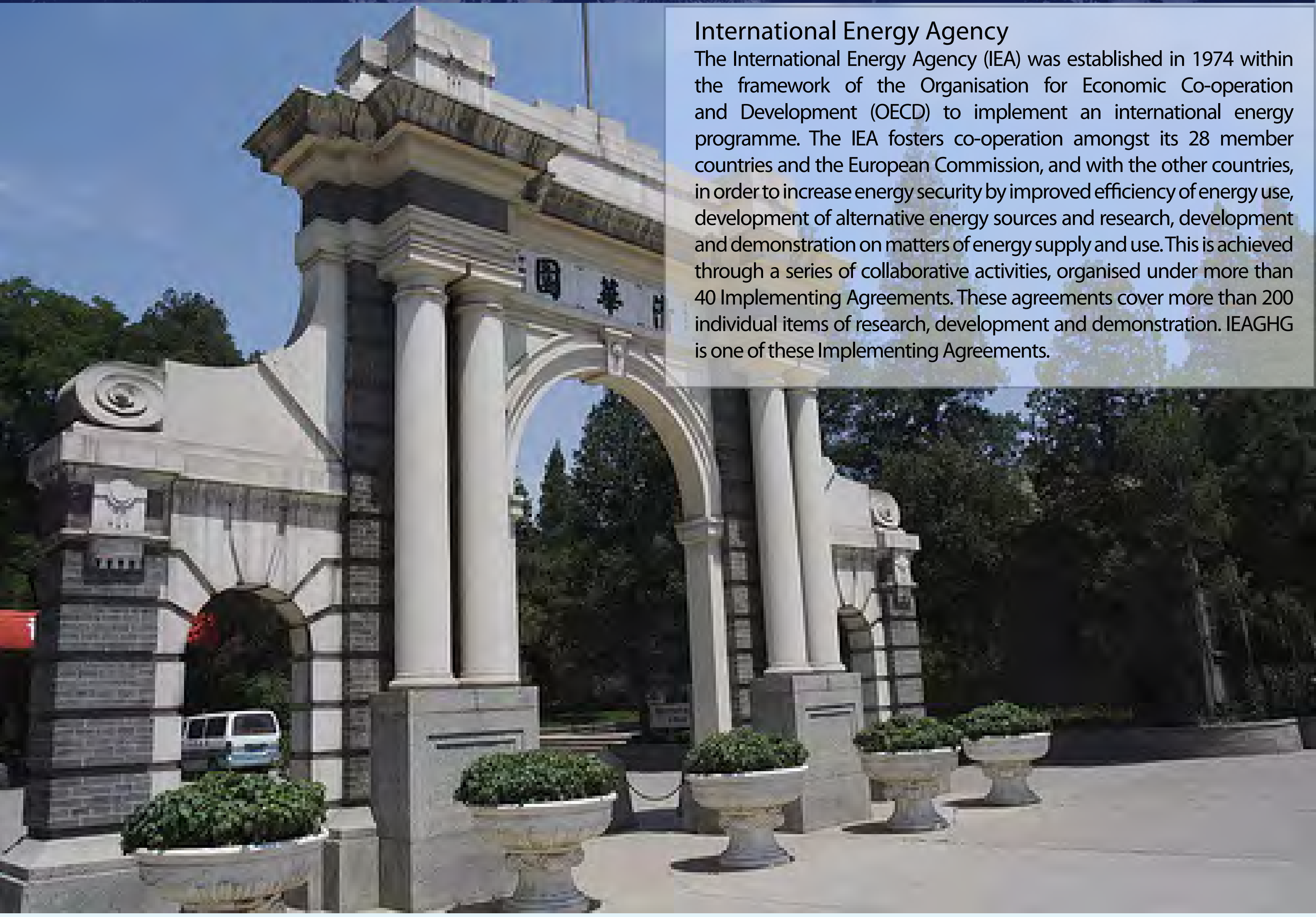
Evaluating technology options to mitigate greenhouse gas emissions

4th ieaghg network meeting and technical workshop on high temperature solid looping cycles

IEA GREENHOUSE GAS R&D PROGRAMME



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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: Pond at Qing Dynasty garden on Tsinghua University campus / Entrance of conference centre at Xijiao Hotel / Delegates in the conference room with poster presentations in the background / The Old Gate at Tsinghua University

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The Great Wall at Badaling / Conference room

Scientific and Organising Committees

A scientific committee has been formed to organise and manage the technical sessions of the network meeting. The scientific committee members for this meeting are:

Ningsheng Cai, Tsinghua University, China
Juan-Carlos Abanades, CSIC-INCAR, Spain
Edward J. Anthony, CANMET, Canada
Paul Cobden, ECN, The Netherlands
Stuart Scott, University of Cambridge, UK
Adolfo Garza, Cemex, USA
Mike Haines, IEAGHG, UK
Anders Lyngfelt, Chalmers University of Technology, Sweden
Tobias Pröll, Vienna University of Technology, Austria
Andres Sanchez, ENDESA, Spain

The organising committee for this network meeting comprised of:

Ningsheng Cai, Tsinghua University, China
Zhenshan Li, Tsinghua University, China
Jinhua Bao, Tsinghua University, China
Mike Haines, IEAGHG, UK
Laura Davis, IEAGHG, UK
Jasmin Kemper, IEAGHG, UK

Introduction

The IEAGHG High Temperature Solid Looping Cycles Network emerged from the preceding International Workshop on In-situ CO_2 Removal (ISCR) and aims at bringing together researchers and developers of CO_2 capture technologies that operate at high temperatures in cylindrical processes using either circulating or fixed beds of solids.

Within the last few years drawbacks of the conventional amine-based CO_2 capture systems have spurred interest in solid looping processes. Since then the technology has advanced considerably and several pilot plants have been build and brought into operation, e.g the 1.7MW pilot plant at La Pereda in Spain and the 1MW pilot plant at TU Darmstadt in Germany. Progress has been made in particular in carrier/sorbent development as well as in process design and integration. In Calcium Looping, for instance, the use of spent sorbent to produce cement has been demonstrated.

The fourth meeting of the IEAGHG High Temperature Solid Looping Network was held from 20th to 21st August 2012 at the Xijiao Hotel in Beijing and was co-organised by Tsinghua University. Beijing was chosen as the location for this meeting to make the network more accessible to an international selection of participants, especially from Asia.

Although the number of attendees for this meeting was slightly down at about 48, there was a full two day programme with 31 presentations, 10 posters, a plenary discussion and a visit to the "Key Laboratory for Thermal Science and Power Engineering of Ministry of Education" at Tsinghua University.

The Technical Programme consisted of four sessions in total. Three sessions were related to progress made in Calcium Looping in the fields of sorbent development, H_2 production and reactor and process design. One session was reserved for Chemical Looping Combustion and presented advances in carrier development as well as some new process concepts.

Introductory Presentations

Introduction to the Department of Thermal Engineering, Tsinghua University – Ningsheng Cai, Tsinghua University

Thermal engineering is one of 4 departments in the Mechanical Engineering school which is itself one of 16 schools at Tsinghua. It is home to 1 national and 15 key state laboratories. Today the University has links with 205 other universities in 68 countries. Thermal Engineering has 4 key laboratories including those researching IGCC and CO_2 Utilisation and reduction. Work on CCS is undertaken from lab to pilot scale. There is international collaboration with BP, Mitsubishi and Toshiba.

Introduction to the Low Carbon Energy Laboratory – Quiang Yao, Tsinghua University

This laboratory was set up in 2008, has a budget of $130M p.a. and staff of around 800. It co-operates extensively with major companies and US DoE laboratories. It undertakes policy studies in many areas and a key aim is to bring the results of research to the international market but with a strong focus on China. Research resources include 4 nuclear reactors. Recently SEED projects have been set up to research Geoenergy, Biofuels, use of low grade energy resources and bi-phasic sorbents for CCS.

Introduction to the IEAGHG Network on High Temperature Solid Looping Cycles – Mike Haines, IEAGHG

The status of solid looping technology for both combustion and CO_2 capture was compared with that of competing technologies. The need to better understand the strengths, weaknesses and opportunities for the technology was stressed. The history of the meetings including the 4 earlier ISCR gatherings was reviewed and the recent use of mainly European locations noted along with the importance of making the network meetings accessible to an international selection of participants. This year participant numbers were slightly down at about 48, although there was a full 2 day programme of papers and posters. Economic restrictions on travel and the biennial chemical looping combustion conference in Darmstadt at the end of September have undoubtedly restricted attendance.

Session 1: Calcium Looping – Sorbent

Chair: Paul Cobden, Energy Research Centre of the Netherlands (ECN)

The Synthesis of Ca-based, Al_2O_3 Stabilised Sorbents – Christoph R. Müller, ETH Zürich

Formulations of 80-20 to 90-10 Ca:Al give better sorption performance up to 75% better than typical natural Rheinkalk. The key to good performance appears to be making a very thin layer of CaO on the Al_2O_3 support. To increase porosity of the structure resorcinol/formaldehyde was used to make a carbon shell. After precipitating Ca/Al the carbon is burned off leaving 5μm spheres with high porosity. In real tests the decay of activity was much slower than natural material. Uptake capacity increases up to a limit of about 93% Ca after which it drops dramatically. For practical use the fine material would need to be pelletized and work on a suitable process is on-going.

Synthesis of CaO-Based Sorbents by Spray-drying – Wenqiang Liu, Huazhong University of Science and Technology

The aim of this work is to create separate ultra-fine CaO particles and separate them with an inert solid in a matrix. Of 4 mixing methods, dry mixing, suspension mixing of insoluble particle, sol mixing (one component soluble) and wet mixing (both components soluble) the wet method was chosen. Use of acetates, lactates, propionates, formates and citrate tetrahydrate were studied. The support was MgO and formulations in which 20μm particles surrounded 100μm CaO particles were produced. Both oven drying which is slow and energy intensive and spray drying were used and the latter shown to produce effective sorbents. The optimum capture capacity was found to be with 82% CaO. Performance was better than literature reports for natural CaO. However a method to pelletize the powders still needs to be developed.

Nano CaO-based Adsorbents Evaluation by a Circulating Fluidised Bed System – Su Fang Wu, Zhejiang University

Use of nano particles has the advantages of high reaction rate, durability and low attrition. Batch CO_2 sorption tests in a fixed bed and circulating fluid bed reactors were carried out. The tests showed low attrition (<3.5% in ASTM test) with 30nm particles. Batch tests were carried out to measure the breakthrough of a stream containing 7.7% CO_2. In a fixed bed reactor there is 100% capture until about 40% of the bed capacity has been used. Because of the mixing a CFBR always shows some breakthrough but can reach up to 99% absorption.

CO_2 Capture Using Lime Mud from Paper Mill in Calcium Looping Cycles – Rongyue Sun, Shandong University

Lime mud originates in paper making and consists of a mixture of NaOH and $CaCO_3$. Disposal to land fill is becoming increasingly difficult. Both the caustic and chlorine content can be reduced by water washing. Cyclic absorption tests were carried out for both prewashed and unwashed lime mud. Prewashing was found to greatly reduce loss of capacity after 100 cycles. It was also found that a prolonged first cycle of 9-12 hours greatly increased capacity particularly for unwashed lime mud. Also the effect of prolonged carbonation in the 20th cycle was tested. Measurements show that surface area decreases over time but overall pore volume was increased with a reduction in small pores offset by an increase in larger ones.

Sequential Capture Characteristics of CO_2 and SO_2 by Ca-based Sorbent – Zhao Zhenghui, Cranfield University

The capacity for SO_2 of partially spent lime after duty as a CO_2 sorbent has been investigated using simulated flue gas. The capacity for SO_2 was found to drop by a relatively small amount typically by 20% after 40 cycles of carbonation. The spent lime is withdrawn from the carbonator where the temperature is lower to avoid cooling. Tests were performed in a bubbling fluidised bed reactor on 3 different sorbents.

Rate Equation Theory of Gas-Solid Reaction Kinetics for CaL and CLC - Zhenshan Li, Tsinghua University

The reactions of CLC air reaction and CaO looping carbonation were studied. Both reactions show a fast followed by a slow phase. No theory currently describes the complete process. Reaction products develop through a process of nucleation and growth. There is also migration of products between the islands which grow after nucleation. A model has been developed which is based on fundamental properties of the chemical reaction and surface diffusion. The model fits the measurements well and most notably the fitted coefficients appear to be able to account for experiments at different temperatures without adjustment lending considerable weight to the validity of the model.

The Effect of HBr and Sea Water on the Reactivation of Ca-based Sorbents – Belen Gonzalez, Imperial College

Doping with HBr was found to greatly improve the activity and reduce the rate of activity decay of limestone (Havelock). The doping did not however appear to alter the reactivation effect of steam. Measurements showed changes in pore size distribution as a result of the doping. Further tests were carried out using sea water as the dopant and activity improvements were also measured. Questions were raised with regard to the possible effect of dopants and or support materials on acceptability of waste sorbent into cement making.

Session 2: Calcium Looping – Hydrogen Production

Chair: Ningsheng Cai, Tsinghua University

H_2 Production by CFB Ca Looping Coal Gasification – Shiying Lin, Japan Coal Centre

Results of simulations and tests on a H_2 production process using low temperature (700-850°C) gasification of coal at 20 atm combined with a calcium looping cycle were presented. In the full process the H_2 is consumed in a solid oxide fuel cell. The decomposition temperature in the calciner was found to be somewhat less than theoretical, 930°C at 6 atm, 1000°C at 20 atm. The material circulation is sufficient to supply heat to the gasifier as long as the gasifier temperature is not too high (< 750°C). Up to 20% CH_4 remains in the product gas and is reformed before H_2 separation. The H_2 is consumed in a fuel cell and waste heat from this can be used either to make steam and heat feeds or as a heat source for reforming the CH_4. The latter gives a higher cold gas conversion efficiency. An overall efficiency of 76% was calculated in the simulation.

H_2 Production from Biomass with Chemical Looping Gasification Technology – Qinhui Wang, Zhejiang University

This new H_2 from biomass process has been patented. Simulations show H_2 purity of 60% can be obtained when operating gasification below 850°C and at a pressure of 10 bar with a sawdust feed. Experiments have been conducted at 4 bar and 680°C and were able to produce 67% H_2 with a CaO to carbon ratio of 1.2. Optimum pressure for the process is thought to lie between 10 and 15 bar.

H_2 Production from Biogas by Sorption-Enhanced Steam Methane Reforming – Julien Meyer, IFE Norway

The design of a plant under construction at Lillestrom, Norway, was described. The aim is to produce H_2 from landfill gas for delivery at 700 bar, storage at 1050 bar to allow H_2 vehicles to drive between Oslo and Stavanger. A double fluidised bed system will be used. Of note is the use of indirect heating in the regenerator through Inconel U tubes. Space between tubes is > 50x particle diameter so that no fluidisation problems are expected. Design fatigue life of the heating tubes is only 1000 hours although with regular inspections up to 5000 hours may be possible. H_2 purity will be 99.999% achieved through use of a Pd membrane.

The Effect of Impurities on Cyclic Stability of Sorption Enhanced Water Gas Shift – Paul Cobden, ECN

The 6 fixed bed SEWGS pilot plant at ECN was described and plans for a larger 2MW demonstration unit. A number of tests have been carried out on the effect of impurities H_2S (500, 2000, 25000 ppm), COS, NH_3 (2000 ppm) and HCN (200 ppm) on three different promoted hydrotalcite sorbents. H_2S and CO_2 breakthrough have been observed at roughly the same time. COS was not detected as it was found to hydrolyse to H_2S. HCN undergoes partial hydrolysis and breaks through slightly more quickly than CO_2. However the sorbents are fully regenerable. Dual Fluidized Beds System for H_2

Production with CO_2 Capture Based on CaL– Wang Dong, Southeast University

The design of a novel compact chemical looping coal to H_2 production process was described. A feature of the process is the carry through of char to the calciner to act as fuel. The process features also an absorber section above the main carbonator/gasifier bed in which residence time and contacting for further CO_2 absorption is provided. A 2kW hot bench scale has been constructed but has still to be tested.

Session 3: Calcium Looping – Reactor and Process

Chair: Carlos Abanades, CSIC

Experimental Validation of Post-combustion Ca-Looping in a 1.7 MWt Pilot – Borja Arias, CSIC-INCAR

La Pereda pilot plant is a 1.7MW unit processing a stream of the flue gas from a 50MW CFB power plant at La Pereda in northern Spain which has been built in the EU FP7 funded project "CaOling". The feed flue gas is taken from downstream of the ESP and pressurised with a fan through the unit. The captured CO_2 is recombined and the exhaust rerouted to the main power plant flue duct. The calciner is equipped for both air and oxy-fired combustion. The unit was hot commissioned in January 2012 and ran for 800 hours on coal combustion in air mode. There have then been 160 hours of CO_2 capture with the calciner working in air fired mode with no sorbent agglomeration problems. Limestone used has a nominal particle diameter of 110 micron. A brief period of oxy-fired operation has been undertaken but is not yet reported. Initial tests were carried out to analyse the influence of the main parameters affecting the carbonator performance. The effect of the inventory of CaO in the carbonator and the reactor temperature were shown. Steady states with CO_2 capture efficiencies over 90 % were obtained in the La Pereda pilot plant during these tests. SO_2 captures efficiencies above 95 % in the carbonator were reported.

Effect of Steam and SO_2 on Pilot-scale Capture of CO_2 Using CaL – Alissa Cotton, Cranfield University

The effects of steam and CO_2 on 3 kg batches of CaO sorbent pre-calcined at 900°C have been measured in a 25kW thermal test unit. With a synthetic feed of 8% CO_2 a capture efficiency of about 80% is achieved. Modifications to improve this rate are planned. SO_2 was found to decrease porosity and reduce carbonation capacity. Raising steam content to 20, 30 and 40% progressively improves CO_2 capture capacity. SEM images of fully carbonated material under 40% steam indicate increased porosity. Work on analysis of trace elements was also presented. Levels of up to 10 ppb were detected. In some cases elements were only released when there was a larger inventory an effect which cannot yet be explained.

The Effect of Inert Solid Accumulation in Post-combustion Ca-Looping Systems – M. E. Diego, CSIC

The impact of the accumulation of $CaSO_4$ and other inert solids on the CO_2 capture efficiencies and the overall CaL process performance was analysed. For this purpose, three variants of a 1000MW coal fired power plant with capture using limestone sorbent were modelled. One was a PC unit with no FGD, the second a CFB unit with desulfurisation and the third a power plant with desulfurisation and with a sorbent regenerator. The CO_2 capture efficiency was calculated for the three systems for different make-up flows and coals used in the calciner. The increase of the feed of ashes and SO_2 to the system leads to a lower CO_2 capture efficiency due to the sulphation of the active CaO and the reduction of the inventory of active CaO in the carbonator. The results showed the first case to need a large make up of 50% due to the sulphation of the lime. Even when an effective reactivating step is included in the CaL process, there is a need for a minimum make-up flow of limestone to avoid the effect of inerts.

Fully Integrated Simulation of a Cement Plant with a CO_2 Capture CaL - Dursun Can Ozcan, University of Edinburgh

The optimum location for the carbonator was determined to be the outlet of the 3rd preheater in the cement process where CO_2 concentration is higher than at the tail end (30% v 22%) and the temperature of 600°C matches that needed for carbonation. The clinker rate was kept constant and some limits were placed on the purge rate of sorbent to limit power generation to that required overall. Results so far indicate an energy consumption of 2.3 – 3.0 GJ/ton CO_2, lower than for a commercial amine process but further work is required to confirm this.

Comparative Second Law Analyses of Endex and Conventional CaL – Rowena Ball, Australian National University

Exergy analyses were carried out over the control volumes of an Endex-configured looping sorption process, in which the exothermic reaction supplies heat directly to the endothermic reaction and calcination is achieved by pressure-swing, and a comparable conventionally configured system. It was confirmed quantitatively that in conventional CaL the most costly step by far is regeneration of the CO_2 from the sorbent. The Endex process was found to have a second law efficiency advantage of 40% over the conventional process, achieved largely by a significant reduction in the cost of the regeneration step. The gain is offset by an increase in the cost of the separation step, but this increase is relatively modest. The Endex process is a good candidate for thermodynamic optimisation because entropy generation is spread relatively evenly over its subprocesses. The capital cost of an Endex plant may outweigh some of the operating costs savings given by superior thermodynamic performance.

Optimisation of CaL for Power Plant and Integrated with a Cement Plant – Matteo Romano, Politecnico di Milano

A model of a USC power plant with full heat integration and cryogenic CO_2 clean-up was developed. A detailed model of the carbonator was implemented in Matlab. Efficiencies for varying make up to coal ratios were determined. Equipment costs were estimated in the model using exponential laws. Results indicate a cost of CO_2 avoided of €30–38 per ton. A similar analysis was performed for a cement plant producing 3600 tpd of clinker. Critical parameters are the purge rate and the amount of purge which can be used to substitute raw feed. Indications are that costs could be as low as €28 ton CO_2 avoided.

Cold Model Test of 3 Fluidised Bed Reactors Combining CaL and CLC – Hongming Sun, Tsinghua University

The process modelled uses three fluidized bed reactors (air reactor, calciner, fuel reactor) to realise the combination of calcium looping and chemical looping combustion. Heat balance in calciner is achieved by supplying transferring heat from air reactor to calciner via oxygen carrier which is mainly FeO/Fe_2O_3, and CaO solid flux is prohibited in the loop between air reactor and calciner. The characteristics including bed hold-ups and residence times were all modelled and agreement was found between conditions in the cold flow model and the theoretical model. The process feeds blast furnace gas to the fuel reactor (carbonator) and uses coke oven gas to fluidise the material in the calciner and appears to have the potential for low energy demand.

Session 4: Chemical Looping I

Chair: Stuart Scott, University of Cambridge

Performance of CaO/CuO Based Composite – Changlei Qin, University of Queensland

The presentation described the performance of a CuO/CaO composite for a combined Calcium & Chemical Looping process. Addition of steam, thermal pre-treatment of the CuO and use of MgO as a precursor can all help to prevent agglomeration and accelerated loss-in-capacity. However, as Cu is an expensive material, minimisation of Cu losses through efficient recycling plays an important role in the future development of these composites.

CuO-based Al_2O_3/CeO_2-supported Oxygen Carriers for CLOU – Christoph Müller, ETH Zürich

Compared to conventional CLC processes CLOU allows for an efficient combustion of hydrocarbon fuels without a prior gasification step. Due to their high O_2 capacity and fast decomposition reaction Cu-based carriers are most promising. The best performance was achieved with $CuMgAl_2O_4$ which showed a high and stable O_2 capacity close to the theoretical value. The chosen support material and the preparation method have a strong impact on morphology and thus can be used to influence the capacity and agglomeration characteristics of the carrier.

Effect of Volatiles in Coal on CLOU – Daofeng Mei, Huazhong University of Science and Technology

An investigation of sol-gel derived $CuAl_2O_4$ supported CuO revealed a steady release of O_2 over time and stable cycles of oxidation and reduction for this CLOU carrier. The presence of volatiles can promote the carbon conversion but at the same time the combustion efficiency and the CO_2 capture efficiency are decreased. It is therefore important to choose a reasonably low-volatile fuel for CLOU processes.

Use of Manganese Oxides Combined with Iron – Henrik Leion, Chalmers University of Technology

The presentation introduced iron-manganese oxides as promising O_2 carriers for CLOU. Generally, the gasification step in CLC is known to be quite slow, whereas the CLOU reactions proceed much faster. The carriers have the advantage to allow for complete conversion and for a magnetic separation. In addition, the Fe/Mn ratio can be used to tune the characteristics of the carrier, such as the activation at different temperatures. Once the particles are stable enough, the experiments will move to a continuous closed system.

Session 5: Chemical Looping II

Chair: Henrik Leion, Chalmers University of Technology

Chemical Looping H_2 Production Using Fe_2O_3/ZrO_2 – Wen Liu, University of Cambridge

Because pure iron oxide loses reactivity very quickly it is often stabilised with Al_2O_3. However, this support material is known as problematic as it can lead to deactivation. So ZrO_2, which is inert and thus does not influence reduction kinetics and thermodynamic equilibrium in a negative way, seems to be a good alternative support material. The experiments showed that this carrier allows for a stable and high-purity H_2 production in Chemical Looping.

Pressurised Chemical Looping Combustion of Coal with Iron Ore – Shuai Zhang, Southeast University

The objective of this study was to prove the feasibility of coal-fuelled pressurized CLC in a 100 kWth pilot scale unit and examine the potential of iron ore as a low-cost O_2 carrier for commercial coal-fuelled CLC. The challenges in CLC of coal lie in the low operating temperature which makes a coupling with power generation systems difficult, and the slow gasification rate. Tests in the 100kWth dual fluidised bed reactor revealed an increased CO_2 capture efficiency and carbon conversion at higher pressures. Hence pressurised Chemical Looping processes may be a feasible and promising option but on the other hand higher cost for pressurization and equipment issues have to be considered.

Gasification and Reforming of Solid Fuels in the Presence of Iron – Stuart Scott, University of Cambridge

For Chemical Looping Combustion solid fuels need to be converted to the gas phase through gasification. When using Fe_2O_3 –based carriers it was observed that these agents remove the mass transfer resistance in the gasification process and thus lead to an enhancement of gasification rates. Moreover, they will effectively combust the volatiles.

Investigation of Chemical Looping H_2 generation with CO_2 Capture – Shiyi Chen, Southeast University

In Chemical Looping H_2 generation which uses iron oxide as a carrier the gaseous fuels cannot be fully converted due to thermodynamic limitations. The presentation introduces a new fuel reactor in which a higher conversion can be achieved. It is also intended to send the high temperature gas product to a SOFC for electricity production.

H_2 Production from Bio-Oil Aqueous Fraction– Changfeng Yan, Guangzhou Institute of Energy Conversion

Steam reforming of bio-oil aqueous fraction coupled with CO_2 capture showed higher H_2 yields and concentrations than traditional steam reforming. H_2 production reaction with calcined dolomite revealed the highest H_2 yield among all carriers investigated. Calcined dolomite loaded with K_2CO_3 improved H_2 productivity by 20%.

Posters

New Progress on Calcium Based Catalyst/Sorbent Materials by SE-SMR – Asunción Aranda, IFE Norway

IFE has developed and patented a novel mixed CaO/calcium-aluminate sorbent with optimum properties for SE-SMR: long-term chemical stability, sufficient sorption capacity and high H_2 yield. Currently "all-in-one" particles including the catalyst are under development to overcome mixed sorbent issues like attrition and segregation with promising preliminary results.

Reactivity Improvement of Iron Ore in CDCL – Daofeng Mei, Huazhong University of Science and Technology

Natural iron ore is a cheap and readily available material and thus a promising O_2 carrier. However it exhibits low reactivity. Ores doped with other metal elements were tested for reactivity first in Hydrogen in a temperature programmed reactor and then with coal in a fluidised bed test reactor. Small improvements in reactivity were observed with Cobalt proving the most effective dopant.

Understanding the Effect of Inert Support on Reactivity Stabilisation for CaL – Zhenshan Li, Tsinghua University

The introduction of inert support materials into CaO particles can drastically improve the cyclic reactivity due to the inhibition of sintering. This study used a simple model to analyse how the Zener pinning force between CaO and support particles might explain this effect on the sintering resistance. The results were validated against literature data and showed agreement. The analysis suggests that there is a critical size of CaO particle beyond which further growth can be completely inhibited by the support, although there is also a mechanism by which encapsulation of the support particles can remove this inhibition of growth. These results are important in gaining a more fundamental understanding of synthetic sorbent performance.

Ca(OH)2 Superheating: A Means to Improve the CO_2 Capture Performance of Lime – Robert Holt, IRL New Zealand

This poster describes IRL's Reactivation Process for CaL, which has three stages: hydration of spent lime in steam, annealing in CO_2 and finally dehydration. During annealing in CO_2 $Ca(OH)_2$ becomes superheated compared to the equilibrium decomposition temperature. The process restores the attrition resistance towards that of the raw limestone. It is proposed to apply the process to a slipstream of the circulating sorbent adjusting this to control the activity of the sorbent to an optimum. This Reactivation Process is proposed as a stand-alone system, with the steam for hydration internally cycled from the dehydration to hydration stages. An average capture activity of 40% is predicted from TGA measurements with repeated reactivation operations after every 7 CO_2 capture cycles. The system offers the potential for average capture activity to be a design parameter set from 20-50%.

Techno-economic Study of the Zero Emission Gas Power Concept (ZEG) – Julien Meyer, IFE Norway

The ZEG concept, which is a combination of SE-SMR to produce H_2 and a SOFC producing electricity as well as providing the heat for the sorbent regeneration, has been compared with a more conventional pre-combustion reference case. The results show that the ZEG technology shows a positive and relatively high NPV for most price scenarios even when there is no revenue from the captured CO_2.

Effect of Sorbent Type on the SEWGS Process in a Fluidised Bed Reactor – Yang Liu, Tsinghua University

This work investigated SEWGS based on CaL with natural sorbents for CO_2 captured from a blast furnace (BF) gas. Because of its relatively high N_2 content BF gas is not amenable to oxy-combustion capture. In natural sorbents both CaO and MgO act as a catalyst. It was observed that once the CaO is covered by $CaCO_3$ product, the MgO, which remains uncovered and thus stays catalytically active, can still continue catalysing the WGS reaction.

Sorbent Enhanced Steam Gasification of Biomass – James Butler, University of British Columbia

Preliminary breakthrough experiments in a BFB together with some cyclic tests have been carried out on biomass gasification with CaO for CO_2 capture. Removal of CO_2 during biomass gasification increases the yield of valuable product gases by shifting the equilibrium towards the desired products. When CaO is used as a sorbent, the formation of $CaCO_3$ also provides the majority of the heat required for gasification. Although the study found a slightly decreased quantity of tar when CaO is present, the overall generation was still quite high due to the low gasification temperatures and thus remains an issue in gasification.

Elevated Temperature PSA Technology for Pre-combustion CO_2 Capture – Shuang Li, Tsinghua University

The study investigated the application of layered double hydroxides (LDH) in a PSA for post-combustion CO_2 capture in IGCC plants. K_2CO_3 promoted LDH showed a good cyclic stability and a higher CO_2 capacity than non-promoted LDH, even under elevated pressure.

A Novel Ca-Ni-based Hydrotalcite-supported catalytic CO_2 sorbent for SE-SMR – Marcin Broda, ETH Zürich

A new bifunctional catalytic sorbent, containing both the Ni catalyst and the Ca-based sorbent, was synthesised and investigated. The bifunctional catalytic sorbent produced a larger amount of high-purity H_2 than the other sorbents examined which were mixtures of catalytic material and limestone. The good performance is attributed to the fact that both Ca and Ni are co-precipitated as nanoparticles on a spinel matrix. Because the CaO particles are very small much of the carbonation reaction occurs in the initial fast phase.

Kinetics of Nano CaO Reactions with CO_2 – P. Q. Lan, Zheijiang University

The authors developed a gas-solid reactive adsorption model to describe nano CaO reaction with CO_2. The results of experiments were analysed using the model for nano CO_2 which had undergone multiple pre-treatments. They determined that the reaction time and the conversion in the rapid reaction regime are reduced by pre-treatment.

Plenary Discussion

Moderator: Mike Haines, IEAGHG
Panel: Paul Fennel, Stuart Scott, Henrik Leion, Carlos Abanades, Dennis Lu, Paul Cobden

The initial question addressed to the panel was aiming at an evaluation whether science or technology will be the driving force for future development and deployment of CaL, CLC and CLOU.

Stuart Scott responded that the point of science is to support the technology. It is not possible to go for a certain technology without a detailed scientific understanding of it.

Paul Fennel clearly stated that both elements are of great interest for the scale-up of CaL and CLC.

Henrik Leion and Dennis Lu also subscribed to this view by underlining that both cannot be separated and that the scientists need to be involved in the process of development and deployment at all times.

However, Henrik made the remark that the CLC community had suffered from focussing too much on the science part and thus a correct balance between science and technology is needed.

In contrast, Carlos Abanades pointed out that technology has to be the real driver and needs to be ready for deployment. Technology should enable the process to be operated efficiently and be simple at a large scale. It is important that fundamental research is useful and applicable.

Paul Cobden explained that in the future CO_2 capture may become the most important driver. Nevertheless, the science has to be done to make the technology cheaper and more efficient.

The next question posed was related to the comparison of CLC with pressurised oxyfuel combustion.

Dennis answered that high pressure is favourable for many processes and this also applies for CLC.

Mike pointed out that an exergy analysis may be important here and that there is still a high penalty because of the ASU. Oxyfuel combustion may become a competitor once the efficiency of the overall process increases.

Henrik raised concerns over the cost of pressurisation of flue gas in general which led Stuart to the conclusion that only pressurised CLC should be compared with pressurised oxyfuel combustion, as both are 2nd generation technologies.

Finally, the question regarding the economics of the solid looping technologies was raised.

There was a broad consensus among the panel members that all CaL, CLC and CLOU have the same problem of not being economically feasible yet.

Stuart said that as researchers we can also provide value by providing fundamental understanding of the various physical and chemical processes which take place. It is sometimes hard to say whether an oxygen carrier is better or worse as we are not considering the full economic implications of the benefits/costs. We should be looking to understand mechanisms and causes since this general knowledge will help move the technology forward.

Mike responded that more publications comparing the performances of the different processes are needed. However, one has to be careful when doing cost analyses for different locations, as they may not be suitable for comparison without constraints.

Carlos pointed out he thinks it should not be too difficult or take too long to come up with a first cost estimation using rules of thumb. It is important for new concepts to first believe in the concept itself, then do the necessary research and finally go on to the economics. He also stated that the transformation between heat and electricity is well established and can be used as a basis. In addition it is crucial to gain sufficient data to identify and exclude the non-feasible processes.

Dennis added that similar reactor types and process technologies already exist, so it would be a good idea to approach engineering companies when starting a techno-economic evaluation.

Meeting Conclusions

At this meeting further steady progress is evident in formulation and testing of sorbents, integration of both CLC and CaL processes with an extending range of industrial processes and in the emergence of encouraging first results from larger scale testing of the process in MW scale demonstration units. A better understanding of the science behind sorbent performance is needed to make the search for better materials more effective. There is also an emerging need to develop a set of credible techno-economic performance figures for the technology to justify further and potentially increasing R&D expenditures as phase in which larger demonstration units are required is entered. Finally the environmental performance of the processes needs to be assessed more rigorously especially as this may represent a considerable advantage over competing systems.

Offers to hold the next meeting in Canada or Cambridge (UK) were gratefully received. After considerable debate the meeting proposed to accept the offer from the University of Cambridge (UK) for the 2013 meeting. A decision on whether to hold a meeting in 2014 in view of the plans to hold the biennial CLC conference somewhere in Europe around the same time will be made at a future date. One alternative is to move to biennial meetings.

All participants agreed that this meeting had been most successful and expressed their sincere thanks to the staff at Tsinghua University for their hard work and excellent organisation.

Evaluating technology options to mitigate greenhouse gas emissions

IEA Greenhouse Gas R&D Programme

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