Advanced Solid Cycle with Efficient Novel technologies

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Executive summary

ASCENT project has been conceived as a platform for comparing the performances of the three different CO_2 capture technologies for hydrogen plants and hydrogen/power co-generation plants. Project activities were organized in three categories: (i) assessment of technologies and benchmarking, (ii) joint R&D activities and (iii) cross-cutting activities..
The main achievements are (i) energy assessment and (ii) techno-economic analysis of the integration of ASCENT technologies: Calcium-Copper cycle (Ca-Cu), Sorption-Enhanced Reforming (SER) with either indirectly heated calciner or oxy-fuel calciner, and C-Shift process in hydrogen production.

Assessment of the ASCENT technologies and benchmarking – The main achievement are (i) Energy assessment and (ii) techno-economic analysis of the integration of Ascent technologies Ca-Cu, SER with indirectly heated calciner and oxyfuel calciner and C-Shift processes in hydrogen.

R&D activity – the main outcomes of the R&D activity are below summarized.

- Summary of the achievements in the combined Ca-Cu chemical Loop development (WP2)– The main results achieved in this work package are related to (i) Selection of the functional materials for Ca-Cu looping process; (i) the experimental conduction of the CaCu cycle at proof of concept scale (total amount of complete cycles carried out is more than 200) and (ii) the validation of reactor models.
- Summary of the achievements in the Fast Sorbent mediated water-gas shift (WP3) – The main achievements have been: (i) choice of lead sorbents according to shared criteria; (ii) testing of chosen sorbent material at real WGS conditions understanding the amount of water vapour needed in the process, the sorbent stability and performance at sour conditions; (iii) A new C-SHIFT process configuration has therefore been suggested.
- Summary of the achievements in the SER looping cycle (WP4)– The main achievements were: (i) development of production methods for sorbent and combined sorbent-catalyst materials, selection of promising materials for proof of concept, production at kg-scale; (ii) development of particle and reactor models for detailed understanding of the material functions. (iii) Validation of material performances through an experimental pre-proof of concept; (iv) the experimental validation of the SER reactor models along with its implementation under industrially relevant conditions; (v) the conduction of the experimental proof-of concept of the SER process.

Impact of the project – The safety and sustainability analysis of the ASCENT technology has been carried out using a multicriteria approach: the analysis and key impacts obtained covered safety, environmental LCA and socio-economic factors provided. The results demonstrate that **globally the ASCENT technologies fare well or show equivalent trends in terms of the safety and sustainability impacts assessed**.

Dissemination and exploitation of the project results were planned to boos the deployment of carbon capture technologies in Europe and worldwide by creating a durable network of excellence integrating R&D capacities and relevant industry.
Impacts on the scientific community and industry are summarised below:

- The consortium of the ASCENT project has hosted the second EU-Australia workshop in the SwissTech Convention Centre of the École Polytechnique Fédérale De Lausanne (EPFL) back-to-back to the GHGT 13 in order to share latest results achieved in the European and Australian research in carbon capture technologies.

- ASCENT members have participated to the Mission Innovation workshop organized by USA and Saudi Arabia in Houston in order to identify future research challenges. The ASCENT consortium is proud to contribute with the other EU initiatives in paving the future of the worldwide research in the advanced carbon capture processes and demonstrating the value of continued EU research, including the contribution of the UK.
- Manufacturing processes of the developed materials are eminently feasible; there is no currently apparent reason why any of these materials cannot be made on a large scale. The equipment to produce them such as large pelletisers and hydrothermal synthesis units already exist. Given the will and resources, it is expected that the manufacture of the sorbents could be successfully scaled up to pilot scale and then commercial scale over the next few years.

1. DESCRIPTION OF THE PROJECT CONTEXT AND THE MAIN OBJECTIVES

1.1 Description of the project

ASCENT project has been conceived as a platform for comparing the performances of three different CO_2 capture technologies for hydrogen plants and hydrogen/power co-generation plants. Project activities were organized in three categories: (i) assessment of technologies and benchmarking, (ii) joint R&D activities and (iii) cross-cutting activities.
The global objectives related to these three categories are as follows:

- The assessment of technologies and benchmarking takes a broad approach and examines the potential merits of benchmarks for evaluating and comparing the performance of the three investigated processes in order to set industry performance targets.
- The lead objective of the Joint R&D actions is to provide a robust proof-of-concept with industrially relevant conditions and materials at full scale for future demonstration.
- The joint aim of the Cross-cutting activities is to define and put in practice dissemination and exploitation plan (i.e. Dissemination, Exploitation activities) along with the administration plan (Management) to increase the internal and external project awareness and spread the excellence.

The whole project has been conceived as composed of the following eight work packages: the assessment of technologies and benchmarking consists of WP1 (Performance criteria and benchmarking), the Joint R&D activity consists of WP2 (Combined Ca-Cu Chemical Loop: process development), WP3 (Fast Sorbent mediated water-gas shift) and WP4 (SER looping cycle). Cross-cutting activities consist of WP5 (Safety and sustainability impact assessment), WP6 (Dissemination) and WP7 (Exploitation) and WP8 (Management).

The key feature of the ASCENT project is that it increases value by bringing together new technologies related to the pre-combustion capture via chemical looping combustion, sorption enhanced shift and sorption enhanced reforming in a combined activity; meaning that some work that would otherwise need to be repeated three times within three separate projects can be performed just once, and that all three technologies will be appraised with a common set of rules.
Simplified schemes of all three concepts are shown in Figure 1. In the first concept, Ca-Cu, a Calcium-Copper looping cycle matches two endothermic-exothermic reaction pairs in the same equipment. The heat needed to drive the endothermic steam-methane reforming reaction is matched with in-situ heat production from the calcium carbonate formation reaction. At the same time, the heat required to regenerate a calcium carbonate material is matched with in-situ heat production through the reduction of CuO to Cu metal. This fixed-bed pressure and temperature-swing process unites the chemical looping combustion and Ca-looping into a single concept, producing hot pressurised hydrogen ready to be used in a gas turbine.
In the second concept, CSHIFT, a highly innovative fluidized bed reactor system is used to match the heat requirements of reaction and regeneration of medium temperature carbon dioxide acceptor materials (300-600°C) with pressure swing technology. This is an ENDEX reactor system, and allows hydrogen production at pressure with subsequent carbonate regeneration at reduced pressure and thus reduced temperature. This fluidized-bed pressure-swing concept builds on and combines the ideas of flash calcination for the production of highly reactive CO_2 capture materials together with the in situ CO_2 capture in a continuous process.
In the third concept, SER, a Nickel-Calcium dual fluidized bed looping cycle is used to generate a hydrogen-rich fuel to be used in a power cycle. Although a pressurized reforming reactor may be

employed for integration with a hydrogen-fired combined cycle, SER process is best operated at low pressure and combined with a high temperature fuel cell system. The endothermic steam reforming reaction producing hydrogen is thermally balanced by the exothermic carbonation reaction of the Ca-loop to provide a thermally balanced conversion. The multi-functional solid material is able to both catalyse the steam reforming reaction, remove the CO_2 formed, and provide the heat needed for the combined reactions. The hydrogen produced is then preferably fed to a high temperature fuel cell system that generates both electricity and the heat necessary to regenerate the carbonated solid material. The integrated concept combines a highly efficient sorption-enhanced steam reforming process, run in a dual fluidized bed reactor system, with a highly efficient high temperature fuel cell with optimal heat integration.

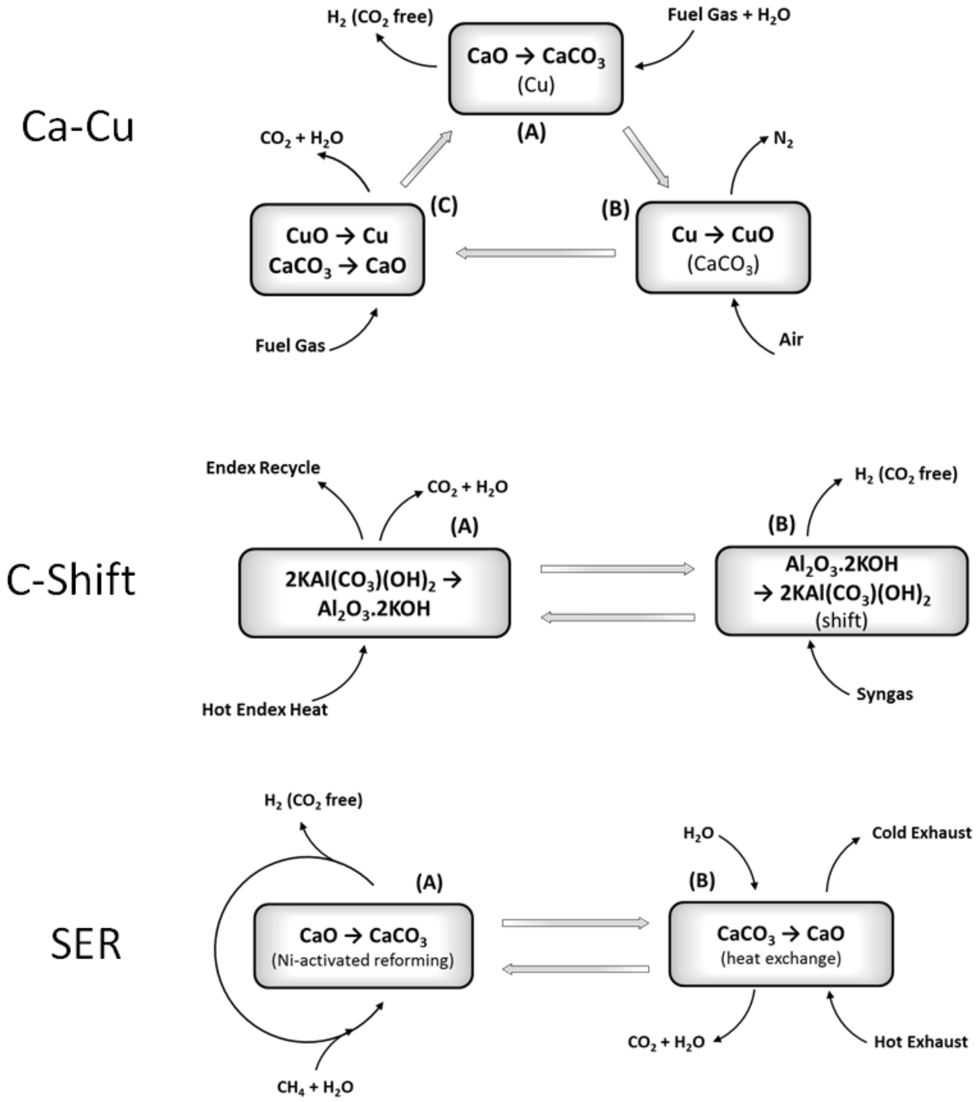

Figure 1 Conceptual cycles for the Ca-Cu, CSHIFT and SER reaction systems respectively

The objectives per each single WP are summarized below:

Performance criteria and benchmarking (WP1)

- Definition of the reference commercial technologies with and without CO2 capture for electricity and hydrogen production (benchmark technologies). Calculation of mass and energy balances of these plants: input data for the LCA analysis of the benchmark technologies;

- Definition of performance criteria for the catalyst and the sorbent of the Ca-Cu, CSHIFT and SER processes, when integrated in full scale plants for power and hydrogen production: input data for technology development;
- Comparative assessment of technology; 'benchmarking' based on agreed system boundaries and key performance indicators;
- Evaluation of the cost of electricity, hydrogen and CO2 avoided for the benchmark technologies: reference for Ca-Cu, CSHIFT and SER-based plants;
- Technical analysis and economic evaluation of plants integrating the SER, Ca-Cu and CSHIFT processes: input data for the LCA analysis (WP5);

Combined Ca-Cu Chemical loop: process developmen (WP2)

- To formulate process models (flow-sheeting) to select optimum solids composition and operating conditions;
- To synthesize stable materials to run the Ca-Cu looping process at least during 200 cycles in differential reactors and 100 cycles in an integral reactor;
- To determine the reaction kinetics of the materials involved in every process stage;
- To develop detailed particle and reactor models and through validation of the models with experimental data;
- To carry out the proof of concept at lab scale but at industrially relevant operating conditions by running at least 100 complete cycles.

Fast Sorbent mediated water-gas shift (WP3)

- To develop sorbents that maintain fast sorption/desorption kinetics with <1% degradation of cyclic sorption capacity during 100 cycles under industrially relevant conditions
- Thus to identify sorbents with fast enough kinetics such that the combination of WGS activity and CO_2 capture leads to >90% decarbonisation in a single pass with reactors preferably not more than 12 m in height.
- To find a cheap way to prepare said synthetic sorbent in an analogous way to those traditionally produced in situ from mineral feeds (such as activated limestones, dolomites and hydrotalcites). To find optimal process configurations and process cycles which give low physical particle degradation
- To understand sorbent particle degradation mechanisms and be able to use this knowledge to improve sorbent/process performance
- To understand the properties of sorbents in the presence of other sour gases than CO_2, i.e. H_2S, to reduce steam use in water-gas shift below 2 mole steam per mole CO in the gas phase and reduce H_2S slip in the hydrogen product to <10 ppm.
- To develop a model of the operation of CSHIFT cycles over a range of process parameter conditions that can be used in WP1 for the optimization of the pre-combustion power scheme with high efficiency, low emission and low cost CO_2 avoided, minimizing the energy penalty

SER looping cycle (WP4)

- Define a set of performance criteria for the materials to be developed and determine realistic process conditions for process simulation and proof of concept.
- Develop production methods for sorbent and combined sorbent-catalyst materials using different synthesis and granulation techniques, produce batches of granulated materials at kg-scale suited for the experimental proof-of concept.

- Prepare agglomerates of combined sorbent-catalyst materials using different methods and starting materials, in batches of different sizes, adapted to the proof of concept experimental set-up.
- Fully characterize the developed materials with advanced analysis and test techniques
- Develop particle and reactor models for detailed understanding of the material functions and use the models as mathematical tools for representative process simulations and techno-economics studies.
- Validate material performances through an experimental proof of concept.

Safety and sustainability impact assessment (WP5)

- To identify and analyze the potential process safety risks that could be critical for the 3 technology lines using advanced solid adsorbents with capture of CO2. The main gaps in terms of safety for the different technology lines will be identified and recommendations will be outlined for the safe deployment and operation of these technology lines.
- Assessment of the life cycle environmental impacts of the selected technology lines, implementation of the environmental profile to these lines and comparison with existing alternatives. The LCA methodology will allow dealing with the specific carbon capture dimension of the investigated technologies.
- Assessment of the socio-economic impacts (SEA) of the ASCENT technologies focusing on the advantages and disadvantages for the society. SEA will also discuss conditions for a successful adoption of the ASCENT technologies by industry and for market deployment.
- Finally, the results from the previous tasks will be put in perspective with the legal framework and its possible evolution in order to identify potential gaps that would be needed to facilitate the large scale implementation of these technology lines in the future.

Dissemination (WP6)

- disseminate results obtained from various work packages of the project;
- Implement web-site;
- create preliminary awareness of the project during the first phase;
- create the basis for the exploitation of ASCENT.

Exploitation of the developed sorbent technologies (WP7)

- To develop a comprehensive exploitation plan for the commercialisation of the outcomes and developments of the studies.

Management (WP8)

- To co-ordinate and manage the project's resources;
- To supervise the progress of the project in implementation tasks and achieving deliverables and milestones within the fixed timetable;
- To enable project cohesion and encourage co-operation between partners;
- To strengthen and develop links between partners to pave the way for future consortium expansion;
- To ensure that all the European Council's requirements for reporting are met.

1.2 The consortium of the project

The consortium as a whole is represented by the value chain shown below in Figure 2. This is a representation of the three related pre-combustion decarbonization technology line in the process, working through the sorbent supplier, research partners, lead developers in support of the SMEs.

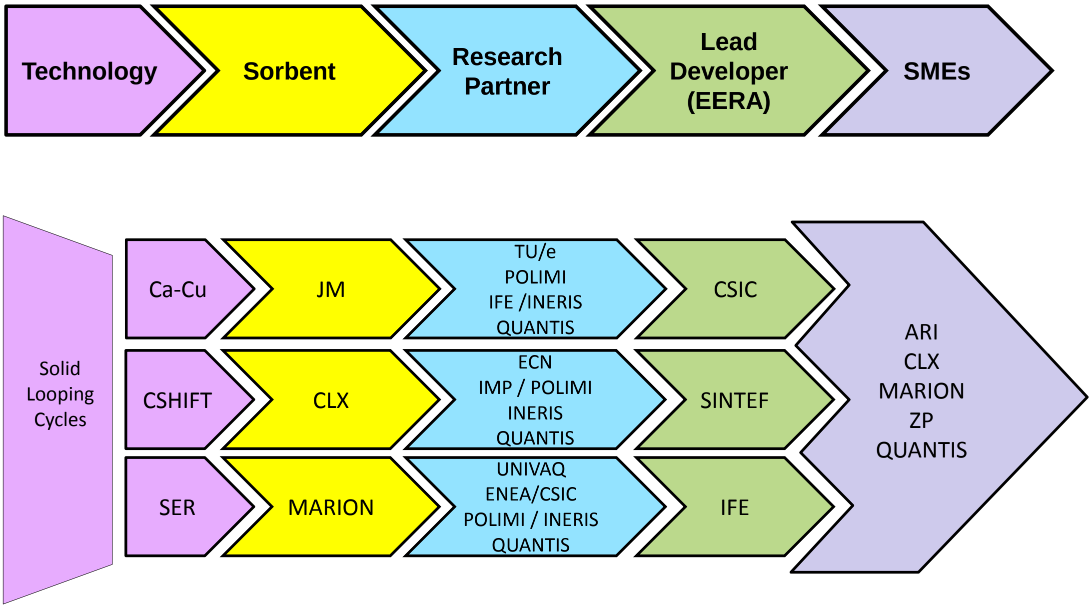

Figure 2 ASCENT value chain

Altogether, the ASCENT project includes 4 universities (UNIVAQ, TUE, POLIMI, IMP), 5 industrial companies (JM, ARI, MTEC, ZEG and CALIX), 4 research centres (ECN, IFE, QUANTIS and SINTEF), a public research institute (INERIS) and two national research agencies (CSIC and ENEA). The partners are located in 5 Member states of the EU: Netherlands (TUE, ECN, ARI), United Kingdom (IMP, JM and CALIX), Italy (UNIVAQ, ENEA and POLIMI), France (MTEC and INERIS), Spain (CSIC), and two Associated Countries, Norway (IFE, SINTEF and ZEG) and Switzerland (QUANTIS). Of the partners in ASCENT, 3 are SMEs (ARI, MTEC and QUANTIS) and 2 are enterprises (CALIX, ZEG).

In addition, some of the consortium members have a long record of previous collaboration in research projects on related subjects. The university partners and research bodies are being involved in the permanent European research network EERA to strengthen the relations between the institutions in view of a long term collaboration in the frame of an international program for R&D in the pre-combustion CO2 capture. In addition, some of the partners have been involved in academic staff and student exchanges, including joint PhD programmes, and are cooperating in permanent research networks.

2. DESCRIPTION OF THE MAIN R&D RESULTS

2.1 WP1 Performance criteria and benchmarking

2.1.1 First review period

Summary of the achievements – The main achievements are (i) the development of reference plants with and without CO_2 capture and (ii) preliminary definition of plants configurations integrating SER, Ca-Cu, CSHIFT and SER processes.

Overview.

Development of reference power with and without CO_2 capture – Methodology and results obtained have been agreed and shared with the University of New South Wales (UNSW) which is a twinned partner of the project. Within the first review period, the process models of the following power plants have been developed:

- Natural gas combined cycle (NGCC) without CO_2 capture
- Natural gas combined cycle with post-combustion CO_2 capture by MEA chemical absorption process.
- Natural gas combined cycle with pre-combustion CO_2 capture by Auto-thermal reforming (ATR) and chemical absorption MDEA processes

- Natural gas SOFC-based power plant without CO_2 capture
- Natural gas SOFC-based power plant with CO_2 capture by low temperature CO_2 separation.

- Coal-fed integrated gasification combined cycle (IGCC) without CO_2 capture
- Coal-fed integrated gasification combined cycle with CO_2 capture by physical absorption by Selexol process.

Performance of the presented plants is evaluated through performance indexes commonly used in studies on capture plants, e.g. electric efficiency, specific emissions and CO_2 avoided. The specific primary energy consumption for CO_2 avoided (SPECCA) index, introduced in EBTF work to evaluate energy and environmental performance in a single index, is also used.

NGCC - The basis of design is largely derived from the EBTF (European Benchmarking Task Force) document. The NGCC without CO_2 capture and with post-combustion CO_2 capture are directly taken from the EBTF document.

The main results are as follows:

- The reference combined cycle achieves an electric efficiency of 58.42%, with specific emissions of 350 kg/MWh.
- The NGCC with post-combustion CO_2 capture achieves a CO_2 capture efficiency of 91.2% and an electric efficiency of 49.90% (-8.5% points less than the case without capture), leading to a CO_2 avoided of 89.7%.
- The NGCC with pre-combustion CO_2 capture achieves a CO_2 capture efficiency of 91.6% and an electric efficiency of 47.12% (-11.3% points less than the case without capture), leading to a CO_2 avoided of 89.5%.

- SPECCA of 3.35 and 4.71 MJ/kg$_{CO2}$ result for the post-combustion and pre-combustion plants respectively.

SOFC-based plants – SOFC-based plants were completely developed within Ascent. Due to the lack of commercial maturity of SOFCs and the lack of widely accepted benchmarks, these plants where defined on the basis of open literature information and previous experience of the partners in this field. Two types of SOFC-based power plants have been defined, namely: (i) a slightly pressurized SOFC in hybrid configuration with a gas turbine cycle (i.e. with a topping SOFC "substituting" the combustor of a bottoming gas turbine) and (ii) an atmospheric pressure SOFC with bottoming heat recovery steam cycle.

The main result achieved is:

- The low values of the SPECCA index obtained with respect to the combined cycle cases highlight the interesting properties of SOFCs, that are intrinsic O_2 separators and hence produce concentrated CO_2 effluents undiluted with N_2.

IGCC – The IGCC plants are also mainly based on the EBTF document, including some modifications defined in previous FP7 projects Demoys and Democlock.

The main results achieved are as follows:

- The reference IGCC with CO_2 capture has an electric efficiency of 37.70%, corresponding to an efficiency penalty of about 9.6 % points with respect to the IGCC w/o capture.
- CO_2 avoidance of almost 87%, and SPECCA of 3.02 MJ/kg are obtained from the balance.

Preliminary definition of plants configurations integrating SER, Ca-Cu, CSHIFT and SER processes – It was proposed a preliminary integration of Ca-Cu, SER and C-Shift processes in full scale power plants. Modifications to these configurations occurred during the project, on the basis of the mass and energy balances resulting from the experimental findings and on the results of the economic analysis.

The main configurations were as follows:

NG-fired power plant with CO_2 capture by Ca-Cu process –Ca-Cu process is fed with a high pressure pre-reformed NG/H_2O stream with high S/C for hydrogen production (stage A) and a low pressure pre-reformed NG/H_2O stream with low S/C for CuO reduction (stage C). All the inlet natural gas is desulfurized at high pressure in a conventional Zn-bed. A portion of the natural gas is then expanded to nearly atmospheric pressure in a turbine. Both the HP and the LP natural gas streams are mixed with steam in different S/C ratio and pre-reformed in order to reduce the risk of carbon deposition in the packed beds of the Ca-Cu process, which may occur in the initial part of the bed when active sorbent and oxidized oxygen carrier are not available during stages A and C' respectively. They are then heated up and fed to stages A and C of the Ca-Cu process. The product of these stages is a high pressure H_2/H_2O stream which is used as fuel for the combined cycle after partial cooling, and an atmospheric pressure CO_2/H_2O stream which is cooled by heat recovery and compressed for CO_2 storage. The other main stream entering the Ca-Cu system is the N_2-rich N_2/O_2 mixture for Cu oxidation (stage B). The hot N_2 produced during stage B is then sent to the GT combustor and expanded in the gas turbine. As in all the power plants based on combined cycles, the heat recovery steam cycle is a state of the art three-pressure level with reheat cycle.

NG-fired power plant with CO_2 capture by SER process and SOFC system – A hydrogen-rich fuel is produced at low pressure in a reformer-carbonator fluidized bed reactor, which is fed with desulfurized natural gas and steam. No pre-reforming is expected to be needed in this case, thanks to the uniform temperature of the reactor and the uniform availability of active CO_2 sorbent, guaranteed by the bed fluidization. The H_2/H_2O stream produced in the reformer is fed to the anode of the SOFC. Here, it is partly oxidized by hot air, preheated in a high temperature heat exchanger by the hot SOFC exhausts. H_2 oxidation is completed outside the SOFC in a combustor, using a portion of the O_2-rich gas from the SOFC cathode. This hot stream is used to provide the heat to the SER calciner for sorbent regeneration through tubes immersed in the bed. In the calciner, streams of cooled calciner exhausts and LP steam are used for bed fluidization and for reducing the CO_2 partial pressure in the reactor, in order to reduce the regeneration temperature.

The heat recovery steam cycle is based on a two-pressure level with reheat cycle, differently from all the combined cycle-based cases (which are based on three-level cycles). This is considered a suitable cycle for the size expected for this steam cycle, which will be much lower than in the other cases due to the higher power share produced by the fuel cell and the lower natural gas heat input. A heat input of 100 MW_{LHV} will be assumed for these cases (vs. about 800 MW of the combined cycle plants), which is considered a reasonable compromise for power generation with a technology which is currently not available for large scale plants.

NG-fired power plant with CO_2 capture by SER process and combined cycle

The two configurations differ in how heat is provided to the calciner for sorbent regeneration, which can be obtained by heat transfer tubes immersed in the fluidized bed or by oxyfuel combustion. In both cases, a hydrogen-based fuel is produced in the reformer-carbonator (stream 1), which is fed with desulfurized natural gas (2) and LP steam (3). The hydrogen produced is cooled, compressed and fed to the GT combustor (4).

In case of the indirectly heated calciner, a portion of the hydrogen produced is burned with part of the high pressure air from the GT compressor and fed to the calciner heat exchanger. The hot gas exiting the calciner heat exchanger is then returned to the GT for expansion in the turbine. As in the SOFC-based plant, the calciner is also fed with recycled calciner exhausts and LP steam for bed fluidization and for reducing the CO_2 partial pressure and hence the regeneration temperature.

NG-fired power plant with CO_2 capture by SER Endex process

The plant configuration is the original plant proposed by Calix for the integration of the Endex CO_2 separation process in a NGCC. Natural gas is heated and mixed with IP steam to achieve a suitable S/C ratio. The mixture in the converted in a high pressure adiabatic decarboniser reactor, where steam reforming, water gas shift and CO_2 removal by CaO carbonation are performed. A H_2-H_2O based mixture is produced in this way in this reactor at high pressure, suitable to be used as fuel in the GT. The carbonated sorbent is regenerated in the calciner, which is operated at low pressure and at temperature of around 900°C. Solid circulation between the two reactors is performed by means of the Calix pressurization-depressurization devices. Pure CO_2 is released from the calciner, which is cooled by heat recovery and compressed for final storage. Heat for endothermic calcination is provided by heat transfer between a calciner combustor, where part of the H_2 fuel from the decarboniser is burned with a portion of boosted compressed air from the GT compressor. The hot combustion gases from the calciner combustor are then returned at high temperature and high pressure to the gas turbine, where they are furter heated up to the maximum cycle temperature and expanded in the turbine.

IGCC with CO_2 capture by C-Shift Endex process

For the integration of the C-Shift process, an IGCC plant has also been considered. Due to the uncertainty related to the tolerance of C-Shift material to H2S, two configurations have been considered, where syngas is either desulfurized before the C-Shift process or desulfurized within the C-Shift process. In both plant configurations, coal is gasified in a dry-feed, oxygen blown Shell gasification process, where a CO/H2-based syngas is produced

2.1.2 Second review period

Summary of the achievements – The main achievements are (i) Preliminary economic evaluation of power plants integrating SER, Cu/Ca and CSHIFT processes; (ii) evaluation of the heat and mass balances of selected ASCENT technologies for H2 and power production.

Overview.

Evaluation of the heat and mass of selected ASCENT technologies

During the second review period the following activities can be reported with regards to the application of ASCENT technologies in power plants and H2 production plants:

Ascent technologies integrated in power plants - These power plants consider the use of a syngas produced in a natural gas reforming process with CO_2 capture as fuel. The following four plants are studied in this report:
(i) NG-fired power plant with CO_2 capture by the Ca-Cu process and combined cycle; (ii) NG-fired power plant with CO_2 capture by Sorption Enhanced Reforming (SER) process and SOFC system; (iii) NG-fired power plant with CO_2 capture by Sorption Enhanced Reforming (SER) process and combined cycle; (iv) NG-fired power plant with CO_2 capture by Calix Endex process and combined cycle; (v) ATR and IGCC-based power plants integrated with the C-shift process as a pre-combustion CO_2 capture system.

The preliminary economic analysis of selected cases of all the Ascent power plants has also been performed and discussed during the second review period. The primary goal of this assessment is to define the regions of economic competitiveness of the novel Ascent processes where target Capex-Opex areas are evaluated for the process developers. For the Ca-Cu NGCC and SER-SOFC cases, a preliminary estimation of the size and cost of the chemical island was possible and therefore costs of electricity and of CO_2 avoided are reported in the deliverable.

The main conclusions are here reported:

- Ca-Cu CC, oxy-SER CC and SER-SOFC power plants show efficiencies and SPECCA in line with the benchmark. Benefits over benchmark technologies should be therefore expected form the economics of the systems.
- C-Shift power plants show efficiencies and SPECCA significantly better than the benchmark. For this technology, the development of high temperature lock-hoppers (TRL<5) is needed beyond Ascent.
- Due to the different advancement of the reactor modelling work in WP2-3-4, the process simulations and economic analysis of the different technologies have a different level of uncertainty. For the Ca-Cu process, reactor modelling is at an advanced stage and detailed data have been used for the process simulation work and for reactor sizing. For the SER and the C-Shift processes, more detailed inputs from reactor modelling are expected in the future months from the corresponding WPs.

Ascent technologies integrated in H2 production plants. As for the ASCENT technologies for H2 production: overall results of the heat and mass balances of selected plants were also achieved. Among the key performance indicators, it is recalled that the ‘equivalent’ indicators (subscript ‘eq’) are calculated from the equivalent natural gas consumption, which accounts for the indirect primary energy consumptions and CO_2 emissions associated to the import of electricity and for the credits associated to steam export, as defined in the first review period.
Following the same approach used for power plants and breakeven Capex and Opex have been calculated, defining an area of economic competitiveness of the novel Ascent technologies. These resulting areas for the five Ascent hydrogen plants presented above represent the target Capex and Opex of the novel technologies leading to lower cost of CO_2 avoided than the benchmark FTR plant.
The main results are as follows:

- For the CaCu process, two cases with two operating pressures of the SER stage (25 and 11 bar) have been compared. The low pressure case features higher hydrogen production efficiency and low CO_2 capture ratio. SPECCA of both CaCu cases is significantly better (between 50 and 62 % lower) than the benchmark FTR plant with capture.

- For the SER process, two cases with indirectly heated calciner and directly heated oxy-fuel calciner have been considered. The selected indirectly heated calciner case results in a low CO_2 capture efficiency. This can be increased by increasing the S/C ratio in the reformer, which however causes significantly higher fuel consumption in the external calciner burner, which worsens the SPECCA. CO_2 capture ration is much higher in the oxyfired calciner case, because the carbon species which slip from the reformer are separated in the PSA and burned in oxyfuel conditions in the calciner and are therefore captured. SPECCA in this case is competitive with the benchmark FTR without capture (13% lower), although the electric consumption is the highest among the examined cases due to the consumption of the ASU and of the hydrogen compressor which is needed because of the operation of the reformer at low pressure.
- For the C-Shift plant, hydrogen production efficiency and CCR slightly better than the benchmark are obtained. Differently from the other Ascent cases, this plant needs a primary FTR for methane conversion. As a result, CO_2 capture efficiency is similar to the benchmark case and significantly lower than the Ca-Cu and oxyfired SER cases because carbon contained in the PSA off-gas is oxidized to CO_2 in the air-blown FTR burners and ultimately emitted to the atmosphere. Higher CCR are possible by increasing the S/C in the reformer, but leading to worse SPECCA. The SPECCA of the selected case is about 20% lower than the benchmark case.
- Higher margins have been obtained for CaCu plants, in particular in the high pressure CaCu case, which takes advantage of a smaller reactor volume and therefore a lower amount of sorbent, oxygen carrier and catalyst than the low pressure CaCu case. A lower margin is obtained for the C-Shift reactors, mainly because this plant still needs the high cost primary fired tubular reformer. Intermediate margin is obtained for the oxy-fired SER case.

2.1.3 Third review period

Summary of the achievements – The main achievement in the third review period is the finalization of (i) Energy assessment and (ii) techno-economic analysis of the integration of Ascent technologies Ca-Cu, SER with indirectly heated calciner and oxyfuel calciner and C-Shift processes in hydrogen.

Overview.

Energy assessment – The selected plants for the energy assessment are the following five options: (i) CaCu at 25 bar and 11 bar, (ii) SER with indirectly heated calciner, (iii) SER with oxy-fired calciner, (iv) C-Shift technologies.

Based on the results obtained, the following main considerations can be made:

- For the CaCu process, two cases with two operating pressures of the SER stage (25 and 11 bar) have been compared. The low pressure case features higher hydrogen production efficiency and low CO_2 capture ratio. SPECCA of both CaCu cases is significantly better (between 50 and 62% lower) than the benchmark FTR plant with capture.
- For the SER process, two cases with indirectly heated calciner and directly heated oxy-fuel calciner have been considered. The selected indirectly heated calciner case results in a low CO_2 capture efficiency. This can be increased by increasing the S/C ratio in the reformer, which however causes significantly higher fuel consumption in the external calciner burner, which worsens the SPECCA. CO_2 capture ratio is much higher in the oxyfired calciner case, because the carbon species which slip from the reformer are separated in the PSA and burned in oxyfuel conditions in the calciner and are therefore captured. SPECCA in this case is competitive with the benchmark FTR without capture (13% lower), although the electric

consumption is the highest among the examined cases due to the consumption of the ASU and of the hydrogen compressor which is needed because of the operation of the reformer at low pressure.
- For the C-Shift plant, hydrogen production efficiency and CCR slightly better than the benchmark are obtained. Differently from the other Ascent cases, this plant needs a primary FTR for methane conversion. As a result, CO_2 capture efficiency is similar to the benchmark case and significantly lower than the Ca-Cu and oxyfired SER cases because carbon contained in the PSA off-gas is oxidized to CO_2 in the air-blown FTR burners and ultimately emitted to the atmosphere. Higher CCR are possible by increasing the S/C in the reformer, but leading to worse SPECCA. The SPECCA of the selected case is about 20% lower than the benchmark case.

Techno-economic analysis for ASCENT hydrogen plants – Following the same approach used for power plants presented in the second review period, breakeven Capex and Opex have been calculated, defining an area of economic competitiveness of the novel Ascent technologies with the methodology developed in collaboration with the Australian partners of the University of Sydney. These resulting areas for the five Ascent hydrogen plants presented above represent the target Capex and Opex of the novel technologies leading to lower cost of CO_2 avoided than the benchmark FTR plant.

The main results obtained from capex and opex analysis are as follows:
- Higher margins have been obtained for CaCu plants, in particular in the high pressure CaCu case, which takes advantage of a smaller reactor volume and therefore a lower amount of sorbent, oxygen carrier and catalyst than the low pressure CaCu case.
- A lower margin is obtained for the C-Shift reactors, mainly because this plant still needs the high cost primary fired tubular reformer.
- Intermediate margin is obtained for the oxy-fired SER case.

Techno-economic analysis for ASCENT power plants– In the third period the final techno-economic analysis of power plants with CO_2 capture using Ascent technologies was presented. The following plants have been analysed in the report:
- Natural Gas Combined Cycle power plant with CO_2 capture integrated with the Ca-Cu process (Ca-Cu NGCC);
- Natural Gas power plant with CO_2 capture by SER process and SOFC system (SER SOFC);
- Natural Gas Combined Cycle with CO_2 capture by SER process and an oxyfuel calciner (Oxy-SER NGCC);
- Natural Gas Combined Cycle with CO_2 capture by C-Shift process (C-Shift NGCC);
- Integrated Gasification Combined Cycle (IGCC) based power plant integrated with the C-Shift process as a pre-combustion CO_2 capture system (C-Shift IGCC).

For all the Ascent plants, recognizing that the most uncertain capital and operating costs are those related to the innovative Ascent reactors, an economic analysis aimed at defining the region of economic competitiveness of the novel Ascent processes (i.e. reactors system and material) has been carried out. Based on the results obtained, the following key conclusions can be drawn about the assessed power plants integrated with Ascent technologies:

- <u>Ca-Cu NGCC</u> power plant shows overall performance in line with the benchmark NGCC-MDEA power plant with pre-combustion CO_2 capture. The higher electric efficiency (+0.6%-points) is balanced by lower CO_2 capture efficiency (-2.4%-points). As a result, a SPECCA slightly better than the benchmark (-1.5%) is obtained. The cost of CO_2 avoided of the optimized Ca-Cu

NGCC power plant is slightly lower (-4%) than the benchmark. A wide sensitivity analysis has been performed for the Ca-Cu NGCC plant, aimed at minimizing the cost of CO_2 by optimizing the size of the Ca-Cu reactors and the pressure drops in the Ca-Cu unit and in the main heat exchangers. Reducing the size and the L/D of the reactors as much as possible, compatibly with the construction and operability constrains, appears as the winning strategy because of the favorable effects on the amount of functional material needed and on the lower pressure drop when short reactors are adopted. Further engineering activities aimed at improving the design and reducing the cost of the vessels and of the valves of the Ca-Cu system can improve the economics of the plant. The final plant appears of relatively high complexity, because of the multiplicity of parallel reactors and of the high heat integration between the power island and the chemical island. As a result, the Ca-Cu NGCC plant is expected to be rather inflexible in the possibility of quickly modulating the electric power output and in the start-up and shut-down time. An advantage over the benchmark ATR-MDEA plant is the possibility of co-producing high pressure and high purity hydrogen, which appears as the most interesting option for improving the plant flexibility.

- SER SOFC power plant shows a lower efficiency (-1.4%-points) and higher CO_2 capture efficiency (+9%-points) compared with the benchmark SOFC-based power plant with CO_2 capture by low temperature phase change separation. The resulting SPECCA is higher than in the benchmark (+30%).From the economic point of view, the SER SOFC plant performs better than the benchmark, obtaining a comparable cost of electricity (-0.5%) and a lower cost of CO_2 avoided (-12.5%). The better cost of CO_2 avoided is mainly due to the higher CO_2 capture ratio. It has to be highlighted that the benchmark SOFC power plant has a relatively low CO_2 capture efficiency of 84.9% and an optimization of the CO_2 recovery process (e.g. by distillation column rather than by flash separation) may improve the CO_2 capture efficiency and reduce the advantage of the SER SOFC plant. It has to be highlighted that the SER SOFC power plant has several non-conventional components, such as the high temperature externally cooled SOFC, the high temperature heat transfer loop and high temperature heat exchangers. The estimation of the cost of these components has low reliability because their design and engineering was beyond the scopes of Ascent. The SER SOFC power plant has a rather high complexity compared with the benchmark. This is particularly evident when comparing the system composed by the SER reactors, the high temperature externally cooled SOFC and the high temperature heat transfer loop with a benchmark SOFC, where methane reforming and N_2-free fuel oxidation are performed intrinsically within the conventional SOFC with no need of additional equipment.
- Oxy-SER NGCC power plant shows a lower efficiency (-1.7%-points) a higher CO_2 capture efficiency (+1.3%-points) resulting in a higher SPECCA (+17%) compared with the benchmark ATR-MDEA plant. With the assumed size of the plant, which was defined to match with the size of a large-scale state-of-the-art heavy-duty gas turbine, the size of the SER reactors results to be very large because of their low operating pressure. Therefore, high gas throughput fast fluidized beds should be used in this case. Since modeling of such oxy-SER reactors was beyond the scope of Ascent, sizing and costing of the oxy-SER reactors has not been performed and the cost of electricity and CO_2 avoided was not calculated for this plant. Compared with the SER SOFC plant, the Oxy-SER NGCC power plant includes only conventional components apart from the SER reactor system. However, with the rather low efficiency and the high SPECCA, such system is expected to be hardly competitive with the benchmark. To improve the efficiency of the system and increase its competitivity, the high electric consumptions of the main auxiliaries (ASU and hydrogen compressor) should be reduced, for example by introducing innovative oxygen production processes or by slight pressurization of the SER reactors to increase the pressure of the produced hydrogen. An advantage compared to the benchmark is the possibility ofco-producing high purity hydrogen, which improves the plant flexibility.
- C-Shift NGCC power plant shows much higher efficiency (+4.1%-points) and lower CO_2 capture efficiency (-3.1%-points) compared to the benchmark, resulting in a significantly lower SPECCA (-40%). Modelling of the C-Shift reactor system is believed to be not sufficiently

developed to attempt sizing and costing of the process. Therefore, the cost of electricity and CO_2 avoided was not calculated for this plant, but economic targets have been provided in terms of breakeven Capex and Opex. The technical uncertainties of the C-Shift NGCC power plant are substantially related to the reactors system, since the plant does not include other components too far from the state-of-the-art technology. Uncertainties in the C-Shift process are largely related to the fluid-dynamics of the reactors and to the solids circulation system between the two reactors with substantial pressure swing, which rely on lock hoppers. Such uncertainty also affects the heat and mass balances of the plant, since lock hoppers will require compressed gas to operate, which was neglected in the heat and mass balance calculations of this study. The integration of the C-Shift process in an ATR-based plant leads to a simplified configuration, because the low temperature WGS, the syngas cooling and the CO_2 absorption sections are avoided. On the other hand, if the ATR is an air-blown unit, the C-Shift power plant is not suitable for co-production of high purity hydrogen, reducing from this perspective the plant flexibility.

- C-Shift IGCC power plant shows higher efficiency (+1.6%-points) and similar CO_2 capture efficiency compared to the benchmark, resulting in a lower SPECCA (-20%). The same remarks expressed for the C-Shift NGCC plant apply here, with the additional uncertainty on the fate of the H_2S. The assessment of the behavior of the sorbent in presence of H_2S was beyond the scope of Ascent.

2.2 WP2 Combined Ca-Cu Chemical Loop: Process Development

2.2.1 First review period

Summary of the achievements – Selection of the most promising synthesis routes for the manufacturing of combined materials (CO2 sorbents, Cu based material, Ni based catalyst) Sorbent materials have been synthesised using three different inert supports (mayenite, magnesium oxide and magnesium aluminate) and applying two different methods (mechanical mixing and co-precipitation). The material synthesises were (i) CaO-mayenite sorbent; (ii) CaO-MgO, synthetic dolomite sorbent; (iii) CaO-Al_2O_3 and CaO-$MgAl_2O_4$ sorbent; (iv) CaO-$Ca_{12}Al_{14}O_{33}$-CuO composite materials (Physical mixing); (v) CaO-$Ca_{12}Al_{14}O_{33}$- CuO composite materials (Chemical mixing). For the details please refer to the first review report.

Overview – the main outcomes in term of materials and syntheses are below reported.

1.Synthesis of Ca based CO_2 sorbent

Two different synthesis routes have been selected and used for producing CO_2 sorbents aiming to disperse the Ca on the support to avoid the typical sintering of natural Ca based sorbents. In the first route, MgO is used to dilute the CaO in the sorbent emulating natural dolomites. In the second route, calcium aluminate cement in different proportion is used as binder. The alumina present in the cement partially reacts with CaO to generate mayenite that has proven to be an excellent support for synthetic CO_2 sorbents. The results have shown that both routes generate materials with a CO_2 capture capacity changing with cycles but that stabilises around 25% (g CO_2/g sorbent) after 20 cycles.
The main differences between sorbents are related to the inert phase and the preparation method. Sorbent materials have been synthesised using three different inert supports (mayenite, magnesium oxide and magnesium aluminate) and applying two different methods (mechanical mixing and co-precipitation).

The produced CO2 sorbents with the respective synthesis procedure are of the main outcomes of the first reporting period:

CaO-mayenite sorbent - CaO-mayenite ($Ca_{12}Al_{14}O_{33}$) sorbent has been prepared through mechanical mixing starting from CaO from calcined limestone, and Ca aluminate cement (a commercial product from cement industry mainly composed of aluminium, iron and calcium oxides). The materials have been mixed in the correct proportions in order to get CaO contents between 80-95 % wt. Afterwards, water has been added drop wise with a continuous mixing to get a homogeneous paste. Then, the material has been either pelletized by extrusion to get pellets of 1-1.5 mm in diameter or kept in powder form. Materials have been dried in a furnace at 120 ºC for 12 hours and subsequently they have been calcined in air at 900 ºC for 2 hours. Agglomeration method has been used to prepare a material with 40 % in weight of inert phase and several fractions with different particle.

CaO-MgO, synthetic dolomite sorbent - A series of synthetic dolomite sorbents with different CaO:MgO molar ratios have been prepared using a co-precipitation method. Calculated amounts of $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ were dissolved in deionised water giving solution with a total concentration of 3 M and CaO:MgO molar ratios of 100:0, 75:25, 50:50, 25:75 and 0:100. A 2M solution of $(NH_4)_2CO_3$ was used as precipitation agent and added drop wise to the mixture under vigorous stirring at room temperature. The precipitates were aged for two hours and subsequently washed during vacuum filtration until the pH was reduced to 7. The filter cakes were then oven-dried at 120 °C for 12 hours and calcined in a muffle furnace under air at 875 °C for 2 hours.

$CaO-Al_2O_3$ and $CaO-MgAl_2O_4$ sorbent - A series of CaO sorbent with magnesium aluminate as support have been prepared using a co-precipitation method. Calculated amounts of $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionised water giving a solution with a total concentration of 3 M and $CaO:MgAl_2O_4$ mass ratios of 75:25 and 50:50. A 2M solution of $(NH_4)_2CO_3$ was used as precipitation agent and added drop wise to the mixture under vigorous stirring at room temperature. The precipitates were aged for two hours and subsequently washed during vacuum filtration until the pH was reduced to 7. The filter cakes were then oven-dried at 120 °C for 12 hours and calcined in a muffle furnace under air at 3 different temperatures (825, 875, and 950°C) for 2 hours. XRD preliminary results confirmed the presence of CaO and $MgAl_2O_4$ phases with the appearance of $CaAl_2O_4$ phase at the highest calcination temperature (950ºC).

The main results are as follows:

- TGA tests showed that material with lowest calcium aluminate cement content (5 wt.%) presents the most pronounced decay among the sorbents tested with a residual CO_2 carrying capacity very similar to the CaO from natural limestone tested. This might indicate that a minimum amount of mayenite formed is needed to maintain sorbent stability.
- Inert content of the sorbent material would affect sorbent carbonation kinetics. The carbonation conversion curve of the material with lowest CaO content does not present the abrupt variation in reaction rate typical of rich CaO materials.
- the presence of MgO is not sufficient to avoid the initial loss in activity and the materials tend to their stable capture capacity as the number of reaction cycles increases.
- Sorbents with calcium or magnesium as main component of the binder showed similar performance in term of CO2 uptake.

Synthesis of Cu based Oxygen carriers

For the Cu-based materials, techniques like co-precipitation, impregnation, deposition, spray drying and physical mixing have been used. In general, the materials have proven to be stable along oxidation-reduction cycles with fast kinetics despite the Cu content was higher than 60%. However, some of the synthesis routes can be discarded because particle agglomeration was detected after cycling.

The main result was that co-precipitated material presented a very high chemical stability along cycling; reduction and oxidation kinetics were the fastest, and no important formation of aluminates were detected. For this reason, it was decided to select co-precipitated materials, to be pelletized.

Combined functional materials

Finally, different combined materials have been also synthesised. Among the different combinations the work has started with the development of materials combining CO_2 sorbent and Cu and CO_2 sorbent and catalyst. Two main groups of combined solids were prepared: a first group by physical mixing of copper-containing and CaO-containing materials and a second group by "chemical mixing" or "combined from synthesis" materials.

The main results were that chemically mixed materials compared to the mechanically mixed ones show higher CO2 sorption capacity, due to the lower content of inert phase. For the number of redox steps in the tests, only a slight decrease over the first 5 cycles was observed.

Therefore, it was decided to focus efforts on the chemically mixed materials. Thus, a new set of materials was prepared, following the same hydrothermal method, but varying the inert content and the compacting method to prepare particles

Reforming catalyst

One commercial reforming catalyst (HiFuel R110) and another highly active new PGN-based reforming catalyst have been provided by JM. The catalysts have been characterised.

Sample: HiFUEL R110 NiO/$CaAl_2O_4$ - The catalyst presented a very high activity in the first reforming test performed. Experimental results were close to the theoretically calculated for equilibrium in the whole range of temperatures studied.

Sample: PGM-based reforming catalyst - The active metal reduces at low temperatures. From XRD analysis its crystallite size is under detection limits of the XRD used, the catalyst keeps the structure and phases. Finally, by SEM no differences are observed in the surface after being cycled

2.2.2 Second review period

Summary of the achievements – During the second review period the following results have been achieved: (i) Selection of the functional materials for Ca-Cu looping process; (ii) Detailed experimental investigation at particle scale; and (iii) Development of reactor models) have been finished.

Overview – The key achievements are below summarised:

Selection and testing of functional materials for Ca-Cu looping process

1. Ca-based material

The main results are follows:

- Only two Ca-based material were selected upon the experimental work performed in differential reactors. One material uses mayenite as support of CaO and was produced by mechanical mixing with calcium aluminate cement. The other material was produced by co-precipitation and and uses MgO as support (synthetic dolomite).
- The material with the lowest CaO content is the material whose decay curve is less pronounced, but the material with a molar ratio CaO/MgO of 2, presents slightly higher CO_2 capture capacity up to cycle 40.
- the rate of CO_2 release does not depend on the carbonate content of the material, and it depends on reaction conditions (temperature and CO_2 partial pressure), and particle size (when intra particle diffusion effects play a role in the evolution of calcination).

2. Cu-based material

The analysis of several CuO-based materials synthesized by Johnson Matthey following different routes, with Cu contents between 56 to 75%wt., supported on Al_2O_3 has been evaluated. The synthesis route selected to prepare the materials was co-precipitation that also was considered as suitable route (see first review period).

The key results achieved during the second review period for the Cu base are as follows:

- In general, all of the materials presented similar conversion curves and fast reaction kinetics along cycles, achieving in most cases complete conversion in less than two minutes of reaction.
- It presented high chemical stability, and as it can be observed complete reduction and oxidation conversions are achieved in less than one minute with very repetitive conversion curves along cycles
- The SEM analysis carried out to the oxidized samples showed that there is a homogeneous mixture between CuO and Al_2O_3 in all sample confirming that the two phases are well mixed.
- Both, XRD and TPR analysis for the Cu based material revealed the presence of small quantities of aluminates in fresh and cycles samples. Even though, it seems that this species are easily reducibles and do not affect the chemical stability of the material neither the conversion after cycling.
- Because of the good performance of material, it was decided to synthesized pellets that will be used in the proof of concept. Three types of pellets were prepared, the main difference between them was their density, and small differences in Cu content due to the agglomerate materials added to the powder during the pelletization process. the complete conversion of the pellets takes place in 2 minutes for the reduction stage, and the oxidation between around 4 minutes. There were only little differences among the three pellets that can be more clearly appreciated on the oxidation conversion curves.

3. Ni-based catalyst

The reforming reaction has been studied with samples characterised during the first review period i.e. HiFUEL R110 and a PGM-based reforming catalyst: which have been used in powder form between 100-200μm and less than 200μm, respectively.

The main results for ***HIFUEL R110*** are as follows:

- The catalyst presented a very high activity in the first reforming test performed experimental results were close to the theoretically calculated for equilibrium in the whole range of temperatures studied.After 10 oxidation/reduction cycles the results from the reforming step perfectly compare with theoretical data, the maximum methane conversion is reached.
- The amount of catalyst was reduced 4 times to increase the space velocity. This way, the conditions of application are stressed in order to know the limits of application of the catalyst and highlight any change in the material properties. In the initial reforming test the catalyst showed high activity. After 10 oxidation/reduction cycles the activity showed by the catalyst did not reach the theoretical values of equilibrium.
- Up to 100 oxidation/reduction cycles were performed in thermobalance with the fresh sample. Very high activity was showed by the catalyst in the whole range of temperatures studied.
- the results obtained for the multicycling reforming test of the HiFUEL catalyst in thermobalance showed that the catalyst cycled 200 times in oxydation/reduction cycles presents a high activity with a good comparison between experimental and theoretical data of equilibrium. The methane conversion obtained is more than 90% of the maximum theoretical conversion.

The main results for ***PGM-based reforming catalyst*** are as follows

- Characterization performed to this solid showed that the properties of the catalyst did not change significantly after several oxidation/reduction cycles. The active metal reduces at low temperatures.
- From XRD analysis its crystallite size is under detection limits of the XRD used, the catalyst keeps the structure and phases.
- SEM analyses have revealed no differences in the surface after being cycled.
- The catalyst presented a very high activity at the conditions tested.
- Very high CH_4 conversion is obtained in the whole range of temperatures studied with this fresh catalyst and after 10 cycles.
- Experimental results at four times the initial space velocity perfectly compare with theoretical data of equilibrium. The catalyst showed very high activity under the extreme conditions studied before and after being cycled.

Development of reactor models

The main results achieved within the modeling activities of the WP2 during the second review period are:

- Two one-dimensional pseudo-homogeneous models were formulated and delivered to describe Ca/Cu process: one solved in Delphi developed at TUE and one solved in Matlab developed at INCAR-CSIC in Oviedo.
- The two models have been compared with experimental results and have been compared with each other. Both models are able to capture the most important phenomena occurring during the Ca/Cu cycle. The main difference of the two model described in the previous sections is in the way of solving the equations. The Delphi model developed at TUE uses time step and grid adaptations and a WENO scheme of 3rd order. The Matlab model developed at INCAR-CSIC uses the Matlab tool called ‘ode15s.m’ and a fixed number of grid cells and time steps.
- These models have been used to design the experimental campaign in the available setups for the proof of concept which is topic of the future third review period.

2.2.3 Third review period

Summary of the achievements – The main results achieved in this work package are related to (i) the experimental conduction of the CaCu cycle at proof of concept scale (total amount of complete cycles carried out is more than 200) and (i) the validation of reactor models.

Overview – The results were jointly achieved by CSIC and TUE and below detailed.

1. CSIC activities during the third period

The activities carried out at **INCAR-CSIC** in the period from March 2017 to February 2018 are in accordance with the working plan of Task 2.4: (i) modification of the experimental set up to reduce heat losses and to improve the initial temperature profiles, (ii) study of the reduction/calcination stage with methane and mixtures of methane/hydrogen for the subsequent validation of the reactor model developed by INCAR-CSIC, and (iii) validation of the reactor model with experimental results.

The main key results are as follows:

- The stainless-steel structure used to support both the fixed-bed reactor and the ceramic oven was modified to install an additional oven at the bottom part of the tube. Moreover, the thickness of the insulating coating that surrounds the reactor was increased up to 15 cm (the layer of quartz wool was initially 8 cm thick). A picture of the modified experimental setup is shown in Figure 3.

Figure 3 **Picture of the modified experimental setup at INCAR-CSIC.**

- The evolution of the composition of the product gas and the temperature profiles inside the bed during the experiments has been described using a 1-D pseudo-homogeneous reactor model. A multicomponent system (composed of CH_4, CO_2, CO, H_2, CuO, Cu, $CaCO_3$, CaO, C and inert) has been modelled assuming axially dispersed plug flow, negligible inter-particle mass and temperature profiles, constant void fraction in the solids bed ($\varepsilon = 0.5$) and a perfect distribution of both Ca- and Cu-based particles along the reactor. The pseudo-homogeneous model (in which the terms related to the chemical reactions are omitted) was used to fit the experimental temperature profiles and a value of U of about 2.5 W/m^2K was calculated, which demonstrates that the experimental setup operates relatively close to adiabatic conditions. The results obtained during the heating experiment are represented
- The shrinking core model (SCM) under the assumption of chemical reaction control was used to estimate the kinetics of CuO reduction with CH_4, CO and H_2, as well as the calcination of $CaCO_3$, which is generally accepted in the literature for modelling chemical looping combustion and calcium looping systems.
- The reactor model gives an accurate description of the experimental results. For the chemical validation of the model, reduction/calcination experiments with a Cu/Ca molar ratio present in the reactor is around 3.2 was used..

The activities carried out at **ICB-CSIC** in the period from March 2017 to February 2018 were focused on determining the operation limits for the materials selected (i.e. the CaO-$Ca_{12}Al_{14}O_{33}$ CO_2 sorbent, the CuO-Al_2O_3 material and the commercial reforming catalyst, and the composite material CaO/CuO developed by IFE.

The main results are as follows:

Operation limits of the H_2 production stage via SER, experiments performed at ICB-CSIC.

To determine the operational window for the materials developed and selected for the scaling up of the process, a series of experiments have been performed focussed on the H_2 production stage at ICB-CSIC in the fixed-bed reactor described in the section above. In this way only sorbent and reforming catalyst were present in this series of tests.

A $CaO\text{-}Ca_{12}Al_{14}O_{33}$ material has been selected as CO_2 sorbent, a detailed description of the sorbent manufacturing was a results of the second review period. The catalyst used (HiFUEL R110) is a commercial reforming catalyst provided by the Johnson Matthey Company.

The main results on the investigation of the SER operational limits

- S/C molar ratios higher than 4, barely enhance the H_2 purity in the product gas, especially at moderate pressures. The ratio Z of sorbent to catalyst has been fixed to 5. The operation conditions have been extracted from the modelling and simulation results presented before. Considering the Ni load of the HiFUEL® R110 catalyst tested in this work, a Z of 5 was selected (3.1 % wt. Ni in bed), introducing in the reactor a total weight of solids of 26.4 g with a particle size cut of 600-1000 μm. Under the described conditions, the effect of CH_4 space velocity on gas product composition has been assessed testing CH_4 MHSV between 1.78 and 4 kg CH_4 h^{-1} kg cat^{-1} respectively.
- At the highest space velocity tested (4 kg h^{-1} kg cat^{-1}), it has been experimentally observed that although there is a clear breakthrough curve for the CO_2, the system is not able to reach the SER equilibrium during the pre-breakthrough period of the bed. The percentage of H_2 is clearly below the equilibrium predictions, and this might indicate that the sorbent carbonation rate is not sufficient to sustain the SER reaction;
- The maximum sorbent carbonation rate in bed determined from the experiments corresponds to the experiment performed at 4 kg CH_4 h^{-1} kg cat^{-1} and a gas linear velocity of 0.53 m s^{-1}.

Complete Ca/Cu cycles in fixed-bed lab scale reactor performed at ICB-CSIC.

A series of complete Ca/Cu cycles have been performed at the fixed bed reactor at ICB. These tests, those contain the three functional materials selected during the second review period. Figure 4 shows the experimental fixed bed reactor used at ICB-CSIC.

Figure 4 Experimental fixed bed reactor used at ICB-CSIC.

In this way, there has been experimentation performed with two different beds: In first place a bed A that contains the three separated materials (CaO-based sorbent, CuO-based material and commercial reforming catalyst) and bed B that contains the composite Ca/Cu selected in the second review period and the commercial reforming catalyst.

The key results are below described:

Complete Ca/Cu cycle with 3 separated materials in bed. Bed A. In this bed three stage were performed as follows:

Stage A: Methane Sorption Enhanced Reforming Stage: the system is able to fulfil SER equilibrium conditions at 2.5 kg CH_4/h kg_{cat}, at 675 ºC, 10 bar and an S/C of 3, which corresponds to a linear gas velocity of 0.045 m/s.

Stage B: Oxidation: For the Cu oxidation stage conditions in this work, 5 % vol. of O_2 in the gas feed to this stage has been chosen for the total operating pressure of 10 bar. All the O_2 introduced in the feed gas is reacting, as no O_2 is measured in the gas product. In order not to reduce the moles of $CaCO_3$ to avoid any further $CaCO_3$ decomposition, the conditioning step to stage C has been performed in a concentrated CO_2 atmosphere.

Stage C: Reduction/calcination stage.
In the last reacting stage of the Ca/Cu looping process, the calcination of the $CaCO_3$ present in bed takes place thanks to the exothermic reduction of the CuO formed during the oxidation stage. The reducing gas stream used for the experiments contains 58 % vol. H_2, 29 % vol. CH_4 and 13 % vol. CO (free of N_2). Experimental results showed that, as soon as the reacting gas reaches the bed surface the reduction of CuO takes place, the reducing gases are converted in a narrow reaction front and the solid bed temperature increases, favoring in this way the calcination of the $CaCO_3$. As a consequence of these reduction reactions, the composition of the gas exiting the reactor is a mixture steam/CO_2.

Complete Ca/Cu cycle with composite material. Bed B. Consecutive complete cycles have performed at the experimental rig at ICB-CSIC with the composition that corresponds to bed B. The experimental results show that the combined material presents stability along the cycles performed, and that the operation limits do not differ from those of the separated materials.

2. TUE activities during the third period

During the last period of the project proof-of-concept of the Ca-Cu process has been carried out at TUE. Two different setups have been used for the proof-of-concept, a packed bed for proof at TRL4 and the bigger packed bed reactor for TRL5 proof-of-concept.

Experimental results are below described.

Validation of the Ca-Cu process with the experiments at TRL4

Sorption enhanced reforming, oxidation and reduction steps were studied in the small packed bed reactor explained above under different conditions at atmospheric pressure. Two different bed compositions have been tested: first only CaO and catalyst were present in the bed with a sorbent to catalyst ratio of 5, then Cu was added to the bed with a Cu/CaO molar ratio of 1.8 and a sorbent to catalyst ratio of 3.2.

The key outcomes are:

- A hydrogen fraction of 95% of H_2 and almost full conversion of CH_4 is reached during the SER;
- The experimental results have been used to validate the Delphi model of the packed bed.
- The temperature peak due to the oxidation reaction is moving towards the end of the bed while Cu is transformed in CuO. Also for the oxidation step the model predicts nicely the experimental results.

Proof of concept in the big packed bed reactor at TRL5

The reactor of the TUE laboratory for the final proof-of-concept of the Ca-Cu cycle is showed in Figure 5. The main objective of the proof of concept is to perform more than 100 complete cycles, meaning SER, Oxidation and reduction. To perform these cycles the bed was filled with the commercial Ni catalyst (HiFUEL) supplied by Johnson Matthey, a calcium-based solid supplied by Carmeuse and a copper-based material developed in the project by Johnson Matthey. The composition of the bed was calculated in order to have 4% of Ni inside the bed and a Cu/CaO molar ratio of 2.1. The particle size of all the solids is around 3 mm.

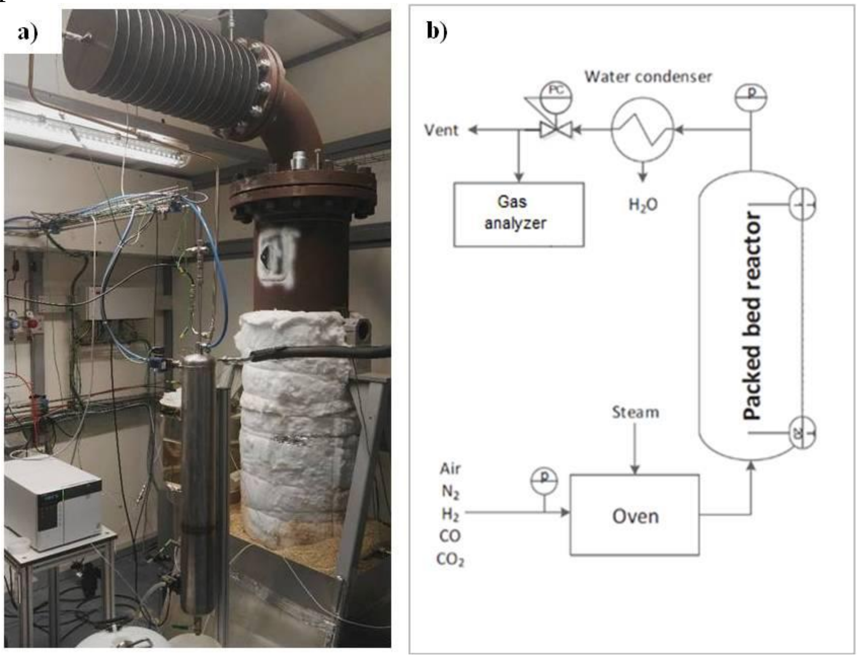

Figure 5 Picture (a) and schematic overview (b) of the packed bed reactor setup.

Sorption enhanced reforming has been studied under three different steam to carbon ratios (S/C 3, 4 and 5) and 2 different pressures (2 and 7 bar). The flow of methane was kept constant at 4 l/min and the flow of steam was varied according to the steam to carbon ratio. The temperature was around 620 for all the experiments. In all these cases the oxidation step was done with 10% O_2 and the reduction step with 40% H_2, with 100 l/min as total flow rate.

The key results for the SER stage are as follows:

- Ten complete cycles have been made for each condition to reach steady state and prove the reproducibility. The temperature in the bed is quite constant during all the cycles due to the high heat losses;
- Increasing the pressure, the SER is less favored as expected by the thermodynamic. The hydrogen fraction is about 4% lower in the case at 7 bar compared to the case at 2 bar. The breakthrough is a bit retarded in the case at high pressure since the CO2 produced is lower.

The key results for the oxidations steps are:

- The oxidation step was studied under different concentration of oxygen: 3%, 5%, and 10%.
- Good reproducibility was confirmed by the repetition of 10-15 cycles. The experiments are very reproducible, since both the temperature and the gas profiles are the same for all the cycles

The aim in the reduction step is to release the highest amount of CO_2. The reaction that gives the higher amount of heat is the reduction of CuO with H_2. To be able to calcine the $CaCO_3$ the stochiometric Cu/CaO molar ration if hydrogen is used is 1.8. In this case a Cu/CaO molar ratio of 2.1 was chosen taking into account the presence of heat losses.

The key results for the reduction steps are:

- Good reproducibility of the process confirmed by the replication of 10 – 15 complete cycles which have been achieved;
- Increasing the hydrogen fraction more CO_2 is released since the temperature reached in the reactor is higher. Moreover, the breakthrough is sharper, and the amount of CO_2 released before the H_2 breakthrough is higher. Further increasing the H_2 fraction would bring to higher amount of CO_2 released.

The total amount of complete cycles carried out is more than 200 (thus double the required number in the DoW of Ascent). The solids are still performing good and the results are still reproducible.

2.3 WP3 - Fast sorbent mediated water-gas shift (CSHIFT)

2.3.1 First review period

Summary of the achievements – An important achievement of the first review period was to select the sorbent to be used for the later proof-of-concept work. Hydrotalcites (HTCs) type sorbents were selected based on their inherent catalytic activity for the water-gas shift (WGS) reaction and usability in the presence of acidic gases such as H_2S. The main achievements in the first period were testing and characterisation of potassium promoted Mg-Al containing HTC sorbents in a pressurized packed bed reactor. Also, a spouted fluidized bed reactor for fast pressure-swing operation and steam injection was successfully upgraded and commissioned. For the details, please refer to the first review report.

Overview.

Selection of the sorbent criteria and preparation – A literature survey to assess and evaluate intermediate-temperature CO_2 sorbents that could provide an alternative to high-temperature CaO-based sorbents for applications in an intermediated temperature (300-800 ˚C) CSHIFT process was carried out. The reactor for the proof-of-concept of the CSHIFT process is showed in Figure 6.

Figure 6 Proof-of-Concept equipment CSHIFT process

The main result of this preliminary activity were:

- the selection of hydrotalcites (HTCs), MgO/MgCO3-based sorbents, promoted-aluminas and alkali ceramics promising candidates for the CSHIFT process. These materials are both capable of absorbing/adsorbing large quantities of CO_2 in the desired temperature range of 300-500 ˚C and pressure interval 1-40 bar and they can be via pressure swing operation;
- a range of different hydrotalcite (K_2CO_3-doped and undoped) pelletised particles have been prepared from commercial HTc powders for fluidised bed use. Two new methods based on co-precipitation and a one-pot hydrothermal preparation method have been tried for preparing HTc materials from MgO and Al_2O_3 precursor materials;
- HTc materials prepared from a semi-calcined dolomite supplied by Calix as the MgO source have also been prepared and partially characterized;
- Breakthrough of CO2 and H2O can be observed after approximately 10 minutes with the CO2 outlet concentration reaching the inlet concentration after ~30 mins indicating that CO2 sorption via the faster uptake mechanisms was complete;
- The work demonstrates that much higher CO2 capacities of over 10 mmol/g can be achieved than was previously thought.

Process development – The key results are:

- A generalized Random Pore Model has been developed and applied to the calcination of limestone, to highlight the impact of the initial porosity of the limestone, and to the carbonation of nascent lime to highlight the impact of fast kinetics. Based on the vast amount of experimental data on HTc the first CSHIFT particle model validation with linear driving force approach and first estimate of Random Pore Model (RPM) parameters were established.
- Initial breakthrough description of the fast surface carbonates is satisfactorily described by the model. RPM parameters are currently not able to predict the bulk carbonation and product layer diffusion kinetics.

2.3.2 Second review period

Summary of the achievements – The main achievements of the WP3 are focused mainly to (i) the choice of lead sorbents according to shared criteria; (ii) modify of high-pressure fluidised bed reactor for P-Swing operation at the proof-of-concept scale. (iii) Continuation of the Proof-of-concept testing in fast high pressure fluidised bed reactor scanning over a wider range of conditions.
Overview.

Proof-of-Concept in Pressurised Fluidised Bed Reactor – Upgrade of a high-pressure fluidised bed reactor to allow for steam injection, pressure-swing operation and H_2S use has been completed and commissioning experiments involving CO_2 capture with High Mg:Al ratio hydrotalcites promoted with K2CO3. The influence of total carbonation pressure (3-10 bar_a), carbonation temperature (200-500 ˚C) and steam concentration (0-40 mol%) on the fast initial sorption kinetics and capacities (measured after 30 s) has been investigated with a K22-MG70-M-PLT-001 sorbent material (22wt% K_2CO_3 Mg/Al hydrotalcite material containing 70 wt% MgO). The effect of K_2CO_3 loading (0-22 wt%) was also investigated with a MA80-M-GRN-001 sorbent material (Mg/Al-hydrotalcite material containing 80 wt% MgO).

The results of this preliminary tests are as follows:

- The sorbents have been tested in a fixed bed reactor for 146 and 492 adsorption-desorption cycles at various conditions. Adsorption took place at 350 °C and regeneration/desorption of CO_2 was done at 450 °C.
- Maximum carbonation rates and uptake capacities for the initial fast sorption reaction of 0.128 mmol $g^{-1}s^{-1}$and 1.03 mmol $g^{-1}s^{-1}$ over a 30 s carbonation time frame have been measured for the K22-MG70-M-PLT-001 sorbent material at 400 ˚C, 10 bar_a 20 mol% CO_2 and 40 mol% steam. The K0-MA80-M-GRN-001 and K22-MA80-M-GRN-001 sorbents exhibited even higher maximum carbonation rates and sorption capacities at the same conditions of 0.14 mmol s^{-1} g^{-1} and 1.4 mmol g^{-1} respectively
-

The materials were characterized by various techniques before and after the multi-cycle tests in order to understand possible material changes during operation and their effects.

The key results are:
- Both pore volumes and surface areas of the sorbents are lower for the spent sorbents compared to fresh ones.
- XRD analyses showed that an extra phase was formed in the materials during operation that could be assigned to a $MgAl_2O_4$ spinel.

P-Swing Cycling Performance (Proof-of-Concept) **–** Most of the research efforts involving the pressurised fluidised bed reactor have been directed towards overcoming engineering challenges to enable operation at pressures and steam concentrations approaching C-SHIFT target conditions
The key results is that the performance indicators (maximum carbonation rate, sorption capacities) show that the K22-MG70-M-PLT-001 sorbent performed poorly during P-Swing cycling. The maximum carbonation rate for the initial fast reaction remained fairly constant for all cycles at 0.04-0.05 mmol s^{-1}.
Further work is necessary in the future third review period to confirm whether these results are accurate, whether pre-saturation with steam does in fact retard carbonation at these conditions and determine the extent of carbonation resulting from stronger interactions that could not be regenerated by pressure-swing.

2.3.3 Third review period

Summary of the achievements – The main achievements during the third review period has been the further testing of chosen sorbent material at real WGS conditions understanding the amount of water vapour needed in the process, the sorbent stability and performance at sour conditions (H_2S) and the sorbent behaviour in a high pressure fluidized bed reactor deriving better estimated for sorption and desorption kinetics. In addition, after initial modelling of the original process concept it was concluded that the process was not able to give the targeted CO_2 capture rate with reasonable use of steam and gas/solid contact times. A new C-SHIFT process configuration has therefore been suggested. Below, each of these topics have been described in more detail.

Overview – The main results are obtained in the following areas

CSHIFT AT SOUR CONDITIONS AND STEAM REQUIREMENTS.

Two selected HtC based sorbents were tested in low steam and sour feeds. The sour feed was characterized by the presence of both H_2S (up to 250 ppm) and CO_2 in the feed.

The main achievements are:

- For the two sorbents that are highlighted in this third review period, i.e. K22MA80 and K15MG70-S, no significant detrimental effect of the presence of 200 ppm H_2S was noticed on the cyclic CO_2 capacity and the steady state CO conversion;
- All sorbents underwent over 100 cycles at S/CO<2;
- Robust cyclic CO_2 capacity and stable steady state CO conversion was obtained during these lengthy periods on stream.
- ^{13}C NMR of post-test samples indicated that no carbon deposition related to coking occurred during the multi-cycling tests.
- The preferred sorbent in this study on the HtC based materials is the is the potassium carbonate-promoted hydrotalcite MG70. MG70 based sorbent gave a slightly higher CO_2 sorption capacity with the activation and test procedures adopted in the work. MG70 is already well described in elsewhere in literature, which is particularly helpful when interpreting complex structural features of activated hydrotalcites.

FURTHER PROOF-OF-CONCEPT EXPERIMENTS IN HIGH PRESSURE FLUIDISED BED REACTOR

The CO_2 sorption isotherm for the K22-MG70-M-001 HTc was updated such that all measurements were taken at a constant system pressure (10 bar) and P_{H2O} (2 bar).

The key results are:

- Applying the measured isotherm data to estimate the sorbent working capacity at NG-CSHIFT relevant conditions i.e. $P_{CO2,carb}$ of 0.33-0.5 bar gives a value of ~0.4 mmol/g. However the predicted working capacity tends to zero when we consider P_{CO2} at the calciner outlet is expected to be $\geq$ 0.5 bar (i.e. no P_{CO2} gradient) unless calcination is effected at a higher temperature or under vacuum.
- Extending the carbonation period from 10 minutes to 30 minutes had only a very small effect on the measured sorption capacity (increase of 0.04 mmol/g to 1.79 mmol/g).
- isotherm projections indicate that the K22-MG70-M-001 sorbent is more promising for pre-combustion CO_2 capture applications involving higher partial pressures of CO_2 e.g. coal-IGCC where P_{CO2} > 10 bar are expected
- preliminary investigations to assess the performance of $NaNO_3$ promoted, high surface area magnesium oxide (or alkali activiated Magnesium oxide, AA-Mag) has been initiated.

RECONSIDERING THE C-SHIFT PROCESS CONCEPT

Initial discussions on modelling indicated that a co-current one-step adsorber could not give the needed capture rate. This is a consequence of the fact that due to the sorption, the partial pressure of CO_2 will gradually decrease in the co-current flow direction, but since the sorbed gas will be in constant equilibrium with the partial pressure of CO_2 in the surrounding, also the effective loading will decrease. Alternative processes therefore had to be evaluated. In the following we have discussed two alternative carbonator concepts; either (i) a fully counter-current version – a moving bed in which the sorbent flows downwards counter-current to the syngas, and, secondly, a (ii) process with several co-current adsorption steps in series (here called 'risers in series') where the sorbent flows co-current in each individual riser while, on a global basis, the sorbent flow is counter-current. Initial evaluation and process modelling of the two concepts have been carried out.

Co- versus counter-current C-SHIFT process.

The CSHIFT concept was originally imagined to be a co-current process, with gas and solids moving down a reactor together. Whilst this is beneficial in several ways, there are benefits to running the units in a counter-current fashion. To determine whether using counter-current units would improve the plant's performance, MATLAB codes of the calciner and carboniser were developed.

The main results obtained with the modelling activities are:

- One important benefit of counter-current is that higher loadings on the sorbent leaving the carboniser should be possible, since it leaves when in contact with higher CO_2 partial pressure gas.
- Similarly, if steam is injected into the bottom of the calciner and the solid passes downwards towards it, the CO_2 partial pressure in the last few seconds of the sorbent's residence in the calciner will be rather low.
- While the required residence time in the carboniser is cut by around 30% by switching to counter-current operation, the calciner shows a roughly 50% reduction in residence time. Although the halving of residence time makes the calciner more feasible, the 900 second duration is still very long.

Different strategies for reducing it further were investigated; one of these was vacuum desorption, in which the calciner is run at sub-atmospheric pressure. This reduces the partial pressure of CO_2, pulling CO_2 off the sorbent and into the gas stream.

The modelling results showed that, although the residence time of the sorbent could be reduced by around 90% based on the original simulations, the flow rate of sorbent required suggested that this combination of hydrotalcite and Endex may be unfeasible from a technical point of view, let alone economic

Risers-in-series - One way to keep a high gas velocity and at the same time reach the capture rate needed, is what we call the "Risers in series" concept. In all four risers (I-IV) the sorbent powder and gas flow in co-current direction. However, the sorbent exiting riser IV (only having used a fraction of its total sorption capacity) is used as input to riser III; the sorbent leaving riser III being used as input to riser II, etc. The sorbent exiting riser I (potentially being fully loaded) will be sent through a lock hopper for regeneration at standard CALIX "flash-calcination" conditions. The regenerated sorbent will be re-entered to riser IV.

Pros

- The co-current solid-gas flow make it possible to use high gas velocities
- Also high capture rates can be achieved since the sorbent in each riser compartment stays within the compartment – or are re-injected to a riser compartment in which the CO_2 concentration is higher

- Each riser should be around ¼ of the riser height needed for full conversion (in the original CALIX riser concept)

Cons

- The concept is complex with several cyclones and powder re-cycling steps – may be harsh to the sorbent powder.
- We have arbitrary chosen four risers in series, the optimal number should be found based on a compromise between performance and process complexity (cost).

Simulations were then carried out using the initial parameters for kinetics using a series of risers. To each riser, fresh sorbent was added.
The key results coming out from the models are:

- Five risers in series were needed to reach 91% capture rate, the low capture rate mostly being due to the low CO conversion.
- Using a less conservative WGS activity of the column will intensify the process considerably where ten times faster WGS activity was used in the simulation. Higher WGS activity can be achieved either by adding a catalyst or by impregnating catalytic sits onto the sorbent. In this case more than 97% capture rate was achieved.
- The results show that around 88% capture rate is achieved mostly due to the lower amount of CO2 capacity in the process.

2.4 WP4 - SER looping cycle

2.4.1 First review period

Summary of the achievements – The main achievements in the first review report were (i) the definition of performance criteria of the Combined Sorbent-Catalyst Materials (CSCM) to be developed; (ii) the definition of industrially relevant process conditions for the SER looping process, both for the reformer and regenerator reactors; (iii) the development of production methods for sorbents, catalysts and combined sorbent-catalyst materials.

Overview
The main results of the first review period are below described.

- **Definition of performance criteria of the sorbent and Combined Sorbent-Catalyst Materials** – A set of performance criteria that the sorbent material and the combined sorbent-catalyst material (CSCM) have to meet has been delivered in the first months of the project. The main performance criteria which were defined are: (i) amount of active CaO in the solid; (ii) amount of Ni in the CSCM; (iii) sorption capacity; (iv) cycle stability; (v) air jet index; (vi) particle size and density; (vii) heat capacity;
- **the definition of industrially relevant process conditions for the SER looping process, both for the reformer and regenerator reactors** –The most important parameters include reactor pressures and temperatures, steam to carbon ratio, fluidization velocities, gas compositions in the reactors, minimum CO_2 capture rate, minimum hydrogen purity and maximum loss of fines rate (due to attrition in the fluidized bed reactorsystem);
- **Development and production of the combined sorbent-catalyst materials** – Attempts on several methods and precursors usage were carried out by WP4 partners (cenospheres wet impregnation and thermal treatment, wet mixing and wet impregnation methods with different nickel precursors, active phases deposition on olivine grains).The main result was the development on an hydrothermal synthesis method to produce a mayenite supported CaO-based sorbent. The method uses calcium hydroxide and aluminium hydroxide (alternatively aluminium oxo-hydroxide) as precursors. The two main steps are first the production of a hydrogarnet phase (Ca3Al2[(OH)4]3), followed by a calcination step to

decompose the hydrogarnet to form mayenite Ca12Al14O33 and free CaO. The synthesis method uses abundant and cheap precursors, is simple to up-scale, and should therefore lead to the production of a low-cost sorbent material. The sorbent material has been characterized in detail. A SER multi-cycle test has been run in a laboratory scale fixed bed reactor using the sorbent material mixed with a commercial Ni-based reforming catalyst. The tests show the high performance of the hydrothermal sorbent material with a stable sorption capacity close to 23 gCO_2/100g sorbent, and a high hydrogen concentration above 95 vol% (dry basis). In parallel, a hydrothermal method for producing a pure mayenite support for the development of a novel Ni-based reforming catalyst has been investigated in detail by IFE in order to minimize the amount of impurities in the material. $Ca(OH)_2$ and AlO(OH) have been chosen as starting materials. Different parameters have been varied, like stoichiometry, mixing time, calcination time and calcination temperature. **The findings from the mayenite synthesis study (hydrothermal method) are summarized below:**

- 5 h hydrothermal synthesis was found sufficient to yield high purity (> 95 wt%) mayenite.
- The best ratio between mayenitewt% and impurities was found for the system with 9 wt% Al excess in the starting stoichiomentry, calcined at 1000 °C for 4 h.

2.4.2 Second review period

Summary of the achievements – The main achievements in the second review report were: (i) selection of promising materials among the materials synthesised during the first review period; (ii) development of particle and reactor models for detailed understanding of the material functions (iii) validation of material performances through an experimental pre-proof of concept

Overview – The main results of the second review period are below detailed.

Selection of one promising material among the materials synthesised during the first review period – The materials have been produced following the selected preparation methods selected during the first review period in order to meet the performance criteria agreed during the first months of the project. The reproducibility and upscaling of the production methods have been validated by the WP4 material supplier MTEC.

For the production of sorbent and **CSCMs** the main results are below described:

- The HYDROSORB sorbent contains 30 wt% free CaO and is produced by high shear granulation of a hydrogarnet powder, the product from the hydrothermal synthesis.
- A production route involving a mechanical mixing of sorbent and catalyst powders prior to granulation and thermal treatment has been selected to produce the CSCMs. A Ni loading of 6 wt% has been chosen for the CSCMs. Both a commercial reforming catalyst (HT-catalyst) and a new developed catalyst (NiM-catalyst) have been used. The new reforming catalyst uses, like the sorbent, a mayenite support (Ca12Al14O33). The sorbent and the new catalyst support have been produced using a hydrothermal synthesis described in the first review period. The NiM-catalyst powder is produced by incipient impregnation of a mayenite powder obtained by hydrothermal synthesis.Both CSCMs (CSCM-HT and CSCM-NiM) were produced using a high shear granulation technique.

As far as the granulated **HYDROSORB** sorbent is concerned the following main results were achieved:

- **HYDROSORB** granules with satisfactory sphericity were obtained by high shear granulation.
- The calcined **HYDROSORB** material is quite sticky and has a tendency to agglomerate, causing difficulties in the sieving process.
- The granulated sorbent showed a high pore volume in the fraction of 600-800 nm and a high porosity of 67%, resulting in a relatively low particle apparent density of 0.890 g/cm3 .

- The granulated **HYDROSORB** material mixed with the commercial HT-catalyst (2-particle system) showed very good chemical stability in SER multi-cycle with regeneration at 850 °C in steam/H2 and no reduction between cycles. Sorption capacity close to 17 g-CO2/100 g mixture was obtained. The small added H2 concentration (6.5 vol% relative to steam) was proven beneficial in protecting the catalyst from oxidation. However, some limited growth of Ni-crystal size has been measured after multi-cycling.
- The crushed HT-catalyst material showed Attrition Jet Index (AJI) values lower than the one of a commercial Fluid Catalytic Cracking (FCC) catalyst additive used at large scale in fluidized bed reactor environment (5.5% compared to 8.1%, 5 hours test), indicating that the HT-catalyst can perform well mechanically in the SER process. It was however difficult to measure properly the AJI of the granulated **HYDROSORB** sorbent due to presence of fines making the material very cohesive.

As far as the granulated **CSCMs** are concerned the following main results were achieved:

- An efficient dry mixing of the sorbent and catalyst powders prior to granulation is important to obtain homogeneous granules and a proper dispersion of catalyst in the CSCM material.
- The CSCM-HT granules show the presence of relatively big catalyst grains due to the granulometry of the catalyst powder used (0-75 µm). However, a satisfactory Ni dispersion has been observed in the material. A Ni loading of 6 wt% proved to be sufficient to provide enough catalytic activity for SER reforming;
- The mechanical mixing production route for the CSCM-HT proved to be robust, reproducible and reliable as the produced granules showed similar chemical compositions and SER multi-cycling performance;
- The CSCM-HT material shows satisfactory SER multi-cycle stability only when regeneration is carried out in CO2, implying a minimum regeneration temperature of 925°C;
- Ni crystal growth has been identified as the main reason to loss of catalytic activity when high temperature reduction is not applied between each cycle. Measurements of Ni crystal size after SER multi-cycling show that the Ni crystal growth is limited when the SER cycle includes the high temperature reduction step;
- A new complex oxide MgNiO2/MgO.NiO phase has been identified after SER multi-cycling, even when high temperature reduction is applied between each cycle, due to the presence of a MgO phase in the HT-catalyst;
- CSCM-HT granulated materials showed satisfactory chemical stability and performance in a SER multi-cycle with regeneration in CO2 and high temperature reduction between cycles. A stable sorption capacity close to 10 g-CO2/100g CSCM has been obtained for the CSCM-HT produced by MTEC after 100 SER cycles;
- The granulated CSCM-HT material showed Attrition Jet Index (AJI) values quite similar to the one of a commercial Fluid Catalytic Cracking catalyst used at large scale in fluidized bed reactor environment (close to 8%, 5 hours test).

In parallel UNIVAQ continued the investigation of wet mixing plus wet impregnation synthesis method, developing several CSCM with different CaO and Ni contents. Eventually, efforts were focused on the CSCM resulting from the impregnation with 10 wt% of Ni of CaO-mayenite with 15 wt% of free CaO (named **CaO15Ni10-IMP**):

- The material was characterized by ICP-AES, XRD, BET and BJH methods, TPR, TGA, SEM and TEM with EDS (before and after catalytic tests), assessing the effectiveness of synthesis methods in producing desired phases;
- Preliminary catalytic tests in cooperation with ICPEES - University of Strasbourg were carried out, to locate suitable operation conditions for SER;

- 205 SER/regeneration cycles in fixed bed micro-reactor, with mild regeneration in pure N_2, demonstrated the promising performance of this material (CH_4 conversion more than 96 % and pre-breakthrough H_2 fraction higher than 90 % dry, dilution-free basis).

2.4.3 Third review period

Summary of the achievements – The main achievements in the third review report were: (i) the experimental validation of the SER reactor models along with its implementation under industrially relevant conditions; (ii) the experimental proof-of-concept of the SER process and of the materials developed.

Overview – The main results of the third review period are below detailed.

As far as the **SER model development** is concerned the following main results were achieved:

- **Particle scale model –** A grain model that describes the simultaneous reaction and diffusion process within the combined sorbent/catalyst particle, as a function of radial position and time has been developed. Good agreement with experimental results was obtained with experimental data collected in a thermo-gravimetric analyser (TGA) chosing a CaO grain size of 100 nm.
- **Validation of the SER reactor model –** The grain model has been integrated in commercial codes for the simulation of the hydrodynamics of the SER reactors. Reactor models have been formulated via Eulerian-Eulerian (EE) and Eulerian-Lagrangian (EL) approaches and validated by means of SER fluidized bed reactor. A preliminary validation of the model with data collected in the literature has been also reported. In particular the models have been useful to estimate the operating parameters (e.g. superficial velocity, carbonation conversion of particles) where the SER reactor achieves the chemical equilibrium. Kinetics of both CO2 capture and methane reforming were selected upon experimental validation with fluidised bed reactor.
- **Modelling and simulation of the SER reactor under industrially relevant conditions –** The most promising configurations for the integration of SER processes which were further detailed are (i) SOFC-based power plant integrated with the SER process using a dual bubbling fluidized bed (DBFB) reactor configuration (100 MWth LHV); (ii) Combined cycle-based power plant integrated with the SER process using an oxy-fuel regenerator (862 MWth LHV). These two configurations have been then modeled and simulated under industrially relevant conditions properly selected with an EL approach. In particular, the EL approach has been used to simulate multi-component, multiphase industrial reactors with poly-dispersed particulate materials.Some of the parameters evaluated were transport disengaging height (TDH), molar fraction of the main components and velocity field. Figure 7 shows the modelling main results obtained for high velocity riser.

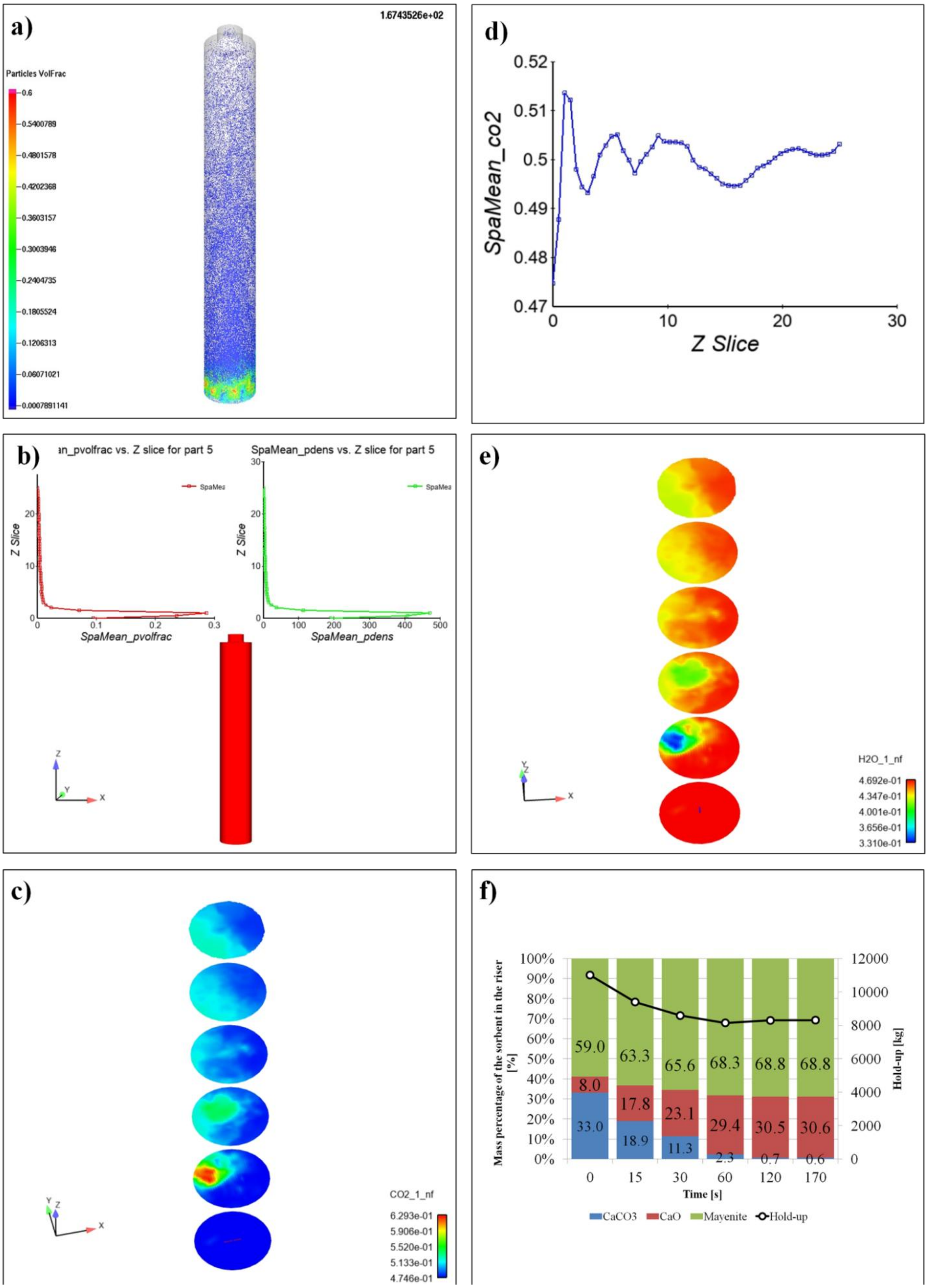

Figure 7 Simulation results for the high velocity riser (oxy-fuel regenerator): (a – b) particle volume fraction; (c) CO2 molar fraction at different heights; (d) average CO2 molar fraction along the axis; (e) H2O molar fraction at different heights; (f) solid line represents the solid inventory whereas the bar chart indicates the evolution of sorbent in the inventory

As far as the experimental **proof-of-concept of the SER** is concerned the following main results were achieved:

- **Adjustment of production methods and production of proof-of-concepts materials** – Some adjustments of the production methods for the HYDROSORB material and the CSCM-HT materials were necessary to obtain materials with required specifications. Concerning the HYDROSORB sorbent, an optimisation of the granulation phase (powder loading, binder feeding rate, mixing time) was carried out to reduce the concentration of fines to facilitate the sieving step. For the CSCM-HT, finer catalyst particles have been used to obtain to better distribution of the catalyst in the CSCM granules and to promote a better mechanical stability.
- **Proof-of-concept methodology and experimental set-ups used** – The methodology chosen for the validation of the proof-of-concept is based on the following:
    - Validate the SER chemical performance and long-term chemical stability of the materials in multi-cycle thermo-gravimetric analyser (TGA) and micro-fixed bed tests;
    - SER pre-proof-of-concept in multi-cycle SESMR/regeneration tests, by a micro-fixed bed automated test rig, for long duration experiments (2-3 weeks non-stop, counting from 40 to 200 cycles per test).
    - Validate the SER chemical and mechanical performance of the materials in fluidized bed environment in a laboratory scale fluidized bed reactor (FBR) set-up, and validate operating parameters;
    - Validate the SER chemical and mechanical performance of the materials in a small pilot scale fluidized bed reactor set-up to prove the upscaling feasibility;
    - Validate the mechanical performance of the materials in an air jet attrition set-up following an ASTM standard procedure and comparing results with reference materials used in industrial fluidized bed environment;
    - Validate the SER models developed with experimental results obtained in the small pilot scale fluidized bed reactor set-up.

The details of the results are below described:

- **TGA multi-cycle tests** – A very satisfactory chemical stability of the 2-particle system is obtained: a stable sorption capacity of 17 g CO_2/100 g mixture is obtained for 30 consecutive cycles. The SER reaction kinetics is also fairly stable for the 30 cycles;
- **Micro fixed bed multi-cycle tests** – The micro fixed bed tests have been carried out, exploring different SER and regeneration conditions:
    - for the 2-particle system composed of HYDROSORB mixed with commercial HT-catalyst 2 tests were carried out: 208 cycles with pure CO_2 regeneration with post-regeneration Ni reduction; 40 cycles with 50 % steam in N_2 as regeneration medium);
    - for the CSCM-HT 2 test were performed with regeneration in pure CO_2, with or without the post-regeneration Ni reduction (205 cycles and 200 cycles, respectively);
    - for the CSCM-Ni-IMP 4 tests were carried out: 205 cycles with regeneration in pure CO_2, without post regeneration Ni reduction; 100 cycles with regeneration in pure CO_2 and post regeneration Ni reduction; 100 cycles with regeneration by steam/CO_2 mixtures in different fractions.
- **Laboratory scale fluidized bed reactor tests (FBR)** – Several tests have been performed in a laboratory scale fluidized bed reactor (5.3cm ID, 180 to 225g material) at CSIC to determine the operating parameters. Relevant test conditions similar to the ones used in the TGA and micro fixed bed tests have been applied. The results indicates that a weight sorbent/catalyst ratio Z=3 for the 2-particle system is more suited to reach SER equilibrium. Secondly, for Z=3, the 2-particle system is able to convert 0.63 $kg_{CH4}/kg_{cat}.h$ at 650 °C for a

steam/CH_4 molar ratio = 4 and a fluidization velocity of 0.1 m/s, reaching an equilibrium H_2 concentration of about 96 vol%. Very good SER performance reproducibility along cycles was obtained, with 4 vol% H_2 addition to steam in the regeneration step. Concerning the CSCM-HT, satisfactory SER performance has been obtained for reforming at 650°C and fluidization velocities up to 0.1 m/s, with good reproducibility. Equilibrium hydrogen concentrations up to 96 vol% (dry basis) have been obtained.

- **Pilot scale fluidized bed reactor tests** – Two consecutive cycles have been run in a small pilot scale batch fluidized bed reactor (20 cm ID, 11 kg material) at IFE for the 2-particle system. Granulated HYDROSORB (200-300µm) and crushed commercial reforming HT-catalyst (120-180µm) have been used with a sorbent to catalyst weight ratio equal to 3. SER reforming has been performed at 650°C and 0.1 m/s fluidization velocity, with a steam to methane molar ratio of 4, and regeneration at 850°C in N_2/steam with a small H_2 addition to protect the catalyst from oxidation. Biomethane (97 mol% methane, 2 mol% CO_2, 0.8 mol% N_2 and 0.2 mol% O_2) was used as fuel in this test. Satisfactory SER performance has been obtained with a hydrogen concentration of 92 vol% (dry basis). Figure

Figure 8 Fluidized bed for the proof-of-of concept of the SER reactor

- **Attrition tests** – Attrition tests following the ASTM standard D5757 to calculate the *Air Jet Index (AJI)* have been carried out. AJI values of 8.9 wt% and 6.1 wt% for the HYDROSORB and the commercial HT-catalyst respectively have been obtained and compare well with values for a reference FCC catalyst additive used in industrial fluidized bed environment (8.1 wt%). AJI values of 9.2 wt% and 8.5 wt% for the CSCM-HT calcined and carbonated respectively, have been obtained and are quite similar to values for a reference FCC catalyst additive.

- **SER model validation** – A very good agreement between EL simulation results and experimental results gathered during the proof of concept tests was obtained. The simulations show that most of the methane conversion is achieved in the lower part of the expanded bed where the gas bubble size is moderate. The calculation of the H_2 molar fraction at the exit of the fluidised bed reactor as function of time shows that the SER reaction is fast and a steady state average H_2 concentration is obtained after about the first minute. The hydrogen concentration value from the simulation is in line with the experimental values gathered during the SER FBR tests at laboratory scale and small pilot scale.

As a conclusion, the SER looping cycle proof-of-concept results presented in this report prove the feasibility of using both the HYDROSORB sorbent in a 2-particle system (mixed with a commercial reforming catalyst) and the CSCM-HT (produced by mechanical mixing of HYDROSORB and commercial catalyst powders) for the SER process. Multi-cycle chemical stability in relevant operating conditions, satisfactory SER performance in fluidized bed reactor environment, and relatively low attrition jet index resulting in acceptable mechanical stability, have been verified.

3. POTENTIAL IMPACT

While the development of innovative technologies such as ASCENT relies heavily on the techno-economic aspects, new technologies may also induce impacts on the environment, society, health and economy. The sustainability and safety of the emerging technologies are gaining importance and considered as an integral part in the development of new processes. The evaluation and understanding of the sustainability and safety impacts is thus very important while going towards a higher TRL so that strategies can be implemented for a sustainable development and deployment in the future.

The safety and sustainability analysis of the ASCENT technology has been carried out by WP 5 using a multicriteria approach: the analysis and key impacts obtained covered safety, environmental LCA and socio-economic factors provided - while the economic aspects are dealt with in detail by WP1. The results obtained will serve in guiding the development of ASCENT technologies outlining the positive impacts brought about by the ASCENT technologies. It will also help in raising awareness among the stakeholders about safety and sustainability. The results in terms of comparison with the existing technologies, the different configurations analysed, and the different recommendations will help in making choices and fixing strategies for further development

The main results and conclusions for ASCENT are explained below:

3.1 Safety and risk assessment

3.1.1 Safety impacts assessment

The safety comparison studies were completed for ASCENT technologies based on the comparison method which was validated with SER configurations in the first reporting period, which was then applied to the technologies of WP2 and WP3.

The comparison results show that ASCENT technologies have main advantages over the reference cases in a safety viewpoint. This was demonstrated from the different results obtained using different approaches. The **safety gains** of the ASCENT technologies were mainly attributed to the **intensification of the processes, milder operating conditions and process parameter**. Thus, it can be concluded that g**lobally the ASCENT processes perform well in terms of safety aspects when compared to the reference cases.** These trends were obtained in the absence of the technically safety barriers which may be further installed to eliminate risks and improve the points which were highlighted as negative with respect to the reference cases.

3.1.2 Risk analysis of the ASCENT technologies

The process hazard analysis method was employed for assessing the risks related to the ASCENT technologies. The different accident scenarios associated with the ASCENT technologies were identified and analysed in detail.

- The different accident scenarios associated with the ASCENT technologies were identified and analysed in detail. The loss of containment in reactors, equipment and the formation of explosive atmosphere were identified as the main scenarios. These scenarios should be kept in mind while going towards higher TRL and in particularly choosing the best safety barriers.
- The points where attention is needed during the future phases of development were highlighted. Recommendation in terms of technical and organisational barriers have been provided for the different accident scenarios.
- The cost, efficiency and reliability of the safety barriers must be considered as they may change depending upon the choice and process configuration.

The results obtained at the present TRL may change with the increase in TRL, evolution of the sorbents, process design and the scale of the process. Hence it is necessary to update the safety assessment results while going towards higher scales.

3.1.3 Regulatory studies for the deployment of ASCENT technologies

The review of regulatory requirements related to health and safety for the future deployment of the ASCENT technologies were carried.

- The regulation requirements reviewed were classified broadly into 2 categories namely:
    - the manufacturers of the ASCENT plant in terms of equipment, reactors
    - the operators of the plant ensuring the protection of environment, safety of workers and installations.

The regulatory limits related to the emissions for key substances like copper, nickel, CO and dust at work place and to the environment have been provided. The evolutive side of the regulations applicable to ASCENT technologies must be monitored particularly for the regulation for nanomaterial / nanostructured material as of today. Most of the regulations concerning future deployment of ASCENT technologies are applied to power plants, chemical and petroleum industry.

3.2 Life Cycle Assessment

The innovative carbon capture technologies developed in the ASCENT project require energy, raw materials, consumables and also generate waste and emissions to the environment. To ensure a sustainable and responsible development, it is thus necessary to assess the environmental impacts of the ASCENT technologies and compare them with conventional reference technologies, in order to first understand the generated impacts and make sure that these new technologies will effectively reduce the environmental footprint of the carbon capture system in comparison with the existing conventional technologies (or at minimum that the proposed technologies do not have higher environmental impacts) over the whole value chain.

Fifteen power plant technologies are assessed in the LCA work, including nine reference technologies, with and without CO_2 capture, and six ASCENT technologies.
The purpose (or function) of the different technologies studied is to produce electricity from a fossil fuel source (natural gas or coal). Power generation is the main goal of the different technologies studied; as a result, the chosen **functional unit[1] is 1 kWh of electricity produced**.

3.2.1 Data availability and quality.

A strong focus has been put to ensure the best quality of data for this assessment, as these are key. The data used for the environmental assessment are based on primary data collected from the project partners directly or through deliverables and technical documents. When primary data were not available directly from project partners, secondary data were used, i.e. data collected from expert inputs from the other WPs (in priority) or the network of LCA experts, as well as from literature.

3.2.2 LCA Results

Results have been generated per life cycle stage (infrastructure, feedstock, consumables production, direct emissions, consumables end-of-life, waste) for five endpoint indicators (climate change, resources depletion, water withdrawal, human health, ecosystem quality) for the nine reference and

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[1] The functional unit (FU) is a reference unit for which the life cycle assessment is performed.

six ASCENT technologies assessed. Mid-point indicators have also been used for detailed analyses and sensitivity analyses.

- **Overall the ASCENT technologies have equivalent or lower environmental impacts** compared to the reference technologies. Furthermore, for all technologies, the climate change, is globally higher for the technology without carbon capture, compared to the technologies with carbon capture, as expected.
- For each indicator and each technology, **feedstock and/or direct emissions are the main contributors**, except for the human health indicator for the IGCC technologies, for which the waste stage has a larger contribution due to the ashes that are to be disposed of.
- When considering the life cycle, the consumables (sorbents and catalysts) production stage has negligible contributions for all indicators, however, consumables have an important indirect influence on the direct emissions stage. An efficient carbon capture technology will reduce direct CO_2 emissions; **consumables thus play an important role** in each technology.
- For almost all the **ASCENT technology consumables, the impacts for all indicators are lower** than those of the reference technology consumables. **Impacts are correlated to the quantities of consumables** needed, though the **consumables' composition** (and not only quantity) **is** also an **important factor to consider**.
    - Indeed, human health and ecosystem quality results for consumables production indicate that the nickel catalyst and copper material in the NGCC + Ca-Cu technology may be problematic from an environmental perspective. Thus, optimizing the composition and, even further, the amount of Ca-Cu material needed for the carbon capture (e.g. by increased carbon capture capacity) is of importance for the development of this particular material.

Finally, whereas the consumables production is within the control, to a certain extent, of each ASCENT partner technology developers, it is of interest to assess the end-of-life of these materials (sorbents and catalysts) in more detail as this is linked to the composition of the consumable but also because the partners can give recommendations regarding the use and fate of these material. As an illustration, some technologies were identified presenting a risk of metals leaching in landfills due to the presence of nickel and copper what has potential impacts on the ecosystem quality aspect. The monitoring and recovery of metals at the end-of-life of the consumables is thus an important aspect to consider. More detailed assessments of the consumables' production processes of these materials should be done as the technologies develop and progress.

3.3 Socio-economic analysis

The socio-economic analysis is a valuable tool for establishing the balance between these impacts and for providing some clarifications on the opportunities for improvement.

The socio-economic analysis of ASCENT power plant technologies has three objectives:

- to characterize and assess advantages and disadvantages of ASCENT technologies from society's point of view;
- to allocate a value to the advantages and disadvantages provided by the various technological options.
- to identify what societal challenges the ASCENT project is expected to positively contribute to;

The first two objectives have been achieved through **a cost-benefit analysis.**

The last objective has been achieved using **a strategic foresight-based approach.**

Cost-Benefit Analysis – The cost-benefit analysis (CBA) focused on the comparison between configurations of reference power plants and ASCENT power plant. The following ASCENT processes were integrated in a power plant configuration:

- the calcium-copper looping process (Ca-Cu);
- the carbonated shift process (C-shift);
- the Sorption Enhanced Reforming process (SER).

Impacts on health and the environment have been characterized for each plant configuration in the ASCENT life cycle assessment (WP5). Impacts related to global warming, health and ecosystems are further considered in the cost-benefit analysis. They are non-monetary impacts or "externalities". Valuation methods have been used for giving a value to those impacts, translating them into costs and benefits. They are based on estimates of the social cost of carbon, the value of life year, and restoration costs of ecosystems.

Two indicators have been used for benchmarking plant configurations:

- the "**health and environmental (H&E) costs per MWh produced**" which represents the costs borne by health and environmental impacts generated by plant production. The lower are these costs, the better is the health and environmental performance of a technology;
- the "**health and environmental Net Present Value per MWh produced" ($NPV_{H\&E}$)** which measures the social benefit brought by a technology. It is a new indicator modifying the Net Present Value (NPV), a common economic indicator, for integrating contribution of environmental economics. This indicator takes into account H&E costs, operational and capital costs and benefits provided by electricity sales. A higher $NPV_{H\&E}$ indicates a higher net social benefit from the technology.

H&E costs: **ASCENT power plants** integrating **C-Shift, SER-SOFC and Ca-Cu process show good H&E performances** in terms of H&E costs per MWh when compared to their respective benchmarks.

$NPV_{H\&E}$ costs: $NPV_{H\&E}$ has been estimated for: (i) natural gas power plant with CO_2 capture by Ca-Cu process and for (ii) natural gas power plant with CO_2 capture by SER and SOFC system, and then, compared with their respective benchmarks. The results a are presented as variations of the $NPV_{H\&E}$ compared to the relevant reference plant configurations without CO_2 capture and with the assumption of a high carbon cost (100 $US\$_{2017}$ per ton of CO_2 in 2030).
When high carbon costs are considered, these two plant configurations are demonstrated to be beneficial to the society, compared to NGCC plant without carbon capture. The Ca-Cu based power plant configuration has comparatively better performance when high carbon costs and high selling prices are considered. But the Ca-Cu based power plant is deeply penalized in this model by the H&E costs borne by the extraction of fossil natural gas. When these costs are neglected, and high carbon costs considered, the Ca-Cu based power plant show better performance than any of its benchmarks. The benefits provided by this plant configuration can therefore be optimized by combining it with low H&E impacts sources of natural gas such as biogas.

The main conclusions are that:

- Regarding NG fired plant configurations producing power with a turbine, the indicator shows similar performances for the Ca-Cu based power plant and NGCC and MEA based power plants.
- The $NPV_{H\&E}$ shows the better performance of the SER-SOFC based plant configuration compared to its benchmarks.

$NPV_{H\&E}$ is an innovative and performing indicator for measuring the net benefits provided by a technology to the society. It allows to summarize both "economic" and H&E related benefits and costs, “paid” and “perceived” at different time periods. However, its calculation requires a lot of input data. Economic, health and environmental impacts of technologies at the early stage of development are subject to large uncertainties. Moreover, the time scale of development of ASCENT technologies is 10-15 years where notable changes can appear in the technological, economic, political and societal spheres. In this context, the CBA as a quantitative assessment must be understood as early recognition and analysis tool. It must be used for guiding future researches, applications and optimization paths.

3.4 Societal Challenges

A strategic foresight-based approach was applied to complete the study the societal challenges. It is based on the building and the exploitation of a structural matrix which identify and characterise the importance and the relationships of 27 factors which may influence the deployment of ASCENT technologies. The deployment of ASCENT technologies depends on a number of political and technology requirements. A first one is unanimously recognized as very important and identified as a main trigger: the need for an evolution of the EU-ETS for increasing the price of CO_2 emissions allowances. This would mechanically rise the production costs of power plants (and H_2 production plants) intensive in CO_2 emissions and therefore foster the development of carbon capture technologies, such as the ASCENT technology. On the side of technological requirements, the need for the availability of CO_2 storage (and its public acceptability) is a key factor. More specifically to ASCENT power plants configurations, the full deployment of ASCENT technologies would require cooled SOFC (for SER based technology), high temperature lock hoppers (for C-Shift based technology) and hot H_2 turbines.

The main conclusions are:

- In the short term, market opportunities are not expected for ASCENT technologies in the power sector. For the next 10-15 years European operators’ efforts for limiting CO_2 emissions will be focused on the development of renewable energy sources (RES), the renewal of old natural gas fired capacities by fully developed and competitive technologies (NGCC) without CO_2 capture and a shift between coal-fired and natural gas fired capacities. However, the penetration of CO_2 capture in the power production sector is assumed to rise after 2030 in view of the achievement of the EU objectives for CO_2 emissions reduction at the horizon 2050 (-80%). The time needed for the full development of ASCENT technologies is consistent with this scenario.
- ASCENT power plant construction would require a greenfield. The size of the market will then depend on the number of NG-fired capacities which will be able to retrofit for adding post-combustion carbon capture technologies to their process. However, the economic model of ASCENT based power plant will have to be find in the probable future energy mix composed by a high share of intermittent RES advantaging rapid start-up back-up capacities.
- Market opportunities exist also in H_2 production for ASCENT technologies, as already illustrated by the possible applications of Ca-Cu process in ammonia production. Opportunities may arise significantly in the case of an acceleration of fuel cell electric vehicles development in the EU market.

3.5 Dissemination activities

Dissemination activities and events during the whole project are 102 and they include:
Research papers: 32; International conferences: 51; Interviews: 2; EU-Australia Workshop: 1; Seminars 3; Newsletters 10; Open magazines: 3. The research papers are distributed as follows: Published: 19; Accepted for publication: 1; Under revision: 3; Open access: 4; Submitted: 3; In preparation: 2,

The main dissemination activities are below described:

Workshop EU-Australia – The consortium of the ASCENT project has hosted the second EU-Australia workshop in the SwissTech Convention Centre of the École Polytechnique Fédérale De Lausanne (EPFL) back-to-back to the GHGT 13. The purpose of this event was to facilitate the diffusion and transfer of latest results in the field of CCS within the Europe and to share the project results obtained with the twinned Australian partners.

The workshop ended with a roundtable for fruitful discussion in order to gather inputs from the attendees for exploring and defining (i) potential future EU-Australian activities in the field of low carbon technologies and (ii) a common and safe framework for facilitating the collaboration between. Indeed, the attendees of the workshop agreed that **interesting synergies and complementarities** have been discovered during the cooperation between EU and Australia which can be exploited in future collaboration.
The event was divided into four sessions: the first one was opened with an introduction of the *ASCENT* project followed by the presentation of some of the current EU FP7 projects on the CCS (Carbon Capture and Storage) technologies: *GREEN-CC, INTERACT, HIPERCAP*. The goal of this first part was to share the gained knowledge and communicate the latest results obtained in the field of advanced and novel CCS technologies studied in these projects.
The central session of the workshop was focused on the current situation of the CCS technologies in the Australia and the main Australian players involved in this topic: The University of Sydney, University of Queensland, The University of Melbourne, University of New South Wales, CO2CRC, CSIRO. Demonstration projects and R&D programs in Australia were also presented (e.g. The CarbonNet project, NSW CO2 storage program). This second part was complemented with (i) a focus on the joined results obtained on the economic optimization of the three *ASCENT* technologies with *The University of Sydney* and (ii) a broad introduction of the Australian coordinated H2020 *LEILAC* project.
The goal of the third session of the event was to inform the audience about the **latest outputs** in the field of materials development, LCA activities and safety risk analysis obtained within the *ASCENT* project.
The workshop ended with a roundtable for fruitful discussion in order to explore and define potential future EU-Australian activities in the field of low carbon technologies. In particular, the purpose of the roundtable was to exploit the current common activities and make use of the synergies and complementarities between EU and Australia in a **realistic and coherent framework of non-committal common interests**.

The roundtable was characterized by a frank and open dialogue on the preparation of the ground for ‘sustainable’ cooperation between EU and Australia for long cooperation in the field of CCS technologies. Twinning activities in all the EU projects presented in the workshop, indeed, have been set out to deliver tailored-made results and not just to foster a mere and general cooperation:

within each projects, indeed, the EU and Australian parties have agreed in advance on a detailed work programme.

Main takeaways:

- It turned out during the roundtable that in order to roll-out this future interaction between Europe and Australia, besides a common scientific programme, the two parties (Europe and Australia) have to access a **common funding source** in order to benefit from the current twinning activities.
- There was a consensus on the non-committal common thematic area with the title: "***Moving towards low carbon technologies via low-cost and environmental benign carbon capture and utilisation***". The main aims of this research action are:
    - reducing emissions from fossil-fuelled power generation and industries:
    - achieving negative emissions if combined with biomass;
    - increasing efficiency in CO2 capture and utilisation;
- Acknowledgement that this research area will be successful if, advancements are made in the following key areas
    - Small and medium application in special/niche markets (e.g. glass market, bauxite);
    - Industrial symbiosis and circular economy
    - Flexibility in power generation;
    - Modular technology solutions.
    - Biomass and bioreactors;
    - Further cost reductions are achieved for CO2 capture technologies;
    - Environmental benign solution have to be pursued to reduce the emission of other pollutants (e.g. NOx);
- A point was made on the need that the CCUS technologies have to be further demonstrated at **industrially relevant conditions** under a number of applications (e.g. cement, steel manufacturing, power generation, coal-fired power); although CCUS was also seen as a niche market unless cheap H2 becomes ubiquitous in the distant future.

The ERA-NET instrument under the Horizon 2020 and Mission Innovation initiative under COP21 could be suggested as methodologies to support and enable a more constructive and solution-oriented dialogue between EU and Australia.

Meeting with the national experts from EU Member States to contribution to the future EU research activities – After the EU-Australian workshop the project coordinator was invited by the Informal Group of RTD Liason Office (IGLO) to attend the IGLO meeting discussing on the issues experienced in coordinating EU project twinned with third country as Australia. The aim of IGLO meeting, indeed would be to discuss in groups focusing on rules for participation of third country (as Australia which is the twinned country in the ASCENT project) in the EU projects with regards to financial, policy and practical problems. The main achievement was to report in the minutes of the IGLO meeting in agreement to the chairman Andrés Martínez Estévez that the "the ERA-NET Cofund was praised as a great example of a funding instrument that is easy for European and third country participants to participate in because it allows for national funding rules to be applied to the funded projects." as the ASCENT consortium agreed with the Australian partners in the EU-Australia workshop in Lausanne.

The minutes of the IGLO meeting have been forwarded to EU parliaments for setting the future 9th Framework programme. This document was the outcome over 50 national experts from EU

Member States/Associated Countries and representatives of third countries (National Contact Points, S&T Counsellors from diplomatic missions to the EU, etc.), which took place during the event.

Harmonization of the ASCENT technologies to the worldwide Mission Innovation strategy – Mission Innovation is a worldwide initiative to accelerate the implementation of clean energy, announced during the COP21 in Paris on November 30, 2015. Several challenges were selected, one of those is the implementation of carbon capture, to enable near-zero CO2 emissions from power plants and carbon intensive industries. A workshop has been held in Houston, Texas on September 25-29, 2017 which aims on early stage breakthrough CCUS technologies. The event was conceived as composed of a number of panels where experts have been invited to discuss the fundamentals of the worldwide research in the field of carbon capture, use and storage within the coming years. One of the panel focused on sorbents and looping systems, and was attended by members of the ASCENT consortium.

The ASCENT consortium is proud to contribute with the other EU initiatives in paving the future of the worldwide research in the advanced CCUS processes and demonstrating the value of continued EU research, including the contribution of the UK. Assuming that all the Mission Innovation partners remain committed to the initial strategy agreed during the COP21, the contribution of the ASCENT representatives within Mission Innovation are expected to have significant and far-reaching consequences in the long term worldwide research on the decarbonisation of industry and power.