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The CO_2 Capture Project (CCP): Results from Phase II (2004-2009)

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Abstract

The CO_2 Capture Project (CCP) is an international collaboration among energy companies supporting advancement of technology in the field of carbon capture and storage (CCS). The main technical results of Phase II of CCP in the development of novel capture technologies are presented. Phase II has been running since 2004 and is coming to a completion in the first months of 2009. Phase II is focused on the development of CCS technologies for natural gas fired power stations and refinery operations.

Keywords: CO_2 capture, scale-up, power generation, refinery, postcombustion, precombustion, oxyfiring, chemical looping

1. Introduction

The CO2 Capture Project (CCP) is a collaboration among eight of the world's largest energy companies (see authors' affiliations) with the mission of addressing the world-wide concern over climate change. This is being accomplished by development of CCS techniques that may favor their early implementation. Since 2000, the CCP has been active on both the capture and storage sides with the high level targets of:

- Development of novel capture technologies for reduction by at least 60% of the capture costs compared to the year 2000 state-of-the-art.
- Development of knowledge for demonstration to stakeholders that geological sequestration is safe and reliable.

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Funding for these activities comes from a number of sources, including an yearly fee associated to membership, government grants (from European Union, US Department of Energy and Norwegian Council for Research), and in-kind contributions, totalizing a budget of about 100 millions US$ by end of 2008.

This paper presents the main achievements of the CCP in the development of novel CO_2 capture technologies, highlighting the contribution given over the development timeline from concept to commercialization.

2. The Phases of CCP

Phase I of the Project (2000-2003) started with an overall review of about 200 novel concepts for CO_2 capture. About 30 promising ideas were selected for intensive R&D programs by external technology providers, and they were co-funded by governmental organizations. By the end of 2003, using a stage gate methodology coupled to detailed economic analysis, about 1/3 of them achieved Phase I targets:

- Technical proof of feasibility at lab scale.
- Potential for consistent reduction in CO_2 capture cost.

A team of CCP engineers identified critical issues for further development of each technology and, working in collaboration with the technology providers, defined a suitable path for scale-up. The calculation of capture costs was performed, both for state-of-the-art and novel technologies, by comparison to "uncontrolled" cases set in well defined scenarios owned by the member companies. Thomas [1].collected all of the technical and economic results from Phase I

During Phase II (2004-2009) the CCP has been supporting further development of preferred technologies emerging from Phase I, setting the following targets:

- Successful scale-up by at least one order of magnitude.
- Address and solve technical critical issues identified in Phase I.
- Confirm or improve economic evaluations of Phase I.
- Achieve the development level of "ready for field demonstration" for at least one technology.

The strong increase in the cost of construction materials experienced over the last 5 years, is affecting the absolute values of CO_2 captured and avoided cost, particularly when expressed in US$, due to the weakness experienced by this currency. Certain targets expressed in the past years in terms of absolute capture costs (e.g. 20-30 US$/ton) are unachievable in the current market situation for some applications of interest to the CCP members. The only realistic target is a percentage reduction compared to actualized state-of-the-art costs, while stakeholders should accept that CO_2 capture and storage is going to be more expensive than could be predicted 5 years ago. The volatility of the markets of raw materials is also making alignment of different cost estimates more difficult and challenging. For this reason, this paper will concentrate on the outstanding technical achievements of the CCP, leaving the roll-out of final CCP economics to a later date in the near future.

3. The Scenarios of CCP

During Phase I, four different scenarios were considered for application of the CCP-supported technologies:

- New-built natural gas combined cycle (NGCC) 400 MW power station in Norway
- Retrofit of heaters and boilers system in a UK refinery (2 million tons/year of captured CO_2)
- Retrofit of a network of gas turbines in Alaska (1.3 million tons/year of captured CO_2)
- New-built petcoke IGCC unit (4.9 million tons/year of captured CO_2)

During Phase II, attention was focused on power generation from natural gas, recognizing this application as challenging, since the low concentration of CO_2 in the flue gas leads to higher capture costs compared to coal power generation, and power generation is going to be the first industrial sector where CCS techniques will be commercially applied. On the other side, the refinery scenario was made more flexible, assessing oil refinery as a multi-source of CO_2, and addressing each type of source with the most promising capture technology. Production of heavy oil or tar, though not directly included in Phase II, is a related application of growing interest where generation of the required steam will result in high levels of CO_2 emission. The other two scenarios of Phase I were not included in Phase II. The extremely high costs of the Alaskan scenario make it an unlikely early deployment opportunity of CCS, while Phase I showed that the additional costs for CCS in a gasification unit are negligible

compared to the huge capital cost of the IGCC itself. In this case, cost reduction should target the gasification unit, rather than the capture technology and this type of development is out of the scope of the CCP.

4. The portfolio of CCP technologies

Technology development in Phase II progressed both in the frame of governmental co-funded and CCP fully funded projects. Technology providers contributed in-kind in several projects. The share of fully funded projects increased compared to Phase I, as it may be expected when activities gradually shift from research to engineering development. Table 1 presents a list of the main governmental co-funded capture projects of CCP phase II.

Table 1: List of major capture projects for phase II of CCP. CLIMIT also includes geological sequestration. NOK stands for Norwegian Krones

Project Acronym	Co-Funder	Starting Date	Duration	Total Budget
CACHET	European Union	April 2006	36 months	13.4 millions €
HMR & BIT in CLIMIT	Norwegian Research Council	June 2005	36 months	46.0 millions NOK
CLCGASPOWER	European Union	January 2006	30 months	2.1 millions €

From the standpoint of "time to market" the CCP has kept the mixed approach of Phase I, including short, medium and long term technologies. While "time to market" is an index including both technical and commercial issues, "time to demonstration" is a more technically sound feature to define the state of development of a technology. In this prospect CCP technologies may be classified as:

- Short Term (ready for demo by 2009)
- Medium Term (ready for demo by 2012)
- Long term (ready for demo beyond 2012)

The commercial availability of novel technologies is expected to gradually reduce the average cost of CO_2 capture for all types of application. Some short term technologies have however potential to achieve outstanding cost reduction in specific applications.

The mixed approach was also kept in the choice of the capture techniques; pre-combustion, post-combustion and oxy-fired technologies are all present in the CCP portfolio. Knowledge gained in Phase I, however, allowed for optimization of coupling between selected techniques and scenarios of application.

Two parallel paths were followed for the power generation scenario. An integrated approach, based on exhaust gas recycle (EGR) was selected as a means to make post-combustion more economically attractive by reducing the size of the absorber and integrating the capture unit with the power station. On the other hand, since Phase I showed that pre-combustion could lead to consistent savings in the medium and long term, an overall approach was followed through the CACHET and CLIMIT Projects to prove and assess a number of novel concepts for syn-gas production and CO_2 separation.

For refinery applications, the technique of oxy-firing was preferred, since Phase I showed this as the lowest cost technique for an overall retrofit of a refinery using state-of-the-art technology. Some pre-combustion techniques were also considered for this application, since syn-gas production units of the required size are already commercially available.

5. Power generation from natural gas in a combined cycle (NGCC)

As reported by Choi et al. [2], the CCP and Nexant developed at the conceptual level an integrated post-combustion process scheme to minimize the costs of capture. This scheme was named "Best Integrated Technology" (BIT) and may in principle be applied to any post-combustion capture technology based on absorption of CO_2. The process flow diagram for BIT as applied to power generation is represented in Figure 1.

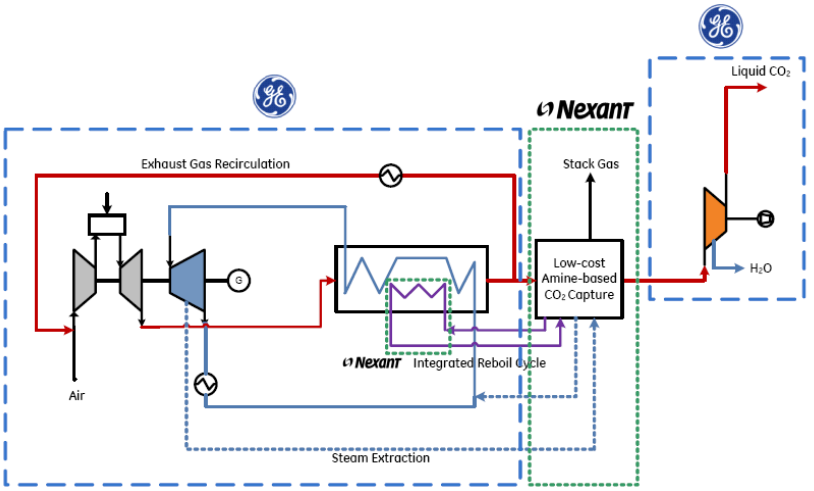

Figure 1 BIT process flow diagram

The positive economic evaluation achieved in Phase I was caused by two main items:

- EGR for the combined-cycle power plant of 50% of the flue gas stream, increasing the CO_2 concentration in the flue gas from the usual 4 vol. % to 10 vol. %
- Integrating the Heat Recovery Steam Generator (HRSG) with the solvent reboilers to eliminate some reboiler shells from the capture plant and reduce net steam extraction to the capture plant.

EGR leads to lean combustion (~ 13% vol. of oxygen for 50% EGR) which may affect operation of the combustion chamber. The CCP has therefore collaborated with one of the main turbine vendors (General Electric) to investigate experimentally the feasibility and limitations of EGR and to update the BIT process scheme and evaluations. Tests with actual EGR were performed on a prototype combustion rig with ~1% thermal load of a full 9FB machine (1/6 of a can). The experimental setup included two combustors, water quenching, re-firing in second stage, piping and preheating. The tests have demonstrated EGR up to 35 % under relevant conditions for up to 30 hours and the feasibility of deploying EGR on Dry Low-NO_x (DLN) turbine, confirming good performance of the DLN nozzle. Modifications of existing equipment might allow demonstration of 40% EGR. Additional to flame stability, concentration of carbon monoxide in the flue gas is the main index used in the assessment. The revised BIT process scheme shows power generation efficiency close to 50% using a 30% wt. solution of monoethanolamine (MEA) as solvent with a penalty of ~ 8 percentage points compared to the uncontrolled case. The use of more advanced new generation solvents may further reduce this gap. The next step for development of the EGR technology may be a full can test ($1/12^{th}$ of a 9F turbine) or a field demonstration retrofitting an existing E- or F-type machine.

Phase I also showed that pre-combustion may be the winner in the long term. A technology under development by StatoilHydro (at the time Norsk Hydro), Hydrogen Membrane Reforming (HMR), showed outstanding potential for long term cost reduction. HMR is based on the development of novel, high temperature (~1000C) ceramic membranes permeable to hydrogen and is applicable to pre-combustion decarbonization schemes for CO_2 Capture. Figure 2 shows an example of a HMR gas power cycle principle with two reactors, one for syngas (hydrogen, carbon monoxide and carbon dioxide) generation and one for hydrogen production. The first reactor combines steam reforming of methane to syngas and combustion of permeated hydrogen by air. The next reactor is used for separating hydrogen and CO_2, generating carbon free fuel for power production. Reforming reactions take place at a pressure of 20 bars and temperatures of 700-1000°C. Alternatively the second membrane reactor can be omitted and hydrogen can be produced by means of conventional CO-shift and CO_2 separation technology. Generated N_2/H_2O gas can be used as sweep gas in the downstream membrane process or used as diluent for hydrogen in the gas turbine for NO_x control. CCP calculations assume, in line with guidelines from European vendors, that the hydrogen stream to the gas turbine may contain up to 50% vol. of hydrogen. The development of burners able to deal with higher concentrations is likely to improve prospects for future deployment of pre-combustion power generation.

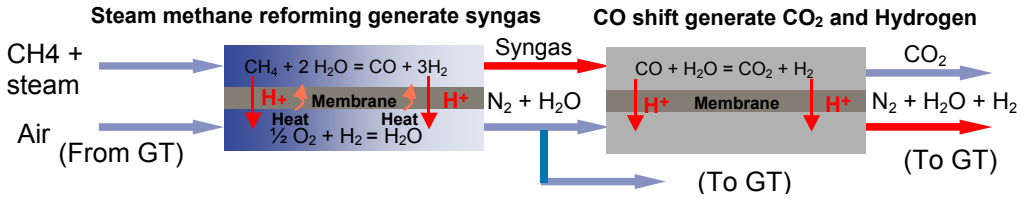

Figure 2 Example of a HMR gas power cycle.

During phase II, the membranes were scaled-up from 10 cm tubes (4 mm internal diameter) to 7x7 cm monoliths with 1.5 mm active channels. Smaller monoliths (2x2 cm) were tested under process conditions at 1000°C and 20 bara and methane conversion was close to equilibrium. An updated process scheme was also developed taking into account the drawbacks of the previous one, targeting:

- Reduction in the overall membrane area: only one stage of membrane reforming is now considered vs. 3 stages in Phase I. CO_2 capture is achieved in a conventional amine unit.
- Use of conventional turbines. The air extraction ratio was reduced from 60% to 20%

This scheme (Figure 3) maintains the potential economic benefit of Phase I, achieving efficiency higher than 50%.

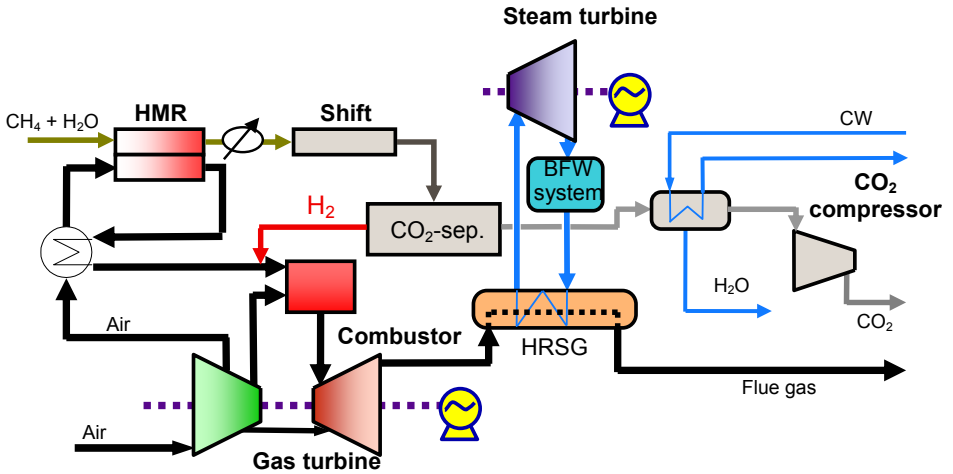

Figure 3 HMR Process scheme with 1-stage of membrane

The HMR development is now entering a 2-year program for qualification and optimization of the membrane materials. The following phase will be focused on testing of a pilot unit.

The success and prospects of HMR pushed the CCP toward a thorough investigation of novel radical concepts for pre-combustion power generation in the EU co-funded project CACHET (2006-2009). Five long-term concepts for hydrogen production for power generation are under study. All of these concepts, involving either chemical looping syngas production, direct hydrogen production by water splitting, low temperature membrane reforming using noble metal membranes and advanced schemes for heat integration between the reformer furnace and the gas turbine, achieved proof of technical feasibility during the project. Critical issues for further development were also determined. Process schemes are under development by a process optimization company, PDC (Process Design Center), and they will be compared to a state-of-the-art air-fired auto thermal reforming (ATR) process combined with methyldiethanloamine (MDEA) washing. At the moment, though all of them may be an improvement compared to the state-of-the-art, achieved efficiencies are lower than 50%, currently considered as an access limit to compete with post-combustion capture. Some of these technologies may be used for hydrogen production with CO_2 capture.

CACHET is also continuing development of two technologies already in the CCP portfolio during Phase I. These are medium-term separation technologies that may be integrated into existing process schemes for syngas production, specifically coupling the Water Gas Shift (WGS) reaction to a separation technique:

- Membrane Water Gas Shift (MWGS) coupling WGS to a noble metal hydrogen permeable membrane (not necessarily in the same vessel).
- Sorbent Enhanced Water Gas Shift (SEWGS) coupling WGS to a solid sorbent for CO_2 capture.

In both cases, the WGS reaction is driven to completion making CO_2 capture easier and cheaper. These technologies seem to be good candidates, coupling good economics to shorter development time.

MWGS is based on the development of ultra-thin palladium membranes started by Sintef in Phase I, as described by Klette et al. [3]. Very thin palladium layers (< 5µm) deposited on a stainless steel porous support are utilized to remove the hydrogen from the syn-gas produced by the reforming and the water gas shift reactions. Good performance of tubes a few centimetres long was demonstrated during Phase I in the water gas shift environment. During Phase II the membrane coated tubes have successfully been scaled-up. 50 cm long membranes have been successfully produced with palladium/silver using a two-step method in which the thin defect-free Pd-alloy film is prepared by sputtering deposition onto the 'perfect surface' of a silicon wafer. In a second step, the membrane is removed from the wafer and transferred onto a porous stainless steel support. A bench scale reactor module based on the scaled-up tubes with hydrogen production roughly equivalent to 4 - 8 kW has been constructed at ECN and testing is currently under way. The next step of development should be a modular pilot unit in the 100 kW range in a non-integrated version of the technology (separate WGS reactors and membrane vessels), based on the modules developed in CACHET.

SEWGS, developed by Air Products in Phase I, uses a solid adsorbent able to preferentially adsorb CO_2 and thereafter applies pressure swing absorption (PSA) and water gas shift (WGS) within a single vessel to simultaneously convert CO/H_2O to CO_2/H_2 and to capture CO_2. A complete process flow diagram for application to power generation is represented in Figure 4.

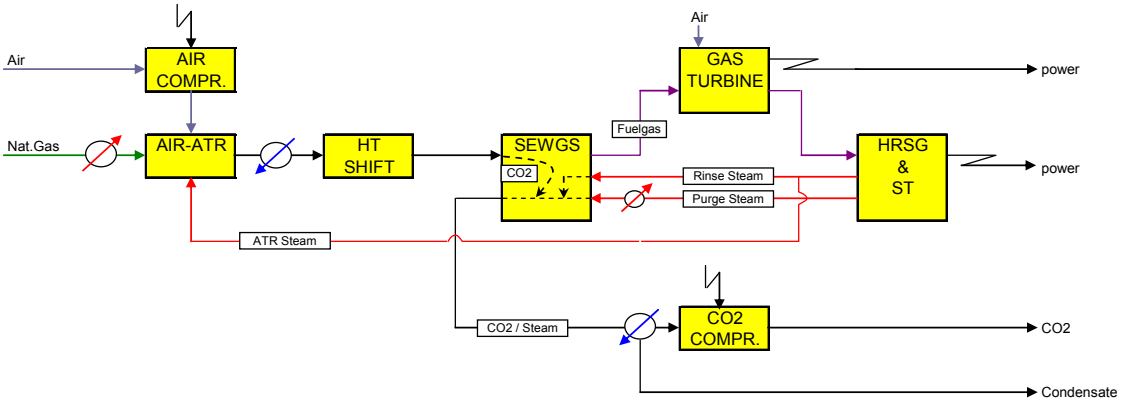

Figure 4 SEWGS process scheme

In Phase I suitable adsorbents (modified hydrotalcites) were developed and tested in a single laboratory reactor with alternating cycles of adsorption and desorption. In the frame of CACHET, a multi-column test rig (6 columns) representing a complete continuous commercial cycle has been constructed at ECN. Columns are of the same height as future commercial columns (6 meters), so that further scale-up should be straightforward. Testing is under way, as well as optimization of the process scheme to maximize efficiency.

6. CO_2 Capture in the refinery

Several sources contribute to the overall greenhouse gas emissions of an oil refinery. Their relative importance depends on the specific configuration of the selected refinery. Three major sources may however be identified:

- Steam boilers and process heaters
- Regenerator of the Fluid Catalytic Cracking (FCC) unit
- Hydrogen production

During Phase I the CCP studied the overall retrofit of a set of refinery heaters and boilers, assessing oxy-firing through a large centralized Air Separation Unit (ASU) and Flue Gas Recycle (FGR) as the state-of-the-art option resulting in lowest capture cost (~ 40% lower than post-combustion baseline). The development of novel technologies for air separation may further increase this advantage in the future, even if some additional costs for final purification of CO_2 might be added, depending on the specification requirements. For a new-built case, or for a single boiler application such as steam production for extraction of heavy oils or oil sands, another peculiar form of oxy-fired technology, Chemical Looping Combustion (CLC), has the potential to become the preferred option.
CLC is an approach to oxy-firing that is based on a solid carrier able to chemically adsorb oxygen from air (oxidation in the air reactor) and release it in the presence of a gaseous fuel (reduction in the fuel reactor) with immediate complete combustion. Central to the technology is a two-reactor system with continuous circulation of solids, as schematically shown in Figure 5.

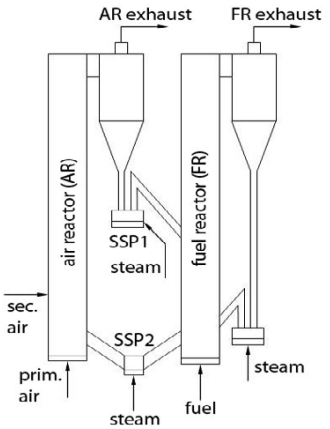

Figure 5 CLC conceptual dual reactor scheme

From the safety point of view, CLC has the advantage of performing oxy-combustion without the presence of free gaseous oxygen. Complete air separation with co-production of pure nitrogen is not needed, decreasing the theoretical energy consumption. The CCP supported formation of a partnership, including Chalmers University of Technology, Consejo Superior de Investigaciones Cientificas (CSIC), Technical University of Vienna and Alstom Boilers, that brought the technology from the almost pure conceptual level (2000) to development of a very active Ni-based oxygen carrier and that demonstrated the operation of a 10 kw unit with continuous solid circulation at Chalmers (2003) in the EU GRACE Project. Development continued in Phase II in the frame of the EU co-funded project CLCGASPOWER with further scale-up to a 120 kW unit at the Vienna University and optimization and scale-up of carrier production. Though more extended runs on the Vienna unit are needed to assess mechanical and chemical durability of the carrier, the technology may be considered ready for another big step in the scale-up path. The preliminary design for a 10MW demonstration unit has been prepared as a deliverable of CLCGASPOWER.

The fluid catalytic cracker (FCC) unit is the single largest emitter of CO_2 in most refineries. CO_2 is emitted through the regenerator exhaust, where coke, deposited on the catalyst, is burnt with air. Capturing CO_2 from this post-combustion stream is likely to be very expensive due to the low concentration and low pressure of flue gas stream. In the oxy-fired FCC catalyst regeneration concept, pure oxygen instead of air is used to burn the coke in the regenerator and flue gas is partly recycled to avoid temperature runaway. Building on results from testing in a small pilot by Petrobras, one of the CCP member Companies, a study to develop a cost basis for a base case (post-combustion) and a set of oxy-fired cases for CO_2 sequestration from a FCC regenerator was awarded to Randall Technologies. The case considered retrofitting an existing unit operated by Petrobras at Landulpho Alves refinery. The unit capacity is 10,000 cubic meters per day and total CO_2 production around 3500 metric tons per day. The study confirmed that retrofitting an FCC regenerator to oxy-firing is technically feasible and economically advantageous when compared to post-combustion capture. Based on these results Petrobras is planning a demo run on a large pilot unit in a Brazilian refinery in 2009.

7. Conclusion

The CCP has been a focal point for development of CCS technologies for oil and gas applications over the last decade. Development of technologies selected in the initial assessment was financially supported through the years and periodically reviewed by the CCP Capture Team, both technically and economically. The progress of technical development for the main technologies in the CCP portfolio, as well as the next possible step in development are summarized in Table 2.

Technology/Year	Main Technology Providers	2000	2004	2008	Near Future
BIT (Best Integrated Post-Combustion Technology)	**General Electric, Nexant**		**Conceptual study**	**1/6th of 9F turbine can testing**	**Full can testing or field demo**
HMR (Hydrogen Membrane Reforming)	**StatoilHydro**	**Concept**	**8cm single tube**	**7x7 cm monolith**	**Further material qualification before pilot**
MWGS (Membrane Water Gas Shift)	**Sintef, ECN, Dalian Research Institute**	**Lab scale fabrication technique for ultrathin Pd layers**	**Tested 2 cm long tubes**	**Tested modules with 50 cm long tubes**	**Pilot unit based on developed modules**
SEWGS Sorbent Enhanced Water Gas Shift)	**Air Peoducts, ECN**	**Sorbent screening**	**Single column testing**	**Multicolumn testing**	**Pilot unit**
CLC (Chemical Looping Combustion)	**Chalmers University, Alstom, TUV, CSIC**	**Small scale lab testing**	**10 kW circulating unit**	**120 kW circulating unit**	**1-10 MW unit**

Table 2: Summary of CCP achievements

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