CCSP Carbon Capture and Storage Program

Final report 1.1.2011–31.10.2016

Preface

The work presented in this report was carried out in the Carbon Capture and Storage Program (CCSP) research program, coordinated by CLIC Innovation Oy, with funding from Tekes – the Finnish Funding Agency for Technology and Innovation, during 2011–2016. The CCSP consortium consisted of 18 industrial partners and 9 research partners. Industrial partners are Fortum Oyj, Ramboll Finland Oy, Vibrometric Oy, Helen, Gasum Oy, Neste Oyj, Amec Foster Wheeler Energia Oy, SSAB Europe Oy, Neste Jacobs Oy, Fortum Power and Heat Oy, Stora Enso Oyj, ÅF-Consult Oy, Oil and Natural Gas Corporation (ONGC) Ltd., Oulun Energia, Tapojärvi Oy, Nordkalk Oy Ab, Andritz Oy, and Outotec Oyj. Research partners were VTT Technical Research Centre of Finland, Aalto University, Lappeenranta University of Technology, Geological Survey of Finland, Tampere University of Technology, University of Oulu, Åbo Akademi University, University of Tampere and the Finnish Environment Institute SYKE.

Contents

Appendices

1. Introduction

Carbon Capture and Storage (CCS) is considered to be one of the main options for reducing CO_2 emissions alongside renewable energy, more efficient energy use and nuclear power. The concept of CCS includes capture of CO_2 produced by a power plant or an industrial plant, transportation of CO_2 to a suitable storage location, and permanent storage of CO_2 (injected deep underground or converted to inert carbonates) in isolation from the atmosphere (Figure 1). CCS could significantly reduce CO_2 emissions and contribute significantly in achieving the deep emission cuts required by the newly signed climate agreement for limiting the global temperature rise to less than 2°C. Finland has good opportunities to achieve a GHG emission reduction of 80% by 2050 if all the technology options are available (Koljonen et al. 2012). CCS was especially found important for heavy industry, which has less mitigation options than the energy production industry has.

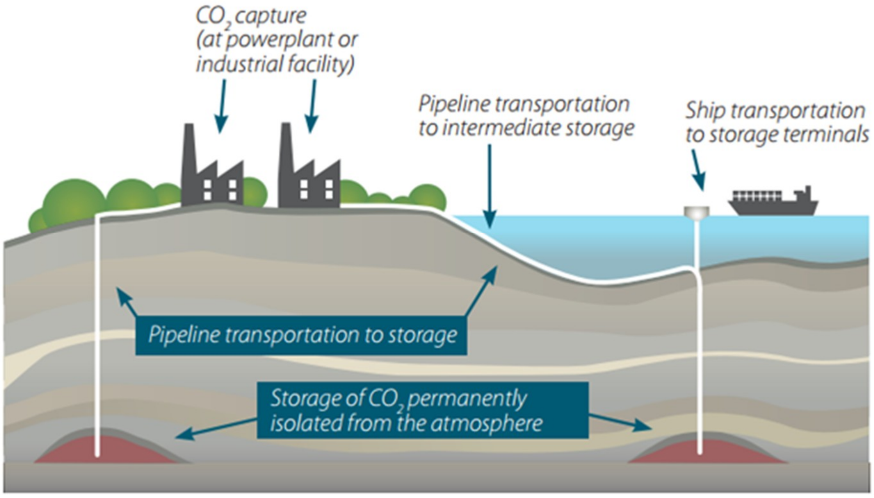


Figure 1. The basic principle for Carbon Capture and Storage (CCS).

1.1 CCS – Significant opportunities for Finland and Finnish stakeholders

The development of CCS technology faces many challenges. CO_2 capture processes are currently very energy intensive and development is needed to bring costs down. Also, CO_2 needs to be transported to a suitable storage site for secure and permanent storage. Although CCS technology has not yet been implemented at a full-scale power plant, several demonstration projects are underway in the world. According to GCCSI (2012), eight projects are in operation, storing 23 Mt CO_2 per year, mostly in conjunction with enhanced oil recovery (EOR).

CCS offers significant opportunities to early implementation in Finland. Being a large consumer of power and heat, Finland has a unique opportunity in integrating CCS with combined heat and power (CHP) plants. As Finland is a large consumer of biomass, adding CCS to bioenergy solutions (bio-CCS) would enable removal of CO_2 from the atmosphere. CCS is the only technology that can significantly reduce CO_2 emissions – typically by 90% – not only from power plants but carbon intensive industry as well, such as oil refining and steel manufacturing. Finding CCS solutions for heavy industry is therefore important for reducing CO_2 emissions from the Finnish industry.

For the Finnish technology developers and providers CCS could provide a significant market share in the future. Chemical looping combustion (CLC) is a new CCS technology that benefits from Finnish expertise in fluidized bed boiler. Monitoring technologies is another Finnish expertise that can help making CCS a safe and secure emission reduction and improve the social acceptance of CCS.

Mapping the geological storage potential in areas close to Finland is important, as the Finnish bedrock does not have any formations suitable for underground storage of CO_2. However, Finland has also large reserves of minerals that could be used for converting CO_2 into inert carbonate minerals. Also, CO_2 can be used as a feedstock for producing chemicals and fuels. CCSP is already bringing these technologies closer to commercialisation, with the laboratory pilot at Aalto University for converting CO_2 and steelmaking slag into pure calcium carbonate being a prime example of this.

1.2 Overview of CCSP

CLIC Innovation Oy's Carbon Capture and Storage R&D program (CCSP) was prepared for strengthening the position of Finnish industry and research organisations in the CCS technology field and aimed for a leading position in certain selected fields of CCS. The objective for CCSP was to develop CCS-related technologies and concepts, leading to essential pilots and demonstrations by the end of the program. A further objective was to create a strong scientific basis for the development of CCS technology, concepts and frameworks, and to establish active, international CCS co-operation.

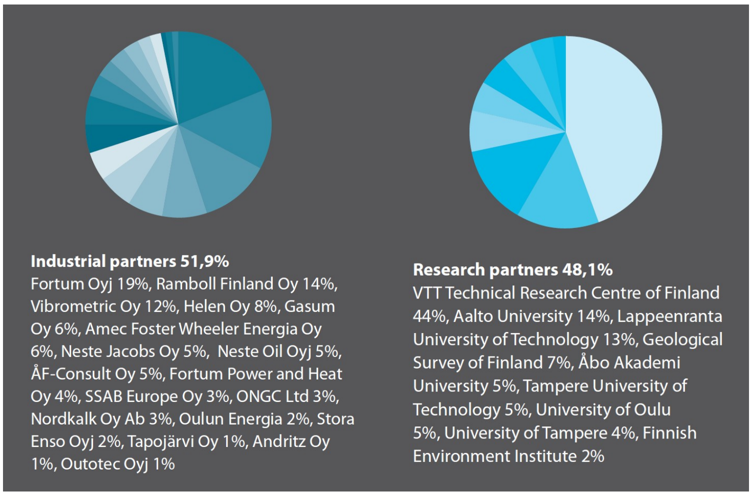
The CCSP program run from 2011 to 2016 and had a total budget of 15 M€, with Tekes – the Finnish Funding Agency for Technology and Innovation providing the main part of the funding. The program consortium consisted of leading research organisations and industry having significant background and references in their own field related to the CCS chain. The consortium consisted of 9 research organisations and 18 industrial partners (Figure 2). The total budget for the program was 15 million euro. The CCSP consortium was managed by CLIC Innovation Oy.

Main research areas were:

- CCS applications
    - Solutions for combined heat and power (CHP) plants
    - Multi-fuel power plants
    - Bio-CCS
    - Heavy industry
- Long-term breakthrough technologies
    - Chemical looping combustion (CLC)
    - CO_2 mineralization
    - CO_2 utilisation by algae cultivation and other novel concepts
- Monitoring technology
    - Development of methods and technology for monitoring of CO_2 capture and storage
- Framework for CCS
    - Regulation and legislation issues
    - Sustainability and public acceptance of CCS
    - Infrastructure and CO_2 storage capacity

By the writing of this report the program had produced:

- 44 peer-reviewed, international journal articles
- 99 conference articles
- 9 Ph.D. Theses
- 26 Master’s Theses
- over 90 internal technical reports



Industrial partners 51,9%
Fortum Oyj 19%, Ramboll Finland Oy 14%, Vibrometric Oy 12%, Helen Oy 8%, Gasum Oy 6%, Amec Foster Wheeler Energia Oy 6%, Neste Jacobs Oy 5%, Neste Oil Oyj 5%, ÅF-Consult Oy 5%, Fortum Power and Heat Oy 4%, SSAB Europe Oy 3%, ONGC Ltd 3%, Nordkalk Oy Ab 3%, Oulun Energia 2%, Stora Enso Oyj 2%, Tapojärvi Oy 1%, Andritz Oy 1%, Outotec Oyj 1%

Research partners 48,1%
VTT Technical Research Centre of Finland 44%, Aalto University 14%, Lappeenranta University of Technology 13%, Geological Survey of Finland 7%, Åbo Akademi University 5%, Tampere University of Technology 5%, University of Oulu 5%, University of Tampere 4%, Finnish Environment Institute 2%

Figure 2. Budget share of industrial partners and research partners participating in CCSP.

2. Summary of the results

This section presents a summary of the main results achieved in the program.

2.1 Role of CCS in Finland

- According to the scenario analyses done in CCSP, one third of the above targeted reduction of greenhouse gas emissions in Finland by 2050 could be achieved cost-effectively with CCS
    - Biomass-related CCS applications represent the main part of this potential (over 80%), while CCS applications in carbon intensive industries stand for the rest.
    - Excluding CCS from the technology portfolio in Europe for reducing greenhouse gas emissions more than doubles the estimated price of emission allowances by 2050.
- Most technologies for CCS are ready for application but currently there are no financial motivations to reduce CO_2 emissions. Financial support for early application of CCS in Europe is needed to ramp up the CCS deployment.
- Demonstration of CCS in Finland for combined heat & power plants combusting biomass and peat as well as for pulp and paper plants is recommended
- In order for bio-CCS to be applied, the benefit from the negative net emissions of bio-CCS needs to be acknowledged and accounted for in the EU ETS and other climate policy frameworks.
- Utilisation of CO_2 will not directly have much effect on reducing CO_2 emissions. However, combined with renewable energy systems it could be a route for providing carbon neutral fuels, chemicals and other products in the future.
- Certain concepts for utilisation of CO_2, like converting slags and ashes into more valuable products by CO_2 mineralization, already seem commercially viable.

2.2 CCS applications

- Several techno-economic assessments were conducted to analyse CCS in CHP environment. Even if CHP applications have limitations in terms of the economy of scale compared to larger condensing power plants, utilisation of recovered heat from the flue gas condenser and CO_2 compressors (and ASU in the case of oxyfuel) as valuable district heat enables important additional incomes, especially in the case of moist biomass.
- A techno-economic assessment of application of CCS with various technologies in the iron and steel industry was carried out. The results showed that the direct site emissions could be reduced by 0.3–2.9 Mt CO_2/a. The cases resulting in significant reductions represent 48–73% of direct site emissions. The net GHG impact of emission reductions were between 45–62% of the site emission reductions.
- The retrofit of CO_2 capture for a pulp and paper mill was assessed technically and economically. Results showed that for 90% CO_2 capture from a Kraft pulp mill the excess steam available onsite will be sufficient to cover the steam requirement in the CO_2 capture plant. For an integrated pulp and board mill an auxiliary boiler will be needed.
    - The levelized cost of market pulp with CO_2 capture is sensitive to policy frameworks, especially in regard to the accounting of negative CO_2 emissions. As a result of retrofitting CO_2 capture in the pulp and paper industry the levelized cost of pulp could increase by up to 30% (Kraft pulp mill) and 35% (integrated pulp and board mill), depending on the prevailing policy framework.
    - The cost of CO_2 avoided for the pulp and paper industry ranges from 50 to 90 €/t, depending on the prevailing policy framework.
- Different carbon capture technologies suitable for steam methane reforming (SMR) plants producing hydrogen were compared (Andtsjö 2013, D216). It was concluded, that the most attractive stream in SMR hydrogen production to be used for carbon capture is the off-gas from hydrogen purification. The estimated production cost for captured CO_2 was in all cases clearly higher than the present emission allowance cost of CO_2.
- The data from the multitude of CCS-concept evaluations performed in CCSP and the previous CCS Finland project were assembled into a single “summary” toolkit, which was used for analysing the techno-economic CCS potential in Finland. The results from this work show that with a CO_2 emission allowance price of 50 €/t, CCS would be economically feasible for 8 Mt CO_2/a, including transport and storage costs.
    - Most of the cost-effective CCS applications in Finland would be in the biomass power & heat sector and in the pulp and paper-industry. However, this requires that “negative” emissions from

bio-CCS are acknowledged and included in the EU emission-trading system.

2.3 Capture technologies

- New methods for sampling, analyzing and measuring environmental emissions from CO_2 capture plants and assessing their health impacts have been developed. One of the methods developed has been found to be one of the most accurate in the world for analyzing and measuring potentially harmful amine emissions. The method has noticed for accreditation, making it the first accredited method in the world for measuring amine emissions from carbon capture facility.
- Comprehensive modelling tools were developed for simulating the oxy-fuel combustion in circulating fluidized bed boiler.
    - A new weighted sum of gray gases model (WSGGM) was developed to specifically support modelling of radiative heat transfer in oxygen fired conditions.
    - A correlation based zone method was developed and applied to study radiative heat transfer in backpass of the oxy-CFB boiler.
    - The new zone method was coupled with a 3D process model to study radiative heat transfer in large scale oxy-CFB furnaces operated in various process conditions and boiler loads.
    - The effects of higher CO_2 and H_2O concentrations on limestone reactions were studied in bench-scale measurements and the data was applied for development of a transient particle-scale model and a steady-state full-scale model for oxy-CFB. Both model approaches were applied for simulating the limestone reactions and sulphur capture in oxygen-fired conditions.
    - A dynamic simulation platform was developed by linking two powerful simulation tools, APROS for boiler and turbine islands and Aspen Dynamics for the gas systems (ASU and CPU), allowing efficient simulation of an oxyfuel power plant.
    - A flexible heat exchanger network synthesis method for optimization of heat integration in a oxyfuel power plant was developed.
- CO_2/H_2S solubility, phase equilibrium, vapor pressure and density data for several aqueous amine and heat stable salt systems were measured. The obtained data were described with models suitable for rigorous simulation of the studied systems.
- Pre-combustion capture technology was studied for a greenfield natural gas fired GTCC power plant. Based on the modelling the efficiency of the

natural gas fired GTCC power plant was 11 %-units lower than corresponding power plant without CO_2 capture.

- Chemical looping combustion was developed in small pilot scale, especially for biomass combustion
    - Various chemical looping concepts for power generation with near-zero CO_2 emissions have been evaluated.
    - One of the world's first tests with chemical looping combustion of wood pellets in pilot scale (20 kW_{th}) was carried out, proving that chemical looping works with biomasses. Observations and measurements support the assumption that higher temperatures could be allowed for a bio-CLC reactor system than for an ordinary biomass combustion boiler, leading to higher steam values.
    - Comprehensive modelling tools were developed for simulating different chemical looping processes with gaseous and solid fuels. The modelling tools were applied for design, optimization, and process scale-up studies.
- Calcium looping for CO_2 capture was studied by modelling and cold model tests.
    - Model for describing reactive properties of calcium materials in continuous cycling were developed.
    - Fluidization properties of calcium based materials were tested in cold model tests.
    - Dynamical simulation model for calcium looping (CaL) capture was developed to study feasibility of process.
    - Feasibility of CaL process was evaluated in combination of CHP power plant.
    - Advanced CaL process concept based on solid heat carrier was presented and evaluated.
    - To summarise research needs and the state of the art of CaL process modelling an extensive review article was published in cooperation between CCSP researchers (LUT) and Italian (Politecnico di Milano) and Spanish (CSIC) research groups (Martínez et al., 2016)

2.4 Transportation and geological storage of CO_2

- Transport options and economics from North-European emission sources, with a focus on Finland and the Baltic Sea area were assessed.
    - The cost for transporting CO_2 from Finland to final geological CO_2 storage sites abroad is higher compared to that from the coastal regions in countries around the North Sea. However, by joint transport infrastructure projects the industry and power

    production around the presented regions can reach significant cost reductions for CO_2 transport.
    - The results indicate that shared CO_2 transportation infrastructure by ships would often be the best transport option from the Baltic Sea region to final storage sites at the North Sea. Especially the heavily industrialized regions on the shore of the Gulf of Finland can benefit from a shared transport infrastructure
- The concept of intermediate CO_2 rock cavern storage was developed and a general emplacement strategy of the storage envisaged, taking into account energy consumption, physical and geological processes inside and around the storage.
    - The cost of conventional intermediate steel tank storage was compared to storage in excavated rock caverns.
    - Simulations indicate that the most favourable store depth is 100 metres or deeper and the most favourable storage temperature is between −20 and −40 °C. In these cases the prevailing hydrostatic pressure best matches the CO_2 vapour pressure and the thickness of the frozen zone is likely to grow thick enough to ensure safe containment of CO_2 inside the store.
    - Feasibility studies indicate that if the concept were to be proven, there would be economic benefits from investing into caverns instead of modular on-ground tanks for larger intermediate storages for CO_2.
- The bedrock in Finland is composed mainly by crystalline and low porosity rock types which lack a potential for CO_2 storage in deep saline aquifers. The distances from Finnish point sources to potential storage sites is quite long, but in comparison to the rest of Europe, the offshore storage potential is very large in areas surrounding Finland..Currently, the nearest identified and demonstrated geological storage sites are located in the North Sea. In addition to the excellent potential of the North Sea, there is also a high storage potential in the Polish-German basin. Russia could also be interesting from a storage perspective but has not been studied in much detail.
- The nearest potential storage sites from Finland are located in the Baltic basin. The storage potential of the Baltic basin was studied in the BASTOR (Baltic Sea Storage of CO_2) project, initiated as collaboration between the CCSP and the Swedish CCS project consortium. Results indicated large storage potential but limited injectivity.

2.5 CO_2 mineralisation

- Europe's first pilot plant that converts CO_2 and slag into pure calcium carbonate has been designed, constructed and tested during the program. The pilot plant can produce about 10 kg of calcium carbonate per batch. The solvent can be regenerated and recycled. Up to 80% of the calcium in the slag can be extracted, while more than 70% of the CO_2 injected can be utilized and converted into calcium carbonate.

  - Researchers have successfully demonstrated that the concept is in its current stage technically and economically feasible for producing calcium carbonate suitable for applications where ground calcium carbonate is normally used.
  - Remaining challenges are the utilisation of slag residue and washing of calcium carbonate product when producing fine-grained calcium carbonate. For the process itself the removal of the solids (spent slag, PCC product) from the aqueous streams effectively is still a challenge. Avoiding losses of ammonia and excessive use of water (for PCC product washing) while efficiently binding the CO_2 fed to the system are other issues that need further work while the concept is being further scaled up and commercialized.
- The possibility to integrate a mineralisation process for natural minerals with a lime kiln was investigated.
  - Two process routes for serpentinite (magnesium silicate-based rock available in Finland in vast amounts) carbonation, under development at Åbo Akademi were both identified to be suitable for application at an industrial-scale lime kiln.
  - Depending on the heat integration, process simplicity and magnesium (hydro)carbonate product aimed at, magnesium extraction from rock would be followed by carbonation either in a gas/solid (fluidised bed) reactor at elevated temperatures and pressures or in aqueous solution.
  - The carbonation process would operate on flue gas directly, without CO_2 pre-separation while process simulation showed that energy input requirements for *fixing* CO_2 into carbonates will be less than what is typically reported for *capture* of CO_2 as part of conventional CCS that would involve underground storage.
  - While the considered test cases imply the use of serpentinite feedstock it was not possible to produce a successful scenario for application of the technology at one of the lime kilns operating in Finland. The limitation of having only wall-rock and other side-stone from limestone quarries available as feedstock rock (none of which containing significant amounts of magnesium silicates) rather than overburden rock from a nickel or gold mine (for example) meant that no feasible case study could be worked out.

2.6 Utilisation of CO_2

- Possibilities for utilisation of CO_2, either by chemical conversion or as a commodity as such was studied.
    - Various concepts in which CO_2 can be utilized chemically were screened, identified.
    - The viability of selected CO_2 utilizing reactions was analysed by thermodynamic calculations and experimentally. Finding an active, selective and stable catalyst is of vital importance. Typical catalytic systems used in the selected reactions were listed.
    - Sustainability assessment were conducted for CO_2 based reaction routes and corresponding commercial routes. Several CO_2 based reactions were found to be promising and feasible, especially synthesis gas and hydrogen production by dry reforming and some hydrogenation reactions (e.g. methanol synthesis).
    - Using CO_2 as a supercritical region has gained a growing interest. In supercritical applications, CO_2 acts a dual role as a reactant and a solvent.
- Possibilities for utilisation of CO_2 by biological conversion into microalgae was also studied.
    - Literature reviews on CO_2 supply methods, energy requirements, waste water utilisation, and cultivation in extreme pH conditions were performed.
    - Various routes to different microalgae products with CO_2 utilisation were identified. Conceptual level techno-economic analyses were performed for four concepts that produce lipids, biofuels and/or fertilizer.
    - Microalgae suitable for cultivation using vent gases from a natural gas processing facility were screened by employing a 20 L photobioreactor (PBR). CO_2 tolerance of various species was studied by sparging CO_2 and monitoring pH. Mixtures of species were also tested.
    - Larger-scale cultivation of selected species was tested using a 0.3 m^3 CO_2 absorption column for absorbing CO_2 from vent gas in connection to a 0.2 m^3 raceway pond. The produced algae was harvested and sent for anaerobic digestion studies. The experiments were successful, with a microalgae yield of 18 $g/m^2/day$ achieved, which on anaerobic digestion yielded about 0.4 m^3 CH_4/g volatile solids fed.
    - A techno-economic assessment was performed for large-scale (400 ha) production of microalgae with novel technologies. Data was acquired from Global Algae Innovations. Based on results it seems that with novel technologies and larger facility size the production of biomass for feed purposes may be economically

    feasible and result in a profit. However, a 400 ha facility size was too small to make the system viable.
  - Since cultivation of microalgae in extreme pH conditions could facilitate CO_2 delivery, a literature review on suitable species and experiments with selected species were performed. The cultivations confirmed that acidophilic algae can take up CO_2 equally efficiently at low (3) pH as at neutral (pH 6 to 7.5) pH and that similarly, alkaliphilic algae can take up CO_2 (bicarbonate) as efficiently at pH 9 as at neutral pH.

2.7 Framework for CCS

- Decision to invest in CCS is not only a technological, economical or legal question, but also an environmental, social, and even ethical question that relates to public acceptance and on the principles of sustainable development.
- The urgency for significant reductions in global greenhouse gas (GHG) emissions highlights the importance of carbon sinks, i.e. solutions that can remove CO_2 from the atmosphere, and the possibility for offsetting historical emissions. The later the global GHG emissions turn to decline, the greater is the need for sinks or so called “negative emissions”. Achieving negative CO_2 emissions is possible by applying carbon capture in processes using biomass as feedstock (bio-CCS).
- The implementation of various technological options for carbon capture and transport can due to environmental, safety and health (EHS) issues be a lengthy procedure, which has to be started several years before the installation is taken into use.
  - Although CO_2 is generally not classified as a hazardous substance, various sections in the Finnish legislation will apply when carbon capture technologies are introduced at power plants and other industrial establishments in Finland.
  - The EHS hazard potential of the carbon capture needs to be recognised early in a CCS project so that the associated risks can be managed effectively along with the risks caused by other parts or processes of the industrial plant.
- CCS could be an effective means for reducing greenhouse gas emissions from energy production and to mitigate climate change. Depending on the case specific conditions, CCS might provide possibilities for reducing other than climate change impacts as well, especially if ship transport of CO_2 and fuel sourcing are optimised.
- However, we should also be aware of the potential risks related to handling large amounts of CO_2, and of the potentially increasing other environmental impacts that might take place locally, for example due

to increasing need for fuels and transport, or the substances handled and emitted as part of CCS process.

- Many of the potential economic, environmental and social impacts of CCS are case specific, and depend on the context, location, system and neighbouring communities in which CCS would be implemented to. As a consequence, economic, environmental and social impacts would need to be carefully assessed in case any decisions to implement CCS in Finland would be made.
- Currently CCS technology is not a burning issue in Finland. The key stakeholders interviewed stated that they followed the development of the technology at some level, but their main interests are elsewhere. Due to the current energy production mix in Finland, the absence of storage sites in Finland, the high costs and impaired energy efficiency, the deployment of CCS technology was seen as unrealistic in the near future. Hence we argue that deployment of CCS technology in Finland is framed with low expectations at the moment.
- In the study focused on media attention to CCS four temporal periods were identified based on the frequency of CCS-references in the Finnish print media. The periods were as follows: (1) the period of nearly non-existent visibility (1996–2003), (2) the period of rising awareness (2004–2006), (3) the peak of attention (2007–2010) and (4) the period of decreasing interest (2011–2015). Bio-CCS or reference to it was mentioned only very rarely in the Finnish print media data in 1996–2015.
- Guidelines for public and stakeholder engagement should pay attention to legal requirements and formal phases related to planning and decision-making of a single CCS project (Figure 80), but at the same time it would be important to propose a policy for developing and taking voluntary activities of public and stakeholder engagement in the field of CCS. Recommendations regarding public engagement should take into account both different levels of decision-making (i.e. policy, local/project) and different phases of a programme or a project.

3. Role of CCS for Finland

A working group was appointed by CCSP's Program Steering Group for assessing the role of CCS for Finland. As a result, Finland's energy system up to year 2050 was modelled, both with and without CCS as a climate change mitigation method. The results were analysed and discussed, and a Summary for Policy Makers was written. The contents of the Summary is repeated below. The Summary is also available as a separate document on the CCSP final report web page (http://ccspfinalreport.fi/)

3.1 Importance of CCS

Carbon Capture and Storage (CCS) is one of the technologies needed in Europe to cost-effectively reduce CO_2 emissions in order to meet the target for 2050[1] set by EU's energy strategy and especially the stringent "well below 2 °C" target of the Paris climate agreement. Although Finland is migrating towards fossil-free power production, CCS is still needed. CCS is an essential tool also for Finland for reducing CO_2 emissions in the heavy industry sector, and it has an important role to play in the bioeconomy: combining CCS with biomass (bio-CCS) would form a carbon sink (or "negative" emissions).

According to the analyses done in the Carbon Capture and Storage Program (CCSP), CCS is a cost-effective method also for Finland for reaching the 2050 target[2]: up to 19 Mt CO_2 emission reductions per year could be achieved with CCS by 2050 – roughly one third of the target. On the other hand, excluding CCS from the portfolio of available methods for reducing greenhouse gas emissions in Europe more than doubles the price of emission allowances by 2050. According to the calculations, the annual mitigation costs around year 2050 would in Finland

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[1] The EU has set itself a long-term goal of reducing greenhouse gas emissions by 80-95% when compared to 1990 levels by 2050.

[2] In our calculations the target for Finland and Europe by 2050 was set to a reduction of greenhouse gas emissions by 80 % when compared to 1990 levels.

amount to 3000 million euro[3], but emission allowance trade would in return generate 500 million euro per year. The exclusion of CCS would increase the direct annual mitigation costs by 200–800 million euro per year by 2050. In this case Finland would have to purchase emission permits to meet the 2050 target, which would cause an additional burden of up to 2100 million euro per year. In Europe, the total annual mitigation costs around year 2050 would amount to 120 billion euro[3], while excluding CCS would increase the direct annual costs by 45–60 billion euro.

The results from scenario analyses done CCSP (D147) show that CCS is expected to have a significant role in emission reduction in Europe already around year 2030. In Finland, implementation of CCS is not required until after 2030, because the share of fossil energy in the energy mix decreases by 2030 due to the planned investments in nuclear power capacity and renewable energy.

Bio-CCS is a too important climate mitigation technology for Finland to overlook. According to the analyses done in CCSP, most of the cost-effective CCS applications in Finland would be in the biomass power & heat sector and in the pulp and paper industry. With bio-CCS alone, Finland could by 2050 reach up to 15 Mt CO_2 emission reductions per year – roughly one fourth of the 2050 target.

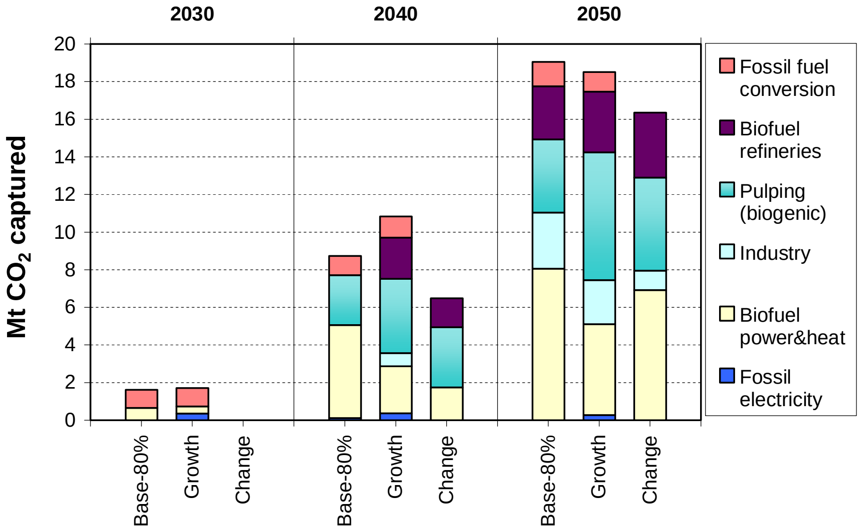

Figure 3. The role of CCS in scenarios targeting a reduction of greenhouse gas emissions of 80 % by 2050: in the “Base-80%” scenario a slower technology learn-

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[3] These costs were calculated only for the “Base-80%” scenario.

ing and penetration of renewables increases the demand for CCS. In the “Change” scenario fossil-CCS in energy production is excluded as a mitigation option to show the impacts of “fossil-free” energy production.

According to our analyses, the need for bio-CCS in Europe could become as large as 400 Mt CO_2/a by 2050 (7-8 % of the total target for reduction of greenhouse gas emissions for EU by 2050). The implementation of bio-CCS in Finland could even enable Finland to become a net seller of emission allowances. Bio-CCS is also an opportunity for Finnish technology providers, as they have the know-how to develop the technology and are already developing it.

Utilisation of CO_2 (or Carbon Capture and Utilisation; CCU) will not directly have much effect on reducing CO_2 emissions, but can have an important role in renewable energy systems, in which CO_2 would be captured for converting renewable (wind, solar, hydro) electricity into hydrocarbons to be utilized in various processes (transportation, chemicals, P2G). By this approach, the entire energy system would be carbon neutral if biogenic sources of CO_2 were used. In addition, certain concepts developed in the CCSP program, like converting slags and ashes into more valuable products by CO_2 mineralization, already seem commercially viable due to the high market value of the products.

3.2 Barriers for deployment of CCS

With 15 demonstration plants already in operation globally and 7 more being constructed, the technology for CCS is ready for application. There are no technical barriers either for storage of CO_2 in underground geological formations – tens of millions of tonnes of CO_2 has been injected and stored safely and securely in deep saline reservoirs for more than 15 years, and in oil and gas reservoirs for decades. However, in Europe there is currently no commercial driver for the industry to start implementing CCS. As an extensive deployment of CCS in Europe would decrease the costs for achieving the targets set out by the climate agreements, financial support for early application of CCS in Europe is needed to ramp up the CCS deployment.

As Finland has no suitable underground geological formations, CO_2 would need to be transported abroad for final storage. Therefore, application of CCS in Finland is 10–20% more costly than in Europe on average. For CCS applications in Finland ship transportation would be favourable over transportation of CO_2 by pipeline. Ship transportation benefits largely from “CO_2 hubs”, where CO_2 can be collected from several sources and distributed to final storage sites, but this requires intermediate (i.e. temporary) storage of CO_2 close to the terminals. The work in CCSP has indicated that building intermediate storage facilities in the Finnish bedrock could be a cheaper alternative than the use of steel tankers. Although the closest operational storage sites are currently located in the North Sea and Barents Sea, work in the CCSP has identified potential storage formations in the bedrock of the Baltic Sea. Although ship transport of CO_2 for storage is not currently covered by the European Emission Trading Scheme (ETS), it is possible for Member States to decide to include it under the scheme.

A low public acceptance is one crucial barrier in deploying CCS technologies and has contributed to halting of a couple of projects in the past. CCS has been seen as an excuse for continuing the use of fossil fuel. However, the work done in CCSP shows that the main potential for CCS in Finland is with biomass-related applications, not for fossil fuel-related CCS applications, except in carbon intensive industries. People have also been concerned with geological storage of CO_2, although the industry has good experience from safe and secure storage of CO_2. From a Finnish perspective, international collaboration is needed in relation to geological storage, as CCS applications in Finland would require transportation of CO_2 abroad. Research carried out in CCSP shows that there is hardly any public discussion about CCS in Finland and the majority of the media coverage of CCS has had a positive tone. In the future, special attention should be paid to stakeholder and public engagement and communication in fostering social acceptability of CCS policy.

Currently, there is hardly any incentive for investing in CCS in Europe, mainly due to the low price for CO_2 emission allowances in the European Emission Trading Scheme. In addition, there is no incentive for bio-CCS, as CO_2 emissions from biomass are not part of the ETS. In order for bio-CCS to be applied, the benefit from the negative emissions of bio-CCS needs to be acknowledged and accounted for.

3.3 Why CCS should play an important role in Finnish RD&D

- The Paris Climate Agreement and EU Energy Strategy set the long-term targets for the EU member states, including Finland, at a radical reduction of greenhouse gas emissions by 2050. Business opportunities for Finnish CCS technology export are expected to arise from the global demand for CCS. Rapid deployment of CCS in Europe is expected by 2030. However, action is needed now because of the significant lead times in CCS deployment and in order to retain economically important CO_2-emitting industries and associated employment in Europe[4]. Large-scale demonstration plants are needed for gaining vital experience from large-scale operation and further development of the technology. Considering the biomass re-

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[4] European Technology Platform for Zero Emission Fossil Fuel Power Plants (ZEP): Response to issues paper No. 9 – CCS and CCU, April 2016.

sources and technological expertise in the field, Finland could be the ideal place for demonstration of smaller-scale CCS applications for bio-CHP plants and larger-scale CCS applications for pulp and paper mills. This would both strengthen opportunities for Finnish technology export and contribute to emission reductions in Finland.

- Although application of CCS is slightly more expensive in Finland, the significant potential for negative CO_2 emissions through bio-CCS could more than compensate for this, making early application of bio-CCS in Finland a business opportunity for export of emission allowances. However, this requires that “negative” emissions from bio-CCS are included in the ETS.
- In order to enable export of CCS technologies and emission allowances, technology development and application of CCS in Finland need financial support. The EU’s NER400 Innovation Fund could provide needed support for bio-CCS implementation.
- Similarly to CCS, the vast majority of processes for utilisation of CO_2 require also capture and purification of CO_2. Therefore, the knowledge and expertise gained from R&D into CCS applications can also be used for CCU applications.

3.4 Proposed actions

For speeding up the deployment of CCS applications in Finland, and for realizing the business opportunity for CCS technology providers, the following is needed:

1. Planning of stakeholder and public engagement as well as communication activities
2. Incentives for application of bio-CCS and decarbonizing the industry
3. Demonstration of CCS for combined heat & power plants combusting biomass and peat
4. Demonstration of CCS for pulp and paper plants
5. Demonstration of CO_2 hubs in Europe and intermediate storage in Finland
6. Continued development and piloting of future technologies related to CCS and CCU
    - Hot solids looping technologies for biomass (for instance, chemical looping combustion and calcium looping capture)
    - Combined valorisation of mineral resources and CO_2 mineralisation, processing residues from mining activities while extracting valuable metals and fixing CO_2 into carbonates with market value.
    - Concepts utilizing captured CO_2 as a process medium to produce materials, transportation fuels, power-to-gas, or other chemistry products.

4. Applications of CCS

Capture systems for heat and power production and industrial processes are specific for each case. Each plant type needs particular processes, models and studies. In CCSP target is to find CCS application concepts for combined heat and power (CHP) plants and different heavy industries as these are among the largest point sources of CO_2 emissions in Finland (Figure 3). CCS is one of the few technological options available for energy intensive industry to reduce their carbon footprint. In addition to concept studies for CHP production and industrial processes, a systematic innovation process is being employed for finding new cost-efficient CCS concepts.

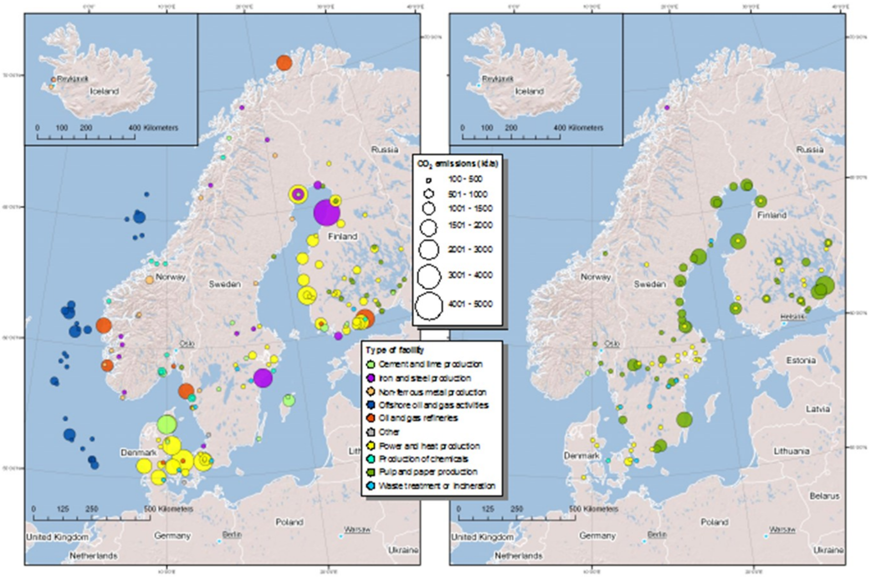


Figure 4. Maps over CO_2 emissions from facilities emitting > 0.1 Mt CO_2/a in the Nordic countries in 2007 (left: fossil and inorganic CO_2 emissions; right: biogenic CO_2 emissions) (Teir et al. 2010).

4.1 CCS for Combined Heat and Power (CHP) plants

Identifying influences of CCS integration to CHP systems are essential in the Finnish energy production infrastructure. In CCSP, influences were assessed on plant and system level focusing on the economic feasibility of these greenhouse gas mitigation options. This included comparison of different carbon capture technologies, differences between fuels and plant types as well as plant operation aspects. The evaluations were based on process modelling and assessment of costs related including investment costs, additional fuel costs and changes in the production costs of electricity and heat.

4.1.1 Oxy-combustion in multifuel boilers

A majority of the CCS studies carried out abroad have focused on coal-firing in condensing power plants. Although carbon capture technologies require energy for capture, most of them produce also an excess of low-grade heat, which could be utilized e.g. in district heating. In addition the utilization of biomass fuels in CCS is a potential pathway to “negative” CO_2 emissions. Adapting CCS technology to a CHP plant using biomass is a concept with a lot of unknown aspects and several opportunities for process integration.

A study was carried out to analyse the optimization and dimensioning criteria of a CHP plant utilizing 1st generation CCS technology – oxy-fuel combustion. The plant concept uses a full-scale oxy-CFB boiler (Circulating Fluidized Bed) and is studied using different fuel bases (varying mixtures of coal, peat, forest residues, wood pellets, etc.), especially focusing in high shares of biomass. The target for the study was also to define the basis for further analyses of effective 2nd generation CCS technologies in a CHP system environment.

The analysed CHP plant is connected to a heating system having heat demand of ca. 4 TWh per year serving industrial, office and municipal customers. The new CHP plant will cover ca. 35 % of the peak winter heat demand generating around 90 % of the steam energy and ca. 45 % of the annual district heat energy demand.

The CHP plant will be based on circulating fluidized bed combustion (CFB) enabling multi-fuel combustion with biomass (mainly forest residue), straw, peat and coal – at the reference point bio fuels share ca. 40%. The case CFB boiler will have the capability for air and in study case with oxy combustion with the total amount of CO_2 emissions ca. 1 Mt per year.

The design covers the boiler, flue gas recycling systems and flue gas condensation with only coal and with different bio fuel shares in different load situations and the selection and design of the turbine section. The total designed capture rate of CO_2 is 95 % and the designed purity levels of O_2 and CO_2 both 95 %.

The new oxy-CHP concept was developed and modelled using Fortum's power plant simulator Solvo® and Fortum's earlier CCS studies. The plant layout, capacities and fuel distributions were modelled according to the study design figures. The model consists of the components needed to calculate the power plant's energy balance. The additional oxy-fuel combustion components are taken into account; ASU has been created for Solvo® as its own component and the CPU's electricity consumption has been approximated by a function while the modelled solution is still under development.

Boiler concept, different load level analysis and flue gas recirculation arrangements are based on the design of Foster Wheeler Finland Oy. The efficiency in heat and electricity production varies very much depending on the bio fuel share as can be seen in Table 1.

Table 1. Efficiency in heat and electricity production of the various cases.

	Reference Case A	Reference Case B	Case 1 oxyfuel	Case 1 oxyfuel	Case 3 oxyfuel
Fuel mix (% of fuel energy content)	Coal 100 %	Bio 45 % Coal 55 %	Coal 100%	Bio 45 % Coal 55 %	Bio 100 %
Efficiency in Heat production (%)	66 %	67 %	69 %	77 %	85 %
Efficiency in electricity production (%)	30 %	30 %	20 %	18 %	16 %

According to the investment studies the capture CAPEX of the CCS cases 1 to 3 is some 80% higher compared to reference cases without CCS (cases A and B).

The preliminary analysis show that in pure coal fired cases the price of EUA (Emission Unit Allowance) required for Case 1 to reach the non-CCS reference case is on the level of around 70 €/tCO_2. This is around double compared to the results of ZEP´s calculations for large hard coal fired condensing power plants.

A finance model was created to analyse the operation of the CCS CHP plant in a complex district heating systems with different fuel and related cost elements of the system based on energy balance and free cash flow analysis. A paper to present some of the study results including comparison of CCS and biomass co-firing was published (Arasto et. al, 2014, D211). A preparatory analysis to examine the effects of different bio fuel shares in combustion was prepared. Moreover the analysis to utilize certain 2nd generation CCS technologies in the same district heating systems replacing the oxy-fuel boiler was - here calcium looping (CaL) and chemical looping (CLC) technologies were studied.

Additionally VTT conducted a feasibility case study of biomass co-firing in a CHP plant. The studied fuel-shares with and without CCS consisted of pure biomass, pure peat and biomass-peat co-firing and these options were compared in the same operational environments. The case study is based on greenfield 482 MW_{fuel} CHP-plant equipped with a modern CFB-boiler which is using oxy-fuel technology in the CCS applications. The results showed that the costs for CCS are heavily dependent not only on the characteristics of the facility and the operational environment but also on the chosen system boundaries and assumptions. In the case of Bio-CCS the feasibility of CCS is dependent on the CO2 allowance price level shift into biomass prices. In combined heat and power plants, significant improvements can be achieved with heat integration, especially, in the production of district heat. Besides the publications (Kärki et. al, 2013 & Kärki et. al, 2012 & Tsupari et. al, 2011) a web based cost estimation tool (D215) has been produced from this case study. All cost estmation tools are available for use on the final report site: http://ccspfinalreport.fi

4.1.2 Post-combustion in multi-fuel boilers

Post combustion capture in multifuel fired CHP plants has been studied in two case studies. The 1st one is a greenfield, 736 MW_{fuel} CFB-boiler using coal and biomass. A Post Combustion-type amine based CCS process was selected as the carbon capture technology and specifically MEA solvent was selected as absorbent based on a survey prepared earlier in CCSP.

The aim of the 1st study was to determine the impact of a CCS process on the power plant’s characteristic figures, such as net electric power, district heat output and electric efficiency by using an integrated heat balance calculation model covering both the power plant and the CCS process. In addition, the study covers also following areas: specifying the requirements for flue gas cleaning, determining the effects of the wide range of fuel quality to the CCS plant, identifying the main interfaces required by the CCS plant.

The portion of the total flue gas stream to be treated in the CCS plant was defined to be 50 %, which is likely to be close to the optimum considering the prevailing boundary conditions. Since the power plant is designed as a multi-fuel power plant firing biomass for the most part (on the average about 70 - 80 % of the fuel input the balance being coal), treatment of the entire flue gas stream is not feasible.

Economic analyses of the plant concept with and without CCS were conducted by VTT. From the results in can be concluded that with the current price levels (and near future prospects) the operation of fuel flexible CFB plant without CCS was found to be the most feasible case among the compared ones. In comparison to break-even prices obtained for CCS/U in other applications in Finland, CHP environment seems to be favourable for CCS/U. Even if CHP applications have limitations in terms of the economy of scale compared to larger condensing power plants, utilisation of recovered heat from the flue gas condenser and CO2 compressors (and ASU in the case of oxyfuel) as valuable district heat enables important additional incomes, especially in the case of moist biomass.

The second case is a 315 MW_{fuel} CFB boiler using peat and biomass. The plant is retrofitted for PCC. At first background information collection and analyses to conduct techno-economic assessment for multi fuel-based CHP were carried out. The main inputs were based on Master's Thesis work conducted by Oulun Energia. The goal was to investigate the effects of different post combustion capture ratios in different plant operation (condensing-, mixed- and CHP-modes) and energy market situations on techno-economic feasibility. The main output was a Flash-based toolkit to visualize the costs and CO_2 impacts with different inputs by selecting key variables using interactive menus (CC-Skynet™ toolkit). From the results it was concluded that the required CO_2 allowance price would need to be in range of 60-100 €/tn to make the studied CCS solutions more economical than operation without CCS.

4.1.3 CCS in gas turbine power and CHP plants

Application of CCS technologies to gas turbine solutions is of special interest as fuel switch from coal to gas as well as unconventional gas and synthetic natural gas (upgrated from biogas or even produced from water and carbon dioxide via electrolysis and methanation) are potential solutions for future energy supply. Different technical CCS solutions that could be applied to gas turbine installations include oxy-, pre- and post-combustion technologies and chemical looping. The focus was on finding optimal technological solutions for combined cycle gas turbine (CCGT) plants including specifications for process modelling and case studies.

The effect of carbon dioxide capture and storage on the CCGT power plant with combined heat and power was evaluated by concept studies. Both thermodynamics and cost effects were investigated for a retrofit CCS unit, combined to an existing power plant (Laine 2011, Kärki et al. 2013), and for a greenfield power plant with CCS (Pirhonen 2011, D254). To determine the impacts of CCS, models of the power plant were created and operation of the power plants with and without CCS was simulated.

The removal and compression of carbon dioxide from flue gases (post-combustion capture) was the only considered option for retrofitting a carbon capture unit into an existing power plant (Laine 2011). Chemical absorption with aqueous monoethanolamine (MEA) was chosen as solvent for the capture plant. The carbon dioxide capture plant and compression unit were integrated into the power plant in order to minimise changes required to the existing power plant process. The overall efficiency decreased depending on the mode of operation 15–17 %-units (Table 2).

Pre-combustion capture technology was studied for the greenfield power plant (Pirhonen 2011). The chosen pre-combustion technology consisted of natural gas reforming, a water-gas shift (WGS) process and a CO_2 capture unit placed before the power plant in order to separate CO_2 from the gas before combustion. Chemical absorption with aqueous mixture of methyldiethanolamine (MDEA) and diethanolamine (DEA) was chosen as solvent for CO_2 removal (Pirhonen 2011). The process steam generation was highly integrated between the heat recovery steam generator (HRSG), reforming and WGS sections (Figure 5). The results showed that the efficiency of the power plant with CCS capture was 11 % units lower than the corresponding power plant without carbon capture (Table 2).

In order to improve the feasibility of the greenfield power plant concept, the following modification options were identified: excluding the pre-reformer, the use of oxygen instead of air in the autothermal reactor (ATR), excluding the low-temperature WGS reactor, and using physical absorption instead of chemical absorption (Figure 5). The most potential options identified were to exclude the pre-reformer and low-temperature WGS reactor (Figure 6), thus decreasing the total plant investment costs by 8% without having any significant effect on the efficiency of the plant. The pre-reformer was considered unnecessary, since the natural gas used in this case contains only minor amounts of heavier hydrocarbons. However, excluding the low-temperature WGS reactor reduced the total carbon capture efficiency from the base case of 90% to 79% (Suomalainen et al. 2013).

Table 2. A summary of the results from the studies of combined cycle gas turbine power plant with and without CCS (Laine 2011, Pirhonen 2011).

	Greenfield (pre-combustion)		**Retrofit [1] (post-combustion)**	
CCS	Without	With	Without	With
Thermal energy of natural gas (LHV, MWth)	841	1003	919	919
Net electrical **efficiency (%)**	48	42	46	40
Overall plant efficiency (%)	89	78	90	74

[1] Mixed mode of operation

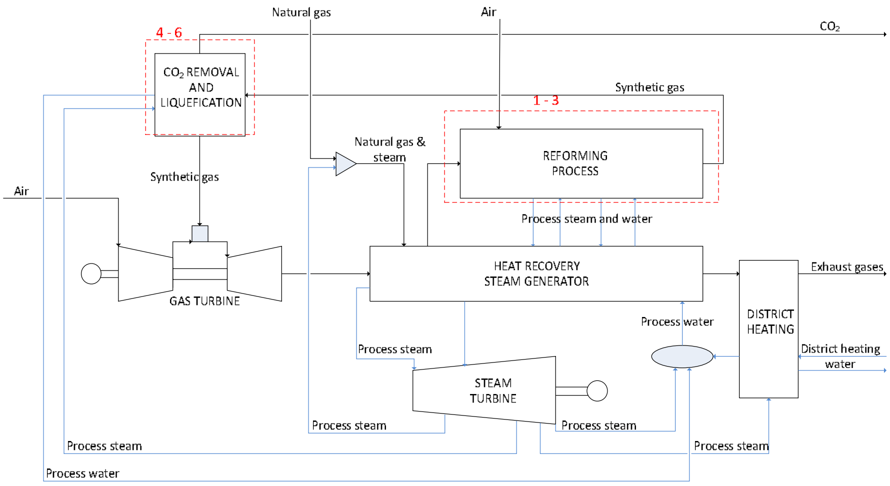


Figure 5. Simplified flow sheet of the natural gas-fired CHP plant using pre-combustion technology for CCS (potential modification options numbered and marked in red) (Suomalainen et al. 2013).

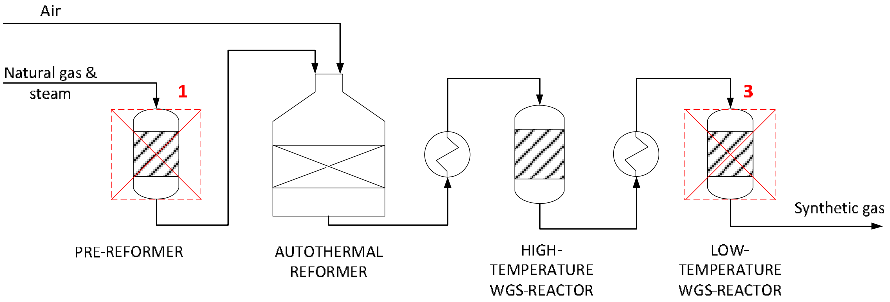


Figure 6. Selected modifications for the reforming process (Suomalainen et al. 2013).

Two GTCC power plant concept studies with flue gas recycling (FGR) were carried out assuming greenfield installations onshore in Finland. These were an air blown gas turbine combined cycle (GTCC) power plant with 50 % FGR and a conventional oxy-turbine combined cycle (SCOC-CC) power plant using nearly pure oxygen. The working fluid of the gas turbine was mainly nitrogen in the air blown GTCC concept whereas in the nearly pure oxygen concept the working fluid was CO_2. SCOC-CC resulted in CO_2 content of 85 mol% (wet) in the recycling flue gas, and due to the lower specific heat of CO_2 than nitrogen the pressure ratio over the gas turbine needed to be significantly higher in order to obtain the design turbine inlet temperature. Both cases were compared to a reference case without CO_2 capture and to a reference case with CO_2 capture using MEA absorption (Table 3). In the SCOC-CC case the air separation unit (ASU) led to lower overall electrical efficiency of the plant and higher production costs compared to the reference MEA absorption case. Instead the flue gas recycling improved electrical efficiency and economic feasibility compared to the reference MEA absorption case thus being an option to improve the electrical efficiency and economic feasibility in case of CCS, without needing significant modification to the GTCC power plant components.

Table 3. A summary of the combined cycle gas turbine power plant cases with flue gas recycling (D254).

	Reference	**Reference-post-combustion (MEA)**	**Post-combustion (MEA) with FGR**	**Conventional oxy-turbine combined cycle**
CO_2 capture (%)	0	90	90	98
Thermal energy of natural gas (LHV, MWth)	925	925	925	925
Net electrical **efficiency (%)**	48.0	44.2	46.0	40.7
Overall plant efficiency (%)	86.0	70.4	74.0	80.2

A Master's thesis (Rynö, 2012) studied how much the efficiency penalty can be reduced by utilizing waste heat from the process for production of district heating with conventional heat exchangers and heat pumps, district cooling with absorption chillers and electricity with Organic Rankine Cycle (ORC) process. By utilizing the waste heat only with a heat exchanger the power plant efficiency was around 75 %. By utilizing the waste heat more effectively with mentioned methods, the efficiency raised to 89 – 91 % depending on the method. ORC turned out to be uneconomical with CHP but profitability can be possible for heat pumps and absorption chillers.

As the profitability of CCS investment is extremely sensitive for example for CO_2 price, electricity price and utilisation rates (with and without CCS), additional economic analyses were carried out based on the results of Laine (2011), Pirhonen (2011) and Suomalainen et al. (2013). Economic analyses were conducted by VTT utilising the same uniform toolkit (CC-Skynet™) as for several other case studies conducted in CCSP. In these studies, the effects of CCS on the local CHP systems are included within the studied system boundaries in order to evaluate the economics and emissions from investor's (local energy company) point of view. The effect of CCS on greenhouse gas (GHG) emissions and operation economics are compared to the reference systems with varying parameters of operation.

4.1.4 Evaluation of flexible CCS-CHP concepts and systems

Increasing share of intermittent renewable wind and solar power are likely to cause more volatility in the electricity systems, setting greater requirements for balancing power in the future. Combined heat and power (CHP) plants with CCS have diverse operating options that allow the plants to adjust their power-to-heat ratios according to the markets. A simplified example of such an option would be to stop capturing CO_2 during peak electricity prices, making more steam available for electricity generation while reducing power demand in the CO_2 compression stage. This added flexibility of CO_2 capture in a CHP network would likely have a positive effect on the profitability of CCS.

In the framework of CCSP, the possible positive effects of enhanced CO_2 capture flexibility to a combined heat and power (CHP) system's net profitability was examined using optimization modelling, technology review and market scenario assessment. A system model was used to (i) compare economic performance of CO_2 capture against fuel switch options under high emission allowance prices and (ii) quantify added value of flexible CO_2 capture compared to conventional CO_2 capture in the case CHP system. The demand side of the case district heat (DH) network is a representation of the capital of Finland, Helsinki. The supply side of the studied CHP system consists of coal- (PC and IGCC) and gas-fired (NGCC) CHP plants, a multi-fuel CHP plant with a circulating fluidized bed (CFB) boiler and an oil-fired district heating plant. The cash flow of the system is maximized assuming the optimal use of flexible pre- post- and oxy-combustion as CO_2 capture concepts. Fuel-switch to bio-based renewable fuels is included as an alternative emission reduction technology. The market and fiscal environments reflect the current and anticipated situations in Finland. The flexible CO_2 capture concepts assumed for the CHP plants include: (i) solvent storage in post-combustion capture (in PC, CFB & NGCC plants); (ii) hydrogen-rich gas storage in pre-combustion capture (in IGCC plants); and (iii) liquid oxygen storage in pre-combustion capture (in IGCC plants) and in oxy-combustion (in PC and CFB plants).

The flexible operating modes and parameters such as start-up times and ramp rates of plants with CO_2 capture are based on literature review. Available literature on the flexibility of CO_2 capture in a CHP environment is very limited. Naturally, more research results, such as by van der Wijk *et al*. (2014), are available for flexibility of CCS in power production. Compared to condensing power production, CHP production is constrained by a heat demand of the district heating network which has to be fulfilled each moment. From a CCS perspective, DH-systems are interesting as they would allow utilization of some of the energy lost in the capture processes as valuable heat. Therefore, it is interesting to assess the possible positive effects of flexible CO_2 capture to the CHP system's net profitability.

System emissions and cash flow was calculated for four different CHP systems, each having a different combination of three CHP plants and one district heat boiler. First, base case results (BASE 1-4, see Table 4) for each CHP system were modelled, assuming no emission reduction technologies. Second, the systems were remodeled assuming a fuel-switch to biomass-based fuels in all the plants in the system (BIO 1-4, see Table 4). Third, the model was run with flexible and non-flexible CO_2 capture technologies. As both the multi-fuel circulating fluidized bed and the pulverized coal CHP plants had the option to use either oxy-combustion or post-combustion CO_2 capture, each system needed to be modelled as two separate cases, opting between the two capture technologies. Altogether the main results consist of 24 model runs, hereon referred to as cases listed in Table 4.

Table 4. Descriptions of the base, fuels-switch and CO_2 capture cases.

Case	Plant and capture technology combination	Purpose
BASE 1	PC + CFB + NGCC + DHBO	Reference case for BIO 1, FLEX 1-2 and NOFLEX 1-2
BASE 2	PC + CFB + IGCC + DHBO	Reference case for BIO 2, FLEX 3-4 and NOFLEX 3-4
BASE 3	NGCC + IGCC + PC + DHBO	Reference case for BIO 3, FLEX 5-6 and NOFLEX 5-6
BASE 4	NGCC + IGCC + CFB + DHBO	Reference case for BIO 4, FLEX 7-8 and NOFLEX 7-8
BIO 1	PC + CFB + NGCC + DHBO	BASE 1 with fuel-switch
BIO 2	PC + CFB + IGCC + DHBO	BASE 2 with fuel-switch
BIO 3	NGCC + IGCC + PC + DHBO	BASE 3 with fuel-switch
BIO 4	NGCC + IGCC + CFB + DHBO	BASE 4 with fuel-switch
FLEX 1	PC-OXY + CFB-OXY + NGCC-POST + DHBO	BASE 1 with flexible[1] oxy-combustion capture opted
FLEX 2	PC-POST + CFB-POST + NGCC-POST + DHBO	BASE 1 with flexible post-combustion capture opted
FLEX 3	PC-OXY + CFB-OXY + IGCC-PRE + DHBO	BASE 2 with flexible oxy-combustion capture opted
FLEX 4	PC-POST + CFB-POST + IGCC-PRE + DHBO	BASE 2 with flexible post-combustion capture opted
FLEX 5	NGCC-POST + IGCC-IRE + PC-OXY + DHBO	BASE 3 with flexible oxy-combustion capture opted

FLEX 6	NGCC-POST + IGCC-PRE + PC-POST + DHBO	BASE 3 with flexible post-combustion capture opted
FLEX 7	NGCC-POST + IGCC-PRE + CFB-OXY + DHBO	BASE 4 with flexible oxy-combustion capture opted
FLEX 8	NGCC-POST + IGCC-PRE + CFB-POST + DHBO	BASE 4 with flexible post-combustion capture opted
NOFLEX 1	PC-OXY + CFB-OXY + NGCC-POST + DHBO	BASE 1 with inflexible[2] oxy-combustion capture opted
NOFLEX 2	PC-POST + CFB-POST + NGCC-POST + DHBO	BASE 1 with inflexible post-combustion capture opted
NOFLEX 3	PC-OXY + CFB-OXY + IGCC-PRE + DHBO	BASE 2 with inflexible oxy-combustion capture opted
NOFLEX 4	PC-POST + CFB-POST + IGCC-PRE + DHBO	BASE 2 with inflexible post-combustion capture opted
NOFLEX 5	NGCC-POST + IGCC-PRE + PC-OXY + DHBO	BASE 3 with inflexible oxy-combustion capture opted
NOFLEX 6	NGCC-POST + IGCC-PRE + PC-POST + DHBO	BASE 3 with inflexible post-combustion capture opted
NOFLEX 7	NGCC-POST + IGCC-PRE + CFB-OXY + DHBO	BASE 4 with inflexible oxy-combustion capture opted
NOFLEX 8	NGCC-POST + IGCC-PRE + CFB-POST + DHBO	BASE 4 with inflexible post-combustion capture opted

[1]) Flexible CO_2 capture: All flexible operating modes are available for the CHP plants through use of storages for syngas and nitrogen (pre-combustion), lean and rich solvent (post-combustion) and oxygen (oxy- and pre-combustion).

[2]) Inflexible CO_2 capture: Only operation under partial load and/or venting of CO_2 is possible.

Flexible CO_2 capture (as in cases FLEX 1-8) means that all operating modes are available for the CHP plants through use of storages for syngas and nitrogen (pre-combustion), lean and rich solvent (post-combustion) and oxygen (oxy- and pre-combustion). Cases with inflexible CO_2 capture (NOFLEX 1-8) are calculated allowing only operation under partial load and/or venting of CO_2 on top of normal operation or stand-by.

The default emission allowance price assumed in the model runs is 100 €/tonCO_2. Equal district heat boiler (DHBO) capacity was included in each case. No emission reduction technology is applied in the DHBO except in the fuel-switch cases (BIO 1-4) where fuel oil is fully replaced by pyrolysis oil.

The results are based on optimization algorithm maximizing the operational cash flow of the CHP system subject to constraints caused by the heat demand of the network. The system cash flow does not include capital costs due to plant investments or revenues from heat.

The summary of case results are presented in Figure 7 and Figure 8. Looking at system cash flow, both fuel-switch (BIO1-4) and CO_2 capture cases (FLEX 1-8 and NOFLEX 1-8) have considerably better performance compared to the reference cases (BASE 1-4). Furthermore, CO_2 capture in general performs better than fuel-switch. Similar conclusions can be drawn from the system emissions (Figure 8).

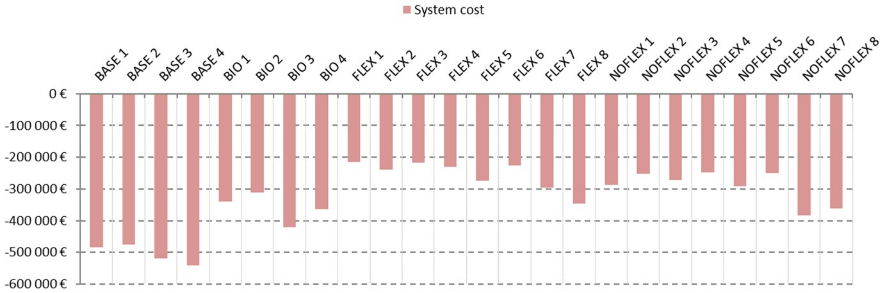


Figure 7. Summary of system costs in the modeled CHP cases.

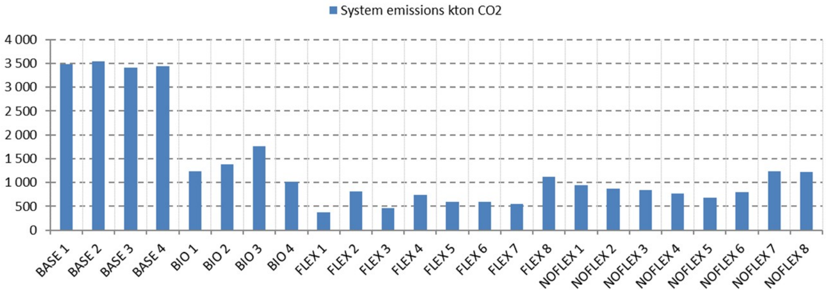


Figure 8. Summary of system emissions in the modeled CHP cases.

To assess the effect of different market assumption on the cost optimal operation of the CHP system, results were calculated using a lower emission allowance price (50€/tCO_2) and higher electric market price variation. The volatile electricity spot price scenario was created by increasing the price variation from the 24-hour average price by 50%. Using such definition for the volatile market scenario, the actual effect on cumulative value of electricity is neutral over the studied timeframe of one year.

Increasing the variation in the electricity spot prices had little to none effect on the cost-optimal operation of the CHP network, based on the system costs which remained nearly unchanged throughout the cases.

Halving the emission allowance price reduced the systems costs in every case, most of all in the reference cases BASE 1 - 4. Therefore, the difference in system costs between the reference cases and fuel-switch and CO_2 capture cases was reduced. With the emission allowance cost of 50€/tCO_2, the emission reduction technology cases still resulted in lower system costs than the reference cases, however.

The operation of a case CHP system was optimized applying alternative CHP plant configurations, fuel-switch options and both flexible and inflexible CO_2 capture. The work is set apart from the body of CCS flexibility system studies by Alie et al. (2016), van der Wijk et al. (2014), Saint-pierre & Mancarella (2014), Nimtz & Krautz (2013), Oates et al. (2014) and Davison (2011) by assuming a CHP environment consisting of several plants in a closed DH network system. Saint-pierre & Mancarella (2014) assessed the benefits from flexible CO_2 capture in a CHP system, but assuming only a single pulverized coal CHP plant in the system with a post-combustion CO_2 capture.

The aim of this study was to compare fuel-switch and alternative flexible CO_2 capture technologies in a large CHP system, modelled to resemble the production and consumption capacity of the DH network in the city of Helsinki. The scope of the system optimization covered only the operational profitability and emission reduction performance of the system, including CHP plants in the model which do not exist in the real-life counterpart DH system.

Based on the cost optimal results of the case CHP system, flexible CO_2 capture increases the net cash flow of the case CHP networks while further reducing CO_2 emissions compared to conventional CO_2 capture. Flexibility of CO_2 capture increased the operational cash flow (without capital costs or revenues from heat production) by up to 25%. The cost and emission reducing effect of flexible CO_2 capture is partly explained by a lower demand of DHBO operation. The heat boiler was assumed to be oil-fired and without CO_2 capture in all cases except the fuel-switch cases. The effect was most dramatic on the flexible oxy-combustion CHP plants.

A common rationale behind the recent CCS flexibility studies, such as by Nimtz & Krautz (2013) and Mac Dowell & Staffell (2016), is to assess the ability of power plants with CO_2 capture to balance out the electricity grid by responding to the changes in the intermittent solar and wind power production. Considering the economy of a CCS investment, flexible CO_2 capture could have a potential in mitigating the impact of overall electric efficiency penalty, since the plants would have more options to react to the electricity markets. In the case CHP environment however, revenues from electricity did not differ between flexible and inflexible cases as strongly as the DH output from the CHP plants. Therefore, the model results indicate that CO_2 capture flexibility increases the operational profitability of the case CHP system more due to ability to provide for changing DH demand than opportunities in the electricity markets.

The results allowed a comparison of CCS against the option to switch to renewable fuels in all the plants connected to the DH network. Using emission allowance prices of 50 - 100 €/tCO_2, CO_2 capture was more efficient in increasing the operational cash flow and in reducing the CO_2 emissions of the case CHP system than fuel-switching. The difference was narrowed along with falling emission allowance prices.

4.1.5 CLC –based concept studies

Techno-economic studies about performance of industrial scale (about 500 MW_{fuel}) CLC power plant and CHP plant have been conducted. The studied fuels are coal and biomass, and co-firing of these fuels with different mixes. Primary focus was on economic evaluations of the CLC plant operation with different input parameters (e.g. efficiencies) and market prices (e.g. electricity and CO_2 allowances) and on comparison to both oxy-fired CFB plant and normal air-fired CFB plant. As a summary, significant economic benefit could be achieved by CLC in comparison to oxyfuel in the case of condensing production (Tsupari et al. 2015; Tsupari et. al, 2014). In CHP systems, the benefit of CLC can be somewhat diminished in comparison to condensing case, if most of the excess heat from oxyfuel process can be utilised as district heat (depending on local system, properties and prices). However, overall economics of CHP is better than in condensing case. In addition, a paper to present feasibility of solid fuel CLC plant investment in the future energy systems including high share of solar and wind has been published (Tsupari et. al, 2014). In that paper, the benefit of lower variable costs of electricity production by CLC was presented. That benefit is emphasized in future energy systems including high shares of solar and wind, because utilisation rate of 1st generation CCS plants would probably be low in such systems. The highest utilisation rates can be achieved by bio-CCS as “negative emissions” could create an additional income for the plants enabling feasible operation also during low electricity prices (Tsupari et al. 2015).

A simulation model to calculate mass and energy balances of a chemical looping oxygen uncoupling (CLOU) based power plant concept was created using Aspen Plus process simulation software.

The concept was modelled as a condensing plant which produced district heating only from CO_2 liquefaction unit. A simplified schematic figure of CLC based CHP plant is presented in Figure 9. The heat recovery steam generation was integrated in between the air reactor and fuel reactor. Superheating and reheating was located in heat exchanger of fluidised bed from fuel reactor. Oxygen carrier in the process was copper oxide (CuO/Cu_2O). Part of flue gas was recycled to fuel reactor to be used as fluidising agent. Captured carbon dioxide was compressed and liquefied to 6.5 bar and -52 °C which conditions fulfil the requirements for ship transportation. Recovered heat from CO_2 liquefaction unit was used for district heating.

Carbon capture efficiency was assumed to be 97 % based on the carbon conversion in the fuel reactor reported by Abad et al (2012). Remaining carbon was assumed to exit as CO_2 from air reactor or as char in ash. Auxiliary power load in the present plant model includes main compressors and pumps but excludes fuel preparation and feeding, ash handling, cooling water pumps, fans of the condenser and miscellaneous utilisation. Based on analysis on mass and energy balances the net electrical power production could be 181 MWe corresponding to net electrical efficiency of 37.5 %. District heat production from carbon dioxide liquefaction unit was 7.4 MW.

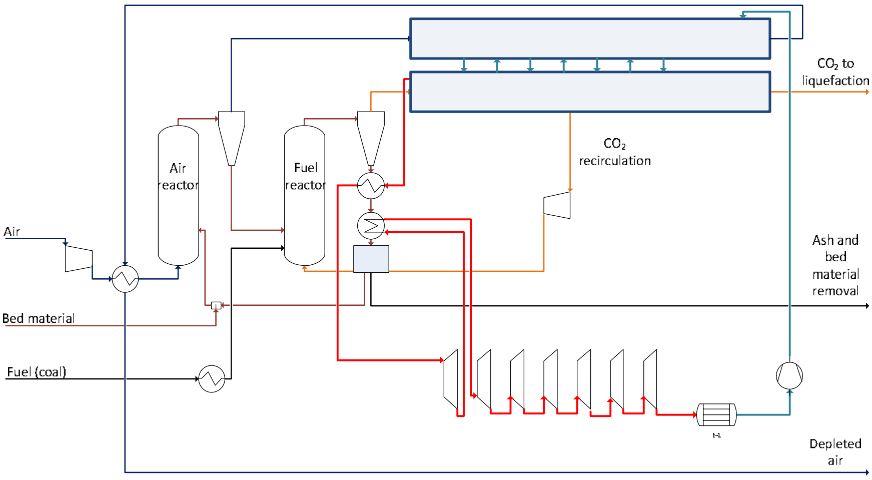


Figure 9. A simplified schematic figure of chemical looping oxygen uncoupling (CLOU) based condensing power plant fuelled by coal.

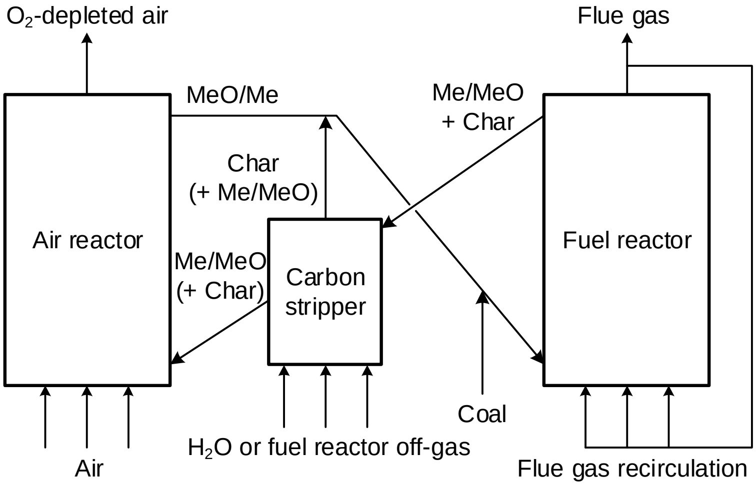


Figure 10. Schematic figure of chemical looping with oxygen uncoupling (CLOU) process (Peltola et al, 2015a).

A comparative performance assessment of three conceptual steam turbine-based CHP installations generating process steam, district heat, and electricity with inherent CO_2 capture was conducted (D360). The processes considered for comparison were (i) CHP with oxy-combustion-based carbon capture, (ii) CHP with CaL-based carbon capture, and (iii) CHP with CLOU-based carbon capture. The main characteristics of the CCS-equipped plants were compared with those of a reference plant without CO_2 capture. In order to assess the mass and energy integration aspects and to quantify the key performance indicators, each process was first simulated using a specific boiler/reactor system model, after which the results from the boiler/reactor system models were employed as inputs for overall plant flowsheet models developed in SOLVO®. The results from SOLVO® simulations are given in Table X. Since ASU is not needed in the CLOU case, the net electricity production of the CLOU plant is 100.7 MW, which is 33.2% higher than that of the oxy-combustion plant and 29.6% higher than that of the CaL plant. In the oxy-combustion plant, the high moisture content of the flue gases due to flue gas recirculation leads to a 10.5% increase of district heat generation compared to the CaL case and a 2.5% increase compared to the CLOU case. Overall, CLOU gives the highest net efficiency (102%) considering the CCS cases. It should be noted that as the plant efficiencies are calculated on LHV basis, efficiencies higher than 100% are possible due to flue gas condensation.

. SOLVO® flowsheet simulation results.

	Air	**Oxy-fuel**	**CaL**	**CLOU**	Unit
Coal input	215,0	215,0	215,0	215,0	MW
Biofuel input	215,0	215,0	215,0	215,0	MW
Fuel total	430,0	430,0	430,0	430,0	MW
Gross electricity	139,7	133,9	124,8	137,0	MW
Net electricity	125,8	75,6	77,7	100,7	MW

District heat	242,9	293,7	265,9	286,4	MW
Process steam 20 bar	35,0	35,0	35,0	35,0	MW
Process steam 5 bar	15,0	15,0	15,0	15,0	MW
ASU	0,0	21,4	12,0	0,0	MW
CPU	0,0	23,5	22,7	22,6	MW
CO_2 to CPU	0,00	43,92	42,30	42,15	kg/s
Total CO_2	43,92	43,92	46,36	44,92	kg/s
Carbon capture rate	0	100	91	96	%
CO_2 content to CPU	0,00	87,31	92,86	93,40	w -%
Power plant net efficiency	97	98	92	102	%

4.2 CCS in oil refining

One of the tasks of CCSP is to find CCS solutions suitable for oil refineries. In order to identify different CCS solutions for oil refineries, the CO_2 containing gas streams were first identified and their potential for CO_2 capture evaluated (Lampinen 2012, D209). The off-gas streams of hydrogen production was found to be the most potential streams, while certain combustion flue gas streams were also found to have some potential. The gas streams in hydrogen production are an attractive target for CO_2 capture due to their high CO_2 concentration and the low number and level of impurities. Hydrogen production via steam reforming or with a gasifier can account for 20% of the CO_2 emissions from a refinery. In a medium size oil refinery, with annual CO_2 emission about 3 Mt, this amounts to about 0.6 Mt of CO_2 per year.

Different carbon capture technologies suitable for steam methane reforming (SMR) plants producing hydrogen were compared (Andtsjö 2013, D216). Technology alternatives were screened for two gas streams: the off-gas from hydrogen purification, and the flue gas from the SMR unit's furnace. After the evaluation of the technology alternatives, the applicability of a cryogenic capture process to both streams was selected for an engineering analysis. Also, the technical applicability, investment cost and operating costs were estimated. It was concluded, that the most attractive stream in SMR hydrogen production to be used for carbon capture is the off-gas from hydrogen purification. Between the two analysed gas flows, the hydrogen purification off-gas was economically clearly more competitive than the flue gas. For CO_2 capture from the flue gas, the cryogenic process was found to be less feasible than amine absorption. Regarding the SMR hydrogen purification off-gas, the combined cryogenic and methanol absorption process was found to be economically more advantageous compared to the analysed cryogenic process. The estimated production cost for captured CO_2 was in all cases clearly higher than the present emission allowance cost of CO_2 (Andtsjö 2013, D216).

4.3 Carbon capture technologies for on-site production of pure CO_2 for in-line PCC process

A study was made on the implementation of a carbon capture process at an integrated pulp and paper mill. The purpose of the capture application is to take advantage of local plant emissions by enriching the flue gas CO_2 concentration for use as raw material for the production of precipitated calcium carbonate. An onsite CO_2 capture process implemented either in connection with the recovery boiler or the lime kiln will take advantage of emissions from the existing process gases and thus eliminate the need for purchasing PCC (precipitated calcium carbonate) for the paper production process. Furthermore, this integrated process of utilizing CO_2 as raw material for paper filler production would decrease the overall CO_2 emissions from the plant. The purpose of this study was to evaluate the technical possibility of implementing a carbon capture process in an integrated pulp and paper mill and to coarsely evaluate the related cost of such an investment.

When considering the investment decision for a CO_2 capture plant at a pulp and paper mill, it is recommended to optimize the plant and evaluate whether there is excess steam available (low or reasonable cost) that can be applied in an MEA capture unit. In that case there is no reason to increase the investment in order to implement a high-efficiency capture plant. The challenge is the different flue gas composition, gas pressure and the presence of new impurities that degrade the amines and generate amine degradation products that can be harmful. Also the process scale can be challenging. The results of the evaluations show that the payback time is increasingly affected by the cost of the steam by time.

Calculation of the payback time includes both capital and operational expenses. The cost of CO_2 produced will increase with increasing investment cost. No CO_2 emission allowance were included, so in the case CO_2 capture for PCC production is allowed in future emission allowance schemes the cost of CO2 produced will decrease accordingly. Likewise, changes in the steam cost or in a possible CO_2 emission allowance will be seen as a direct consequence in the CO_2 production cost.

4.4 Bio-CCS as a carbon-negative solution

The need for carbon-negative solutions as safeguards against irreversible climate change is increasingly being recognized on an international level. Biomass with Carbon Capture and Storage (Bio-CCS) has the potential as a carbon negative solution against climate change (Figure 11); contributions that are increasingly likely to become indispensable. Lately, Bio-CCS has started to receive a lot interest, especially in Europe where the expansion of renewable energy is high on the agenda with the 20-20-20 and 2030 targets. The importance of carbon negative solutions seems to be highlighted more and more by global climate stakeholders, such as IPCC and IEA. VTT has taken a globally acknowledged position as a leading actor and an expert in the field of Bio-CCS as a large scale carbon negative solution.

Finland and Sweden have large biogenic CO_2 emissions, mostly from pulp and paper industry and from power plants co-combustion biomass (Figure 4). Photosynthesis binds carbon from the atmosphere and the carbon is again released during biomass combustion, making the process carbon neutral. Capturing and permanently storing biogenic CO_2 emissions from these processes would thus lead to net negative emissions and therefore create a carbon sink.

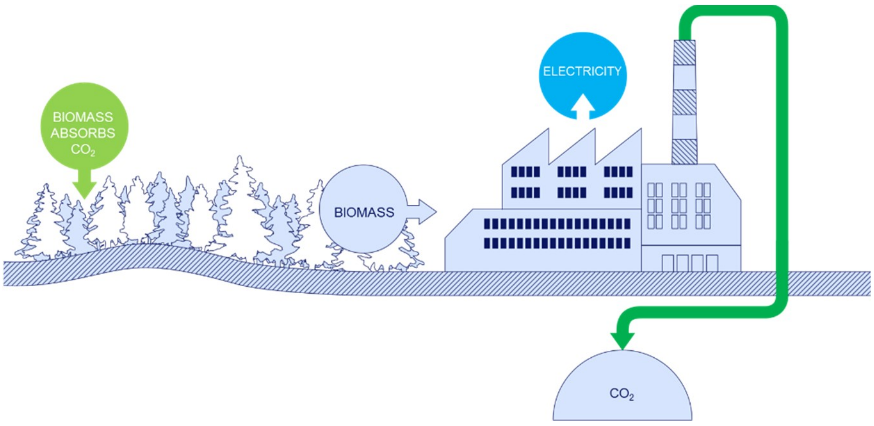


Figure 11. Principal of Bio-CCS and its impact in example from power sector.

A report on Bio-CCS was published by the European Biofuels Technology Platform and Zero Emissions Platform with a significant contribution from VTT through CCSP (EBTP & ZEP 2012). The report concludes that Bio-CCS and negative emissions can make a significant contribution to climate change mitigation and that Bio-CCS is currently the only large-scale technology that can remove CO_2 from the atmosphere. Liquid biofuels production may be an appealing target for deployment with near-pure CO_2 streams but as with all bio-based production, the utilization of a constrained resource must be taken into account; is CCS adding significant value (economic, GHG reduction, public perception) to certain biomass utilization technologies and therefore should the biomass utilization be directed accordingly? Generally the same technologies considered for capturing of fossil CO_2 could be applied for biomass based processes as well. The main differences and restrictions are mainly related to shares of biomass in co-firing, regional availability, typical sizes of installations and availability of sustainable raw material. Current policies for lowering greenhouse gas emissions do not recognise negative emissions from power plants, and thus no fiscal incentive exists for capturing CO_2 from biomass installations. To make Bio-CCS deployment happen in Europe, biogenic CO_2 emissions must be acknowledged, and carbon-negative solutions must be incentivized in the EU ETS.

A Bio-CCS roadmap for Finland has currently been updated in CCSP. The objective of the roadmap work is to understand the complexity of the issue and to get a realistic estimate how big contribution these Bio-CCS technologies actually could provide. The underlying question for a country with biomass resources available is: what is the best way of utilizing the constrained biomass resources. Constructing this Bio-CCS roadmap for Finland is based on existing infrastructure, sustainable resource potential, prices and national targets. Sectors considered are power production (condensing and CHP), pulp and paper, iron and steel, liquid biofuels production and oil refining with technologies related. The first estimation of the techno-political potential of Bio-CCS has been reflected to global perspectives and disseminated on several international forums to estimate the realistic development potential of this solution. The most significant questions in respect to these carbon negative solutions is the availability and sustainability of available raw materials. The alternatives of 2nd generation feedstock, such as algae, are next in global agenda, with emphasis on global perspective in addition to the Nordic approach to biomass and wood use.

A toolkit for economic evaluations of CHP plant operation has been prepared on issues related to Bio-CCS. The toolkit provides scenarios for dedicated biomass, multifuel (50/50 bio-peat) and dedicated peat fired plants with selectable user input parameters. Comparison of oxy-fired CFB plant and normal air-fired CFB plant is in the focus to provide information on CCS feasibility. The toolkit available here: http://virtual.vtt.fi/virtual/combust. More info about the conducted case studies can be found in Tsupari et al. (2011).

The first estimation of the technical potential of BioCCS in Finland has been evaluated based in existing installations and policy goals (Figure 12). The impact of different Bio CO_2 accounting options to feasibility of plant investments was also conducted during the period in order to stress the importance of acknowledgment of capturing of biogenic carbon also within different policy instruments such as EU-ETS. The current roadmap approach based on biomass utilisation typical to northern coniferous belts is tried to be expanded towards more global view with extensive communication and seeking of global partners in the topic. As Bio-CCS seems to be more a policy incentive, cost and sustainability issue than a technical issue this is also stressed in the work, e.g. with proposed new task to IEA bioenergy agreement being one of concrete the actions. During the programme CCSP and VTT have been acknowledged as global leading partners in relation to Bio-CCS in power sector and industrial applications with several presentations and dissemination requests globally.

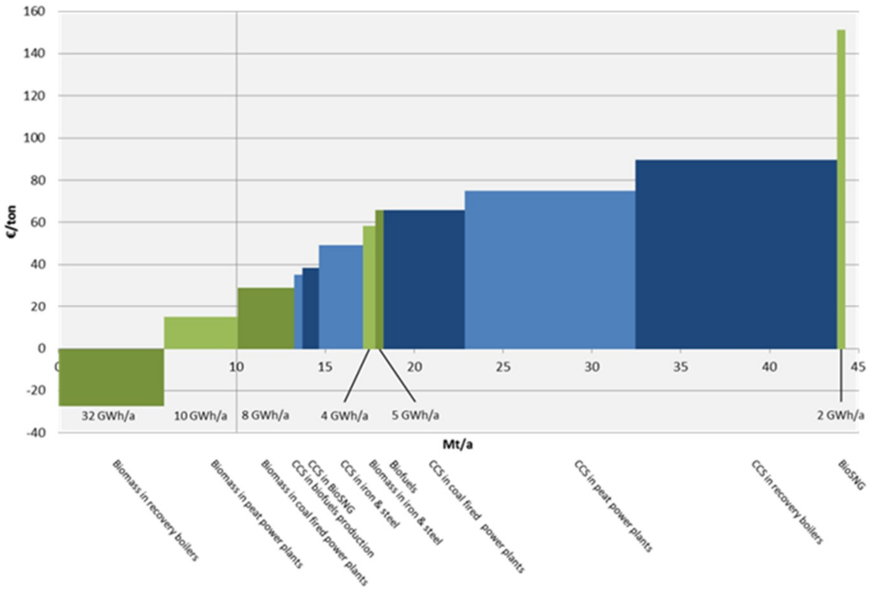


Figure 12. The technical potential of Bio-CCS in Finland.

4.4.1 Evaluation of bio-CCS potential for pulp & paper industry

The pulp and paper industry is a major energy-intensive industry that has the potential to demonstrate deployment of both industrial CCS and bio-CCS. The majority of the CO_2 emissions from a pulp and paper mill are of biogenic origin (75 – 100%). With sustainable management of the raw materials these CO_2 emissions could be considered CO_2 neutral, and adding CCS technology can realize CO_2 negative emissions.

A techno-economic feasibility study has been undertaken in cooperation with the IEA Greenhouse Gas R&D Programme on estimating the technical feasibility and cost of retrofitting CO_2 capture to the pulp and paper industry. Two reference cases were developed:

- CO_2 capture in a Kraft pulp mill (Base case 1A) producing 800 000 air dried tonnes (adt) of softwood Kraft pulp annually
- CO_2 capture in an integrated pulp and board mill (Base case 1B) producing 740 000 air dried tonnes (adt) softwood Kraft pulp and 400 000 3-ply folding boxboard annually.

Both reference mills are energy independent and export excess electricity to the grid.

Performance balances (mass, steam, electricity, heat, fuel) for the reference cases were evaluated using WinGems process simulation tool. The amine-based post-combustion CO_2 capture plant and CO_2 compression train were evaluated using Aspen Rate-Based Distillation process modelling software. A capture rate of 90% was evaluated. The models were validated against industrial data and the CO2 capture model was reviewed by a technology vendor. The following CO_2 capture cases were evaluated for both reference mills, totalling 12 different CCS cases:

- CO_2 capture from recovery boiler (REC)
- CO_2 capture from multi-fuel boiler (MFB)
- CO_2 capture from lime kiln (LK)
- CO_2 capture from recovery boiler and multi-fuel boiler (REC + MFB)
- CO_2 capture from recovery boiler and lime kiln (REC + LK)
- CO_2 capture from recovery boiler, multi-fuel boiler and lime kiln (REC + MFB + LK)

The total CO_2 emissions from the reference cases and the different CCS cases are presented in Table 5.

Table 5. Allocation of fossil and biogenic emissions in the different CCS cases.

Capture case description	**Total emissions (whole site)**	**Biogenic based CO_2 emissions**	**Fossil based CO_2 emissions**	**Total CO_2 captured**	**Overall CO_2 capture rate**
	[MTPY]	**[MTPY]**	**[MTPY]**	**[MTPY]**	**[%]**
Kraft pulp mill with CCS					
Recovery boiler	683 636	597 054	86 582	1 477 526	68.4
Multi-fuel boiler	1 891 678	1 805 097	86 582	270 696	12.5
Lime kiln	1 974 532	1 974 532	-	101 209	4.9
Recovery boiler and multi-fuel boiler	412 736	326 155	86 582	1 749 596	80.9
Recovery boiler and lime kiln	495 628	495 628	-	1 580 126	76.1
Recovery boiler, multi-fuel boiler and lime kiln	224 728	224 728	-	1 851 025	89.2
Integrated pulp and board mill with CCS					
Recovery boiler[2]	833 005	746 423	86 582	1 477 526	63.9
Multi-fuel boiler	1 891 678	1 805 097	86 582	270 696	12.5
Lime kiln	1 974 532	1 974 532	-	101 209	4.9
Recovery boiler and multi-fuel boiler[2]	644 832	558 251	86 582	1 749 596	73.1
Recovery boiler and lime kiln[2]	715 085	715 085	-	1 580 126	68.8
Recovery boiler, multi-fuel boiler and lime kiln[2]	574 021	574 021	-	1 851 025	76.3

Steam from the pulp mill steam turbine island is required for the CO_2 capture plant stripper reboiler and reclaimer.

Major changes to the pulp mill when retrofitting a CO_2 capture plant are the modifications to the existing steam turbine island. A conventional back pressure/extraction (HP) steam turbine and condensing (LP) steam turbine in dual casing was considered. The steam turbine island produces steam at 30.0 bar, 13.0 bar and 4,2 bar (a). Steam is required in the CO_2 capture plant for the amine solvent regeneration (ultra-low pressure (ULP) steam at 2.0 bar(a)) and in the amine reclaimer (4.2 bar(a)). ULP steam is produced by extracting 4.2 bar(a) steam and de-superheating this to ULP steam at 2.0 bar(a).

Modifications to the steam turbine were made based on the idea of minimizing the impact on the HP turbine section, and thus maximizing gross electricity output. The reduced steam flow through the LP section is controlled by a clutch to reduce the impact on the generator. Figure 13 illustrates a simplified schematic block diagram of the steam turbine island where steam to the CO_2 capture plant is extracted at 4.2 bar and de-superheated.

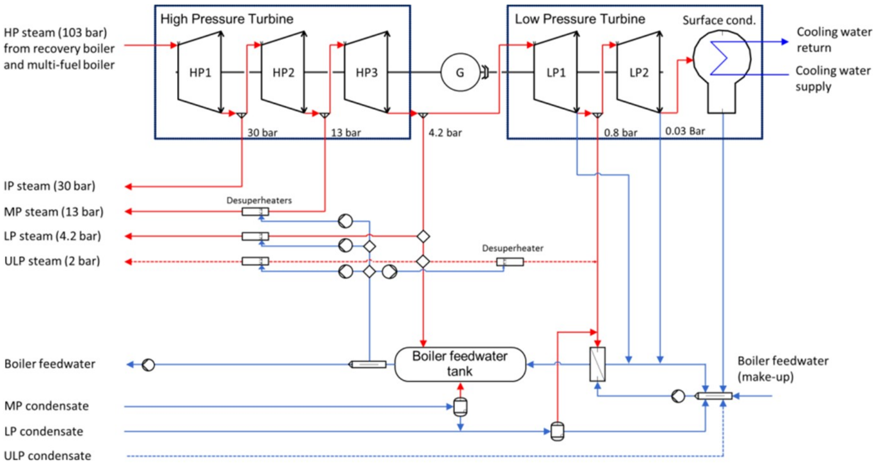


Figure 13. Steam turbine island with steam extraction options. 4.2 bar(a) steam is extracted from the HP section of the turbine and de-superheated to 2.0 bar(a) ULP steam for the CO_2 capture plant regenerator. Condensate from the CO_2 regenerator is returned to the boiler feed water line.

4.2 bar(a) steam was not always sufficient for the heat requirement in the CO_2 capture plant. Three alternative steam turbine configurations for supplying steam and electricity to the CCS plant were evaluated:

1. Extracting 4.2 bar steam from high-pressure side of turbine and reducing it to 2.0 bar de-superheated steam. CO_2 compressors are electrically driven.

2. Extracting 13.0 bar, reducing it to 2.0 bar de-superheated steam. CO_2 compressors are electrically driven.

3. Extracting part of the steam from 13 bar and using steam-driven CO_2 compressors that will provide 2 bar steam for utilization. Remaining need for steam is extracted at 4.2 bar in the steam turbine and reduced to 2 bar de-superheated steam.

The effects of the CO_2 capture plant integration on the pulp mill steam turbine island is presented in Table 6.

Table 6. Steam and electricity balance of Kraft pulp mill and integrated pulp and board mill with CO_2 capture (REC = recovery boiler, MFB = multi-fuel boiler, LK = lime kiln, MP = medium pressure steam used to fulfil steam requirement in CO_2 capture plant).

	Base case	**Pulp mill with CCS**						**Base case**	**Integrated pulp and board mill with CCS**					
	1A	**2A-1**	**2A-2**	**2-A3**	**2A-4**	**2A-5**	**2A-6 MP**	**1B**	**2B-1 CO2MP**	**2B-2**	**2-B3**	**2B-4 CO2MP**	**2B-5 CO2MP**	**2B-6 CO2MP**
Steam demand														
Pulp mill														
Steam 30 bar [t/h]	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4
Steam 13 bar [t/h]	171.0	171.0	171.0	171.0	171.0	171.0	171.0	167.3	167.3	167.3	167.3	167.3	167.3	167.3
Steam 4.2 bar [t/h]	255.2	255.2	255.2	255.2	255.2	255.2	255.2	351.8	351.8	351.8	351.8	351.8	351.8	351.8
CO_2 capture plant														
Steam 13 bar [t/h]	-	-	-	-	-	-	-	-	189.5[b]	-	-	223.9[b]	213.2[b]	247.6[b]
Steam 4.2 bar [t/h]	-	0.9	0.2	0.1	1.1	1.1	1.3	-	0.9	0.2	0.1	1.1	1.1	1.3
Steam 2.0 bar [t/h]	-	255.8	45.2	31.0	289.3	284.2	335.3[a]	-	255.8	45.2	31.0	289.3	284.2	335.3
Auxiliary boiler														
Steam 30 bar [t/h]	-	-	-	-	-	-	-	-	1.5	-	-	2.3	2.2	3.4
Steam 4.2 bar [t/h]	-	-	-	-	-	-	-	-	2.7	-	-	4.3	4.1	6.5
Steam supply														
Ex: Steam turbine														
Steam 30 bar [t/h]	20.4	20.4	20.4	20.4	20.4	20.4	20.4	20.4	21.7	20.4	20.4	22.5	22.4	23.5
Steam 13 bar [t/h]	171.0	171.0	171.0	171.0	171.0	171.0	171.0	167.3	286.4	167.3	167.3	284.9	279.6	256.5
Steam 4.2 bar [t/h]	255.2	256.2	255.4	255.3	256.3	256.3	256.5	351.8	355.4	351.9	351.9	357.1	356.8	359.4
Steam 2 bar [t/h]	-	255.8	45.2	31.0	289.3	284.2	335.3	-	66.3	45.2	31.0	65.3	71.0	87.8
Ex: Auxiliary boiler														
Steam 13 bar [t/h]	-	-	-	-	-	-	-	-	64.9	-	-	100.9	95.4	151.9
Ex: Back-pressure steam turbine														
Steam 2 bar [t/h]	-	-	-	-	-	-	-	-	189.5			224.0	213.2	247.6
Electricity demand														
Pulp mill [MWe]	61.0	61.0	61.0	61.0	61.0	61.0	61.0	94.3	94.3	94.3	94.3	94.3	94.3	94.3
CO_2 capture plant [MWe]	-	23.5	4.4	2.8	28.5	26.9	31.4	-	7.8	4.4	2.8	9.9	9.2	10.9
Auxiliary boiler [MWe]	-	-	-	-	-	-	-	-	1.6	-	-	2.4	2.3	3.7
Total [MWe]	**61.0**	**84.5**	**65.4**	**63.8**	**89.5**	**87.9**	**92.4**	**94.3**	**103.6**	**98.7**	**97.1**	**106.6**	**105.8**	**108.9**
Electricity supply														
Ex: Steam turbine														
HP section [MWe]	130.4	130.4	130.4	130.4	130.4	130.4	113.7	130.6	124.2	130.6	130.6	124.5	124.5	127.3
LP section [MWe]	37.9	7.7	33.0	34.7	-	4.3	-	27.1	-	21.8	23.5	-	-	-
Total [MW_e]	**168.3**	**138.1**	**163.4**	**165.1**	**130.4**	**134.7**	**113.7**	**157.7**	124.2	**152.4**	**154.1**	124.5	124.5	127.3
Electricity export to the grid [MW_e]	**107.3**	**53.6**	**98.0**	**101.3**	**40.9**	**46.8**	**21.3**	**63.4**	**20.6**	**53.7**	**57.0**	**17.9**	**18.7**	**18.4**
Electricity export to the grid [MWh/adt]	**1.13**	**0.56**	**1.03**	**1.06**	**0.43**	**0.49**	**0.22**	**0.67**	**0.24**	**0.56**	**0.60**	**0.21**	**0.22**	**0.22**

[a] For case 2A-6 MP steam at 13.0 bar(a) is de-superheated to ULP steam at 2.0 bar(a) and the mass flow is incorporated in the ULP steam demand to the CCS plant.

[b] For the CO2MP cases MP steam at 13 bar(a) from the auxiliary boiler is fed directly to the CO_2 compression train (compliment with the MP steam from the steam turbine island).

The study shows that it is technically feasible to implement a CO_2 capture plant in an existing pulp and paper mill. In a Kraft pulp mill the excess steam onsite is sufficient to cover the steam requirement for more than 90% capture of total site CO_2 emissions. For an integrated pulp and board mill, which has a higher steam consumption in the existing processes, it may be necessary to invest in an auxiliary boiler or import electricity from the grid to cover the additional steam demand represented by the CO_2 capture plant. It is recommended that specific site studies evaluate the mill performance with partial CO_2 capture to find the best possible solution for the specific site.

A discounted cash flow was evaluated for the levelized cost of pulp (LCOP) both for the reference cases and for the CCS cases. The levelized cost of pulp for the Kraft pulp mill reference cases was 523 €/adt. In the case of the integrated pulp and board mill the levelized price of board was fixed in order to make the LCOP comparable in the two cases.

The levelized cost of pulp and the cost of avoided CO_2 were evaluated for six different policy frameworks:

- Scenario 1: No CO_2 emission tax applicable and no incentives for biogenic CO_2 emissions
- Scenario 2: CO_2 emission tax at 10 €/t, but biogenic CO_2 emitted is not recognized as CO_2 neutral (biogenic CO_2 is not exempt from tax)
- Scenario 3: CO_2 emission tax at 10 €/t, and biogenic CO_2 emitted is recognized as CO_2 neutral (biogenic CO_2 is exempt from tax)
- Scenario 4: CO_2 emission tax at 10 €/t, biogenic CO_2 emitted is recognized as CO_2 neutral (biogenic CO_2 is exempt from tax) and renewable electricity incentive at 10% of the electricity selling price (40 €/MWh)
- Scenario 5: Same conditions as in Scenario 3 with an additional negative CO_2 emission credit at 10 €/t.
- Scenario 6: Same conditions as in Scenario 4 with an additional negative CO_2 emission credit at 10 €/t.

The levelized cost of pulp for the different policy framework scenarios is presented in Table 7 and the cost of CO_2 avoided is presented in Table 8.

Table 7. Levelized cost of pulp for retrofit CCS in the pulp and paper industry

	Reference mill	**Recovery boiler**	**Multi-fuel boiler**	**Lime kiln**	**Recovery and multi-fuel boiler**	**Recovery boiler and lime kiln**	**Recovery boiler, multi-fuel boiler and lime kiln**
			Kraft pulp mill				
Scenario 1 No CO_2 emissions tax, no incentives for biogenic CO_2 em.	523	643	553	543	659	652	676

Scenario 2 CO_2 emissions tax 10 €/t, biogenic CO_2 not neutral	550	651	577	568	664	658	679
Scenario 3 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral	524	644	555	543	660	652	676
Scenario 4 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral, renewable electricity incentive	519	642	550	539	658	650	675
Scenario 5 Same conditions as in Scen. #3, negative CO_2 credit 10 €/t	524	625	551	542	638	632	653
Scenario 6 Same conditions as in Scen. # 4, negative CO_2 credit of 10 €/t	519	623	547	537	637	630	652
Integrated pulp and board mill							
Scenario 1 No CO_2 emissions tax, no incentives for biogenic CO_2 em.	523	671	556	545	695	687	714
Scenario 2 CO_2 emissions tax 10 €/t, biogenic CO_2 not neutral	550	680	580	570	702	694	719
Scenario 3 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral	524	672	557	545	696	687	713
Scenario 4 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral, renewable electricity incentive	519	669	553	541	694	684	711
Scenario 5 Same conditions as in Scen. #3, negative CO_2 credit 10 €/t	524	652	554	543	672	665	688
Scenario 6 Same conditions as in Scen. # 4, negative CO_2 credit of 10 €/t	519	649	550	539	670	663	686

Table 8. Cost of avoided CO_2 for retrofit CCS in the pulp and paper industry.

	Recovery boiler	Multi-fuel Boiler	Lime kiln	Recovery and multi-fuel boiler	Recovery boiler and lime kiln	Recovery boiler, multi-fuel boiler and lime kiln
Kraft pulp mill						
Scenario 1 No CO_2 emissions tax, no incentives for biogenic CO_2 em.	65	91	87	62	62	64
Scenario 2 CO_2 emissions tax 10 €/t, biogenic CO_2 not neutral	55	81	77	52	52	54
Scenario 3 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral	65	91	82	62	62	63
Scenario 4 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral, renewable electricity incentive	66	92	83	64	63	65
Scenario 5 Same conditions as in Scen. #3, negative CO_2 credit 10 €/t	55	81	77	52	52	54
Scenario 6 Same conditions as in Scen. # 4, Negative CO_2 credit of 10 €/t	56	82	78	54	53	55
Integrated pulp and board mill						
Scenario 1 No CO_2 emissions tax, no incentives for biogenic CO_2 em.	82	92	88	84	84	89
Scenario 2 CO_2 emissions tax 10 €/t, biogenic CO_2 not neutral	72	82	78	74	74	79

Scenario 3 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral	82	92	83	84	83	88
Scenario 4 CO_2 emissions tax 10 €/t, biogenic CO_2 neutral. renewable electricity incentive	83	93	84	85	84	89
Scenario 5 Same conditions as in Scen. #3, negative CO_2 credit 10 €/t	71	82	78	72	72	77
Scenario 6 Same conditions as in Scen. # 4, negative CO_2 credit of 10 €/t	72	83	79	73	73	77

Currently the EU ETS recognizes biogenic CO_2 emissions as neutral. If biogenic CO_2 emissions would be considered negative the study shows that the price of EUA would have to increase from the current ~4 €/t to 60 – 70 €/t in order to keep the levelized cost of pulp at the reference case level (523 €/adt). These results are illustrated in Figure 14 and Figure 15.

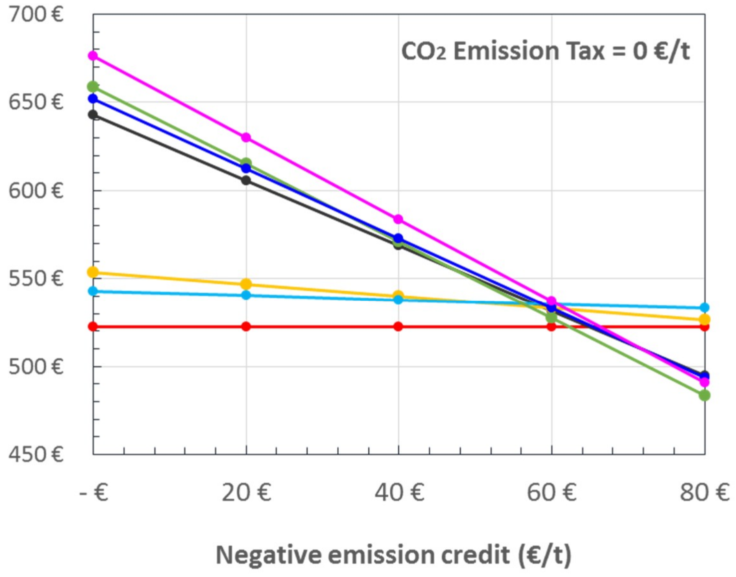


Figure 14. Effect of negative emission credits on breakeven price of pulp (€/adt) with 0 €/t emission tax.

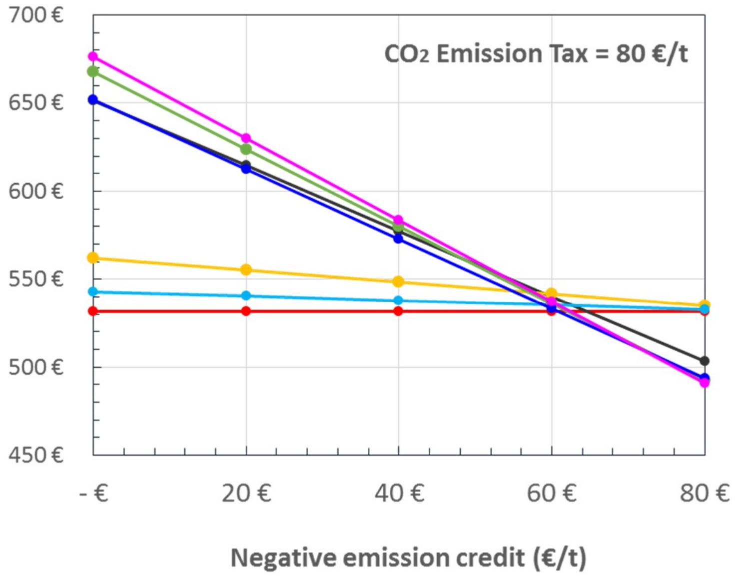


Figure 15. Effect of negative emission credits on breakeven price of pulp (€/adt) with 80 €/t emission tax.

Results from this study shows that retrofitting and integrating a CO_2 capture plant in the pulp and paper industry is highly site specific and the technical and economic effects depend very much on the steam turbine configuration. For a Kraft pulp mill the excess steam available onsite will typically be sufficient for covering the heat demand in the CO_2 capture plant, while for an integrated pulp and board mill, where more of the excess steam is utilized in the board mill an auxiliary boiler will be needed in most cases.

Depending on the prevailing policy framework the pulp and paper industry has the potential to demonstrate Bio-CCS. If the biogenic CO_2 emissions would be considered negative in the EU ETS the implementation of CO_2 capture with permanent storage could represent a business case for the industry, and thus a stepping stone for widespread implementation of not only industrial Bio-CCS, but also for CCS in general. However, it would not only be enough to consider biogenic CO_2 emissions as negative, also the price of the EUA would have a great impact. An EUA price over 60 – 70 €/t would even make CCS in the pulp and paper industry an additional source of income.

A Master of Science thesis was conducted under the title of *Feasibility of carbon capture in kraft pulp mills* to assess retrofit carbon capture in kraft pulp mills. Thirteen different technology options were evaluated based on their technical maturity, technological potential and carbon capture cost. The study focused on

Finnish pulp mills and their development towards 2030, but also the broader context was investigated.

The research methods included a comparison of data from literature, modelling oxy-fuel combustion cases with Balas software and calculating fuel switch options. The technical maturity was evaluated based on the number and quality of existing studies and possible commercial activity. The carbon capture cost data was recalculated under the same assumptions regarding investment cost factors, commodity costs, supporting policies and other possibly available revenue. The technological potential was estimated based on the technical age distribution of Finnish pulp mills. Some of the technologies require large structural changes and were considered only available if the mill is rebuilt. Thus the capture potential in a reference mill was scaled either by the potential in mills to be rebuilt by the chosen time scale of 2030 or the potential in all Finnish pulp mills. Sensitivity analysis were performed for the integrated system.

Results show that carbon capture in kraft pulp mills is probably only feasible if new products, greater efficiency or other sources of revenue in addition to supporting policies are available. This was the case for *l*ignin separation and black liquor gasification to transportation fuels, but the technological potential of these technologies appeared to be limited. In addition, small scale processes like pre-calcination before the lime kiln showed promise for on-site utilization purposes. Large scale implementation of carbon capture in the Finnish pulp mills held a potential of up to 12 Mt(CO_2)/a, at a capture cost of about 50-80 €/t(CO_2) excluding transportation and storage costs. Barriers like higher capture cost relative to power plants, transportation and storage issues and the lack of political support for bio-CCS still remain. This pointed to the direction that the role of pulp and paper industry in mitigating the climate change could be found elsewhere, like in producing carbon containing products, sustainable forestry practices and investments in forestation.

4.5 CCS in steel industry

Iron and steel industry is a significant sector contributing globally to about 6% of anthropogenic CO_2 emissions from energy use (IEAGHG, 2011). Carbon capture and storage is the only widely applicable solution to significantly reduce the CO_2 emissions from iron and steel sector, which is largely relying on the blast furnace-based steel production route.

In CCSP, new process concepts suitable for application in Finnish iron and steel industry has been identified and evaluated. Technologies under more detailed evaluation for capturing carbon dioxide from steelmaking processes are post-combustion capture and oxygen blast furnace technologies. Various technical solutions, technologies and integration configurations have been evaluated for these. For example, three different solvent options for post-combustion capture and two different CO_2 reduction scenarios for oxygen blast furnace process have been analysed. With these processes about 1–3 Mt CO_2/a can be reduced on studied iron and steel mill, accounting for approximately 25–75% of the whole site emissions. Investigation of greater emission reductions with these technologies is not rfeasible, as at integrated steel mill, CO_2 emission sources are scattered around the large industrial site and the flue gases are led to several stacks.

Application of post combustion carbon capture on an existing steel mill is relatively simple in comparison to the extensive process modifications required in the case of oxygen blast furnace (Arasto et al. 2013b). Consequently, the impacts of using an oxygen blast furnace are more diverse as, for example, LPG consumption and electricity purchase will be increased, but significant economic savings are achievable since the coke consumption is reduced. Thus, the oxygen blast furnace also enables a wider range of process optimisation to suit very different operational and economical environments. This is reflected for example with the fact that the sensitivity of the feasibility of the oxygen blast furnace process for the electricity price is higher than in the reference case or with post combustion carbon capture. In other words if the electricity prices rise, the feasibility of carbon capture with an oxygen blast furnace decreases more than the feasibility of post combustion carbon capture. This includes high risk as the CO_2 allowance price penetration to the electricity market price is of significance. However, the cost of globally avoided emissions is heavily dependent on the assumed type of substitutive electricity generation and substitutive fuel usage (Tsupari et al. 2013).

In recent studies, different possibilities and the feasibility of applying carbon capture at an integrated steel mill based on blast furnace process were studied (Arasto et al. 2013a & 2013b). Implications of different capture amounts, different solvents for post-combustion capture and process integration levels to the greenhouse gas emissions and operation economics were compared to the base case for steel production. Furthermore the effect of reducing the carbon intensity of steel production on the final steel production cost was evaluated. The assessment was based on a case study on Ruukki Metals Oy’s steel mill in Raahe. The mill is situated on the north-eastern coast of the Gulf of Bothnia, emitting approximately 4 Mt of CO_2/year. Due to the location of the installation only ship transportation of CO_2 is considered. Carbon capture processes and process integration options were modelled using Aspen Plus and the results were used to estimate CO_2 emission reduction possibilities and carbon abatement costs from an investor's point of view. Different heat integration options and heat utilization scenarios were investigated and optimized with a custom-built CC-Skynet™ economics toolkit. Also, different technologies related to oxygen blast furnace were considered, both for

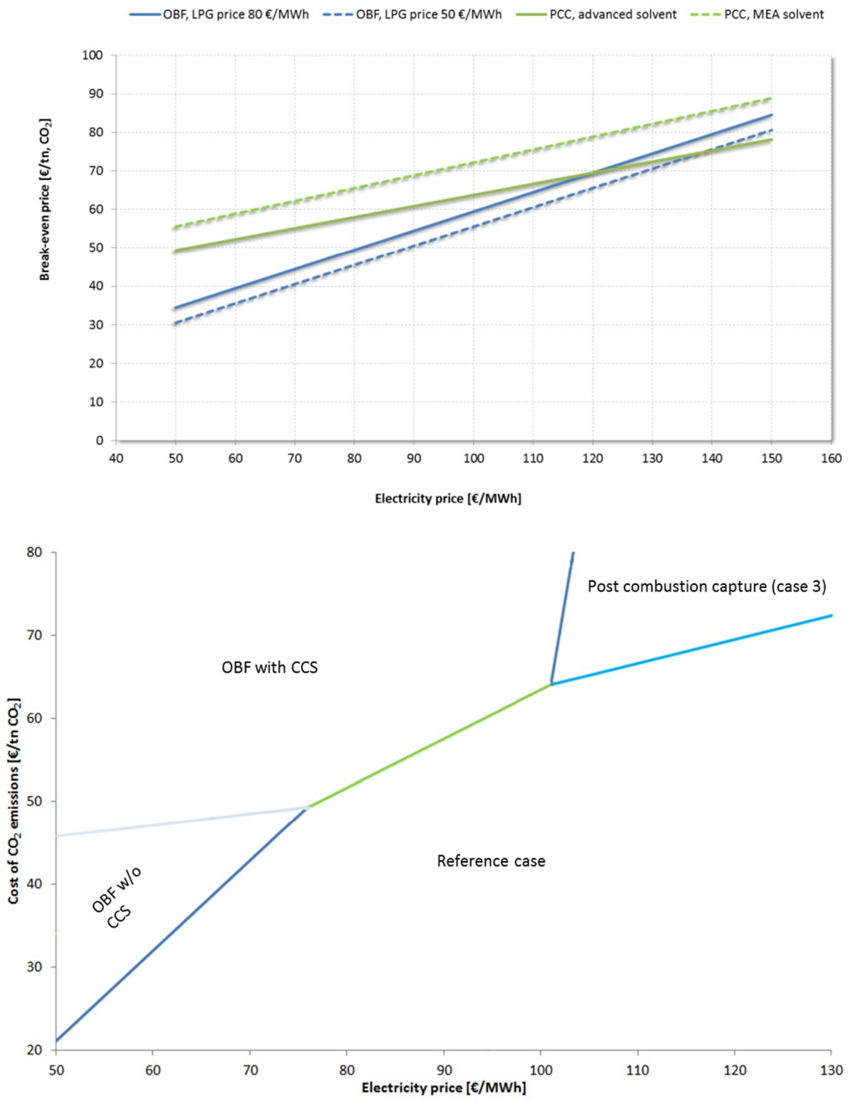


Figure 16. The effect of electricity price to the break-even price (i.e. the price of emissions allowances needed to motivate CO_2 capture instead of buying CO_2 emission allowances) of different technologies for significant CO_2 reductions in a steel mill from the operator's point of view.

oxygen production and for top gas treatment. With a whole chain approach, including CO_2 capture, processing, transport and storage, the results showed a significant reduction potential: up to 2.9 Mt/a using CCS. The cost breakeven point, i.e. when CCS turns more feasible than buying carbon credits in the reference case, for the plant owner were in the range of 50–90 €/t CO_2, for most of the considered cases. However, the breakeven prices are very sensitive for electricity prices (Figure 16). Typically the breakeven prices in steel industry seem to be somewhat lower than in most of the cases evaluated for other Finnish CCS applications, e.g. power plants. In addition, several potential ideas for further optimisation were identified during the work.

International co-operation with ZEP other industries WG, EERA CCS JP, IEA GHG Programme projects and especially MEFOS and ULCOS II projects regarding Oxygen Blast Furnace have been of significant importance for the succession of the work. The intermediate results of the task have had a strong international visibility among research community working on CCS in industry and the policy makers in Europe.

4.6 Evaluation of new CCUS concepts

4.6.1 Evaluation of CCUS technologies under development in CCSP

An evaluation of new CCUS-technologies under development in the Carbon Capture and Storage Program (CCSP) was made in 2013-2014. Technologies that were studied are thermos-catalytic decomposition of methane (TDM), and hybrid CCS concepts. Thermocatalytic decomposition of methane is developed by Tampere University of Technology (TUT) whereas Lappeenranta University of Technology (LUT) and Technical Reasearch Centre of Finland (VTT) develop hybrid CCS concepts.

The evaluation focused on to determine certain key performance indexes for the processes and comparing the concepts according to the indexes. The concepts that were evaluated are described elsewhere in this report.

A brief evaluation for the above-mentioned concepts was made. TDM is an interesting process as it would create a side product, solid carbon, which could be valuable product for certain applications. This process is being researched in lab-scale and its development to commercial level would need to be studied further. Development of hybrid CCS processes aims at to lower CCS costs compared to conventional post-combustion capture. Behavior of calcium in the looping process might cause some challenges but if working properly the process could have significant potential in capture of CO_2 emissions worldwide.

In conclusion all the processes or technologies have great potential in lowering CO_2 emissions. Research is not complete yet and therefore these concepts should be further studied in order to be able to draw conclusion of their full potential, challenges and possibilities in capturing CO_2 in significant scales.

4.6.2 Partial oxy-combustion

In partial oxy-combustion air is enriched with oxygen. Partial oxy-combustion power plant would require both oxygen plant and CO_2 removal unit, leading to more but smaller units than required in either air-blown combustion power plant or oxy-combustion power plant. When comparing oxy-combustion to air-blown combustion, the volumetric flow rate of the flue gas decreases and CO_2 concentration increases with increasing oxygen content in enriched air. The most significant effect to operational cost was the decrease in energy consumption of the flue gas blower and the stripper. The investment costs of the main equipment in CO_2 absorption process were decreased due to the smaller size of the equipment. The investment and operational costs of oxygen plant were not taken into account.

The advantages of other CO_2 removal technologies compared to amine-based absorption process in partial oxy-combustion were also studied. Power consumed for compressing the flue gas to attain economically feasible CO_2 partial pressure (10 bar) for physical absorption was too high to be beneficial compared to amine absorption. Both membrane separation technology and vacuum pressure swing adsorption (VPSA) technology would benefit if the CO_2 concentration increased in flue gas. However, neither technology can reach the same level of removal efficiency and CO_2 purity as the absorption technology today due to material limits (adsorbent efficiency, membrane selectivity).

Special attention was paid to CO_2 removal by water wash absorption which is an old physical absorption technology mostly replaced by more efficient CO_2 removal methods. A concept for CO_2 removal from partial oxy-combustion flue gas by water wash absorption process was designed and simulated using Aspen Plus simulation software. Water wash absorption could be a possible alternative to amine absorption. Water wash absorption is more environmentally friendly and technically a less complicated process but the power consumption of water wash process was estimated to be higher than of amine absorption.

4.6.3 Evaluation of a water wash process

A new concept for CO_2 capture by absorption into water was briefly assessed (Teir et al. 2014). In this concept, CO_2 is captured from flue gas in a pressurized bubble-type absorption column. Desorption of CO_2 takes place by flashing the water at sub-atmospheric pressure (0.4 bar). This leaves a relatively high concentration of CO_2 in the water. The new concept introduces a post-desorber that enables lowering the CO_2 concentration of the water further by flashing the water stream into the flue gas. This enables a higher CO_2 capture efficiency at chosen pressure level than possible with other water CO_2 capture concepts. The preliminary energy requirements and equipment cost seems to be similar to those of amine-based CO_2 capture processes. However, more work is needed to verify these preliminary results.

The water-based CO_2 capture concept requires no chemicals, which is a clear environmental advantage over amine-based concepts. The water requirements are still very high so for the process to be feasible (in terms of energy requirements) it requires an external source of cooling water, i.e. the process needs to be located next to a large river, a large lake or the sea. Also, while the preliminary results indicate that the new water-wash concept could possibly be competitive to amine-based processes for CO_2 capture at a small scale (~50 kt CO_2 per year), more work is needed to assess the performance and cost of the concept at a large-scale power plant (~1 Mt CO_2 per year). Since the water-based concept requires ten-fold more solvent circulation than amine-based processes it is possible that at larger scales amine-based processes may be favourable (e.g. due to space requirements, and technical challenges related to circulation of very large amounts of water). Still, the new water-based CO_2 capture concept seems promising based on this initial assessment and warrants further work.

4.6.4 Evaluation of Cuycha's CCN concept

The target of this work was to evaluate the feasibility of a new carbon dioxide (CO_2) neutralisation concept by literature review and mass and energy balance calculations (D228). In this concept, CO_2 is captured from a gas stream, either by dissolution in pressurized water or using conventional CO_2 separation processes. An acidic CO_2-water solution is obtained, which is neutralized with feldspar. The neutralization of the feldspar is expected to result in a bauxite by-product that could be used as raw material for aluminium production. Three embodiments of the concept are given in a patent application related to the concept, of which two embodiments were assessed.

None of the CO_2 neutralisation concepts assessed were found economically feasible, not even when taking into account revenues from by-product sales. The slow reaction kinetics of feldspar with CO_2 is the main bottleneck of the concept. The scarce experimental data available indicates that pressures over 100 bar CO_2 and temperatures between 100-300 ºC are required to even reach a conversion as low as 9% of the theoretical maximum in 6 h. Completion of the reaction is therefore expected to take days, which is far too slow for an industrial process. The water consumption and the need for dumping of millions of tonnes of bicarbonate waste water is another hurdle for the concepts studied. This can be overcome by using only Ca-plagioclase for neutralisation, resulting in solid calcium carbonates, and not K-feldspar or Na-plagioclase, resulting in a bicarbonate solution.

An alternative process for simultaneous CO_2 neutralisation and aluminium ore production by leaching feldspar in mineral acids was also briefly assessed. It was found technically feasible and less demanding to perform than the main CO_2 neutralisation concepts evaluated, but due to the large consumption of chemicals it was also found economically unfeasible.

4.6.5 Emissions of carbon dioxide capture in power generation when using pre-combustion capture or oxyfuel combustion methods

Carbon dioxide capture from large point sources, such as power plants using fossil fuels, is essential for mitigating further global warming. New combustion methods are being researched to help increase the partial pressure of carbon dioxide in the flue gas of a power plant and to make carbon dioxide capture faster, cheaper and less energy intensive. The most important methods for this are gasification and combustion with pure oxygen instead of air.

Gasification of solid fuels is compatible with so called pre-combustion capture methods, where the carbon dioxide is removed from stream before combustion of the remaining synthesis gas. Combustion with pure oxygen, or oxyfuel combustion, reduces the amount of nitrogen in the flue gas, effectively resulting in only carbon dioxide and water vapour as the combustion products. Both methods result in higher carbon dioxide content in the flue gas compared to the conventional combustion with air.

Several methods exist for separating carbon dioxide from other gases. These methods are based on absorption, adsorption, membrane separation, cryogenic separation or their combination. Each capture method, as well as the two combustion methods mentioned above, has its advantages and disadvantages that concern both the capture capabilities of carbon dioxide and emissions potentially harmful not only to humans and environment, but also to related processes, such as transportation of carbon dioxide.

The emissions of different carbon dioxide capture methods are highly dependent on the capture process due to the different chemicals used in each method. The chemicals used are not the only possible emissions, but also thermal and chemical degradation of the chemicals may result in new, potentially thus far unpredictable compounds. The precise composition and effects of these emissions are not yet fully understood and research concerning their nature is required.

The work done in CCSP (Suvanto 2013) serves to show different possible emissions related to carbon dioxide capture processes and to provide this information for others, in order for them to develop measurement devices required for emission control.

4.6.6 Utilisation of alkaline process streams for CO_2 capture

In this work, the potential to use alkaline streams, such as alkaline by-products, wastes and internal process streams, for capture, storage and/or utilisation of CO_2 was assessed. The study was limited to Finnish industry. Only plants emitting more than 100,000 t CO_2 were assessed (Teir, 2015). In addition, also metal refineries and the mining industry were included in the survey.

The preliminary results from the study show that there is a significant theoretical CO_2 capture capacity in the various alkaline material streams in Finnish industry. However, in all cases there are constraints to the utilisation of these streams for practical CO_2 capture. For instance, the two steel mills in Raahe and Tornio produce about 800,000 t/a of steelmaking slag each, containing a significant share of calcium silicates and calcium oxides/hydroxides that could be converted into calcium carbonates. However, a large part of the slag produced is already being utilized for various purposes in civil and highway engineering, e.g. soil conditioners, road construction, and as a raw material in industrial process replacing natural minerals. Therefore, the practical utilization potential would be less than 100,000 t/a CO_2 per facility. The pulp & paper industry in Finland is based on the Kraft process that process large amounts of sodium hydroxide: the ten largest pulp mills each process 100,000-230,000 t/a NaOH. Most of this is regenerated using calcium hydroxide, requiring only about 10% make-up chemicals. The NaOH use corresponds to a theoretical CO_2 capture capacity of 110,000-250,000 t/a, or 7-17% of the total CO_2 emissions of the plants. As both NaOH and $Ca(OH)_2$ are needed as input for the Kraft process, utilising these streams for CO_2 removal would require additional steps for regeneration or doubling the lime kiln capacity for calcination of produced $CaCO_3$ (to regenerate hydroxide), not necessarily making CO2 capture any cheaper than conventional CO_2 capture processes. The mining industry has by far the largest theoretical CO_2 storage potential, with over 50 million tonnes of mineral waste being produced each year. While waste rock from mining is readily available, natural magnesium- and calcium silicate containing minerals require mechanical, thermal and/or chemical activation in order to speed up their reaction with CO_2 to time scales that are of relevance for industrial processes.

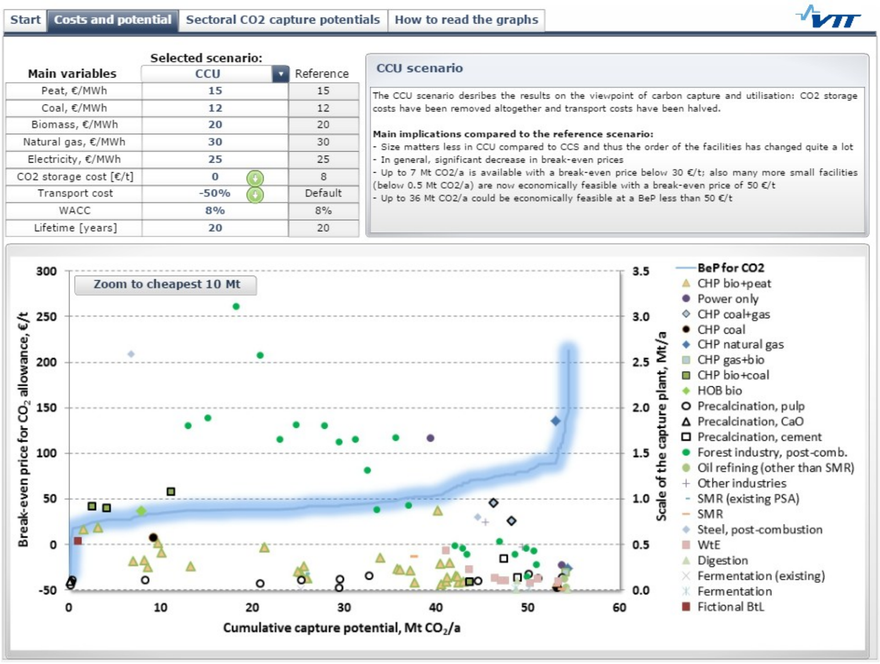
4.7 Summary of CCSP conceptual case studies

VTT has conducted several techno-economic concept studies for CCUS applicability within energy production and carbon intensive industry in Finland based on real industrial plants and their environments. An illustrative summary graph was developed and published in the on-line report as a toolkit (*http://ccspfinalreport.fi/*) in which the potential and costs of CCUS in different applications and market conditions in Finland can be visualised. The main research questions answered are:

- What are the most profitable CCUS applications in Finland in different market situations (e.g. prices of electricity, CO_2 allowances, etc.)
- What CO_2 price is required to turn these CCUS cases feasible over the respective reference cases without CCUS?
- What is the estimated potential for these different applications (in Mt/a of CO_2)?

In the summary tool the analysed application areas are electricity production, combined heat & power (CHP), pulp & paper, oil refining, hydrogen production by steam methane reforming (SMR), steel industry, forest industry, digestion processes and fermentation processes. In energy production special focus has been on CCUS integration to CHP systems in multi-fuel and gas turbine combined cycle (GTCC) solutions, including bio-CCS.

The tool was used for analysing the techno-economic CCS potential in Finland. The reults are presented in D265. According to the analyses done, many of the cost-effective CCS applications in Finland would be in the biomass power & heat sector, BtL refinery and in the forest industry. With a break-even price (BeP) of 50 €/t, including transport and storage costs, the capture of 8 Mt CO_2/a would be economically feasible, of which 3 Mt CO_2/a would be of biogenic origin. It is therefore clear, that the opportunities as well as the challenges of bio-CCS are very relevant for Finland. By halving the transport costs and removing all storage costs, the CO_2 utilisation perspective can be revealed: at a BeP less than 50 €/t up to 36 Mt CO_2/a in total could be captured for CCU; as long as there is use for the CO_2. Of this 36 Mt/a, up to 26 Mt/a is of biogenic origin. The potential for bio-CCU is significantly larger than for bio-CCS because of the typically small unit sizes and inland locations of biomass fired CHP plants and pulp mills.



Main variables	CCU	Reference
Peat, €/MWh	15	15
Coal, €/MWh	12	12
Biomass, €/MWh	20	20
Natural gas, €/MWh	30	30
Electricity, €/MWh	25	25
CO2 storage cost [€/t]	0	8
Transport cost	-50%	Default
WACC	8%	8%
Lifetime [years]	20	20

CCU scenario

The CCU scenario desribes the results on the viewpoint of carbon capture and utilisation: CO2 storage costs have been removed altogether and transport costs have been halved.

Main implications compared to the reference scenario:
- Size matters less in CCU compared to CCS and thus the order of the facilities has changed quite a lot
- In general, significant decrease in break-even prices
- Up to 7 Mt CO2/a is available with a break-even price below 30 €/t; also many more small facilities (below 0.5 Mt CO2/a) are now economically feasible with a break-even price of 50 €/t
- Up to 36 Mt CO2/a could be economically feasible at a BeP less than 50 €/t

Figure 17. An illustrative summary graph was developed and published in the online report as a toolkit (http://ccspfinalreport.fi/).

5. Capture of CO_2

Various technical solutions exist for capturing CO_2 before or after combustion (or conversion, in case of certain industry processes). Some capture processes are already in use by industry for producing CO_2 for industrial use. However, this production is in a relatively small scale as compared to the millions tons per year needed for a capture unit in a full-scale CCS power plant. Several new capture methods are in different stages of development. These were studied in CCSP with a special interest in oxy-fuel related technologies and biofuel solutions.

Cost-effective carbon capture technologies are still not commercially available for large-scale implementation on power plants. Technologies that are the most mature ones include Fluor's Econamine FG+, Mitsubishi Heavy Industries KM CDR, Hitachi H3, Cansolv Technologies, Aker Clean Carbon and Alstom's Chilled Ammonia Process (ACAP). These technologies have been tested at scales on slip streams no larger than 1–40 MWe from coal-fired power plants, the size of a typical coal-fired power plant being 500 MWe.

Most of the capture technologies in development face the following issues:

1. They have not been successfully demonstrated at the scale necessary for power plants;
2. The parasitic loads (both steam and power) required to support CO_2 capture significantly decrease power generating capacity and require more fuel input to produce the same power output; and
3. They are not cost-effective.

Other separation methods such as membranes and chemical looping combustion are being considered as a potential technology that could be employed at a later stage, since these are not as mature as the main carbon capture technologies based on absorption or oxy-fuel combustion. In CCSP, chemical looping combustion was selected for further development as it benefits from the Finnish expertise in fluidized bed combustion technology.

5.1 Oxy-fuel combustion

Oxy-fuel combustion in circulating fluidized bed (CFB) boilers is a CCS technology area where Finnish technology providers are world-leading. Understanding the technical challenges and limitations of oxy-fuel combustion as well as the related cost structures for fossil, biomass and co-firing cases is essential for several actors in Finland. In CCSP, the focus was therefore on further developing models and modelling tools for increasing the understanding of various processes related to oxy-fuel combustion in CFB boilers. As part of this work flexible simulation environments were developed. In order to understand the phenomena and limitations of oxy-fuel combustion boilers, combustor process models for air-firing are further developed and updated to provide estimates for combustion, heat transfer, fluid flow and emission performance under various oxy-fuel combustion conditions. This allows for more accurate unit processes to be utilised in process simulators of a wider scope.

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5.2.1 Dynamic simulation tool for oxy-fuel CFB processes

A dynamic simulation tool has been developed for concept studies of oxy-fuel CFB processes, consisting of an air separation unit (ASU), a circulating fluidised bed (CFB) boiler island and a CO_2 purification unit (CPU). The simulation tool is needed for studying the dynamic performance of (heavily) integrated processes in oxy-CFB power plants and to develop its control strategies. Different linking techniques to integrate two separate dynamic modelling programs, Aspen Plus Dynamics and Apros, have been evaluated (D305). The reason for integration is to utilise the best features of the simulators: Apros is strong in boiler and turbine processes, and Aspen in distillation processes like air separation and CO_2 liquefaction. The proper method for linking (via Matlab/Simulink) was found, tested and implemented. In addition, the possibility to transform AspenPlus models into AspenDynamics models has been successfully tested.

5.2.2 Heat transfer in an oxy-fuel CFB furnace

Due to lack of atmospheric nitrogen in oxygen fired combustion, the partial pressures of CO_2 and H_2O in flue gas are substantially higher than in air fired combustion. Both gas species are radiating gases, which affects the radiation heat transfer both in the furnace and in the backpass. In CCSP, the gray and non-gray modelling of radiative heat transfer in a large back pass channel of a CFB boiler have been made using a zone method, which has been developed at LUT (Bordbar & Hyppänen 2013). A comprehensive comparison has been done to determine the accuracy of the gray gas modelling (Figure 18). In addition some analysis has been done to show the effect of combustion types (air/oxy fired) on the overall radiative heat transfer of a backpass channel.

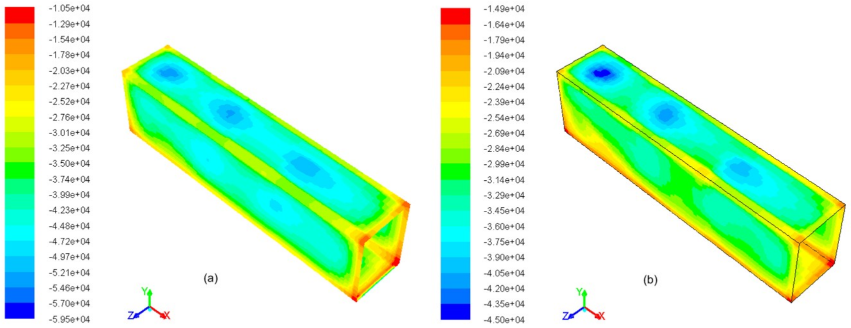


Figure 18. Radiative heat flux (W/m^2) in the walls of a backpass channel for the case of oxy-fired combustion; (a) gray modeling, (b) non-gray modelling (3D color presentation of the data generated in article by Bordbar and Hyppänen, 2015).

The non-gray behaviour of combustion gases has a significant effect on the radiative heat transfer from combustion products. Most of the previously developed models for spectral radiative properties have been developed to support the conventional air-fired combustion scenario and using them for modelling the oxy-fired combustion systems may cause uncertain level of inaccuracy. In CCSP, a new weighted sum of gray gases model (WSGGM) is obtained which is specifically developed to support the oxy-fired conditions (Bordbar et al, 2014). The different formulations presented for new WSGGM eases the use of the model as the molar fraction ratio of H_2O and CO_2 is included in the model and one set of coefficients supports the wide range of molar fraction ratios which may be found in the oxy-fired systems. The model is validated by being applied to several 1D and 3D benchmarks. The model is implemented for non gray gas modelling of radiative heat transfer in the backpass channel.

A correlation based zone method (CBZM) was developed and coupled with a 3D process model to simulate radiative heat transfer in oxy-CFB furnaces. In the earlier process model, the radiative heat transfer within the circulating bed was approximated by diffusion of energy using empirical diffusion coefficients, and the radiative heat transfer to walls was modeled by effective heat transfer between the suspension and the wall. The old approach was improved by using the radiative zone method with the new WSGGM (Bordbar et al., 2014a) to address the effect of inner dilute region in the overall heat transfer of the furnace. The radiative properties of the particles were obtained by using detailed information of solid concentration of 6 different particle size groups and their absorption and scattering efficiencies. The geometric optic was used to calculate the radiative properties of the particles. The modeling principle is presented in Figure 19. A 3D process model is used for solving the fluid dynamics, reactions, and other process data, which are then transferred to the radiation model. The correlation based zone method is used to calculate the radiative source terms in the volume elements and radiative heat flux in the surface faces. The solution is iterative as the solution of the radiative heat transfer affects the temperature field, which further affects other process variables, such as the fluid dynamics and reactions.

The first case study was a 700 MWth oxy-CFB with 23.5%-vol inlet oxygen concentration. The work was reported shortly in a presentation at Liekkipäivä 2014 (Myöhänen & Bordbar, 2014) and later in more details in a journal article (Bordbar et al., 2014b). At full load, taking account for the long distance effect of radiation did not have a very large effect (Figure 20). The temperature field obtained by using the radiative zone method was slightly more uniform, and the total heat flux to the wall was slightly higher. In the upper furnace, where the gas is the dominant phase, the difference was larger, and the effect of long distance radiation was more important.

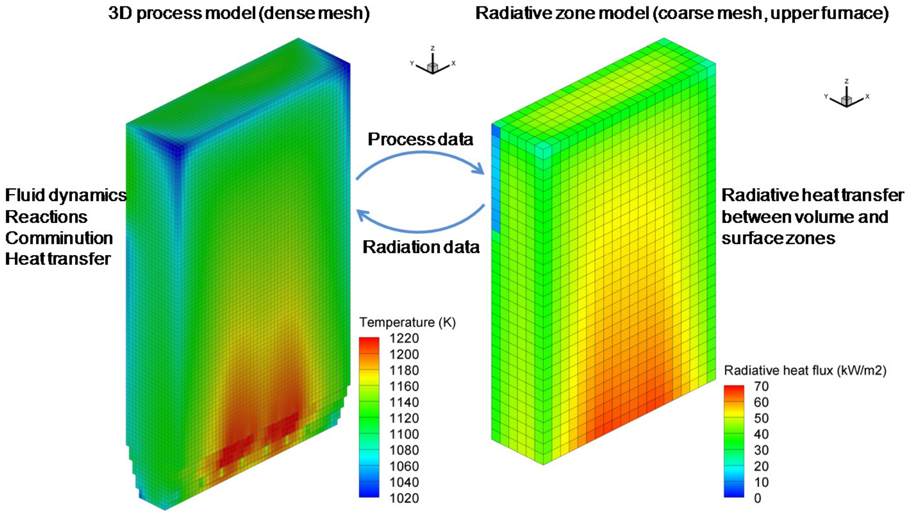


Figure 19. Modeling of radiative heat transfer in a CFB by zone method (Bordbar et al., 2014b).

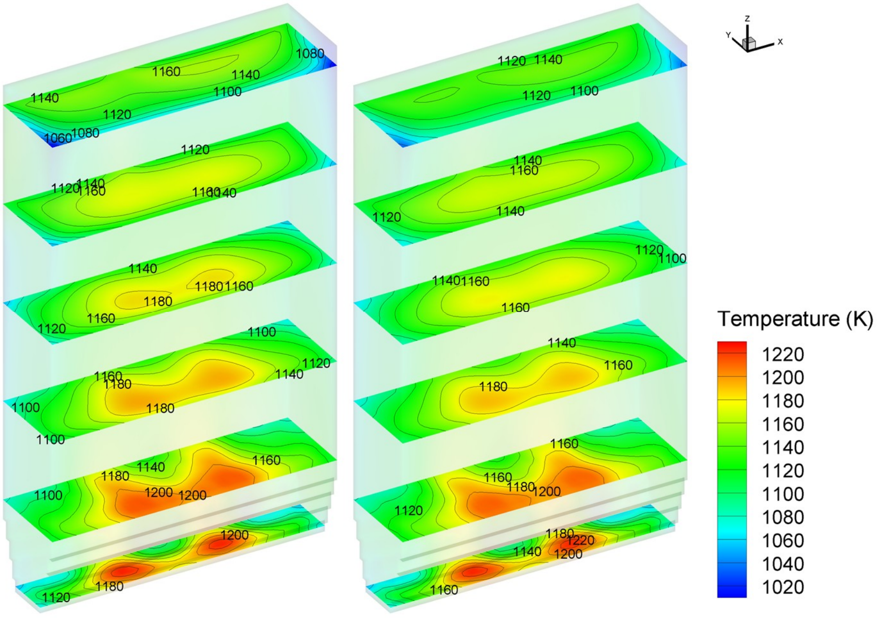


Figure 20. Modeled temperature fields without (left) and with (right) the external radiation model (Bordbar et al., 2014b).

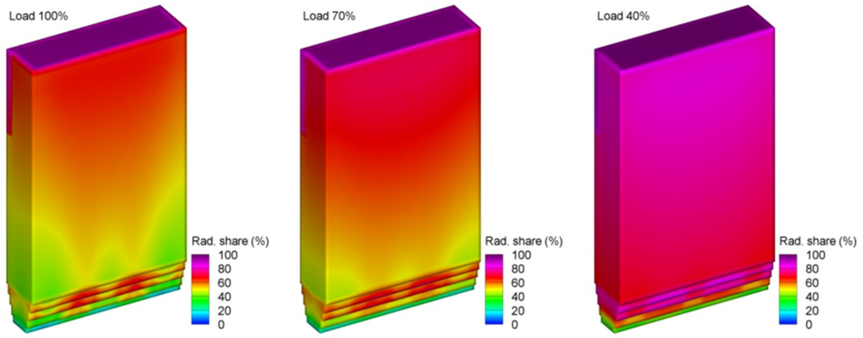


Figure 21. Share of radiative heat flux of total heat flux in a 1200 MWth oxy-CFB furnace at load points 100%, 70%, and 40% (presented by Myöhänen at FBC22-conference, 2015).

The zone method was applied for modelling the radiative heat transfer in a 1200 MWth oxy-CFB furnace at different boiler loads with 40% inlet oxygen (Myöhänen et al., 2015). Figure 21 presents how the share of radiative heat transfer increases as the boiler load decreases and how it is distributed in various parts of the furnace.

The model approach was further developed and applied to calculation of heat transfer in various process conditions: oxygen-fired mode at 40% inlet oxygen with wet and dry flue gas recycle (FGR) and boiler loads 40 – 100 %MCR, operation at full load with 60% inlet oxygen, air-fired mode, effect of wall emissivity, and effect of particle size and segregation. At equal fuel input and fluidization velocity, the furnace temperatures were 10 – 20 °C smaller with dry FGR compared with wet FGR. This was mostly due to higher gas density, which increased the mass flow when the volumetric flow was the same. Because of higher temperatures, the share of radiative heat flux of the total heat flux was slightly higher with wet FGR. Similar to earlier study, the radiative heat flux was dominating at lower load and at upper furnace due to smaller solid concentration.

5.2.3 Limestone and sulphur reactions in oxy-fuel combustion conditions

Another objective is to study limestone reactions in oxy-fuel combustion conditions in CFB boilers and further develop existing particle models. The oxy-fuel combustion conditions can have a great influence on limestone reactions and these effects are not well known. A deeper understanding of these reactions is required for developing the knowledge of reaction phenomena and development of comprehensive oxy-fuel combustion process models. A sub-model of limestone particle model for carbonation has been validated with bench-scale experimental data for the study of non-stationary condition. Limestone reactions in oxygen-fired conditions at different furnace temperatures have been modelled by a steady-state three-dimensional modelling and compared with air-fired combustion (Figure 22, Myöhänen et al. 2013). Particle trajectories in different combustion conditions inside the steady-state 3D model have been determined to produce a gas and temperature history for the particle model. Limestone reactions in these conditions have been studied with the transient particle model (Rahiala et al. 2013).

The study included different cases in air-fired and oxygen-fired combustion conditions and conditions on both sides of the equilibrium curve for calcination. Thus both indirect and direct sulphation mechanisms were studied. Also the effect of the return leg system was studied. The study showed that a complex behaviour consisting of simultaneous reactions is possible depending on the conditions in the return leg. The modelling approach was also used to estimate whether the transient environment has an effect on the limestone behaviour compared to the averaged conditions and in which conditions the effect is the largest. Also the influence of CO_2 on sulphur capture efficiency was studied during fluidized bed desulphurization by experiments and modelling (Rahiala et al. 2013). The effects of CO_2 on sulphur capture in oxy-fuel CFB conditions were studied with experiments and modelling. Experimental results show different effects of CO_2 in different CFB conditions. The experimental results were analysed using a single particle model of limestone to interpret the effect of different conditions on sulphur capture, and the model was able to predict the observed conversion curves.

During year 2014, the focus of the study was in the effect of water vapour on limestone reactions (Rahiala et al. 2014). Sulphur capture in fluidized bed conditions has been studied widely during last decades, but the effect of H_2O has not been studied extensively. Recently, the effect of water vapour in sulphur capture has been found and presented in literature. Water vapour has been found to have an effect both in calcination and sulphation, but the phenomena behind the sulphur capture in presence of H_2O is not clear. In oxy-fuel CFB, the H_2O concentration can be even 30% while in traditional air combustion it is 4-20%. Development of the fluidized beds energy applications requires understanding the behaviour of sulphur capture in presence of CO_2 and H_2O since them both exist in large amounts in oxy-fired fluidized beds. Also when developing the accuracy of the particle model this understanding is needed. Thus the particle model and bench scale experiments were utilized to study the influence of H_2O on sulphur capture in conditions of fluidized bed air and oxy-fuel combustion.

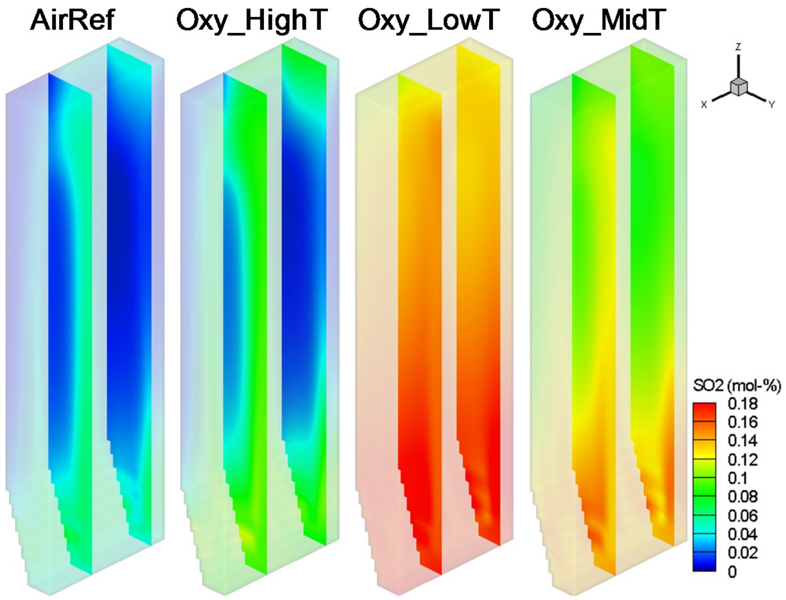


Figure 22. Modelled sulfur dioxide profiles in air-fired (AirRef) and oxygen-fired cases at different temperatures (Myöhänen et al. 2013).

The different conditions included calcination and indirect sulphation experiments with and without H_2O. Some of the tests were repeated during summer 2014 because there were uncertainty of the correctness of the test results. Also, rest of the tests were checked in order to ensure reliability of the results. The results showed that sulphur capture was enhanced when the gas atmosphere included water vapour. Also calcination was enhanced in the presence of H_2O. These limestone reactions in different environments with and without H_2O were simulated with an unsteady multilayer particle model based on control volume method. The model was utilized to interpret the differences between the test results with and without H_2O and to determine conversion curve, conversion profile and the magnitude of reactions and diffusion as a function of radius and time. The results show that different sulphation patterns and conversion degrees can be explained with the different limitations inside particle in time in different conditions. Some recalculations were made with the model during autumn 2014 due to checking and repeating of the experimental tests. A journal article about the effect of H_2O on limestone reactions was submitted to Fuel in August 2016.

The steady-state 3D model was applied to simulate the sulphur capture in a large scale oxy-CFB. The object of study was a 1500 MWth oxy-CFB firing bituminous coal and operated with 40% inlet oxygen concentration. The studied cases included load points 40, 70, and 100 %MCR. With Ca/S-ratio of 2.9, the modelled sulphur retention in furnace was 96% at full load and increasing up to 99% at minimum load due to longer residence time. The furnace temperature was aimed above the calcination temperature, as this has been observed to be the best operating mode in terms of sulphur capture and heat transfer with high inlet oxygen concentration. The main sulphur capture mechanism was indirect sulphation in all cases. Some direct sulphation occurred at the bottom of the furnace, where fresh $CaCO_3$ was available from limestone feeds. Some re-carbonation occurred in cold regions of the furnace, and the share of re-carbonation increased as the load decreased. The model data can be later applied for transient studies by a particle model. This will allow for a better evaluation of the possible cycling effects, which the limestone particles may experience inside the furnace loop.

5.2.4 Development of a flexible heat exchanger network synthesis method

This work presents a multi-objective synthesis method for flexible heat exchanger networks where process flexibility is one of the objectives being maximized (D323). The other objectives are energy efficiency and investment costs needed in the heat exchanger network. The reason for this type of a synthesis method is that in order to be competitive, oxyfuel processes need to be as energy- and cost-efficient as possible, but at the same time the processes need to be as flexible especially if the oxyfuel process operates on CHP-mode and if various fuels are used and also if the electricity prices vary. Heat recovery networks are a key option to improve the process energy efficiency. Flexibility can be increased by designing the needed equipment to consider the flexibility, with installing heat and material storages and especially with designing the overall flexibility in an intelligent way. Typically the flexibility of a heat exchanger network is calculated after the design has been finalized. In this novel synthesis method, flexibility is a separate objective that is considered already during the design phase.

The superstructure with two stages of a hot stream exchanging heat with two cold streams, cold utility, storage and bypass is presented in Figure 23. This superstructure is applied in an oxyfuel process that operates in CHP-mode in changing environmental conditions (DH-load and electricity price). The oxyfuel process has an oxygen storage representing the possibility of having material storages in the process. Additionally heat storage for district heating is applied. Altogether nine hot streams and two cold streams exist. The mass flow rates of these flows can be varied depending on the environmental parameters. Lower mass flows compared to nominal conditions effect the operation costs of the total power plant system. The main novelty is in a method where flexibility, or more preciously flexibility cost, can be considered as a separate objective in process optimization. In the approach flexibility cost is dependent on other objective functions (i.e. energy, investments). The hypotheses here is that when increasing inputs of other objectives (i.e. energy, investments), the process under study comes more flexible and there is a clear cost function for this increased flexibility. This flexibility can then be considered as an additional objective function for the optimization problem. Both multiperiod and stochastic approaches have been developed. Multiperiodity means that the changes in parameters (like start temperature and flowrate of a stream) as a function of time are known in beforehand (like the district heat load under a year), while in stochastic approaches the changes in process parameters are not known beforehand, but can vary between some predefined bounds. Important is to note that in the multiobjective optimization model a design condition is known in the beginning. This assumption will be challenged in future.

The results show that the model can be used in designing flexible and cost- and energy efficient oxyfuel processes that operate under varying conditions.

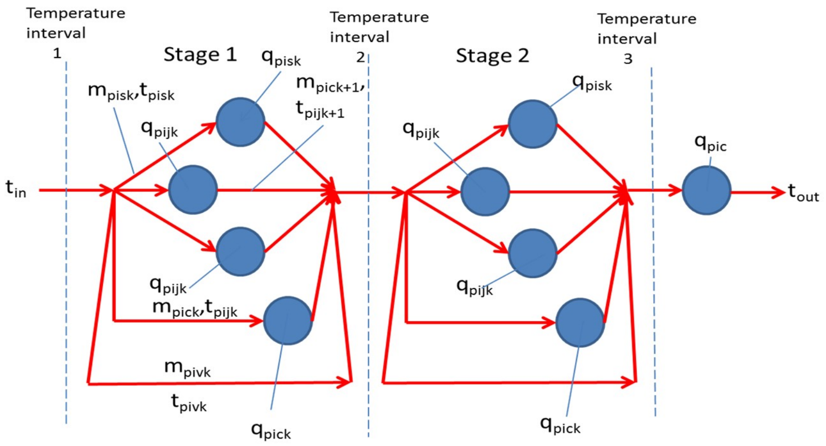


Figure 23. Two stage superstructure for a single hot stream exchanging heat with two possible cold streams, cold utilities, storage and by-pass. Variables: q (heat), t (temperature), and m (mass flow rate). Indexes: p (period), i (hot stream), j (cold stream), k (stage), s (storage), and v (by-pass) (D323).

5.2.5 A Submodel for Calculating Exergy Linked to Aspen Plus

Process simulations provide an opportunity to design and optimize processes so that they are in mass- and energy balance, but they don't directly provide information where thermodynamic losses occur. Other analysis tools that are based on the second law of thermodynamics are needed to provide this information. One of these analysis tools is exergy analysis. In this work two methods for calculating both physical and chemical exergy values of streams are presented (D310). The data for these methods are obtained from AspenPlus simulation software. In the first of these methods, AspenStreams, the physical exergy at environmental conditions of a stream is calculated by copying a stream that either enters or exits a process into an additional stream and changing the pressure and temperature of this stream into the values of the environment. The benefit is that any property method in AspenPlus can be used to calculate the enthalpy and entropy values of the streams in environmental conditions. The drawback is that generating the additional streams is hard to automate. In the second approach, called AspenData, the physical exergy of a stream is calculated using the stream's molar concentration together with a mixing rule and multiplying this corrected molar concentration with the specific enthalpy and entropy of each species. The benefit here is that no additional streams are needed, but the precision of the calculation depends on the precision of the mixing rule. The chemical exergy of both methods is calculated using the Standard Chemical Exergy approach. Both of the methods were tested on an oxyfuel power plant. The results of these calculations show that both methods provided the same results, and hence for oxyfuel processes, the AspenData approach can be seen as the more efficient one. Although the methods presented in this report are applied on Excel Worksheets, the methods could be written as part of AspenPlus code. In general the methods presented in this work could be applied also to other types of process simulation software. The only necessity is that stream enthalpies, entropies and molar concentrations are provided.

5.2.6 Development of CFD calculation of oxy-fuel combustion in CFB boilers

In the present study VTT's steady-state modelling approach for circulating fluidized beds was applied to simulate air and oxy-fuel firing with different fuels, lignite, coal and biomass, in a large scale CFB furnace (D309). The over fire air (OFA) concept developed earlier by Fortum and VTT was applied in all cases but one. The normal operating mode without the OFA was simulated for reference. In air firing flue gas volumetric flow rates varied remarkably depending on the fuel, but In oxy-fuel firing they were more similar due to the modified feed gas O_2 content. According to the results the OFA concept efficiently reduces NOx emission in air firing of lignite. At the same time solids circulation decreases, the furnace heat transfer declines moderately, the lower furnace temperature increases and the unburned carbon remains at the original level. CO burnout is predicted to be a bit weaker in the OFA case.

In air firing of different fuels with OFA heat transfer and the furnace temperature are simulated to increase and solids circulation to decrease along with improving fuel quality. The UBC flow and the exit CO concentration are predicted to be higher with biomass and lignite and lower with coal and the coal/biomass mixture. The simulated NOx and N_2O emission are small with all fuel types thanks to the efficient staging. Additional simulations were carried out to confirm the validity of the results in the case of a smaller commercial boiler with different heat transfer arrangements and geometry. In that case also minimum load conditions were studied. Since at minimum load possibilities for air staging are poorer, the suggested

OFA arrangement as such will not work without significant modifications which need to be further studied.

In oxy-fuel firing the furnace performance is more similar with different fuels due to the fuel dependent feed gas O_2 concentration. The upper furnace temperatures are lower in oxy-fuel cases as a consequence of rise in flue gas heat capacity. Solids circulation and the UBC flow are reduced in cases with increased feed gas O_2. The predicted CO emissions are comparable to air firing. The exit NO, HCN, NH_3 and especially N_2O concentrations increase in connection with flue gas recirculation. With coal the decreased furnace temperature also favours N_2O formation over NO.

5.3 Post-combustion capture

In post-combustion capture, aqueous alkanolamine solutions are commonly used for removal of acid gases from refinery, flue and natural gas. Primary amines used for gas stream purification are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and diisopropanolamine (DIPA). In addition, mixtures of the previous ones are also used as aqueous solutions for carbon capture.

5.3.1 Phase equilibrium measurements and modeling for amine systems capture

Heat stable salts are formed in CO_2 capture processes when oxygen is present in the system. The effects of heat stable salts in CO_2 capture have been investigated in general level, but their effects on phase equilibria have not been studied previously. Heat stable salts are undesirable components in CO_2 recovery systems because they do not regenerate back into alkanolamine in a stripper unit. Thus, heat stable salts tie up the amines at the expense of the amine capacity. Heat stable salts also cause foaming and corrosion in process equipment.

The focus on the work in CCSP is to study heat stable salts effects on CO_2 solubility in aqueous amine solutions. The information of heat stable salts effects on CO_2 solubility is important when CO_2 capture processes have to be modelled accurately.

An expression for the Henry’s law constant in aqueous binary and ternary amine solutions was developed (Penttilä et al. 2011). The Henry’s law constant of CO_2 is needed to describe the molecular or physical solubility of CO_2 in aqueous alkanolamine solutions. The model was developed for the following aqueous amine systems: MEA, DEA, DIPA, MDEA, 2-amino-2-methyl-1-propanol (AMP), MEA+MDEA, MEA+AMP, DEA+MDEA, DEA+AMP, DIPA+MDEA and MDEA+AMP. The Henry’s law constant is needed as part of vapour-liquid equilibrium (VLE) models when acid gas is present in the system. The developed model predicts the Henry’s law constant in aqueous binary and ternary amine solutions either comparably or better than the models found in the literature and it behaves consistently on the whole composition and temperature range.

A new model for the density of aqueous DIPA solution has been developed (Uusi-Kyyny et al. 2013). The Redlich-Kister type polynomial has been generally used to describe the densities of aqueous alkanolamine solutions but in case of aqueous DIPA solution the model is not satisfactory. The Redlich-Kister polynomial describes the whole composition range of aqueous DIPA solution but only at one temperature at a time. That means that each temperature needs its own polynomial correlation which is not practical in VLE calculations. Instead, this model is dependent both on temperature and composition of aqueous DIPA solution.

Ionic liquids (and heat stable salts) have traditionally been considered to be non-volatile by having negligible vapour pressure. Therefore, vapour pressure data have only been measured with indirect methods, which means that the vapour pressure has not been measured but it has been calculated from other measured quantities. Only recently, it has been indicated that it is possible to measure vapour pressure data for ionic liquids with direct methods. In CCSP, vapor pressure data for an ionic liquid/heat stable salt system was measured successfully by using a Vigreaux type distillation column. In addition, a new way to describe the vapour pressure of an ionic liquid/heat stable salt system was developed. The model is different from the models found in the literature. The new model takes into account the reaction that occurs when 2-(hydroxy) ethylammonium acetate (2-HEAA) dissociates into its initial substances, MEA and acetic acid (HAc), prior to vaporizing in vacuum distillation. 2-HEAA reforms from MEA and HAc when the temperature decreases low enough in the condensing unit. This means that 2-HEAA does not possess vapour pressure in the circumstances used in this work but instead the measured vapour pressure is the vapour pressure of the ionic liquid system (Penttilä et al. 2014). The vapour pressure measurements can be applied in the determination of the distillation conditions for purification of spent amine for the removal of heat stable salts.

Densities were measured for the water + 2-HEAA and MEA + 2-HEAA systems and modelled with the Redlich-Kister equation. In addition, solid-liquid equilibrium (SLE) data were obtained with visual method for two different systems: water + 2-HEAA and MEA + 2-HEAA. The enthalpy of fusion and the melting point of 2-HEAA and of MEA were measured with the Differential Scanning Calorimetry (DSC). The enthalpy of fusion was needed for modelling the SLE data. Vapor-liquid equilibrium (VLE) data were measured for the water + 2-HEAA, HAc + 2-HEAA and MEA + 2-HEAA systems but only the water + 2-HEAA and HAc + 2-HEAA systems were successfully conducted. The obtained data is required when the effect of the heat stable salts has to be taken into account in modelling of CO_2 capture (Penttilä et al. 2014, Penttilä 2015) (D326 and D352). The results were published by Penttilä et al. (2014).

The work was continued by the measurements of CO_2 solubility in water + 2-HEAA and water + 2-HEAA + MEA solutions (D327). The measurement results illustrate the effect of the heat stable salt accumulation on the CO_2 capture capability of the aqueous MEA system. Total 224 points were measured for water + 2-HEAA and water + 2-HEAA + MEA systems. The measured data was used in development of a model for description of water + 2-HEAA + MEA systems. The developed activity coefficient model described CO_2 solubility in H_2O + 2-HEAA, H_2O + MEA and H_2O + 2-HEAA + MEA systems with average relative deviation of 6.7 %. The physicochemical model uses reaction equilibrium constants, Henry's law constants and activity coefficients to describe the reactions occurring during CO_2 dissolution into the solution and the vapour-liquid equilibrium of the system. Both molecular and ionic activity coefficients were calculated in the model. The molecular activity coefficients were calculated using the NRTL model while the activity coefficients of the ionic species were calculated using Debye-Hückel type empirical correlation. In addition, adjustable parameters of Henry's law constants for CO_2 solubility in pure 2-HEAA were fitted together with the activity coefficient parameters to achieve the most reliable results. The model was expanded to describe the heat stable salt+MEA+H_2O systems in general. A scientific article containing the measured data and the model was published (Ostonen et al. (2015).

After the heat stable salt study, the emphasis of the phase equilibrium measurements was put on the phase change solvents (D353 and D354). Previously unavailable data for H_2S solubility in aqueous MAPA + DEAA solutions was measured using the static total pressure method. The measurement results indicate that H_2S dissolves sparingly in the aqueous DEEA + MAPA systems compared to CO_2. At low mole fractions of H_2S in the liquid phase (< 0.125), the system was observed to behave according to the Henry’s law. In addition, the H_2S absorption enthalpies were calculated from the temperature behavior of the Henry’s law constants. Finally, unlike in the case of CO_2 absorption, the system was observed not form two phases during the H_2S absorption.

5.3.2 CO_2 capture using amine based solvents

5.3.2.1 CO_2-MEA simulation by Aspen Plus (2011-2012)

A study was made to improve Aspen Plus modelling of system CO_2-MEA because earlier versions, 7.1 and older, predicted too optimistic regeneration energies (D301). In collaboration with software Vendor it resulted in significantly better prediction in comparison to later versions. The results are presented in Table 9.

Table 9. Summary of comparison (D301).

	2006.5	2006.5	2006.5	2006.5	2006.5	2006.5	V7.2	
PurePara	2006.5	V7.1	V7.2	V7.2	V7.2	V7.2	V7.2	
BinPara	2006.5	2006.5	V7.2	V7.2	V7.2	V7.2	V7.2	
ElecPara	2006.5	2006.5	2006.5	V7.2	V7.2	V7.2	V7.2	
HEM+REA	2006.5	2006.5	2006.5	2006.5	V7.2	V7.2	V7.2	
Columns	2006.5	2006.5	2006.5	2006.5	2006.6	V7.2	V7.2	
Capture	2.20	2.21	2.27	2.57	2.47	2.31	2.36	kmol/h
Capture	64.79	64.99	66.71	75.57	72.63	68.07	69.30	%
QR	238.04	238.99	256.09	568.17	169.27	159.00	194.27	kW
QR/CO2	8.85	8.85	9.24	18.10	5.61	5.62	6.75	MW/kg

The results show that

- Pure component and binary interaction parameters have only a minor effect and that in the wrong direction (i.e. increasing QR/CO_2).
- Electrolyte pair parameters have a dramatic effect and that in the wrong direction (i.e. increasing QR/CO_2).
- The calculation of reaction equilibria through Gibbs energies as in V7.2 - and not through given equations - has a dramatic effect and that in the right direction (i.e. decreasing QR/CO_2).
- The column specifications have only a minor effect.

Given the very complicated calculations involved it seems a miracle that the dramatic increasing effect (with respect to QR/CO2) of the electrolyte pair parameters and the dramatic decreasing effect of the parameters affecting the Gibbs free energy change (used in the calculation of reaction equilibria) combined give a QR/CO_2 quite near the desired value.
This new version was used to model pilot unit that was planned to be built at VTT. Attempts were made to take an existing capture pilot that was to be decommissioned in use in CCSP. Unfortunately, the owners of the pilot did not allow this. Therefore, the plans for constructing a pilot have now been abandoned.

5.3.2.2 Modelling of CO_2 recovery from flue gases using piperazine activated MDEA solution

Power plants using fossil fuels are producing large amounts of carbon dioxide, which is one of the primary greenhouse gases. Typically the volume of carbon dioxide in flue gases from power plant operation is about 4-14 %. Post-combustion carbon dioxide capture based on aqueous alkanolamine absorption is a widely investigated method in recovering carbon dioxide. Functionality and cost-effectiveness are essentials when applying a technique to a real large scale power plant for reducing emissions. The alkanolamine absorption process consists of an absorber and a stripper column. Carbon dioxide is captured from the flue gas in the absorber and later on released in the stripper as a pure carbon dioxide for further treating. The aqueous alkanolamine can be recycled between the columns. Alkanolamine is acting as a physical and chemical solvent. This means that in addition to the physical dissolution simultaneously a chemical reaction accelerates the mass transfer. To fully understand the process detailed information about mass and heat transfer, chemical reactions and kinetics, phase and reaction equilibriums as well as physical properties of components are needed.

Aqueous piperazine activated methyldiethanolamine is one of the solvents used in the carbon dioxide capture processes. It is known that methyldiethanolamine has several advantages in the gas treating process and piperazine is used as an activator to accelerate the rate of reaction with carbon dioxide in the absorption process without diminishing the advantages. Challenges of the process are concerning high energy demand of the regeneration process occurring in the stripper column and modelling of the process.

In the experimental part of the thesis (D311) the aim was to test the ability of a commercial simulation program, Aspen Plus V7.3.2, to model the piperazine activated methyldiethanolamine process. In the simulations it was found that there are some deviations between the solubility results and the literature values likewise between the equilibrium results and literature values. The similarity of the results and the literature values varied widely depending on the concentration of the amines and used temperature. However, the physical properties of unloaded amine solutions were simulated sufficiently well. Since there are no research results or practical experiences available about the whole piperazine activated methyldiethanolamine process, the validity of the results when modelling the whole capture process is uncertain. Nevertheless, the results were promising when considering the capture efficiency and the amine recycling. According to the simulations performed in this work the process to be studied is more energy efficient than the monoethanolamine process.

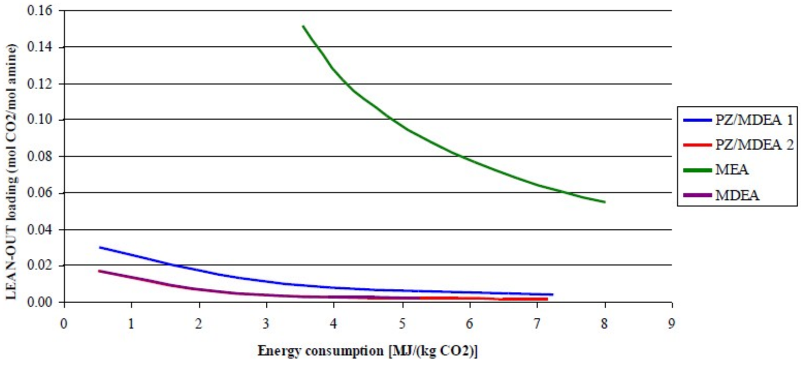


Figure 24. Impact of activated MDEA on energy efficiency (D311).

PZ/MDEA 1 and 2 represent different concentration of MDEA and piperazine in the solvents. The results of the PZ/MDEA 2 and plain MDEA are almost equal. The energy consumption of the PZ/MDEA 2 is slightly smaller. The energy consumption of the PZ/MDEA 1 is a bit larger whereas the energy consumption of the MEA is significantly larger. When considering the concentrations of the amine solutions the order is reasonable. The PZ/MDEA 2 is the most concentrated solution, but because of the PZ content the energy consumption is at the same level than with the little less concentrated plain MDEA. The PZ/MDEA 1 is less concentrated and includes more PZ.

5.3.2.3 Phase change solvents in carbon dioxide capture (D328)

New technologies are under study to find solutions to slow down global warming and climate change. One option is the capture of greenhouse gas carbon dioxide from industrial outlet gases and storage of it. However, the most commonly applied method of using amine as a solvent has the problem of high energy consumption in the solvent regeneration. Capture methods of phase change solvents have been found to give good results for energy efficiency. The phase change solvents have the property of forming third phase for specific carbon dioxide loading, temperature or pressure conditions. The phase can be either liquid or solid. In this thesis the aqueous phase changing solvent blend of tertiary amine 2-(diethylamino)ethanol (DEEA) and diamine 3-(methylamino)propylamine (MAPA) is investigated. When loaded with carbon dioxide it forms two immiscible liquid phases. The upper phase with lower density consists mainly of DEEA and the lower heavy phase consists of MAPA and carbon dioxide. The loaded solvent is lead to a separator where the two phases are separated. The system saves energy as only the loaded heavy phase is lead to stripper for regeneration. Lower regeneration temperature or elevated pressure for the solvent regeneration can also be used. The energy efficiency presented as heat duty per amount of absorbed carbon dioxide is relatively better than for reference MEA. The light phase from the separator is taken to a mixer where it is mixed with the lean solvent recycled from the stripper. After this the mixture is lead back to the absorber. The loading is an important factor as it tells the amount of amine needed to capture certain amount of carbon dioxide. The loading depends on partial pressure of carbon dioxide, change in temperature, type of amine, amine concentration in the solution and nature and concentration of other components in the solution. In this thesis and industrial scale process is considered. Solvent flow rate is determined to capture carbon dioxide for certain loading. The flue gas flow rate and composition of a coal fired power plant of 565 MW is used. Also a gravity settler is dimensioned for the system. To calculate the dimension laboratory measurements have been made over the solvent viscosity and density. The density and viscosity of the heavy phase are high, which makes the separation of the two phases very slow.

Due to long settling time the dimensions of the decanter are enormous. Considering 565 MW coal fired power plant coalescer dimensions should be about 30 m length and 8 m diameter. The settling time could be shortened by using coalescers, rising temperature or with another separation technique like centrifugation.

5.3.2.4 CFD and kinetic modelling of post-combustion CO_2 absorber

Gas flow field in a post-combustion CO_2 absorber has been studied by CFD modelling (D312). The computational domain included the inlet piping, the bottom part of the absorber and the lowest bed. Six different geometries were simulated. Based on the modelling results it can be concluded that:

- 2-sided feed pipe arrangement leads to a smoother bed inlet velocity profile than 1-sided arrangement.
- Rectangular column with 2-sided inlet provides similar results to equivalent cylindrical case.
- Staggering gas inlet pipes i.e. placing them on different levels leads to unnecessary velocity peaks appearing mainly on top of the uppermost inlet pipe.
- Tangential 1-sided inlet leads to a strongly swirling velocity field below the bed, which is not desired.

The process simulations based on the above CFD simulations indicate that the parts of the absorption column with an uneven gas flow distribution suffer from a significantly reduced CO_2 capture efficiency. However, since the gas flow evens out quickly in a packed bed column, the impact of the initial irregularities is negligible. When the liquid distribution is taken into account, the capture efficiency is certain to be affected. This was however not considered in this study.

Results from simulations with the stripping column included, and assuming similar gas distribution as for the absorber, also points to a negligible effect of the gas maldistribution on the CO_2 capture.

These results are for 1-phase gaseous flow field only. In reality liquid droplets fall down from the bottom of the lowest bed creating some degree of resistance to the gas flow. The influence this has on the predicted gas inlet profiles should be studied. This expansion is presented in the following.

Gas flow field in a post-combustion CO_2 absorber was studied further by CFD modelling (D329). When the liquid distribution is taken into account, the capture efficiency is certain to be affected. Considering also liquid flow, anisotropic porous model seems to capture the gas phase maldistribution quite well. It is noticed that it is not guaranteed that a severe maldistribution will smooth out even in a relatively high bed These conclusions can be seen in the following industrial scale calculations for 10 m wide and 8 m high column with periodic boundary conditions in z-direction (“infinite” in z-direction see Fig 31 and 32):

- Severe velocity maldistribution at the inlet. Calculation with laminar flow in bed
- Obtained pressure drop rather low: (dp = 440 Pa) when compared to results of SULCOL (dp = 900 Pa)

Conclusions and recommendatioons:

- The anisotropic porous model for packed beds was created with help of experimental results
- The model seems to capture the gas maldistribution according to the simulations
- Many assumptions: geometry, pure gas flow in columns, incompressible flow → effects of different parameters could be researched.
- Turbulence in packed beds: Now flow in bed is assumed to be laminar, but the flow in the bed is turbulent to some extent.
    - The conventional turbulence models cannot predict the turbulence reliably, the turbulence is overestimated.
    - Experiments or accurate simulations
        - → information on turbulence values in bed
        - → manipulation of the turbulence production term in fluid flow equations.

5.3.2.5 Emissions and contaminants on CO_2 capture using MEA - desk study (2011) (Other technical reports: GBC44-001)

The reclaimer waste is the largest waste quantity and contributes the highest impacts in amine-based CO_2 removal processes due to the possible presence of heavy metal corrosion inhibitors and heat-stable salts. Heat stable salts are formed when CO_2 reacts with acidic or oxidizing components in flue gases, such as O_2, SOx and NOx. In a reclaiming unit impurities are separated by boiling off both amine and water, while amine degradation and oxidizing products remain in the waste stream. In thermal reclaiming sodium carbonate or hydroxide can be added if necessary to liberate the amine from the heat stable acid salts and to minimize corrosion. One mole of amine tied up as a heat-stable salt can be neutralized with one mole of caustic or one-half mole of sodium carbonate.

Other reclaiming technologies used in parallel or separately are:

- Filtering - A slipstream of the circulating amine solution is continuously filtered for solids. The vast majority of filtering media is disposable. Filtering of 50 % slipstream should be sufficient to prevent foaming and significant fouling.

- Electrodialysis - In this technology membranes are used that allow selective passage of anions and cations under an electric field. Electrodialysis has lower energy demands than vacuum distillation and it has lower chemical and water usage than ion exchange. Disadvantages of this technology are the fouling of membrane and overall economics.
- Ion exchange - removes the formate ion and drives the equilibrium to amine and formate. Ion exchange is extremely selective, removing only the formate, none of the formamide. Formamide can all be converted to useful amine, but formate anion remains in the circulating solution.
- Activated carbon filter - used for hydrocarbon removal.

Solvent degradation leads to the need of removing the degraded solvent. Amine reclaimer wastes can contain liquid, semi-solid or solid fractions of wastes generated by amine degradation and by other additives. Solids are often treated by incineration but with liquid biological treatment is potential.

Though this waste is toxic there are micro-organisms that grow at high waste concentrations and also degradeamine. Both the aerobic and anaerobic wastewater treatment techniques can be used for amine wastes treatment. Aerobic treatment can provide higher biodegradation rates while anaerobic processes can be much more energy efficient. A combination of aerobic and anaerobic treatment is promising. Biological treatment can be facilitated by pretreatment with Fentons reagent.

All amines haver a non-zero vapor pressure. As the gas flows rates are large, there might be significant losses even with minor concentrations of amine in the treated flue gas. MEA degradation products, like formic acid, 1-propanamine, 2-butanamine, acetone, ammonia, butanone, ethoxyethene are also released to atmosphere. These are considered harmful chemicals, which can cause irritation and skin burns.

Amines themselves are not so significant risk to human health and the environment but can instead contribute to the nitrogen load and ecosystem nitrogen fertilization. There are also amine photo-oxidation products like nitrosamines, nitramines, aldehydes and amides that pose health and environmental risks. Especially nitrosamines are toxic and carcinogenic already in low levels.

5.3.3 Post-combustion capture technologies

5.3.3.1 Post-combustion capture technologies - A technology survey (2012)
(Other technical reports: GBC44-003; update 2014 GBC44-004)

Cost-effective carbon capture technologies are still not commercially available for large-scale implementation on power plants. Near-term include Fluor's Econamine FG+, Mitsubishi Heavy Industries KM CDR, Hitachi H3, Cansolv Technologies, Aker Clean Carbon and Alstom's Chilled Ammonia Process (ACAP). Mitshubishi, Aker and Kepco has started some new demo projects.

Many new solvents has been proposed. In addition to basic amine absorbent processes a carbon dioxide capture approach called the phase change system has been developed. It is using a solvent with thermodynamic properties forming a third phase for specific CO_2 loading, temperature or pressure conditions. The third phase makes it possible to significantly decrease the energy requirements for the regeneration in the stripper. The phase can be either liquid or solid. Chilled ammonia process forming a solid phase is already widely studied and under development by Alstom. Also deep eutectic solvents and aminosilicones show potential. The studied phase change solvents forming two liquid phases are for example DMX™ developed by IFPEN and tested in the EU OCTAVIUS project and DEEA + MAPA system in the EU project iCap, the process that is ready for an industrial prototype.

5.3.4 Capture of carbon dioxide in fermentation processes (2012) (Other technical reports: RB/TEK/GBC44)

The worldwide usage of fossil fuels produced 30.3 Gtons of CO_2 emissions in 2011. The biggest sectors were 41 % electricity and heat, 22 % traffic and 20 % industry. These amounts are many times bigger than in studied fermentation industries. The most fermented CO_2 emissions came from fuel ethanol production which global emissions were 70 millions of tons in 2010. These emissions were only 0.23 % of global carbon dioxide emissions. Pharmaceutical-, enzyme-, food-, brewery- and wine industries are much smaller emission sources globally when only fermented CO_2 gases are observed. Otherwise these industry areas are very large and they need a lot of energy for their actions which come mainly from fossil fuels and these industry areas produce a lot of CO_2 emissions. For example indirect manufacturing of fertilizers in farming of raw materials produces a lot of CO_2 emissions. In these areas the recovery of fermented CO_2 will come more common in future and the plants try to utilize recovered CO_2 better in-house processes and even sell it forward.

The calculation of CO_2 emissions is not easy. There are many things which affect directly or indirectly to total emissions. The priority number 1 should always be that the whole life cycle of product should be noticed. It is quite usual that if manufactured product has been made by using waste or useless material as a source material it can easily be thought that there are not additional CO_2 emissions or emissions are even negative. This is partially true but it is also partially false because there are always some CO_2 emissions when something is produced. Calculation of CO_2 emissions is always tricky and it depends on used method. There does not exist evidently one standard method which would observe also neutral and negative CO_2 loading which EU is not recognize at the moment. This study concentrated only to CO_2 recovery and emissions which were produced during aerobic or anaerobic fermentation.

5.3.5 Flue gas processing in amine-based carbon capture systems

In CCSP, a literature review of fuel gas processing in amine-based carbon capture systems was conducted (Merikoski 2012). Amine absorption is currently the leading carbon capture method. Amines are chemical derivatives of ammonia that are able to first absorb CO_2 and then release it when heated. There are health and environmental concerns related to amines and their degradation products, so amine emissions to the environment should be minimised.

The amine absorption process is sensitive to SO_x, NO_x, and particulates that may, depending on the fuel, be present in the flue gas from conventional combustion. The normal emission control systems are often adequate to control the other pollutants, but SO_x must be reduced to even lower levels before the absorber. This often requires additional investment. The absorber operates at fairly low temperatures, so the flue gas must also be cooled before the absorber. This increases the cooling demand of the plant.

There are two actively marketed amine absorption technologies in which commercial experience exist. One uses a simpler and less expensive solvent while the other consumes less energy and has smaller amine losses. Amines are lost in the absorption process due to amine vaporisation, amine entrainment in the flue gas and amine degradation. The two first mentioned losses occur in the absorber, so they cause amine emissions to the air. However, degradation accounts for the greatest losses because the amine reclaimer purifying the amine solution to ensure reliable operation of the process removes the degraded amines from circulation.

After absorption and subsequent desorption, the CO_2 is not yet ready for transportation or storage because it must first be purified and compressed to meet the CO_2 quality requirements for its further use. The requirements for ship transport are stricter than for those for pipeline transport, and enhanced oil recovery by CO_2 injection needs purer CO_2 than storage in saline aquifers. Amine absorption produces CO_2 of good quality, so usually only compression and drying are needed before it is ready for transportation and storage.

The work shows that it is technically possible to build and operate large-scale CCS plant with existing amine absorption technology and thus markedly reduce emissions. However, today this is not yet economically feasible because the process consumes much energy and requires large investments.

5.3.6 Extension of electrolyte modelling possibilities

In order to model in reliable way solvent-based CO_2 removal processes, one need to have a good electrolyte model. So far there has been one common called electrolyte NRTL which has been implemented for example in ASPEN Plus. This model, however, has restrictions and the purpose of this study is to implement alternative electrolyte models into modelling tool (D342).

Electrolyte models are needed also for all gas scrubbing processes utilizing electrolytes, as well as in waste water treatment and hydrometallurgy for production of metals.

The modelling target is to handle both gases and solids dissolved in electrolytic liquid phase composing of mixed solvents, as well as reactions between ions formed Additionally in case of liquid-liquid systems, surface active compounds or formation of different micellar structures with solids in liquid the applicability of the model is much widened.

The most advanced models used for electrolytes currently are:

- electrolyte-NRTL model [21-27] (fitted binary interaction parameters)
- extended UNIQUAC [10-16] (fitted binary interaction parameters)
- LIQUAC (original) [32], modified LIQUAC (improved) [30] and revised LIQUAC (latest version, also called LIQUAC*) [29] (fitted binary interaction parameters)
- LIFAC (original) [31], modified LIFAC (improved) [30] and revised LIFAC (latest version, also called LIFAC*) [29] (uses predictive UNIFAC methods)
- MSA-NRTL [8-9] (fitted binary interaction parameters)
- MSE by OLI Systems [18-20] (fitted binary interaction parameters)

The first four were studied in detail in this study.

Flowbat has been used as an in-house flowsheeting program mainly for hydrocarbon and organic compound simulation cases including reactors, distillation columns and heat exchangers etc.. Previous methods to calculate liquid energy values are not suitable for electrolyte systems as the ideal gas concept for ions does not work. Instead, new ways to calculate energy variables are needed. These require modifications to the Flowbat Access databanks and in the simulation program Flowbat itself.

Flowbat pure component thermodynamic and physical property databank has been maintained in a Microsoft Access database. It has been modified to allow entering the data needed for electrolyte system calculations.

As stated earlier, the systems of interest usually contain multiple phases (gas, two liquid phases, solids/precipitates) and several simultaneously occurring equilibrium reactions. The aim is to solve the equilibrium composition of each phase. In equilibrium, temperature and pressure are same in all phases and the total Gibbs energy of the system has attained its minimum value.

Three approaches have been suggested for solving the governing equations. Two has been implemented to Flowbat and tested. In the future the third approach will be implemented as well.

5.3.7 Monitoring of emissions from CO_2 capture processes

When a new technology, as amine-based CO_2 capture plants (Figure 25) or geological storage facilities, is deployed on a large scale the risks have to be fully managed. If not, a promising or even good technology may encounter backlash and fall under social pressure, even if the problems would be solved later. Reliable measurement technologies are necessary for proving the maturity of the technology and develop the process to the safe level.

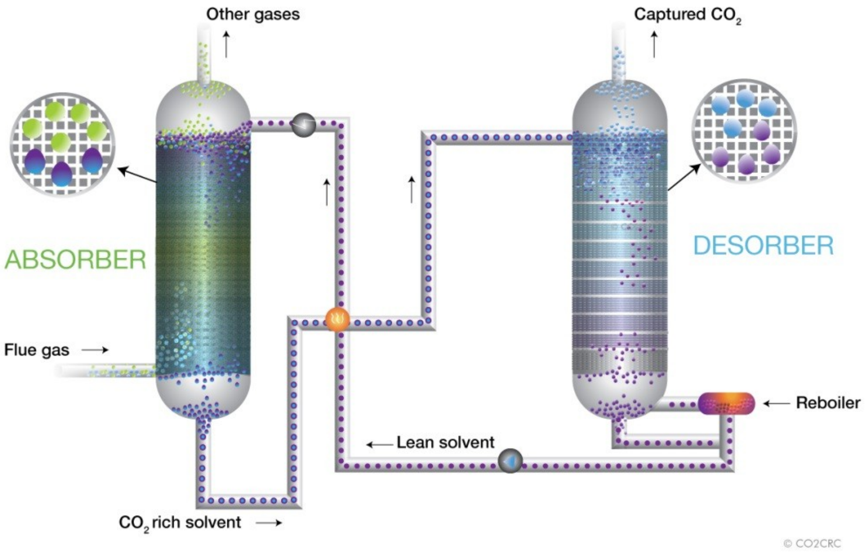


Figure 25. Principle of an amine based CO_2 capture process (Image by CO2CRC).

A carbon capture process is not enclosed (see, for instance, Figure 25), which means that the process causes emissions that will be dispersed into the environment. The amount and quality are related to the used capture technology, but also depending on how the process is implemented. Chilled ammonia and amine-based solvents are the most studied technologies and especially amines are proved to degrade in the process forming potentially harmful components, while ammonia processes produces mainly ammonia slip. As solvent amines are typically non-harmful the focus has been drawn into some selected degradation products, of which some, such as nitrosoamines, has proven to be carcinogenic.

In CCSP, Ramboll Finland Oy started studies related to emissions of ammonia and amine based processes. It was soon apparent that standard sampling or analysis methods for potential emission compounds from these processes were not available. N-nitrosoamines was found to be most significant compound group what comes to environmental issues from post combustion amine plant. The main focus has therefore been on developing robust and reliable N-nitrosoamine detection methods.

During the program several different analysis methods have been established. A couple of common CO_2 capture absorption solvents have been used as a synthetic matrix and methods have been developed accordingly. The main solvent in the tests has been monoethanolamine (MEA). Methods have been developed for several different matrices such as:

- Pure water representing drinking water
- Washer section water representing flue gas condensate and flue gas washing phase
- Solvents representing samples taken from the CO_2 capture solvent
- Absorption medium commercial cartridges, absorption liquids on flue gas sampling

In case of MEA one of these nitrosoamines is N-nitrosodiethanolamine (NDELA). It was observed, that NDELA is both important to analyse and difficult to be separated from the solvent matrix. Development of sampling and analytical methods was started for selected compound groups: alkylamines, solvent amines, nitrosoamines, aldehydes and ammonia. Key challenges were to develop methods allowing for separation of chemically similar compounds from each other and offering detection limits in the order of ng to µg per liter.

A method for the analysis of seven common nitrosoamines described in United States Environmental Protection Agency (EPA) method 521 (Munch & Bassett 2004) and an MEA matrix up to 30 per cent has been successfully developed. With sophisticated mass spectrometers, detection limits under 1 µg/l has been achieved. Finally, a partially working analysis method for the NDELA was establishedHowever, the method is totally different approach compared to the EPA 521 method, and after further development, the method was validated and accredited by FINAS (Finnish accreditation service) in 2015. The analysis methods were developed for all the matrices described above. Moreover, nitrozation prevention practises were established. In addition, methods were developed for 12 carbonyl compounds (mainly aldehydes). The methods are based on derivatization with DNPH. Methods for the selected alkylamines and MEA were also developed.

A prototype for the sampling train for flue gas sampling was established. Isokinetic sampling (sampling velocity the same as the flue gas velocity) should be applied due to high water concentration. Unfortunately, most of the compound groups need a different approach. Methods for the work hygienic purposes were also established for some compound groups.

In 2012, Ramboll established a Round-Robin comparison tests for four different international laboratories involved with analysis of emissions from CO_2 capture plants. The results showed that Ramboll has established methods which are relevant and comparable with the other laboratories in the field, but with lower detection limits. This has gained interest within foreign operators and designers working with CO_2 capture. Based on development and validation work done and round robin test arranged in CCSP, Ramboll got sufficient evidence for requesting accreditation for EPA 521 N-nitrosoamines measurement from CO_2 capture solvents, wash waters and flue gas samples. In the evaluation by FINAS the method was approved and Ramboll possesses now one of the first accreditations for this compound group from CCS-process samples in the world.

Based on the experience with the amine solvents, the analysis methods were modified and tested with the chilled ammonia capture process. After some modifications the methods can be easily applied to analysis of ammonia samples. The ammonia process is much easier what comes to degradation products as N-nitrosoamines or N-nitramines are not expected to be found from the different process streams in a wide extent.

Ramboll started working with some generic N-nitramines by modifying nitrosoamine methods and end up the procedure where sampling and analysis method for the N-nitramines is ready for use to amine and ammonia process samples. Ramboll also attended to a larger Round Robin comparison test with European laboratories to the actual samples and artificial taken from the Heidrun plant. A detailed results are presented at Energy procedia publication in 2015. The total N-nitramine method was evaluated, but it appeared to be unpractical as mercury was one the reagents.

Ramboll made a feasibility study of on-line monitoring instruments potentially applicable to measure emissions from carbon capture unit. There found three categories:

1. On-line monitors showing real-time concentrations of selected components
2. Automated sampling devices connected to analysers (e.g. process GC) analysing samples in selected intervals
3. Automated sample collectors

Two potentially applicable technologies are available for on-line monitoring: Fourier Transform Infrared (FTIR) and process MS-analysers. The challenge with FTIR is that IR-absorption spectrums between the different amines and ammonia are quite similar so the accurate calibration of analyser is important to perform. Mass spectrometers without pre-separation (like GC) may also suffer from interferences between different compounds with the same mass. The sensitivity of these technologies is suitable for solvent amines and some N-nitrosoamine precursors. However, detection limit for continuous N-nitrosoamine monitoring is too high.

Process GC with suitable application will lower the detection limit and selectivity is better than FTIR. The flip side is representativeness of the sample or response time.

Collective samplers are not commercially available but it may be possible to modify continuous PCDD/F-sampler for amine and even N-nitrosoamine applications.

Industrial stack emissions, other than carbon capture processes, are potential source of amines and degradation product to ambient air and environment. On a baseline surveys it has observed that near industrial areas secondary and tertiary amines and corresponding N-nitrosoamines are observed from the ambient air and natural waters in trace level concentration. For example, N-nitrosodimethylamine (NDMA) from malt has commonly monitored in Europe, where it is formed due to NO_x in ambient air. Sensitivity of current on-line monitors is mainly too high for the ambient air monitoring applications. One possible system is automated thermal sampler/desorption combined to GC-MSD. A detection limit for this system is still too high for the N-nitrosoamines, but applicable for the solvent amines. To analyse N-nitrosoamines from ambient air, Ramboll has started to develop “high volume diffusive sampler” which should be able to achieve enough target analyte for the subsequent concentration in laboratory followed with GC-HRMS analysis. One target of the development is to make sampler versatile also for other applications. One of the main challenges is how to verify sampling rate (diffusive coefficient) of the sample due to lack of standard atmospheres of unstable compounds.

In addition to potentially harmful components there are other components of interest in carbon capture process. Anionic degradation compounds and impurities in solvent are often referred as heat stable salts (HSS). These compounds have a significant effect on desorption efficiency of solvent in use.

Method for some anionic compounds (heat stable salts, HSS, as often referred) was established by ion chromatography. The main issue again is the matrix in solvent samples. IFP Energies nouvelles and E-On arranged Round Robin tests for selected components (formate, acetate, glycolate, oxalate, nitrate, sulphate) in 2015. Ramboll participated Round Robin test in very early phase of the method development. Unfortunately on that stage proper purification treatment was not finished and results were poor for some samples. Especially real process samples had very poor background. For the synthetic MEA based samples and background was relatively good, see the picture below:

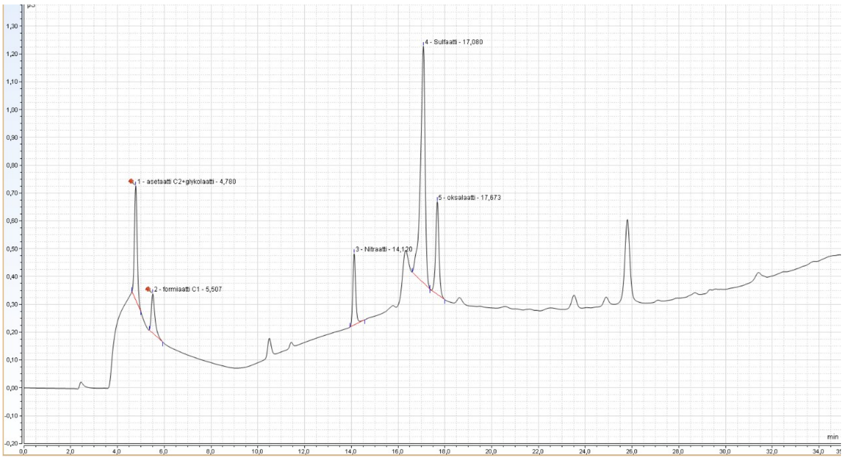


Figure 13. IC-chromatogram of HSS in synthetic matrix (5M lean MEA)

The need for the accurate CO_2 emission measurements from the outlet of the plant is recognized. The challenge is to acquire total uncertainty less than 2,5 % including concentration measurements of CO_2 and flow rate measurements. In Finland one power plant has ended to measure carbon emission on-line from flue gas. The importance of measurement will increase in the case where carbon dioxide is captured. Also existing power plants will benefit the flue gas-approach compared to analysis performed from the fuel, because the easiness of direct measurement. Unfortunately current calibration method in Finland is relatively demanding and alternative approach is under evaluation.

Ramboll performed parallel flow rate measurements with tracer based method to evaluate uncertainty of ISO 10780 method by a pitot tube in real circumstances. In addition, also concentration measurements of CO_2 according to SFS-EN 12039 were performed and compared to know CO_2 concentration produced by burning homogeneous fuel. Ramboll used several different analysers in test. The overall result is that difference of CO_2 emission between “high-tech” approach and typical emission measurement method is 1,5 % - 8,0 % from actual value.

5.4 Looping technologies

Chemical looping combustion is a process where oxygen separation is integrated to process itself, using a dual reactor system (Figure 26). The oxygen needed for combustion is fixed to metallic oxygen carrier in the air reactor, after which the solid oxygen carrier is transferred to the fuel reactor. Combustion – oxidation of fuel when oxygen carrier is reduced – happens at fuel reactor, resulting in an almost pure gas mixture of carbon dioxide and steam. The oxygen carrier is then returned to the air reactor for re-oxidation. This neglects need of air separation unit or post-combustion nitrogen separation.

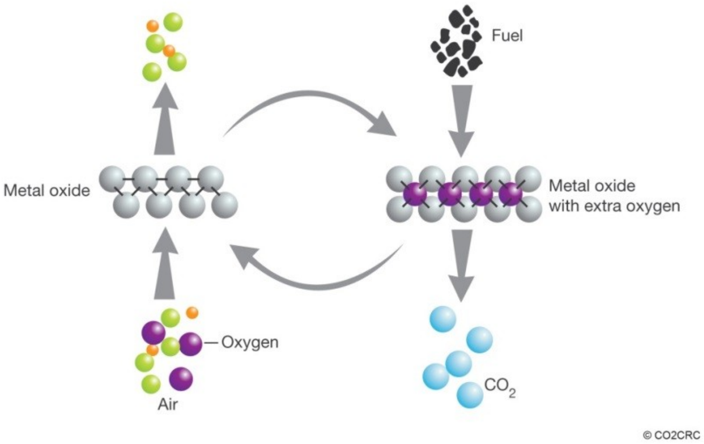


Figure 26. Principle of chemical looping combustion. The left part of the process takes place in the air reactor, while the right part of the process takes place in the fuel reactor (image by CO2CRC).

The potential of CLC in comparison to first generation carbon dioxide capture technologies is high. Ideally, the energy penalty of CLC is around 2.5%-units, which comes mainly from the CO_2 compression, which is low in comparison to the energy penalty for an air separation unit used in oxy-fuel combustion (approx. 7.5%-units).

CLC technology has potential to become a breakthrough CCS technology that would lower the energy penalties and decrease the overall costs of carbon capture. Technology development is still in an early phase after around ten years of research. CLC has been demonstrated in laboratory scale mainly with gaseous fuels. The possibility to apply the technology to solid fossil fuels and renewables (enabling negative CO_2 emissions) opens even a greater opportunity to be superior in cost of CO_2 capture and that promising R&D area is very new.

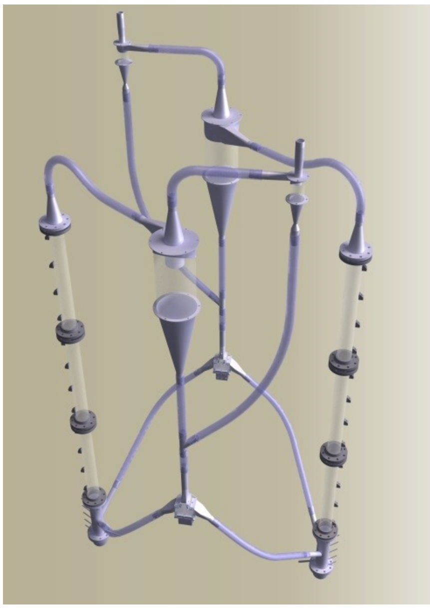


Figure 27. 3D rendered image of the equipment built for solid circulation and hydrodymanics testing at VTT (Tähtinen et al., 2012).

When moving from small scale to commercial unit, typical challenges involve aspects of both physical and chemical nature. Development of various modelling and simulation tools and validating them using experimental results from laboratory and process development unit (PDU)-scale work is essential for the design, optimization, and up-scaling of the CLC process. This is part of the work that was done in CCSP.

5.4.1 Test rig for testing of hydrodynamics

In order to allow control of the combustion process successfully, the ability to adjust and control the circulation of solid oxygen carrier material is important especially at partial loads. Therefore, laboratory equipment for studying CLC hydrodynamics, Figure 27 using a double exit loop-seal was constructed and hydrodynamic tests were performed (Tähtinen et al. 2012, D302 and D314).

Research shows that hydrodynamics and the handling of solids in the process are essential engineering problems to solve for development of the chemical looping combustion process. The cold model tests showed that the concept of two interconnected reactors with two double exit loop-seal can support solid circulation and is adjustable (D315). Results have been compared to similar reactor systems at other research facilities and at the literature. These results and conclusions support technical feasibility of the CLC process and concept. At hydrodynamics point of view it is suitable and connectable to following CCS processes.

5.4.2 Development of oxygen carrier synthesis and characterisation methods

Focus in oxygen carrier development can be divided in to two parts: firstly chemical oxygen carrying capacity and reaction rate, and secondly long time mechanical and chemical durability of the oxygen carriers. Some typical Fe_2O_3/Al_2O_3 and NiO/Al_2O_3 type oxygen carriers were synthetized and granulated. Used granulation methods were spray drying and mixer granulation. Also some Mn/Mg/O based oxygen carriers were prepared. Available spray dryer was found out not to be able to produce large enough granules to simulate actual sized fluidized bed reactor oxygen carriers. On the other hand reactivity and durability of the granulates can be tested with restrictions. Mixed granulated oxygen carriers with optimum granule size can be done but optimum, exactly round shape is not.

A test apparatus and procedure to characterize and tests the oxygen carriers was planned and constructed. The test procedure includes a series of chemical, mechanical and characterization tests both before and after chemical cycling. In this way the effect of repeated oxidation and reduction of the oxygen carrier granules can be found out. The chemical cycling can be done in larger laboratory size quantities compared to small sized samples in thermogravimeter. On the other hand large scale reactors are not needed. Basically pure chemical cycling effect can be separated from mechanical effect of fluidized bed and changes in mechanical properties and chemical properties can be detected.

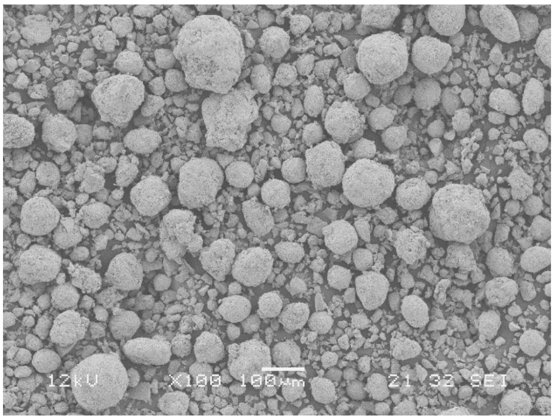


Figure 28. Fe_2O_3-Al_2O_3 oxygen carrier granules.

Construction and initial testing of the test apparatus has been finished and reported in D331 (Laboratory scale oxygen carrier characterisation - test rig design and test procedure). Reference test oxygen carriers of NiO-Al_2O_3 and Fe_2O_3-Al_2O_3 has been formulated, granulated and characterized. Particle size distribution, XRD, morphology, feed rate and crushing strength of the oxygen carriers has been tested. These NiO and Fe_2O_3 type oxygen carriers with Al_2O_3 base were tested in chemical cycling test apparatus. In sintering of the granulated the NiO-Al_2O_3 formed a spinel structure $NiAl_2O_4$, which was found out to not be reactive enough to be able to be reduced using the CH_4-CO_2 gas. In order to test the chemical cycling resistance of the NiO base OC free NiO should be available in the OC structure. This can be done using higher NiO fractions forming a NiO-$NiAl_2O_4$ structure in which NiO would be reactive and the spinel inert. On the other hand use of NiO as oxygen carrier has become rare due to its toxicity and price although it has high oxygen carrying capacity.

Fe_2O_3 type oxygen carriers were reactive enough to be reduced in the used process gas. 100 cycle tests with different setups were done. Also tests with only air with similar fluidization test duration were conducted. It was found out that with using repeated reduction and oxidation very fine particles was formed during the test and the particles coated the OC granules surface. In actual CLC process the fine particles will be removed from the bed and separated from the OC but the fines will be formed anyway. The degradation of the oxygen carrier by the chemical cycling was evident. During a 100 cycle test 10 % of the OC weight was lost with exhaust gas, even with very moderate fluidization gas flow rate and with some of the fine particles gathered on the surface of the OC granules. When the OC was fluidized with air for the same time the OC was basically intact, no fines were detected. This can be concluded to be clear evidence of chemical cycling induced degradation. As very fine particles are formed, instead of primary particles of the granules the degradation mechanisms seems to be surface dusting and not breakage of bonds between individual particles. Figure 29 presents Fe_2O_3 based oxygen carriers morphology after 24 h tests in air and in alternating (CH_4-CO_2)-air for 100 cycles. It can be seen that OC tested in air had original particles visible on the granule surface but chemically cycled OC is covered with very fine particles.

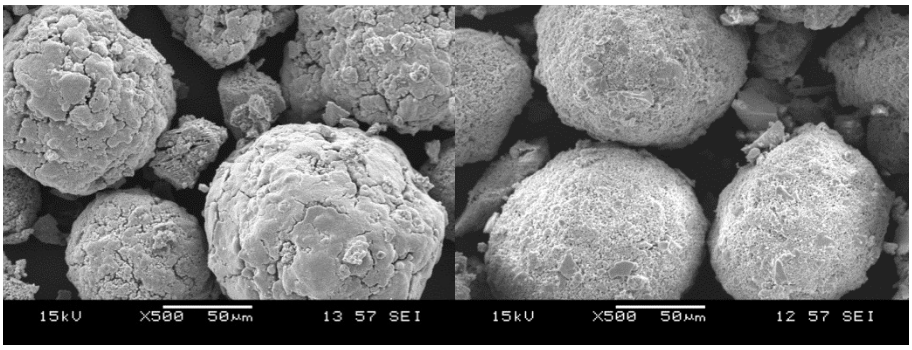


Figure 29. Oxygen carries morphology after 100 reducing oxidising cycles (on left) and after 24 h fluidization in air (on right)

Iron oxide based oxygen carriers are potential for CLC because of their low price and availability as natural minerals. The minerals may not need any expensive processing prior usage. On the other hand oxygen carrying capacity for iron oxide is low. Also, at least the composition and preparation process based structure of the OC tested here seems to have low durability against repeated reduction and oxidation. According to general iron oxide properties (especially hematite Fe_2O_3) its high temperature resistance and cyclic reduction-oxidation resistance may not be as good many other oxides like Al_2O_3, Cr_3O_2 and also even NiO. Especially Fe_2O_3 tend to form porous and poorly protective scales on metal, this phenomenon may be the basic cause for low durability here also.

A second batch of NiO based oxygen carrier was produced with a composition of 70 %NiO/and 30 % Al_2O_3. This composition was chosen in order to have a 50 wt. % NiO – 50 wt.% $NiAl_2O_4$ type structure for better reactivity. Similar preparation schedule was used as with the other NiO OC. NiO-$NiAl_2O_4$ oxygen carrier was reduced in the fluidized bed. It was found out that the NiO was mostly reduced to Ni but some of it was left as NiO. Figure 30 presents SEM pictures of the as-sintered (untested), and 100 x tested samples. Morphology (granule shape and size) was quite unchanged. On the other hand in it can be seen that fragmentation of NiO has occurred. The fragmentation can cause firstly increased reactivity but also disintegration of small particles from the granules. Smaller particle size increases the reactivity due to higher surface area but also by lower needed penetration depth of reactants O_2 and CH_4 and smaller diffusion distances of Ni. At the start all particles are attached to neighboring particle due to high sintering temperature. The disintegration may occur as fragmented particles are no longer as well attached to each other, because the temperature of 800 ºC is not enough to cause sintering effect. The small particles can be carried away by the gas flow, higher make up is needed and reactivity lost.

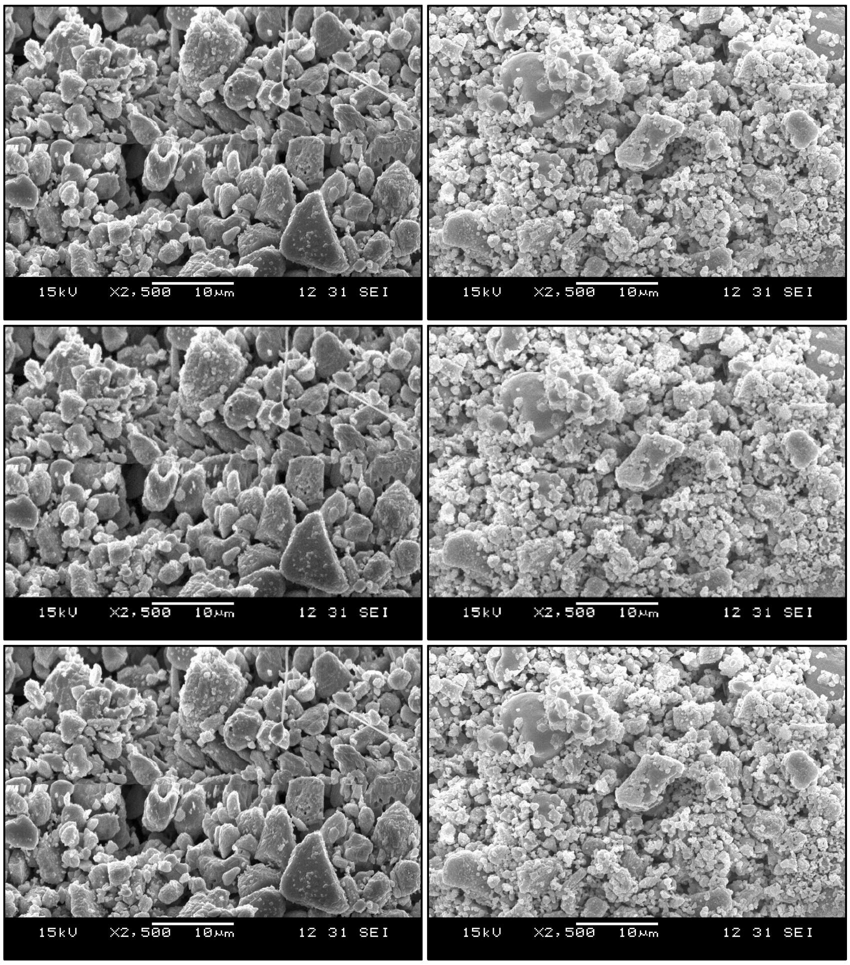


Figure 30. NiO/NiAl2O4 OC as sintered left, after 100x cycle’s right.

In testing of Ilmenite as OC it was noticed that somewhat heavier degradation of the material was evident than with Fe_2O_3 or NiO OC`s. Fine particle formation was heavier, which can cause OC make up need to increase and potential clocking problems. The typical increase in reactivity of Ilmenite based OC can be explained by the generation of fine particles and subsequent increase of specific surface area. The same tendency was noticed both in laboratory fluidization tests and preliminary bio-CLC tests. Also noteworthy is that mild fluidization with chemical (oxidation-reduction) cycling is enough to cause near the same effect as mechanically heavier bi-CLC test.

As a conclusion it can be said that it is possible to study oxygen carrier's chemical cycling stability using the constructed equipment. Iron and nickel oxide based OC were tested for 100 cycles of reduction and oxidation. Tests to evaluate other type OC degradation are recommended. Full report on results of the oxygen carrier tests is reported in D344 (Characterization of oxygen carrier's performance – procedures and results).

5.4.3 Bio-CLC

CLC technology applied for solid fuels works best with fuels having high reactivity and low ash content, characteristic, which are typical for domestic biomass fuels. In addition, CLC shows promise as a future combustion technology even without CCS or with very low CO_2 emission costs. It is expected that high-temperature corrosion problems can be significantly reduced in bio-CLC as compared to conventional biomass. This is because heat will be extracted mainly in the exothermic air reactor, in which there will be no alkali compounds present and very little fly ash. This should allow the use of improved steam data compared to conventional biomass combustion and improved efficiency for power generation.

In terms of CCS, CLC has one of the lowest efficiency losses of piloted capture technologies. Negative emissions combined with high efficiency lead to higher utilisation rate and thus significantly improved economic feasibility in comparison to other CCS technologies, especially in the future energy markets including increased share of intermittent renewables. So far, bio-CLC has only been tested at laboratory or small pilot scale at few places.

The main objective, originally set out in the research plan of CCSP, was to develop technologies and concepts for CCS deployment leading to industry pilots and demonstrations by the end of the program. In 2013 the research had advanced in CCSP program to the stage that a hot test rig for chemical looping combustion could be designed. Unfortunately, the needed investment was close to 1 M€, which was too expensive for inclusion in the program and the plans had to be abandoned. In late 2014 a new opportunity arised: a 200 kW dual fluidized bed (DFB) gasifier is currently being installed at Bioruukki, VTT's new test centre, and could be modified with relatively little expenses to work as a CLC process development unit (PDU) for low-ash fuels (Figure 31). This would enable CCSP to reach its original targets for enabling piloting of CO_2 capture technologies.

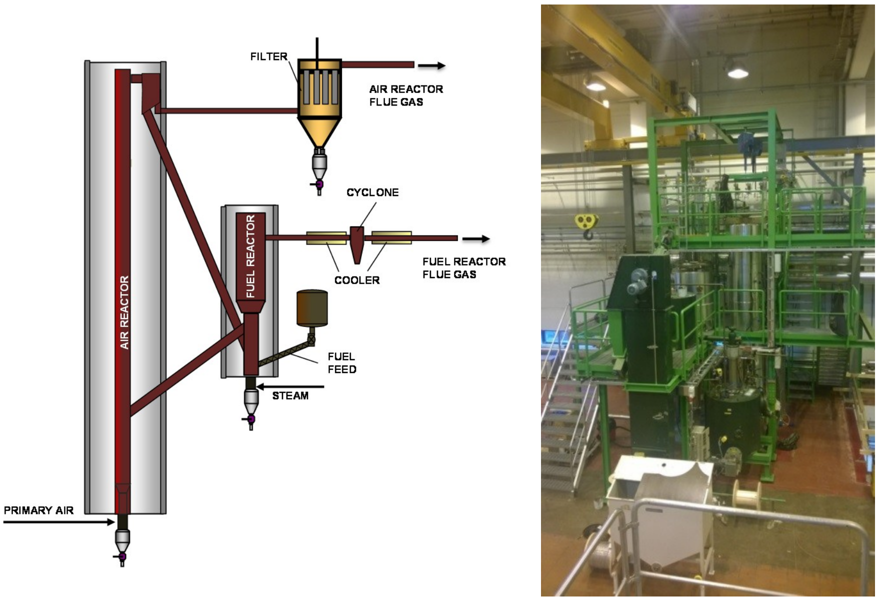


Figure 31. Bio-CLC PDU in Bioruukki, VTT, Espoo.

The required modification works for bio-CLC PDU were ready on January, 2016, and hot commissioning tests were carried out during a following month. The actual test campaign was successfully carried out on April, 2016.

Ilmenite was used as oxygen carrier and the test matrix contained totally 9 test points (16 hours); 3 tests with white wood pellets and 6 tests with heat treated (black) wood pellets as fuels. Stable and controllable operation was achieved, but the temperature in the fuel reactor was some 50°C lower than the targeted temperature (900°C). Due to the low temperature, the fuel conversion to CO_2 remained relatively low, about 70%, and lot of incompletely oxidized C_xH_y and tars were detected from fuel reactor flue gases. The oxygen demand varied between 29…41 % and carbon capture efficiency 83…96 %. Test matrix with varied parameters and key indicators is in Table 10.

During the test campaign very little degradation of the ilmenite was observed. However, it was observed that if poorly fluidized there is a risk for formation of ilmenite agglomerates.

As the fuel is fed and gasified in the fuel reactor, fuel leakage to the air reactor was low and alkaline components were not accumulated to the surface of oxygen carrier particles, it can be concluded that concentrations of vaporized alkali chlorides components in air reactor flue gas are much lower than in conventional biomass combustion applications. The results indicate that the risk of high-temperature corrosion of super heater tubes is lower in bio-CLC than conventional biomass combustion, making it possible to to use higher steam values (temperature, pressure) in bio-CLC improving the power generation efficiency from biomass. Although these results indicate a clear benefit of bio-CLC over conventional biomass combustion, this phenomenon needs to be studied in more detail and by longer tests for verification. The results of bio-CLC PDU tests are reported in D334.

Table 10. Test matrix with two main key indicators.

			Fuel reactor			Air reactor		Key indicators	
Test #	Fuel type	Duration min	Fuel kW	H2O m/s	Bed ºC	Air m/s	Bed ºC	Oxygen demand %	Carbon capture eff. %
1	VAPO white pellet	15	14	0.23	840	5.2	864	34	96
2		10	14	0.12	852	5.2	865	41	93
3		15	14	0.17	848	7.3	847	32	95
4	Arba-flame black pellet	20	15	0.23	845	5.2	869	32	94
5		10	15	0.12	863	5.2	875	38	92
6		25	22	0.17	848	6.0	878	34	88
7		20	19	0.17	852	7.4	868	30	83
8		40	9	0.12	860	7.4	862	29	86
9		15	19	0.12	851	6.5	872	31	87

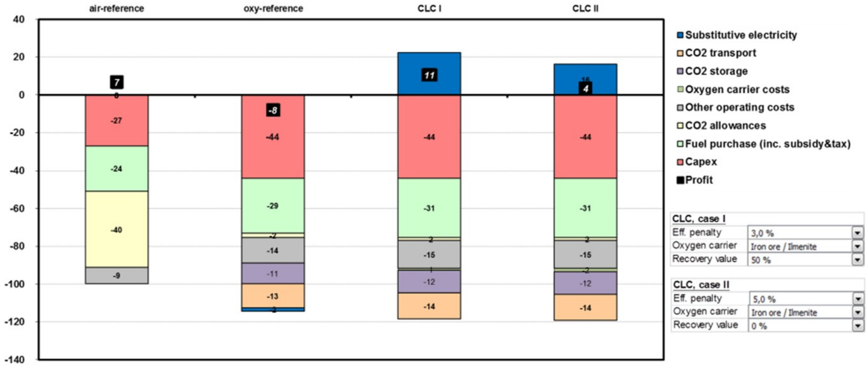
5.4.4 Oxygen carrier cost in power plant operation and investment

Power plant investment feasibility can be divided to capital and operational costs. For chemical looping combustion discussion of oxygen carrier costs at operation have been under discussion. Calculation and analysis show that oxygen carrier related operation costs have small effect to the overall feasibility when part of oxygen carrier economic value is recovered (Tähtinen et al. 2014).

In Figure 32 it can be seen that the feasibility of chemical looping combustion power plant investment does not significantly depend on oxygen carrier based costs if recovery rate is moderate. This can be reached by highly attrition resistant synthetically manufactured oxygen carrier or with ore based, cheap but more fragile oxygen carrier. In both cases there are different business models which can be used.

When higher proportion of value recovery is used, oxygen carrier price or inventory are not so significant factors in terms of overall operational expenditures of power plant. For example, if moderate value recovery of 50% is assumed, oxygen carrier related costs are typically 1-10 M€/a for studied 500 MW_{fuel} coal fired CLC power plant, depending on lifetime, inventory and price of oxygen carriers. Per captured CO_2 ton, costs related to oxygen carriers corresponds about 3 €/tCO_2 by default values. For gaseous fuels, oxygen carrier related costs are even smaller. Three different business operational models have been presented. First option is, buy and sell –model, where vendor sells fresh oxygen carriers to the power plant and power plant sells used oxygen carrier to vendor or third party. Second option is where oxygen carrier is rented from supplier and costs are more easily predicted. Disadvantage of this option is dependency to the supplier. Third option is that

CLC power plant works as preparation facility and used oxygen carrier is product. This kind of applications may be found mining and steel industry.



CLC, case I
Eff. penalty: 3,0 %
Oxygen carrier: Iron ore / Ilmenite
Recovery value: 50 %

CLC, case II
Eff. penalty: 5,0 %
Oxygen carrier: Iron ore / Ilmenite
Recovery value: 0 %

Figure 32. Annual operating costs and overall profits of compared technologies.

5.4.5 Modelling of chemical looping processes

Two simulation tools were developed: (1) one-dimensional dynamic model aimed at investigations of gaseous/solid fuel chemical looping processes in a system of two interconnected fluidized bed reactors and (2) a combined CLC–steam power plant model for predictions of the overall plant efficiency.

5.4.5.1 Chemical looping combustion of gaseous fuels

The one-dimensional model for gaseous fuel CLC was successfully validated based on the data obtained from the operation of a 120 kW_{th} CLC pilot unit located at Vienna University of Technology (Peltola et al., 2013a). Good agreement was observed between the experiments and simulations, and the model structure and submodel forms turned out to be appropriate to describe the studied process.

A scale-up study of the gaseous fuel CLC process was conducted (Peltola et al., 2013b). As a result, an operational design for a CLC reactor system at a pre-commercial scale of 100 MW_{th} was obtained. Certain scale-up criteria were followed for determining the design parameters, and the validated 1-D model was used to assess the performance of the system. The integration of the reactor system with a steam turbine cycle for power production was studied resulting in a suggested plant layout including a CLC boiler system, a simple heat recovery setup, and an integrated steam cycle with a three pressure level steam turbine. A flow sheet model for the plant was set up for efficiency calculations. The compression of CO_2 would reduce the efficiency by about 2 %-points, and taking this reduction into account, the calculated CLC efficiency was found similar to that currently achievable by a modern steam power plant, which does not include energy penalty for CO_2 capture.

A transient Eulerian two-phase CFD model applying the kinetic theory of granular flow was used to simulate two pilot-scale test balances in a CLC fuel reactor fed with methane and a nickel-based oxygen carrier (Vepsäläinen et al., 2013). The kinetic reaction rate coefficient for the oxygen carrier was defined based on the measured total methane conversion, and correspondence with the experimental data was found. The bed Sherwood numbers were derived based on the CFD simulations. The derived Sh_{bed} corresponds to the in-literature presented data and explains the commonly faced problem of obtaining different chemical kinetic coefficients from TGA and bench-scale fluidized bed reactor tests.

5.4.5.2 In-situ gasification-chemical looping combustion (iG-CLC) of solid fuels

In iG-CLC, solid fuel is physically mixed with the oxygen carrier in the fuel reactor. Steam and/or CO_2 are supplied both as fluidizing and gasifying agents. The oxygen carrier reacts with the volatiles and the gaseous products from char gasification, where H_2 and CO are the main components. The gasification of the char generated after the solid fuel devolatilization has been found to be the controlling step of the iG-CLC process.

A 1-D bubbling fluidized bed (BFB) model for the simulation of an iG-CLC fuel reactor has been developed (D357). The model is based on the existing CLC model frame and it considers BFB hydrodynamics coupled with a relevant reaction scheme, as well as heat transfer within the reactor. Preliminary validation of the model was conducted based on the operation of VTT's new 10–50 kW_{th} bio-CLC pilot unit.

5.4.5.3 Chemical looping combustion of solid fuels with oxygen uncoupling (CLOU)

Among the materials suggested for use in chemical looping, copper oxide has attracted significant attention. Materials such as copper oxide allow the direct combustion of solid fuels, without an intermediary gasification step, by spontaneously decomposing from cupric oxide (CuO) to cuprous oxide (Cu_2O), liberating free oxygen in the process.

A CLOU process scheme with medium volatile bituminous coal as fuel and silica-supported CuO as the oxygen carrier has been investigated (Peltola et al., 2014a). The basic relations between the relevant process parameters were quantified via mass, energy, and exergy balance analysis. The work also includes the estimation of various design and operational parameters, thermal considerations, and evaluation of the overall performance.

In order to simulate CLOU of solid fuels, the existing 1-D model frame was augmented with appropriate descriptions for the physical phenomena specific to the process (Peltola et al., 2014b). Then, the performance of a 500 MW_{th} CLOU fuel reactor fed with bituminous coal and a TiO_2-supported CuO oxygen carrier was evaluated (Peltola et al, 2015a). A reference case was first defined and simulated, after which the effect of various process parameters on the results was assessed by parameter variations. For the reference case conditions with a temperature of 960 °C and solids inventory of 400 kg/MW_f in the reactor, a CO_2 capture efficiency of approximately 90% was predicted. A CO_2 capture efficiency of 95% could be reached by optimizing the operating conditions. It was shown that with low-reactive coals, an intermediate carbon separation unit is required to obtain a feasible CO_2 capture rate.

An investigation on feasible solids flow arrangements in a dual fluidized bed reactor system for CLOU with a copper-based oxygen carrier has been performed (Peltola, 2015c). In the simulations, gas velocities between 5–6 m/s, bed pressure drops between 5–20 kPa, and solids circulation rates between 8–29 $kg/(m^2s)$ were considered. The hydrodynamic operating range of the system was found feasible, and compared to current CFB boilers, the maximum circulation rates were not exceeded.

The integration of a copper-based CLOU process in a large-scale (1500 MWth) coal power plant based on ultra-supercritical (USC) steam cycle (270/60 bar, 600/620 °C) has been investigated (Peltola et al., 2015b; Spinelli et al., 2016). The power plant comprised three sections: (i) chemical island in which the oxygen carrier oxidation/reduction takes place, (ii) power island made of the USC steam cycle, and (iii) CO_2 compression/liquefaction section. The core of the plant – the chemical island – included an air reactor, fuel reactor and a carbon stripper unit. The air and the fuel reactor were designed as circulating fluidized beds and the intermediate carbon stripper as a bubbling fluidized bed. The performance of the proposed reactor configuration was evaluated by the LUT 1-D model and the overall power plant performance was computed with the Politecnico di Milano GS® code, a modular code widely used to assess a number of complex energy systems. A comprehensive sensitivity analysis of the main process parameters, namely, reactor temperature, solids inventory, flue gas recycle to the fuel reactor and carbon stripper efficiency, was performed. The total performance of the plant was evaluated based on the net electric efficiency of the power plant and CO_2 avoided. The CLOU process assessed facilitated a highly competitive performance with a benchmark oxyfuel combustion technology. For the selected base case, a net electric efficiency of 42.0% (2.5 percentage points less than a reference plant without capture) and CO_2 avoided of 95.8% was calculated, which justifies R&D activities for this technology.

5.4.6 Calcium looping process

Post-combustion calcium looping (CaL) was first introduced by Shimizu et al. (1999). This technique can capture CO_2 and SO_2 from static sources by utilizing a twin fluidized bed system. Flue gas from a stationary source is processed in a fluidized bed reactor, known as the carbonator. The carbonator captures CO_2 and SO_2 from the flue gas to solid calcium oxide at around 650 ºC. This forms calcium carbonate and calcium sulphate, $CaCO_3$ and $CaSO_4$, which are then transferred to a fluidized bed regenerator, known as the calciner. The calciner regenerates the carbonate back to calcium oxide at around 920-950 ºC. The regenerated calcium oxide is returned to the carbonator where it resumes capturing CO_2 from the flue gases. The formed calcium sulphate is stable in the loop and will accumulate to the system unless fresh calcium carbonate is fed to the system and the used sorbent is removed at a steady rate. The temperature difference between the reactors can be achieved by many means, burning suitable fuels in the calciner in an atmosphere of oxygen and recirculation gas or from external heat sources. This forms a highly concentrated CO_2 gas flow which can be compressed and transported to a storage site after steam and oxygen removal. As a result of solid fuel combustion, ash accumulates in the system which increases the need of solid purging from the loop. The general layout of the calcium loop is presented in Figure 33 (Ylätalo, J., 2013).

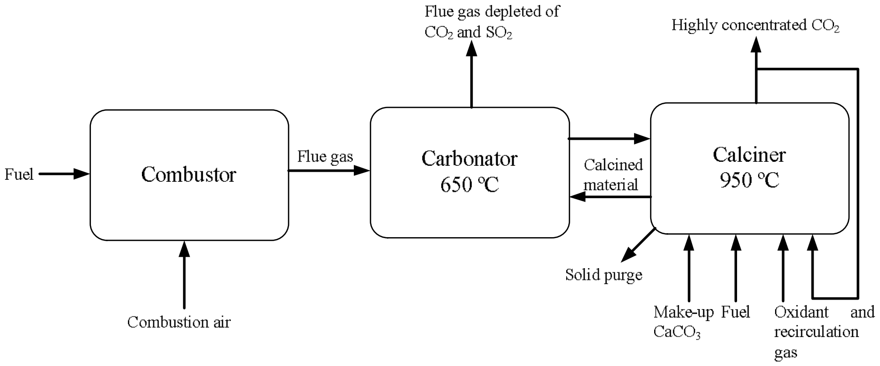


Figure 33. Concept of the calcium looping process (Ylätalo, J. 2013).

One of the biggest challenges of the CaL process is the decrease of carrying capacity over carbonation and calcination cycles. That is why it is important to understand this phenomenon and model it accurately. Natural lime subjected to cyclic carbonation and calcination undergoes a radical change in physical and chemical properties. At LUT the models for the time dependent CO_2 carrying capacities were developed. The CO_2 carrying capacity describes the ability of lime material to receive and release CO_2 in the cyclic calcium looping process. Two different approaches were created that both can be implemented to the dynamic 1D calcium looping model framework. Earlier experimental work from different research groups on the aging of lime material was implemented to framework and continuum equations were written and solved for the different age fractions. Detailed report of the results is published in deliverable report (D337).

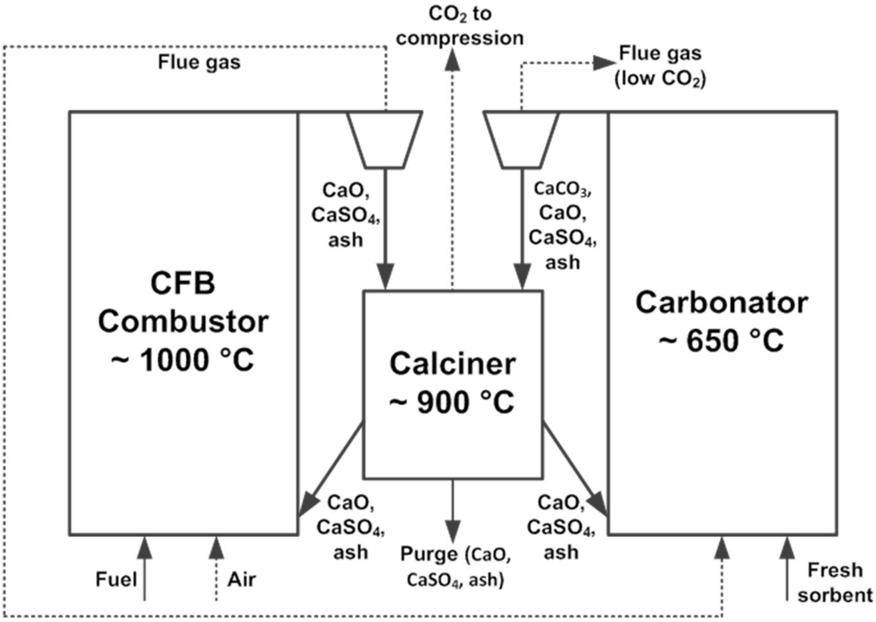


Figure 34. Concept of the calcium looping with sorbent heat carrier (Martínez et al. 2011).

Also scale up and parameter study of the CaL process was conducted at LUT. The reactors of the calcium looping system were dimensioned using initial calculations from a 0D-model and the dimensions and boundary conditions were implemented to the 1D calcium looping model framework. The 1D model framework was used to design heat transfer in the system, optimize solid mass flows between reactors, evaluate design point performance and produce 1D-profiles of process parameters from the reactors. The calcium looping system was also analyzed in partial flue gas loads where the flexibility of the system was studied. The main results of this study have been published in Ylätalo et al. (2014) and in the deliverable report (D338). To support model development cold model tests were conducted for calcium based materials to study hydrodynamic fluidization properties. The results were published in deliverable report (D348).

The CaL process model was used to study two different commercial scale power plants. The 1D CaL reactor model developed at LUT was integrated to steam power process model Solvo. The study was accomplished together with Fortum. The cases included CHP and condensing power plants with fuel mixtures containing different shares of biomass and coal (Parkkinen et al., 2015a). For CHP plant net efficiency of 93.9 $\%_{LHV}$ was achieved with CO_2 capture efficiency of 91.1 %. Results were utilized for comparing feasibility of different capture technologies, such as oxycombustion, CLC and CaL (D360).

Next phase in CaL study was to study advanced CaL process, which utilises solid heat carrier for providing heat into the calciner, Figure 34. In this concept, suggested by Martínez et al. (2011), energy penalty due to oxygen production will be avoided. Feasibility of the concept was studied by mass and energy balance analysis and rough dimensioning of a large scale plant was conducted (Parkkinen et al., 2015b). Carbonation conversion in the carbonator and temperature difference between the combustor and the calciner were selected as studied parameters. The results shows that reasonable conversion degree (around 0.22) is enough to minimize the solid material flow to calciner i.e. the heat demand in calciner. Increasing temperature difference between the combustor and the calciner reduces material flow to the calciner significantly but very high temperatures might have effect on sorbent behaviour. Further improvement for the concept was introduced, where advanced solid separation technologies are applied to separate active large particles from inactive small particles and effect of particle segregation efficiency was studied (D359). Results were promising for the process but many challenges in large scale operation exists and more studies with more sophisticated models have to be done.

To summarise research needs and the state of the art of CaL process modelling an extensive review article was published in cooperation between CCSP researchers (LUT) and Italian (Politecnico di Milano) and Spanish (CSIC) research groups (Martínez et al., 2016).

6. Transportation of CO_2

Although considered a commercially mature technology, CO_2 transportation issues are receiving more attention now as Europe aims to implement its first wave of CCS demonstrations. CO_2 transport networks will go through an intense risk assessment and permitting processes considering the environmental and public health issues, and finally the costs of CO_2 transport will have to be managed effectively as well. Ship transport of CO_2 is still without legal framework under the emission trading scheme, and although pipelines do have one, the European industry does not have experience on large pipelines operating in the high pressure required by CO_2 transportation. Assuming the technical and regulatory issues are solved, the form of the CO_2 transport infrastructure will have an impact on the price range of transportation from capture facilities around Europe, and likely an impact as well on where CCS can or will be implemented. According to the current knowledge, Finland is without any own geological formations suitable for long term CO_2 storage. Therefore, logistics and transportation of the captured CO_2 to foreign storage sites is a central element of all domestic CCS concepts.

Considering on-shore potential for storage of CO_2, suitable geology can be found within the north-eastern Benelux countries Belgium and Holland (GeoCapacity 2009a). The highest on-shore potential seems to be situated in North Germany, south-east from Hamburg and Lübeck. The potential on-shore storage areas closest to Finland are in western Latvia. Beyond EEA, great amount of on-shore storage potential are situated in East Ukraine and West Russia. The most potential off-shore storage areas are on the North Sea between Scotland and Norway and also near the east shores of England. In general, the North Sea and parts of the Norwegian Sea are abundant with potential storage sites. Some off-shore storage potential may also exist in the southern parts of the Baltic Sea (see also section 6).

The European Environment Agency (EEA) releases regular updates to the CO_2 emission point sources containing E-PRTR data. The database covering the industrial emissions for 2007 - 2010 is used as the basis of transport system analysis within this study. The emission release database covers facilities from food and beverage sector, chemical industry, energy industries and energy production, mineral industry, paper and wood processing, production and processing of metals and waste and waste water management. Emissions from the industrial sectors not included in the above are classified as other activities. The CO_2 emission release map over the Nordic countries was updated in CCSP and is presented in Figure 35. Finland has numerous large point sources, which are mainly located in coastal areas.

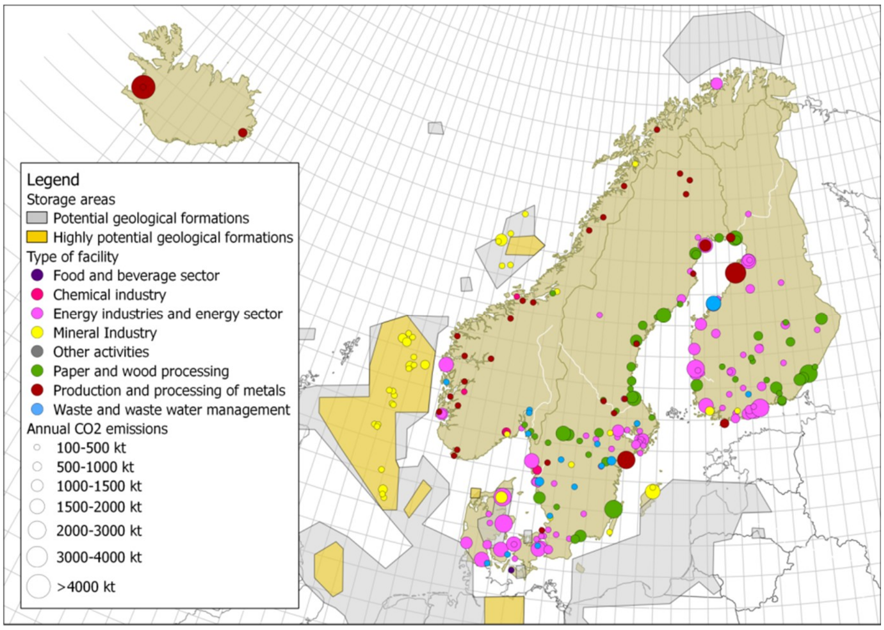


Figure 35. CO_2 emission sources (data from 2010) and potential geological formations for storage of CO2 in the Nordic Countries. Map constructed by L. Kujanpää, VTT, using data from EEA & EU GeoCapacity .

Both pipelines and ships should be considered as possible CO_2 transport options for the Finnish power producers and the industry. Mainly coastal emission sources and long transport distances can favour ship transport over pipeline transport. However, pipelines would likely be used for collection of CO_2 into centralised export terminals to gain the benefits from the economy of scale. Large trunklines from capture plants to the geological storage areas could also be viable options from at least selected regions of Finland.

The research goal in CCSP on CO_2 transport was therefore to generate scenarios and transportation cost estimates on future CCS infrastructure in North Europe, covering both transportation technologies. The possibility to use underground intermediate storage facilities as part of a transportation infrastructure was also studied. The research was conducted from a Finnish point-of-view, since corresponding studies typically view transportation on a global or EU-wide scale.

6.1 North European infrastructure for transporting CO_2 in 2050

A CO_2 transport cost estimation methodology was created and used in assessing the transport costs in four North Europe-wide infrastructure scenarios for year 2050 (D411). For the cost estimation methodology, a set of transport cost equations were generated by fitting a surface to the lowest-cost results for a range of transport distances and annually transported CO_2 amounts. The infrastructure scenarios differed by the weighing between pipeline and ship transport modes and the selection between available storage areas. The scenario results are given in Figure 36. Scenario 1, named “Independent actors”, depicts a situation where closely situated CO_2 capture sites do not engage in joint transport infrastructures. This leads to ships being chosen as the preferred transport modes due to easier implementation and lower investment cost. Scenario 2, the “Areal co-operation” scenario, explores the benefits following from a larger CO_2 flow per transport route and from a shared infrastructure using trunklines. Scenario 3, “Beyond EEA infrastructure” is essentially similar to Scenario 2 with the exception that geological storage outside the EEA is allowed. Finally, Scenario 4, the “Masterminded infrastructure” scenario, tries to sum up the best of the previous scenarios without restrictions concerning on-shore storage.

The scenarios clearly indicated that a shared CO_2 transport infrastructure is in general superior compared to independent transport projects by single CO_2 emitters. The transport cost of CO_2 from Finland to geological storage sites abroad includes a cost penalty compared to the coastal regions in countries around the North Sea. However, by joint transport infrastructure projects the industry and power production around the presented regions can reach significant cost reductions. The ship transport infrastructure benefits from a model where nearby capture plants are connected by pipelines to exporting terminal hubs. The transport cost for an in-land capture plant operator is quite sensitive to the pipeline distance, however.

Co-operation enables more economic transport of CO_2 for smaller capture facility operators. This results by default into heavier emission mitigation impact of the CCS implementation. As an example, a trunkline connecting all CO_2 point sources of over 0.5 Mt/a in the northern Bay of Bothnia to the Norwegian Sea seems to result in competitive costs for all involved parties and in significantly larger annually stored CO_2 volumes than in the case when only few larger plant operators would engage in CO_2 capture and ship transport.

Heavily industrialized areas around North Sea would benefit from a shared pipeline infrastructure. CO_2 could be economically collected by trunklines to the coast, from where large-capacity off-shore pipelines would take the CO_2 to the off-shore storage areas. Shipping would seem a viable option from the northern parts of United Kingdom, northern France and the Nordics, however.

Considering the results from the scenario where on-shore storage would be allowed outside the limits of EEA, the massive trunklines from Finland and the Baltics to Russia seemed uneconomical. Trunklines from southern Baltics and Poland to Ukraine resulted in more promising cost levels, although the costs seemed high towards the upstream of the trunklines. Such joint pipelines would however have a great CO_2 emission abatement impact.

Enabling the use of the on-shore storage potential in Latvia and Germany would result in interesting trunkline option for Finland and the Baltics. Also the resulting pipeline collection network from the German industries would seem one of the most economic transport networks of CO_2 in the North Europe. Finally, if geological storage potential in the southern Baltic Sea would be used, ship transport cost from the surrounding coasts would be reduced considerably.

The results indicate that ship transportation would often be the best transport option from the Baltic Sea region to final storage sites at the North Sea. Increasing the CO_2 transportation capacity of a ship terminal can lower the transportation cost due to a benefit from scale.

Any mature CO_2 storage potential at the Southern Baltic Sea could enable considerable reductions of transportation cost by ships from Finland. However, as part of the CO_2 storage potential lies outside the European Economic Area (EEA) it could pose some additional challenges, as EU's current legislation requires the storage capacity to be inside the EEA.

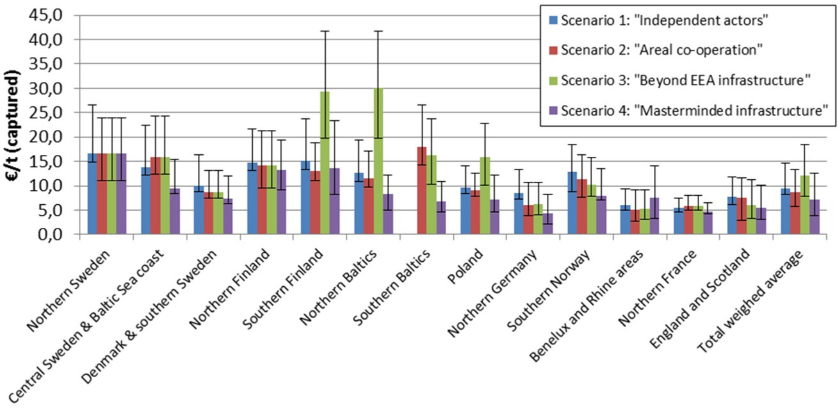


Figure 36. Scenario results on transport costs of CO_2 from capture plants in North Europe.

Uncertainty of the transportation cost results was assessed with Monte Carlo simulation. The results showed considerable variance throughout the range of distances and transport capacities in the study. In Figure 37, an example of transportation costs at 95 % confidence is presented for a 1 000 km pipeline and ship route of 5 $MtCO_2/a$ capacity.

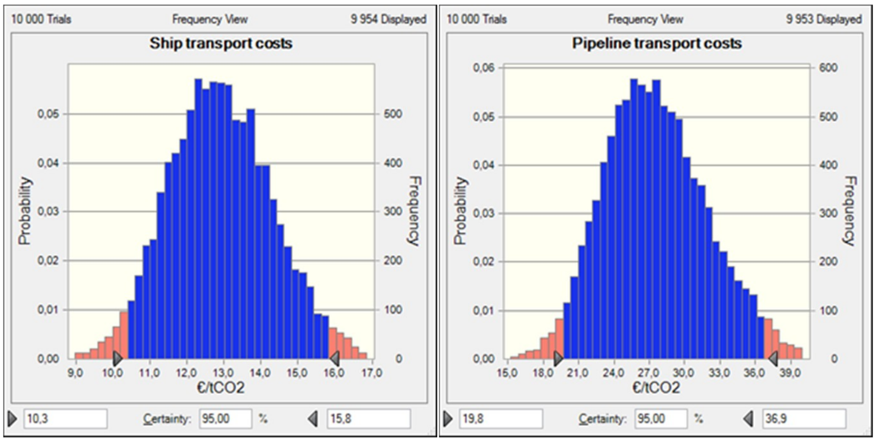


Figure 37. Probability distributions for ship and pipeline transport costs of CO_2. Transport distance is 1 000 km with a capacity of 5 $MtCO_2$/a.

In general, pipeline transportation cost of CO_2 is most sensitive to the capital costs (Figure 38). The interest rate assumptions are having a high impact on the results on both transport modes. The ship fuel price is the most significant model parameter determining the ship transportation costs of CO_2 in the example scale. Regarding both ship and pipeline transportation costs, the parameter values depending somewhat on modeller's preferences, namely interest rates and economic and operating lives, seem to have a high impact among the top 10 most influential model parameters. Due to the considerable variance, contributed strongly by the basic economic assumptions, of cost results, the generation of a further route optimisation model does not seem sensible. The scenario analysis deployed in the work therefore would seem to provide better view on the transport costs and trade-offs between the route options. The uncertain future of the emission point sources and geological storage sites also speak against a route optimisation model for source and sink matching. As such, this study provides new grounds for assessing the position of Finland in the future of North European CO_2 transport infrastructure. Results map the competitiveness of CCS between the regions based on transportation costs, and give ideas on what kind of co-operation would result in a more cost-efficient infrastructure. The scenarios of CO_2 transportation networks are meant to have value both in the design for economic reasonability and in the selection of strategy for CO_2 transportation on corporate or public level.

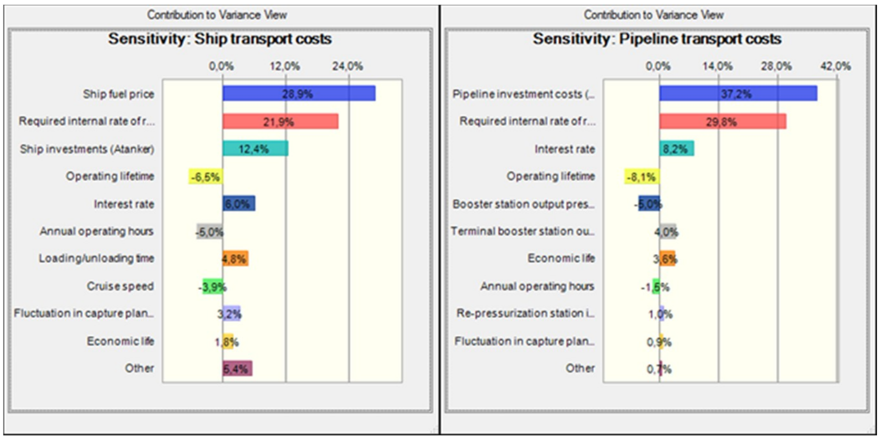


Figure 38. Model parameter contribution to variance in ship and pipeline transportation costs of CO_2. Transport distance is 1 000 km with a capacity of 5 $MtCO_2$/a.

6.2 Terminals and intermediate storage of CO_2

Transporting CO_2 from Finland by ships would require a terminal infrastructure, where the CO_2 is collected into intermediate storages from single or several capture facilities. The main process equipment at a harbour terminal functionally connected to CO_2 transportation are liquefaction plant, intermediate storage facilities and loading equipment. Excluding the costs of harbour infrastructure, the CO_2 conditioning and liquefaction facility and intermediate storage have the highest investment costs among the stationary installations of a CO_2 ship transportation system. The input pressure of CO_2 to the liquefaction process has a high impact on the investment costs. Based on investment costs reported by Metz et al. (2005) and Skagestad et al. (2014), the investment costs of the liquefaction facility amount to 5-20 M€/$MtCO_2a^{-1}$ when CO_2 is obtained at a pipeline transport pressure.

After liquefaction, the CO_2 is stored temporarily at the terminal before loading into a ship. Above-ground intermediate storage facilities take a considerable share of the terminal land surface area. A cylindrical steel tank storage configuration proposed by Statoil & Kinder-Morgan (2003) would take about 0,5 ha per 10 000 m^3 capacity. Alternative options for above-ground intermediate CO_2 storages are underground cavern storages and floating storage facilities. The investment cost comparison between above-ground and cavern intermediate storages is presented in figure 46.

Skagestad *et al*. (2014) reported investment costs of 0.2-0.4 M€/$ktCO_2$ for an above-ground intermediate storage. According to ZEP (2014), investment cost of a floating intermediate storage of CO_2 would amount to 1 000 €/m^3 (translating to 0.9 M€/$ktCO_2$). Required intermediate storage capacity equals 1-1.5 times the capacity of a single ship. Assuming the use of large ships of 20 to 40 kt or more, the intermediate storage investment can have the largest share of the capital expenses of a CO_2 terminal.

Investment costs of the loading equipment depend on the required capacity to transfer CO_2, amounting to 0.4-3.2 M€/kt$CO_2$$h^{-1}$ (Aspelund & Gundersen, 2009 and Skagestad *et al*. 2014). Therefore, the investment cost of a loading facility able to load 40 ktCO_2 in 24h hours would amount to 0.7-5.3 M€.

Increasing the capacity of a terminal can lower the transportation cost due to a benefit from scale (Kujanpää et al. 2014). Larger transported volumes of CO_2, would likely drive upwards the unit sizes of ships and intermediate storages. Conventional intermediate storage units for CO_2 are formed by refrigerated cylindrical steel tanks. A volume of 3 000 m^3 per single tank has been proposed by Elsam, Kinder Morgan & Statoil (2003). Cooled excavated rock cavern storage is a promising alternative technology for intermediate storage of CO_2. A cavern would require less above-ground surface area and seems to be a cost effective solution for large intermediate storages (D410). The economic difference between the storage modes is a result of significantly lower investment cost per storage volume of a cavern compared to steel tanks. The common assumption is that excavated caverns become more economical compared to modular on-ground tanks for large, over 50 000 m^3 intermediate storages for CO_2. The operational and maintenance costs can be assumed to represent only a minor share of the annual cost of the storage facility. The annual costs from liquefaction of boil-off CO_2 from both cavern and tank storages are of the same order of magnitude in comparison to the investment costs. However, the subject does not appear often in the scientific literature, and the available data does not provide basis for a robust analysis (D410).

The higher and lower estimates for both tank and cavern storages for CO_2 in the range of 50 000 to 120 000 m^3 are presented in **Error! Reference source not found.**. Assuming an interest rate of 5% and an economic life of 25 years, the capital cost of a single 3 000 m^3 steel tank equals from 0,224 M€/a to 0,557 M€/a (based on Aspelund & Gundersen 2009 and Svensson et al. 2004). Aspelund and Gundersen (2009) assumed an operation and maintenance costs amounting to 1% of the investment, resulting in this case from 0,0315 M€/a to 0,0785 M€/a. The operation and maintenance costs, represent therefore roughly 14% of the annual fixed costs of an above-ground CO_2 intermediate storage when cost related to liquefaction process are neglected. When the liquefaction cost resulting from the operation of a single 3 000 m^3 tank unit are taken into account and the operation and maintenance cost are neglected, the annual cost of the unit amounts to 0,231 M€/a to 0,564 M€/a. The liquefaction costs, equalling 0,007 M€/a per a 3 000 m^3 tank, represent roughly 1–3% of the annual cost. On a rock cavern of a size of 50 000 m^3, the annual liquefaction cost 0,023 M€/a equals some 2% of the annual cost without operation and maintenance costs.

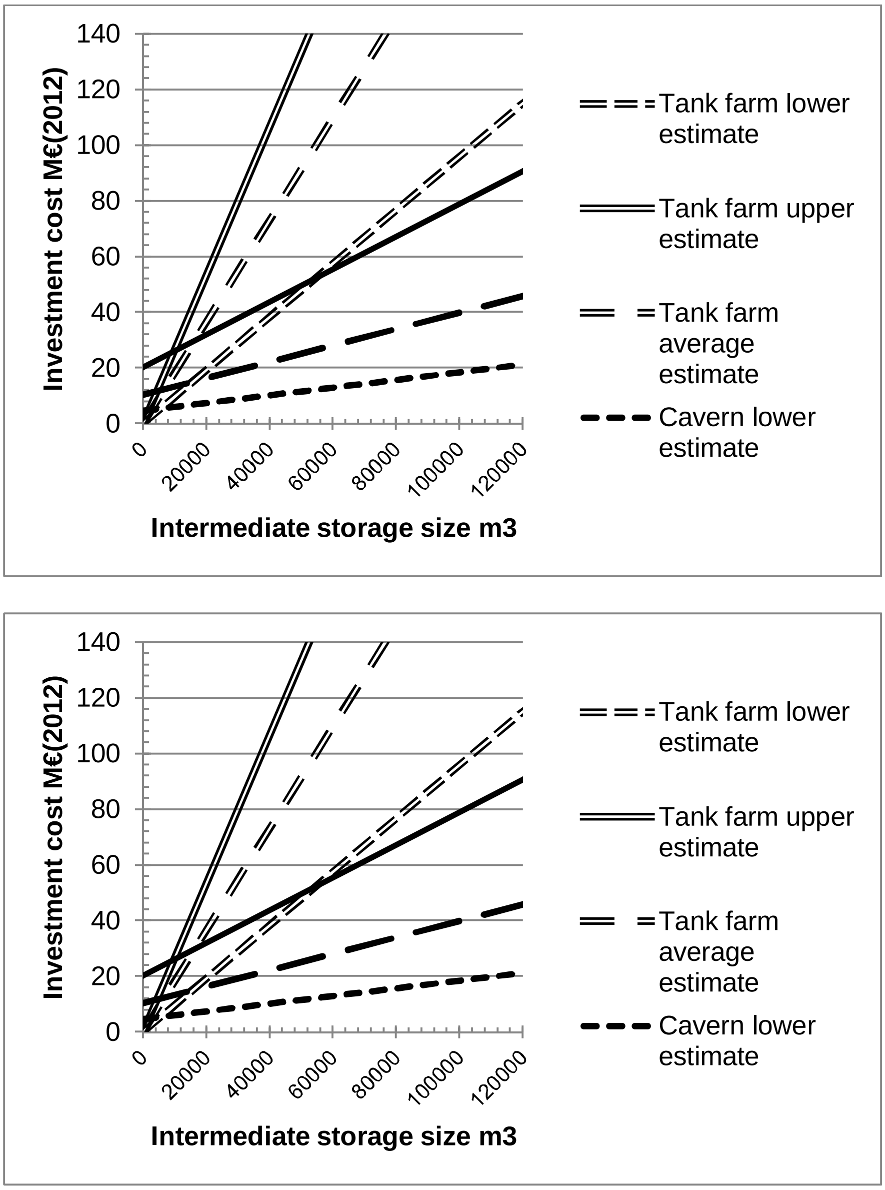


Figure 39. Upper, lower and average investment cost estimates for cavern and tank farm intermediate storages of CO_2. Based on reference costs from Svensson *et al*. (2004), Aspelund *et al*. (2009), Decarre *et al*. (2010), Elsam, KM, Statoil (2003) and CCSP WP4 estimates (Kujanpää et al. 2014).

The intermediate CO_2 cavern storage concept, which has been investigated, involves the storage of CO_2 in excavated, unlined underground rock caverns in liquid form at temperatures between -5 and -40°C. The low temperature will result in a frozen zone around the storage, which is assumed to seal the storage, allowing for pressurisation (D413). The goal of the work has been to define and specify the characteristics and optimal design of the geological intermediate cavern storage concept and compare the investment, operational and liquefaction cost with other conventional intermediate CO_2 storage methods above-ground. Required site selection, characterisation and monitoring procedures have also been described (D410 & D417).

Simulations indicate that the most favourable store depth is 100 metres or deeper and that the most favourable storage temperature is between −20 and −40 °C. In these cases the prevailing hydrostatic pressure best matches the CO_2 vapour pressure and the thickness of the frozen zone is likely to grow thick enough to ensure safe containment of CO_2 inside the store (D416). Based on the modelling, cooling of the storage before the actual storage would also be advantageous and diminish the required cooling capacity. A geological intermediate storage operated at – 40º C would require a cooling capacity of 300 kW. The geothermal energy, generated during the liquefaction process, could theoretically be used for heating purposes

7. Geological storage of CO_2

CCS is a chain of operations, which all have to be organised in a reliable, sustainable and feasible way. Perhaps the most essential and critical part of the CCS chain is the final storage of CO_2. The volumes to be stored are extremely large, which significantly reduces the number of potential solutions. Only a few credible storage methods have been presented, mostly based on geological storages. The applicability of other alternatives is mainly restricted by capacity and/or economy. However, alternative methods are being developed in order to improve their competitiveness. Also, certain options for utilisation of CO_2 could contribute significantly to CO_2 emission reduction locally.

Geological storage of CO_2 is the only storage method, which has been demonstrated in industrial scale and is currently seen as the most potential storage option. From Finnish point of view this means transportation of CO_2 abroad because no potential storage sites have been identified inside the borders of Finland. The nearest identified and demonstrated geological storage sites are located on the North Sea. The Baltic Sea region has some theoretical potential that has been studied in more detail in CCSP. As the distance from Finnish emissions sources is much closer to the Baltic Sea than to the North Sea it provides an interesting opportunity for geological storage. Thus, international R&D activity was established as part of CCSP for focusing on this option.

Successful long-term storage of CO_2 in underground formations requires also various monitoring technologies. The structural geometry and flow pathways of the considered rock formation need to be surveyed using various tools for seismic survey. Furthermore, monitoring is required to verify that the CO_2 remains in the rock formation long after the injection has stopped. Possible monitoring techniques for future CO_2 storage facilities include atmospheric monitoring, soil gas and water sampling and seismic surveys (Figure 40).

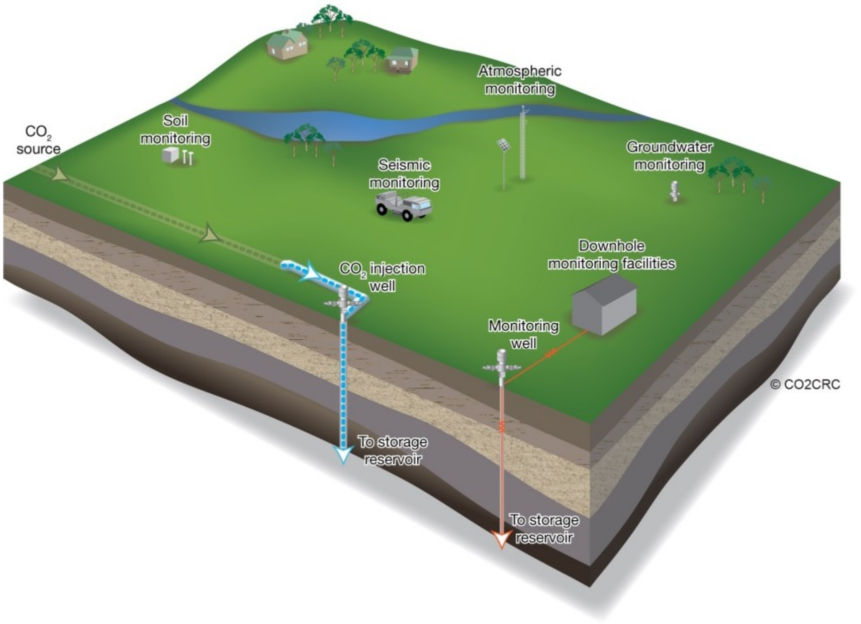


Figure 40. Monitoring techniques for CO_2 storage include atmospheric monitoring, soil gas and water sampling and seismic surveys (image by CO2CRC).

7.1 CO_2 storage potential assessments

Scientist believes the earth has extensive capacity to store injected CO_2, potential storage sites are however quite unevenly distributed (Figure 41). The U.N. special report on CCS (IPCC, 2005) estimates the global CO_2 storage capacity in oil and gas fields, unmineable coal seams and in deep saline aquifers to be at least 2 Tt in total. The highest insecurity is regarding the capacity of deep saline aquifers, which alone could have a capacity of up to 10 Tt. This insecurity is due to the fact that saline aquifers are much less explored, compared to the sedimentary formations that have been found to hold oil and gas accumulations. For assessing the storage potential and comparing potential reservoirs, only theoretical estimates are available for many regions. To fully characterise storage sites, which would allow more precise estimates; more data (seismic surveys and drillings), dynamic simulations and injection experience is needed.

The EU GeoCapacity project (2006-2008) provided calculations on the geological CO_2 storage capacity of Europe. The project gathered results from earlier European projects together with data from countries not covered in detail before, thus providing coverage of the majority of the EU member states and neighbours. The database of GeoCapacity includes a total CO_2 storage capacity of 360 Gt. Since not all of the capacity can be exploited, conservative estimates were also done. According to the conservative storage capacity estimates at least 96 Gt can be stored in deep saline aquifers, 20 Gt in depleted hydrocarbon fields and 1 Gt in unmineable coal beds. A large portion of the European capacity was found to be situated offshore Norway, mainly in deep aquifers in the North Sea (Vangkilde-Pedersen et al. 2009).

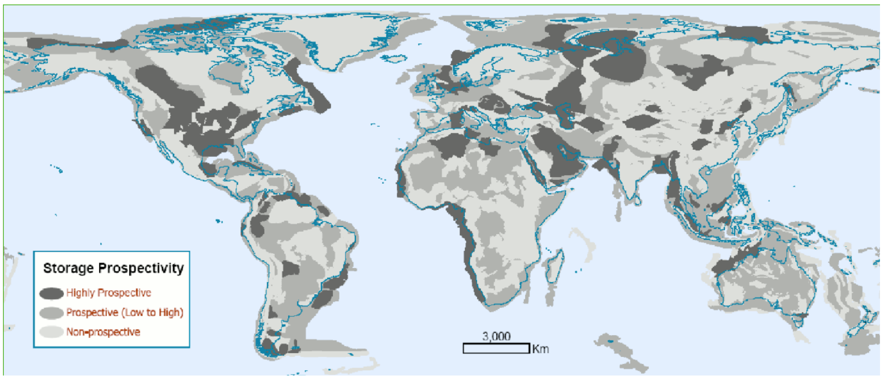


Figure 41. Map of global geological CO_2 storage prospectivity (IPPC, 2005).

The areas of Finland, Sweden and Russia were not covered in the EU GeoCapacity project. While the possibility to find suitable CO_2 storage sites in Finland is highly unlikely (D501), screenings for CO_2 storage capacity in the Swedish territory indicates suitable aquifers at three locations: in the southern Baltic Sea (adjacent to Polish, Russian, Lithuanian and Latvian waters), in SW Skåne and in SW Kattegatt (adjacent to Danish waters) (Erlström et al. 2011). Although quite unexplored, the Russian territory is also likely to hold a large potential for CO2 storage (D518).

Recent studies in i.e. Poland and Norway indicate much higher storage potential compared to the conservative estimates of EU GeoCapacity. Recent studies in Germany however, indicate a somewhat higher capacity in hydrocarbon fields but even more conservative numbers for the deep saline aquifers, compared to GeoCapacity estimates (Knopf et al 2010). The Norwegian Petroleum Directorate (NPD), which has access to all the Norwegian data, released in 2014 a CO_2 storage atlas for the entire Norwegian continental shelf (NPD, 2014). The atlas reported a total theoretical CO_2 storage capacity of 85.24 Gt, of which 72.1 Gt is in the North Sea, 5.6 Gt in the Norwegian Sea and 7.49 in the Barents Sea region. Some storage formations in Norway have reached a high maturity level and 1.27 Gt of the storage capacity can already be regarded as ready for CO_2 injection (1.1 Gt in North Sea, 0.15 Gt in Norwegian Sea and 0.02 Gt in Barents Sea).

A Nordic CO_2 storage atlas was published as a web based GIS database in 2015 (NORDICCS, 2015). This database includes the Norwegian capacities, updated numbers from Denmark and previously non-estimated capacities from Iceland and Sweden.

Distances from Finnish point sources to potential storage sites are quite long, but in comparison to the rest of Europe, the offshore storage potential is very large in some of the surrounding regions to Finland (D534).

7.1.1 CO_2 storage potential at the Baltic Sea area

From Finnish and Baltic Sea region point of view, perhaps the most well-known and significant sites suitable for geological storage of CO_2 are located in the North Sea, which is relatively far away from Finland. However, the Baltic Sea region might also have potential storage sites, but these have not yet been studied systematically.

In the CCSP R&D program, the Bastor-project, has assessed the CO_2 storage potential of the Baltic Sea. Several countries have borders on the Baltic Sea and therefore the Bastor-project was implemented in tight international collaboration. The overall objective of the Bastor-project was to evaluate the CO_2 storage potential in Baltic Sea region. The main focus was on off-shore storage. In practice, the study was implemented by an Irish expert organisation, SLR, who has specialised on evaluation of geological storage capacities. In addition to SLR, an Australian expert organisation, CO2CRC, was used for the implementation of the work.

In CCSP, the first part of the Bastor-project has assessed the potential for geological storage of carbon dioxide in sedimentary basins in the bedrock of the Baltic Sea region (Vernon et al. 2013). A compilation of available digital data from well logs, seismic line data interpretations, mapped structure outlines and published material from existing hydrocarbon fields and identified and mapped structures from Sweden, Poland, Latvia, Lithuania and Kaliningrad have been incorporated into a GIS database for the Baltic Sea region. A detailed screening of regional sedimentary basins identified the Slupsk Border Zone as having suitable structures for storage of CO_2 in depleted oil and gas fields or saline aquifers.

Cambrian sandstone saline aquifers below 900 m have been identified as the principal regional potential storage target with the Dalders Monocline as the most promising area. Eight individual structures were identified as having greatest potential. Detailed 3D geological static models were developed for three of these structures located in offshore Latvia and one cross-border structure – the Dalders Structure (Figure 42).

A theoretical regional CO_2 storage capacity calculation based on the GeoCapacity (2009b) methodology was undertaken. A regional storage capacity for Cambrian sandstones below 900 m was estimated at a total of 16 Gt, with 2 Gt for the Dalders Monocline (Figure 42). Theoretical storage estimates for individual structures for the Baltic Sea regions includes 760 Mt for the Latvian structures and the Dalders Structure, 9.1 Mt for the structures located in Poland, 31 Mt in Lithuania and 170 Mt in Kaliningrad.

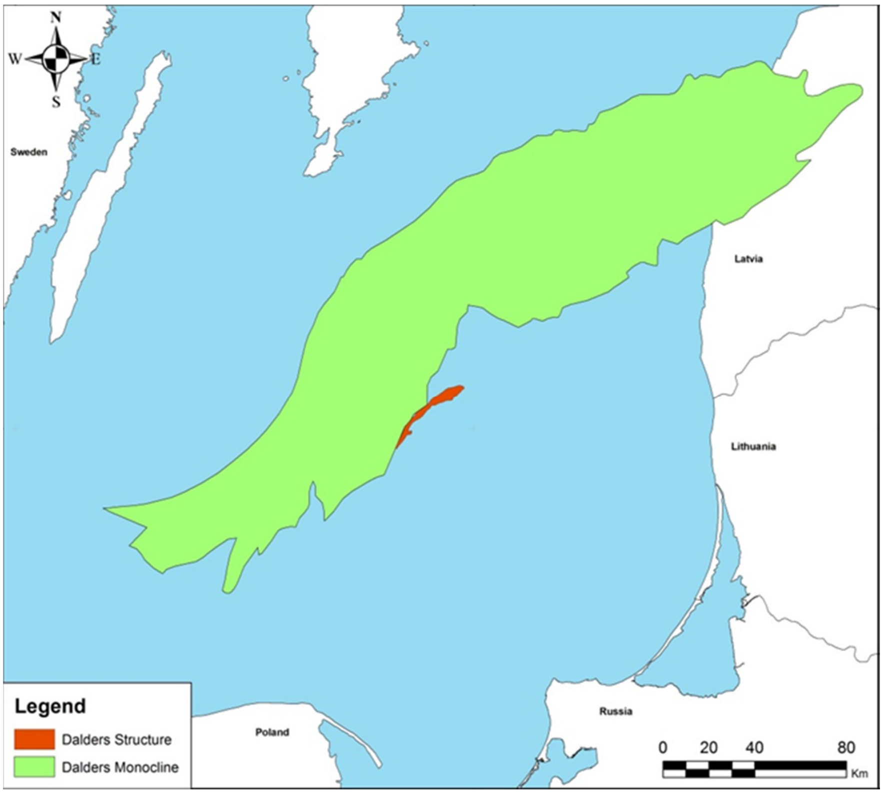


Figure 42. Location of the Dalders Prospect Structure and the Dalders Monocline (Vernon et al. 2013).

During the last year of the collaboration with the Swedish Bastor2 project the potential storage capacity in Baltic Sea region was evaluated by carrying out more detailed analysis and dynamic modelling of selected potential storage sites.

Preliminary dynamic simulation was carried out focusing on the southern part of the Dalders monocline offshore Sweden. The results of the simulation showed that maintaining the reservoir pressure at 50 % above the hydrostatic pressure, would limit the CO_2 injection rate to 0,5 Mt CO_2 per well per annum over 50 year period if five wells are used for injection. Increasing number of wells would increase the total rate but the injection time would be reduced, respectively.

This injection rate does not allow commercial injection of CO_2 and thus these preliminary simulation results do not look very encouraging. However, results should be seen as a preliminary simulation focusing on one potential site and thus this does not mean that Baltic Sea would not offer any potential storage site for CO_2 injection. In this study the simulation was limited to Dalders monocline because of availability of data. Other areas to the north east from the monocline, like offshore Latvia, could include more suitable areas for storage but detailed enough data from this area was not available for the study.

In this phase, the analytic study on CO_2 storage potential in the Baltic Sea region has been completed. As described above, the results do not represent the overall area of Baltic Sea because of availability of raw data for evaluation and simulations. The work should be continued in the future by tightening collaboration with Baltic Sea countries in order to enable more detailed evaluation of the overall storage capacity and to enable efficient information exchange between Baltic Sea countries on CCS and especially on storage potential.

7.1.2 Prospective areas for CO_2 storage in Western Russia

In sharp contrast to the exposed basement of the Baltic Shield, a large part of NW Russia is covered by a several km thick succession of sedimentary rocks, ranging from Proterozoic to Quaternary in age (D518). The underlying Archean to Proterozoic basement has undergone intensive rifting at different stages that created sedimentary basins of different types. The Mezen, Moscow and Volga-Ural basins are examples of basins formed at Proterozoic time while Timan-Pechora and Barents Sea basins are younger basins that evolved during the Paleozoic (Figure 43). The potential for CO_2 storage in Russia has not yet been systematically studied and many regions are still quite unknown, also from a hydrocarbon perspective. The Russian Federation is however extremely rich in oil and gas deposits, accounting for 13% of the world oil reserves and more than 30 % of world gas reserves.

During CCSP an assessment of the situation of CCS in Russia has been reported (D506) and prospective areas for CO_2 storage described (D518).

Mezen and Moscow basins have not been drilled and explored as much as the more potential hydrocarbon areas of Russia. However, some prospective Vendian layers seem to exist in both regions and especially the Devonian sequence of Moscow basin looks promising from a CO_2 storage perspective.

In Volga-Ural and Timan Pechora basins a large potential for geological CO_2 storage most likely exist, both in aquifers and in depleted oil and gas fields. The Paleozoic formations are highly prospective for CO_2 storage in both regions and in Timan Pechora a high storage potential also in the overlying Mesozoic sequence. These regions have for a long time both been active in oil and gas production and exploration and have therefore reached a high level of maturity regarding the availability of data.

The arctic offshore location of the East Barents Sea basin makes it a challenging area for exploration. Although not very well studied, there is a huge hydrocarbon potential in this region and CO_2 storage has already been demonstrated in sediments of Mesozoic age on the Norwegian part of Barents Sea. In addition to the Mesozoic sequence, some parts of the Paleozoic might also offer possibilities for CO_2 storage in the East Barents Sea basin.

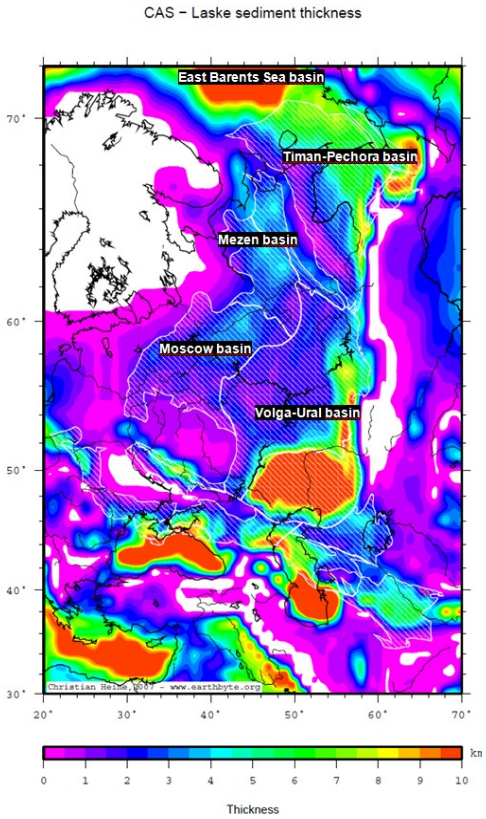


Figure 43. Laske sediment thickness map with sedimentary basins of western Russia outlined (Heine, 2007).

As the BASTOR project concluded there might occur good capacity for storage in the Cambrian sandstone of the Kaliningrad sector of the Baltic Sea. Onshore in Kaliningrad, the Devonian sandstone occurring below a salt bearing strata might also offer another opportunity for CO_2 storage. Possibilities for CCS R&D work and funding between Russia and Finland has been actively explored. A memorandum of understanding (MoU) between CLIC Innovation Oy and VNIGRI (Russian Oil and Gas Institute, St. Petersburg) has been signed. Scope of MoU is to promote cooperation between Russia and Finland on CCS. A preliminary project plan including literature and site screening studies for the Kaliningrad area has also been prepared.

7.2 Seismic characterisation and monitoring of CO_2 storage

Seismic investigations, including those performed in boreholes, have proven useful for choosing suitable storage formations and for monitoring the evolution with time of the injected CO_2. Without this information it is difficult to assess the CO_2 plume position, monitor its extension and interaction with the host formation, or predict its evolution, including potential migration to adjacent formations. The seismic data collection and processing methods are being improved and new technologies developed in order to make geologic CO_2 storage as efficient and safe as possible. Seismic monitoring of a CO_2 plume extension is commonly performed by 3D seismic surveys performed from surface (Figure 44, left-side image). The main advantage of surface methods is the wide coverage of the site from above, which allows the horizontal extension of the plume to be imaged. The resolution can however suffer because of the large distance from the surface to the reservoir. Borehole seismic studies (Figure 44, right-side image) were less used in the past, partly because of logistic difficulties with setting up frequent surveys in boreholes in the presence of CO_2. Such difficulties are currently addressed by developing seismic receivers and sources for boreholes, which would allow the plume to be monitored permanently, from its proximity.

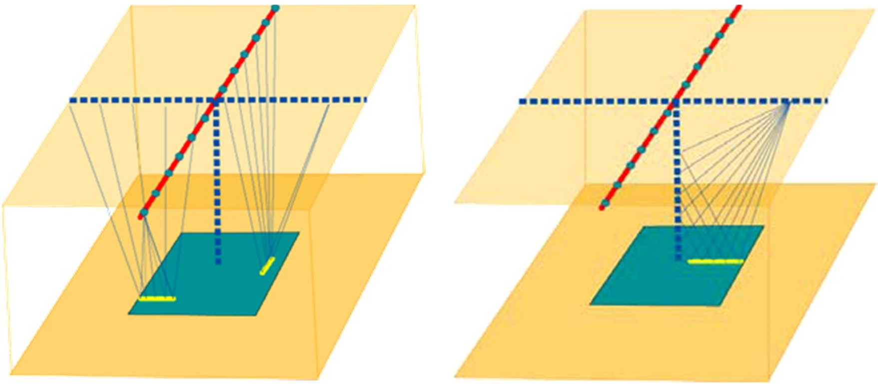


Figure 44. Seismic surveys from surface (left) and borehole (right).

In CCSP, Vibrometric Oy focuses is on developing seismic characterization and monitoring techniques, instrumental for the adequate understanding of the structural geometry and flow pathways of potential geologic CO_2 storage formations.

7.2.1 Reprocessing of seismic data using new methods

Seismic data have been collected in two CCS EU projects, CO2SINK and MUSTANG. Time-lapse VSP (Vertical Seismic Profiling) with its variant MSP

(Moving Source Profiling) and time-lapse seismic cross-hole data sets were analysed as a means of testing the methods and techniques being developed in CCSP. On one side, the development effort was aimed at improving the resolution, reliability and efficiency of the methodology currently used for CO_2 seismic monitoring, while on another side the effort was aimed at designing and building seismic acquisition instruments that meet specific practical requirements associated to CO_2 seismic monitoring in the subsurface.

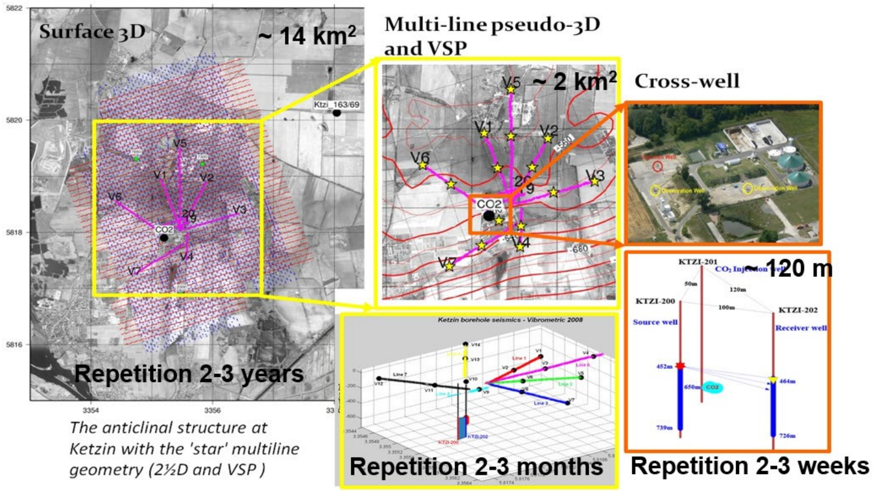
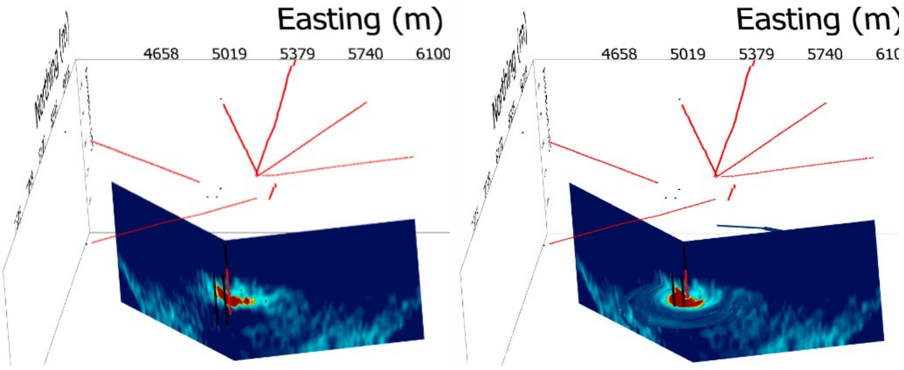
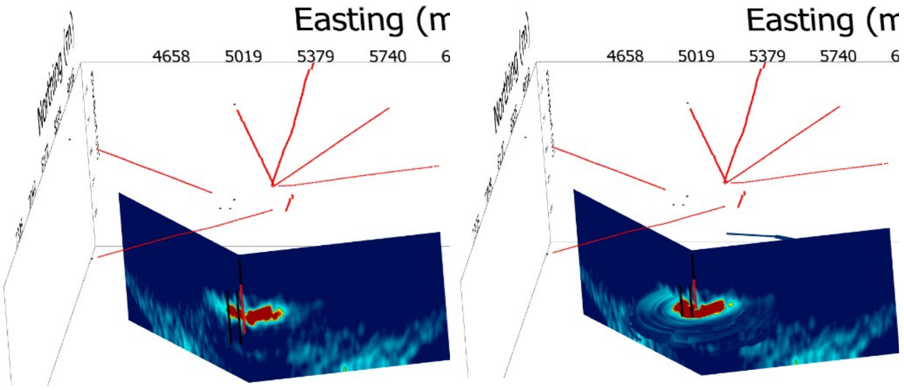


Figure 45. Application of other methods, complementing 3D seismic surveying, proved instrumental for monitoring CO2-related processes that act over shorter timescales. *As a less expensive alternative, 2½D seismic surveys could complement the temporal resolution of the 4D seismic surveys.*

An integrative concept was applied at the Ketzin CO_2 injection test site, in Germany, where a comprehensive seismic monitoring program was unrolling for more than 5 years. Seismic monitoring comprised baseline and repeat observations at different scales in time and space: surface 3D and multi-line 2D, VSP (Vertical Seismic Profiling), MSP (Moving Source Profiling) and cross-well seismics (Figure 45). It was found that VSP/MSP time-lapse surveys can monitor the evolution of the CO_2 plume accurately and in a timely manner, the reservoir layer being imaged with higher resolution than from surface. However, with VSP/MSP the coverage is limited to the vicinity of the observation well, i.e. to a cylinder with a radius of app. 300–500 m (Figure 46 to Figure 47), the restriction is mainly due to the acquisition geometry. Cross-well measurements cover the smallest scale, between wells ~100 m apart but are capable of detecting very small CO_2 amounts, therefore may be useful for identifying unpredicted CO_2 migration (leaks).



BL vs R1



BL vs R2

Figure 46. 3D view of two IP migrated vertical sections calculated at azimuths 75° and 315° from North on the left and the same, together with a time depth slice at the level of the reservoir (630 to 640m depth in KTZI-202). Baseline vs. first repeat appears in the top row and baseline vs. second repeat is shown in the bottom row.

A contribution entitled “Optimized seismic methodology for CO_2 injection monitoring at the Ketzin pilot site, Germany *Calin Cosma and Nicoleta Enescu, Vibrometric”* has been presented at the Canadian Exploration Geophysical Society Symposium “Geophysics and the Environment” in Toronto in March, 2016 (Enescu, 2016). The paper is published in the Proceedings volume.

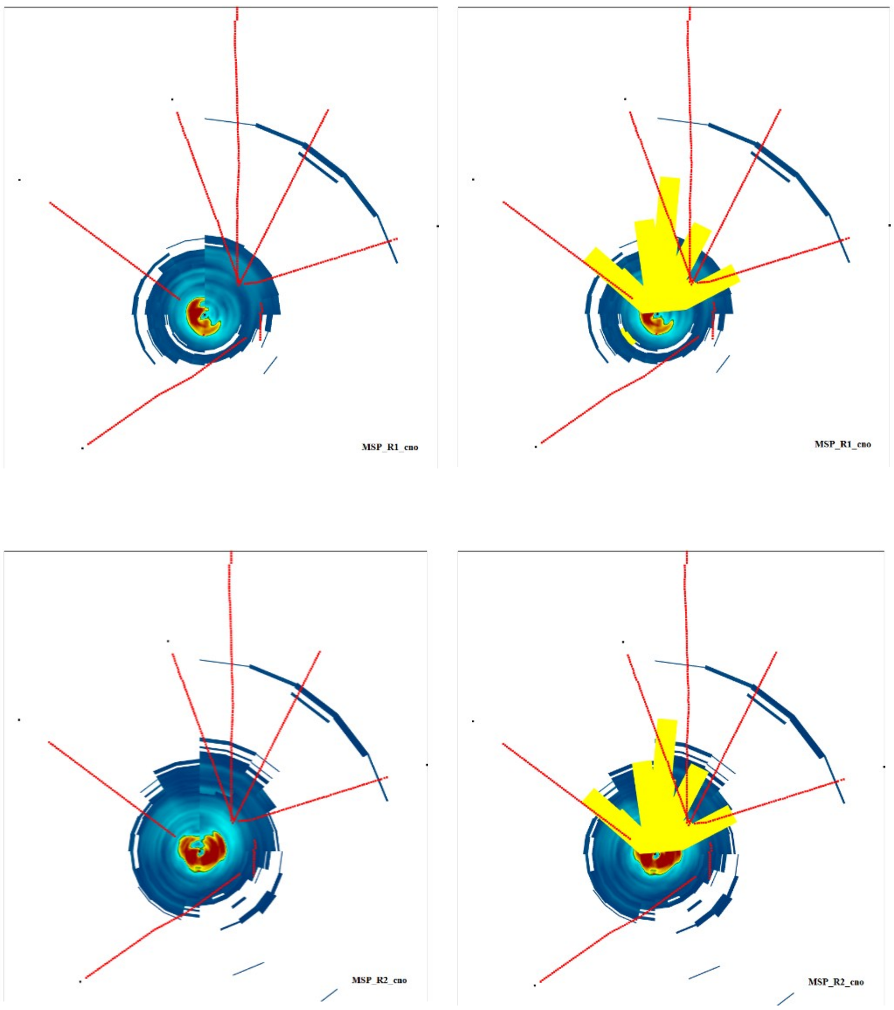


Figure 47. View from above of the time depth slice at the level of the reservoir (630 to 640m depth in KTZI-202) for baseline vs. first repeat (top) and baseline vs. second repeat (bottom). Images on the right side also display reflector elements (yellow) interpreted at the reservoir level from the baseline VSP data (Enescu, 2010).

Difference maps shown in Figure 46 and Figure 47 were computed from the time-lapse analysis of the MSP baseline and repeat surveys and can be compared with the difference maps computed from the 3D data by (Juhlin et. al. 2010) and from the 2D star data by (Ivandic et. al., 2012).

Comparison of difference maps obtained with different type of surveys is relevant only in the regions where coverage exists, considering intrinsic limitations caused by limited coverage for the 2D Star and MSP survey geometries.

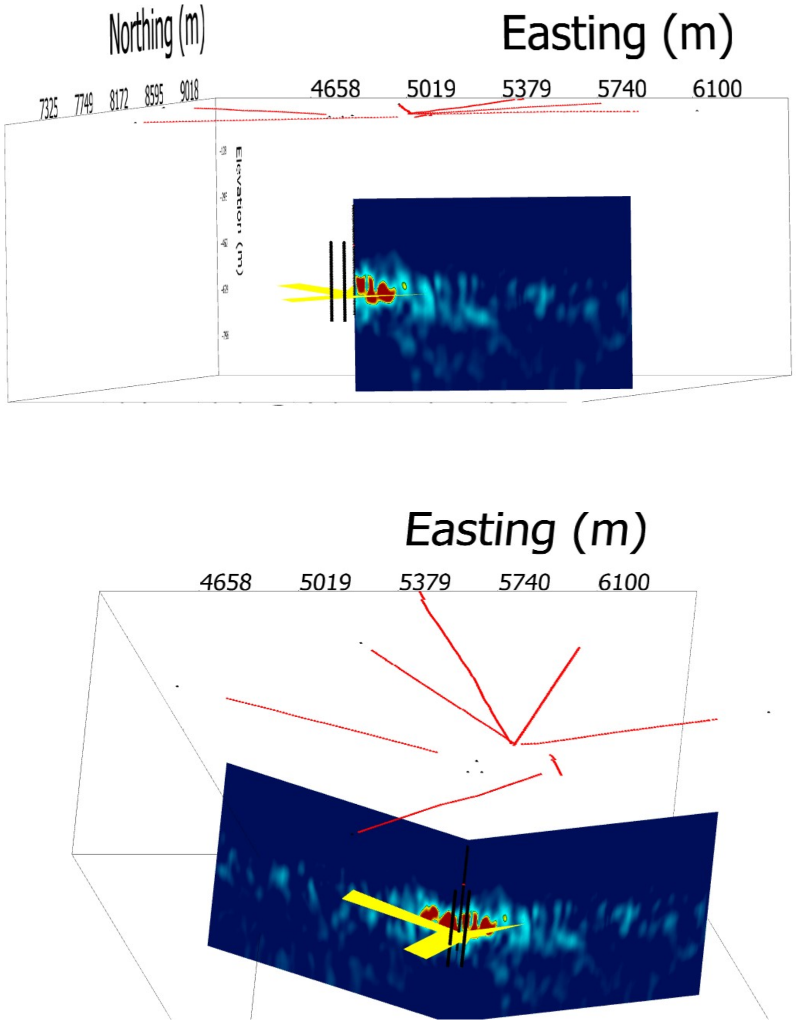


Figure 48. 3D view of two IP migrated vertical sections calculated at azimuths 75°(top) and 315° from North with receiver elements interpreted at the level of the reservoir (630 to 640m depth in KTZI-202), interpreted from the baseline VSP data.

Difference maps shown in Figure 48 and Figure 49 were computed from the time-lapse analysis of the VSP baseline and repeat surveys and can be compared with the difference maps computed from the 3D data by (Juhlin et. al. 2010) and from the 2D star data by (Ivandic et. al., 2012) and the ones estimated from the MSP time-lapse data (shown in Figure 46).

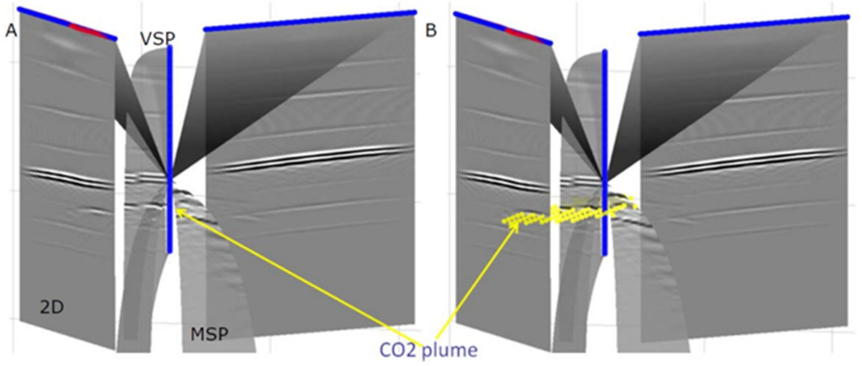


Figure 49. Combined imaging of the CO_2 plume from multi-line surface 2D and borehole measurements, VSP & MSP. Pseudo 3D coverage can be obtained with relatively sparse coverage from surface and borehole (Enescu et. al., 2011).

7.2.2 Development and testing of a receiver chain for borehole seismic surveys

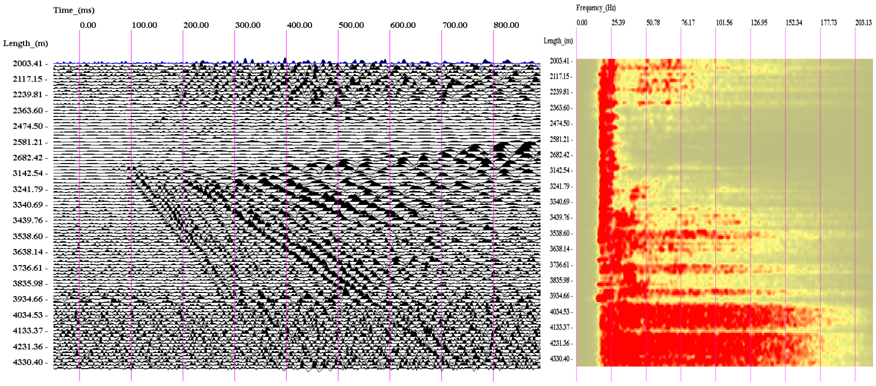
A 16-level wide-band 4-component receiver tool for borehole seismic surveys at CO_2 storage sites was developed by Vibrometric for measurements at depths of 1.6 to 2 km. The frequency band of the instrument was extended downwards to 1 Hz. Preliminary in-situ evaluations were done at the Heletz CO_2 injection site (Israel), as a part of the EU funded MUSTANG project. Comprehensive tests are scheduled to be carried out next winter at the same site as a part of the EU TRUST project.

The development of test instruments and procedures in CCSP is being continued. One priority is to extend the frequency band for both seismic sources and receivers. Modelling results undertaken in this program show that by extending the spectrum towards lower frequencies than commonly used with reflection seismics it may be possible to reduce the number of source and receiver points for monitoring CO_2 geological storage sites and thus make buried permanent installations logistically and economically feasible. Such permanent installations would allow frequent or quasi-continuous measurements to be performed which in turn would lead to a truly 4-D monitoring of the evolution of the storage.

7.2.3 Geophone array for coastal region sites

The ability of performing seismic measurements on shallow sea bottom is likely to become a necessity for storages located in coastal regions. A geophone array which can be deployed on the bottom in shallow water was built in 2012 (Figure 50). The construction was kept simple and light with an ellipsoidal enclosure made of heavier steel at the bottom and lighter plastic at the top, thus allowing the sensor to sit vertically on uneven soft or hard surfaces. A test programme with this tool was performed in Canada and data was collected in 2012. The results proved the viability of the design of the shallow water bottom geophones (Figure 51).

Figure 50. Shallow water bottom geophone units built within the scope of CCSP



Raw data of good quality

Figure 51. Data acquired in Canada (2012) with the shallow water bottom geophones.

7.2.4 Construction and deployment of a near-surface permanent geophone array at the Helez site

The subsurface geophones are intended as a complement to the monitoring arrays deployed in shallow and deep boreholes. The sensors will be installed at several meters depth, whilst the controlling electronics and cables will be buried just under the ground surface away from agricultural and other surface activities. A 30-channel system built as ten, 3-component stations has been tested. Following discussions with partners contributing to the seismic effort of the TRUST Project consortium, an extension of the task has been proposed. The proposed extension consists of two stages: the physical realization of 30 independent x 1-component (vertical) receiver modules instead of the already built 10 x 3-component modules;

The construction of an additional lot of 30 independent x 1-component (vertical) receiver modules, bringing the number of near-surface buried digital receiver modules to a total of 60. The additional 30-channel extension is currently being built.

The resulting 60-channel permanent sub-surface array can be configured as separate single-component or grouped 3-component stations and shares the data recording and processing server with the borehole geophone arrays. The deployment at Heletz is ongoing and will be finalized pending the completion of the experimental facilities at the site.

The development of an application for real time processing of the data collected by the monitoring system is ongoing concomitantly with the integration of the borehole and subsurface hardware. Currently, this task has been extended to include:

a) Concept of quasi on-line processing and interpretation protocols and equipment (initial deliverable);
b) Mini cluster server to perform three main tasks (additional deliverable):
    - Continuous data acquisition from all permanent seismic stations installed;
    - Online detection, selection and processing of relevant seismic events (natural micro-seismic events and artificial source-generated events) ;
    - Communication and data transfer to remote users.

Figure 52. Testing the subsurface permanent seismic array. The steel cylinders house 3-component geophones and/or a vertical low frequency geophone. They are to be installed at approximately 2m depth by means of an auger drill (right). The grey boxes contain the acquisition and transmission electronics and are to be buried at 0.5-1m depth (left), hiding the system from activities carried on the surface above.

7.2.5 Processing and Interpretation of Monitoring data from the Helez site

The seismic program planned at the Heletz site-Israel could not be completed on schedule because of long delays with the completion of the injection and observation wells, which will be ready only this fall. The permanent sensors in three boreholes and the sub-surface sensors designed and built as a part of CLEEN/CCSP project will be installed as planned before the end of the project. The field surveys will however be carried out during the next year.

The concept presented in Figure 53 provides the experimental frame for monitoring small injected amounts of carbon dioxide.

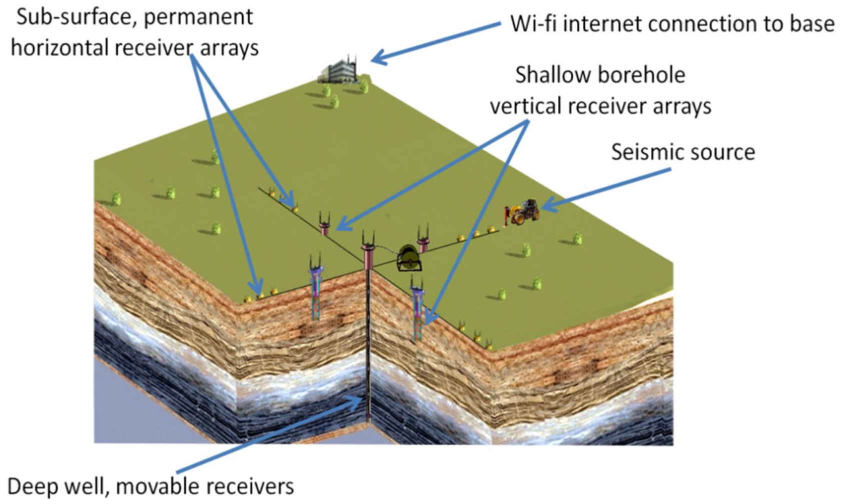


Figure 53. Schematic view of the seismic monitoring setup at Heletz-Israel. Receivers will be deployed close to the reservoir as multi-level strings in several boreholes and an array of geophones buried under the ground surface. Subsurface sources will be installed for quasi continuous use, completed by a mobile surface source.

7.2.6 Conceptual design for a semi-permanently installed shallow underground seismic source

The current seismic source design consists of a relatively low-power impact device that builds up energy by repeated action. A source will permanently be located in a shallow borehole, as shown in Figure 54. The subsurface installation puts the source out of the way of other surface activities and permits its quasi-continuous use for extended periods of time. A sequence of materials with various densities is deployed at the bottom of the hole to match the mechanical impedances of the source to the seismic impedance of the ground, hence maximize the energy transfer. The bandwidth of the source is also be extended by impedance matching. The mechanical and electronic design have been executed and the prototype is under execution. The testing and final installation of a buried semi-permanent source at the Heletz site will start in July 2016 and be completed in October 2016, with up to three prototype versions, of which one will remain permanent.

Figure 54. Design of the subsurface seismic source. A low power multi-impact device produces vertical pulses. The bottom of the borehole is prepared to maximise the energy transfer from the mechanism to the ground.

3.2.6 Intelligent wireless acquisition system, conceptual design and HW design

Typical underground storage reservoirs would lie at depths of 1000 m or more and contain tens or even hundreds of millions of tonnes of CO_2. A likely regulatory requirement is that storage sites would have to be monitored both to prove their efficacy in emissions reduction and to ensure site safety. A diverse portfolio of potential monitoring tools is available; some tried and tested in the oil industry, others as yet unproven. Shallow-focussed techniques are likely to be deployed to demonstrate short-term site performance and, in the longer term, to ensure early warning of potential surface leakage. Deeper focussed methods, notably time-lapse seismic, will be used to track CO_2 migration in the subsurface, to assess reservoir performance and to calibrate/validate site performance simulation models.

In CO_2 monitoring, the purpose of seismic technique is to determine the changes in seismic properties (mostly acoustic impedance) that resulted from CO_2 injection by comparing the surveys among time-lapse seismic data set.

Vibrometric's aim for building the Intelligent Wireless Seismic system is to be able to cope with all challenges presented above, thus to be able to participate in commercial survey and monitoring projects in the near future.

Vibrometric's Intelligent Wireless Seismic (VIWS) system has the following main characteristics:

- Self-positioning of each receiver (GPS equipped)
- Automatic configuration-reconfiguration of the array of receivers
- Selective data downloading
- Automatic asynchronous data downloading (each receiver sends its data function on the availability of the communication channel
- Intelligent power management for continuous wireless monitoring
- Full wireless

The Main Components of the VIWS are (Figure 55):

- Wireless Land Geophone (WLG) which is built with its own electronics for full wireless transmission of data (Figure 56)
- Wireless Unit (WU) which has incorporated the processor for controls, self-configuration and self-diagnostics as well as quasi on-line processing as well as the WiFi newest developed standard for simultaneously multi-channel configuration
- Wireless Hub (WH) which gathers data from a selected number of WU's and transmits it to the Acquisition Station.

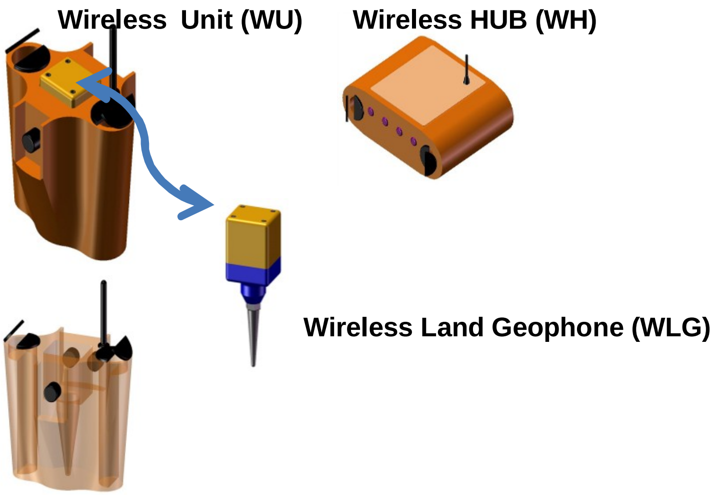


Figure 55. The components of the Vibrometric Intelligent Wireless Seismic System.

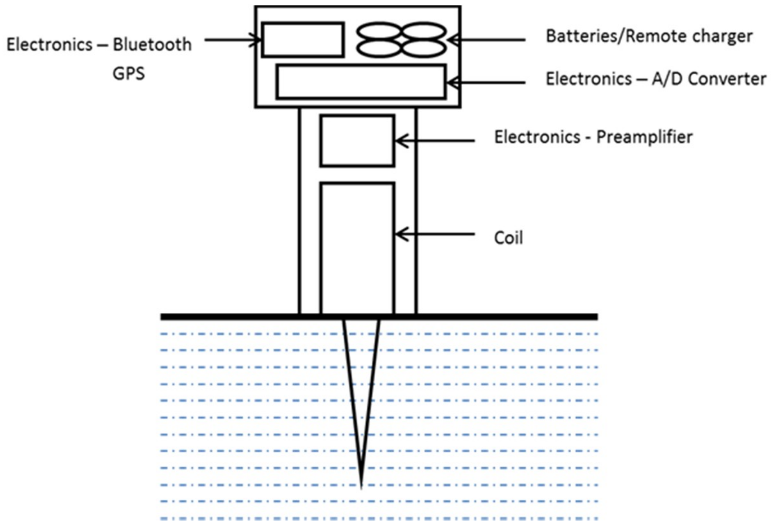


Figure 56. Building blocks of the Wireless Land Geophone (WLG).

The Network architecture is construed having in mind the typical 2D and 3D layouts, but also the simplicity of deployments and transmission. The typical 3D layout is presented in Figure 57.

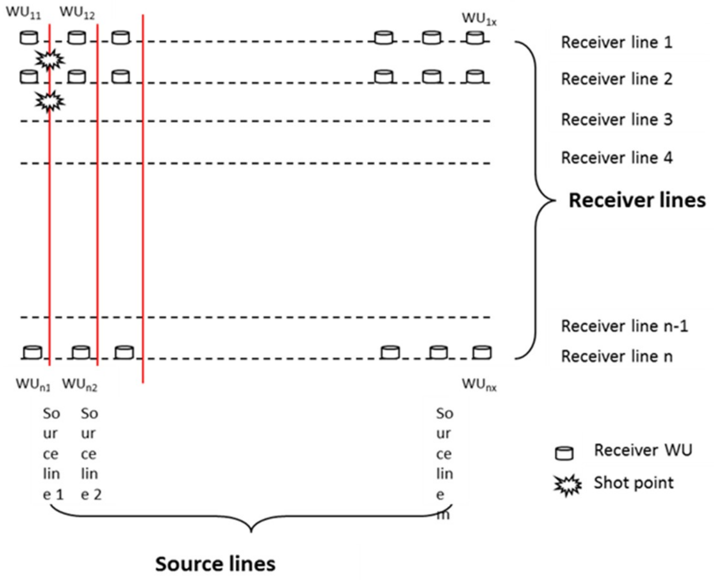


Figure 57. Typical 3D layout of the Network architecture.

The Network protocols are based on the newest WiFi direct which allows simultaneous channel usage and the possibility for WiFi transceivers for acting both as AP and transmitting unit. The proprietary modifications at the Data Link Layer are implemented to allow for dynamic prioritization of chan-nels so that any transmission attempt will not be delay by channel busy with earlier transmission. The transmission on a line will be implemented according to Figure 58.

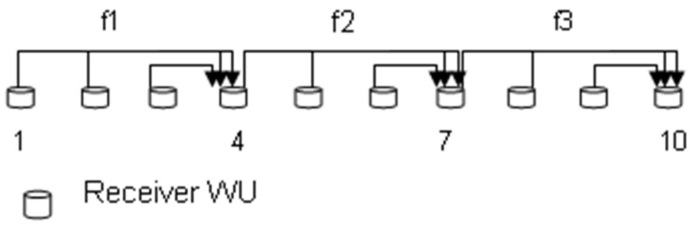


Figure 58. The layout of a seismic line with 3 orthogonal radio channels used simultaneously (f1, f2, and f3).

These are the technical aspects of the above layout:

- WU 1, 2, 3 transmit the seismic data to WU4 on channel f1; WU4, 5, 6 transmit the seismic data to WU7 on channel f2; WU7, 8, 9 transmit the seismic data to WU10 on channel f3; using orthogonal channels, we avoid radio interference.
- These 3-to-1 (many-to-one) transmissions occur simultaneously along the seismic line; the radio channels are reused, e.g. 1-4 on f1, 4-7 on f2, 7-10 on f3, 10-13 on f1, 13-16 on f2, 16-19 on f3, and so on. It is based on the many-to-one capability of Wi-Fi Direct.
- Stations 4, 7, 10,…, operate simultaneously on two frequencies (4 on f1 and f2, 7 on f2 and f3, 10 on f3 and f1, …) having two concurrent Wi-Fi sessions: AP for the previous 3 units and client for the next AP (Wi-Fi direct supports concurrent hosting and client capabilities on single interface)

A sketch of the Vibrometric Wireless Seismic Network is shown in Figure 59.

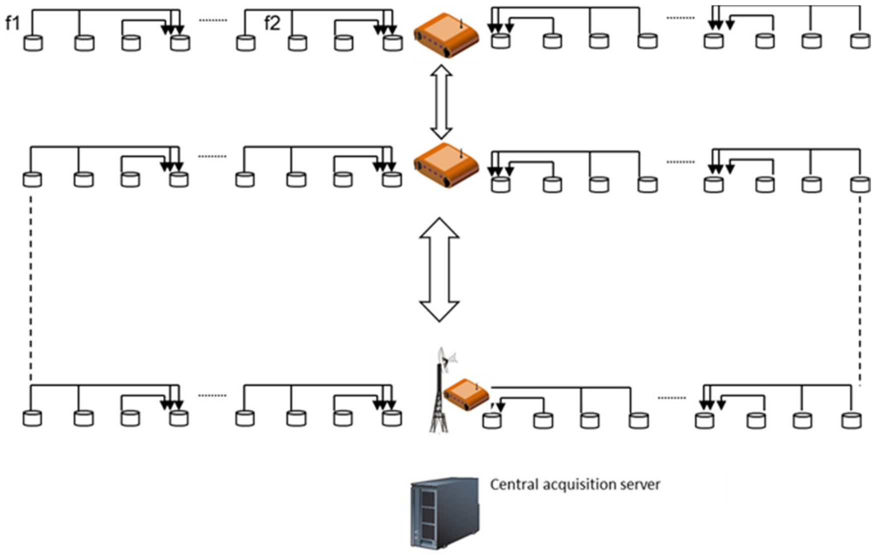


Figure 59. Layout of Vibrometric Wireless Seismic Network..

8. CO_2 mineralization

Beside geological storage, ex-situ mineralization of CO_2 is alternative storage technologies being developed. In Finnish conditions fixation of CO_2 to mineral matter might offer an alternative for CO_2 storage in specific cases. This topic has been studied in Finland for more than fifteen years on laboratory scale and results have encouraged continuing development work towards piloting and demonstration. Expertise and industrial activity in the field of geology and large-scale mineral and ore processing is available in Finland. Besides the earlier identified large potential for central and northern Finland, interesting opportunities for south-west Finland are offered by magnesium silicate mineral resources at Vammala and Suomusjärvi. The development work is further supported by international project cooperation, as Finland's expertise in the field attracts interest from abroad. An aspect that drives the interest of international R&D consortia is the option to apply mineralization directly to CO_2-containing gases, avoiding a costly CO_2 separation step and enabling possible revenues from valuable carbonates and other products

In addition to natural minerals, also alkaline industrial residues and by-products, such as slags and ashes, can be used as a raw material for CO_2 mineralization. These are typically more reactive than natural minerals and therefore some CO_2 mineralization processes for slags and ashes are already commercially available[5]. In CCSP, the focus has been on further development of the so called Slag2PCC concept, enabling fixation of CO_2 by producing PCC from steelmaking slags.

8.1 Fixation of CO_2 by producing PCC from steelmaking slags

The Slag2PCC process route, developed in Finland, aims at converting calcium containing industrial by-products (with main focus on steel converter slag) into

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[5] A first commercial plant using Carbon8's Accelerated Carbonation Technology was started up last year and another plant is being commissioned.

valuable precipitated calcium carbonate (PCC) product (Teir et al. 2011). In this method, an aqueous ammonium salt solution is used to selectively extract calcium from the by-product/waste material (Figure 60). After removal of the solid slag residue, CO_2 is bubbled through the solution producing chemically stable calcium carbonate as an end product. Ammonium salt solution is recovered simultaneously and can thus be reused. Depending on both the properties of the slag material and the details in process design, 1 t of CO_2 could be sequestered in approximately 5 t of steel converter slag, producing ~2 t $CaCO_3$ end product and ~4 t of slag residue. If the produced $CaCO_3$ replaces conventionally manufactured PCC then additional CO_2 emission reductions are gained as the conventional PCC production method is very energy and emission intensive (Mattila et al., Journal of Cleaner Production, 2014).

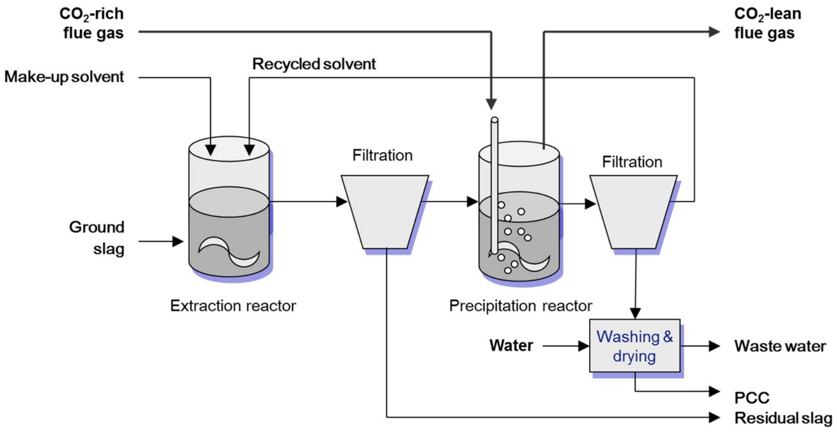

Figure 60. The Slag2PCC process: calcium is selectively extracted from steelmaking slag and it reacts with CO_2 from flue gases to produce precipitated calcium carbonate.

The process benefits from the facts that it proceeds at room temperature and pressure, its end product is likely to have significant market value, and it does not consume significant amounts of chemicals. In addition, it uses raw material that is readily available, has a low price and requires some treatment and handling anyway. Furthermore, it is likely that flue gases could directly be used as a source of CO_2, which would avoid the need for a costly and problematic CO_2 separation step.

The Slag2PCC concept was first developed during the Tekes (the Finnish Funding Agency for Technology and Innovation) funded projects Slag2PCC and Slag2PCC-Plus (2005–2009), while current development work is mainly funded by the CCSP program, Academy of Finland and Aalto Center for Entrepreneurship.

The objective of the current development work is to move the concept further towards commercial application, aiming at processing 25 t/h steel converter slag into 10 t/h PCC.

8.1.1 Pilot rig work

In 2014, researchers at Aalto University, Department of Energy Technology have designed, constructed and tested the world's first Slag2PCC pilot plant test facility that converts steel slag and CO_2 into PCC. The researchers have scaled-up the Slag2PCC process for 400 times, from 500 mL to 200 L. In the calcium extraction process, the pilot plant can handle up to 190 L of liquid solvent and 20 kg of solid steel slag. Based on these amounts, the pilot plant can produce 5-10 kg of PCC depending on the Ca extraction efficiency. The feasibility of the Slag2PCC process route has been successfully demonstrated at the pilot scale.

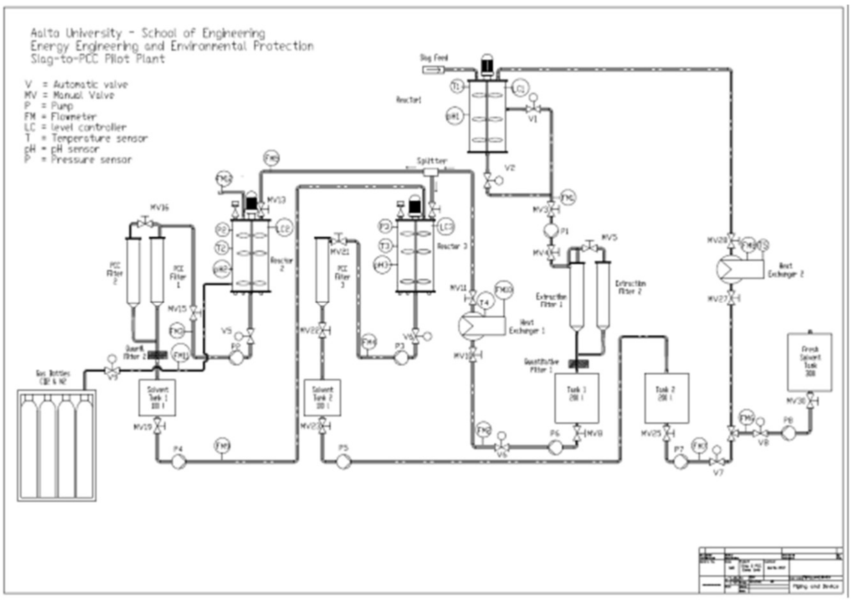

Figure 61. Process design of Slag2PCC pilot plant test facility (D546)

The initial reaction temperature and solvent concentration seem to be significant factors while steering the PCC crystal morphology in the Slag2PCC process. Calcite PCC can be produced at lower temperature (e.g. 20°C), where aragonite PCC is formed at higher temperatures (e.g. 60°C). The carbonation reaction should not take place below the pH range of 7-8 to maximize calcium conversion and to prevent re-dissolution of PCC. Attempts to produce scalenohedral PCC from the Slag2PCC process have so far not been successful on the pilot scale.

The pilot-scale process design was completed in 2012, followed by ordering of the equipment (D515; Figure 61). One of the challenges was that all the equipment in the markets are either designed for the laboratory level or for the industrial level, thus it was difficult to find suitable equipment for the test facility. However, the construction work began in January 2013.

Figure 62. Completed Slag2PCC pilot plant (photo by S.Teir).

Te set-up of the pilot-scale test facility (Figure 62) was ready in January in 2014. Next, a series of simplified tests using only water were conducted. After the found leaks were repaired, a test was done with water and steel slag. This revealed that the performance of the filters was not sufficient, thus a qualitative filter of 0.45 µm was added resulting into a very clean filtrate solution. These tests and repairs were followed with tests using aqueous solution of ammonium salt and steel converter slag.

Three tests were designed to produce two different PCC morphologies: scalenohedral calcite and aragonite. The aim of the first test was to produce scalenohedral PCC by attempting to replicate the experimental conditions suggested by Åbo Akademi University researchers, who successfully produced scalenohedral PCC at the laboratory scale. The second test was an attempt to produce scalenohedral calcite based on traditional PCC production conditions presented in US patents. The third test attempted to produce aragonite by increasing the precipitation temperature while other parameters remained the same as in the second test.

Pure aragonite crystals with lengths of 2-50 μm and a maximum width of ~3 μm were successfully produced in the third test. A variety of crystal morphologies including spherical and disc-like vaterite, rhombohedral calcite and aragonite were formed in the other tests.

8.1.2 Extraction Stage

6.2.2.1. Solvent recyclability tests

Batches of steel converter slag (≤250μm) were mixed with 1 M aqueous solutions of ammonium chloride (NH_4Cl) to selectively dissolve calcium from the slag at room temperature (~20°C). In the first extraction test, a fresh batch of the NH_4Cl solvent was used, and the regenerated NH_4Cl solution after the carbonation stage was reused.

As shown in Figure 63, the first three cycles (Cycle-1, Cycle-2, and Cycle-3) of the recycled solution show almost the same calcium extraction efficiency as with the fresh solvent. The highest Ca-extraction efficiency achieved was 78-% with the fresh solvent and the lowest (60%) extraction efficiency was found for the third cycle (Cycle-3). After the solution was recycled more than 10 times (Cycle-X) including high temperature carbonation tests, the calcium extraction efficiency had deteriorated significantly (to 39%).

On the other hand, the maximum extraction efficiency was achieved already after 30 min of the addition of the slag to the solution, suggesting that the extraction stage requires 30 minutes maximum.

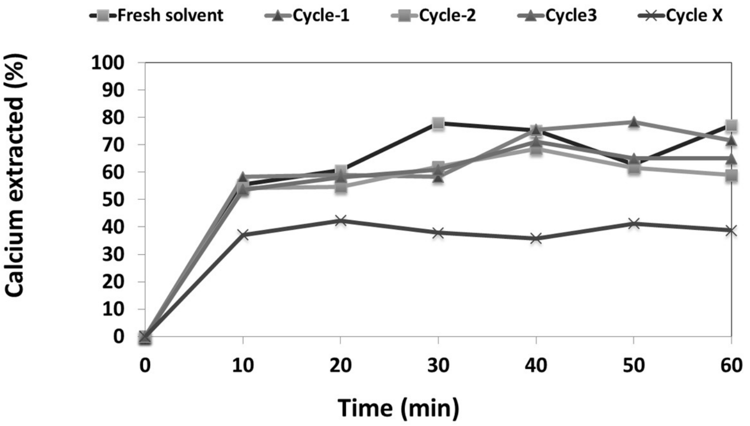

Figure 63. Solvent recyclability tests

6.2.2.2. Two stages extraction tests

One way to increase the Ca extraction efficiency is to use a two-stage extraction process. After filtration, the residual slag from the first extraction stage can be mixed with fresh (or recycled) solution of NH_4Cl to extract the remaining calcium in the slag. Figure 64 shows results from a two-stage extraction test. mmediately Immodestly after the filtration the residual slag was put back into the extraction reactor and mixed with a fresh solvent of NH_4Cl. In the second extraction stage, 24 % of the calcium in the residual slag was dissolved making the total Ca extraction efficiency 94% of the original calcium content of the slag.

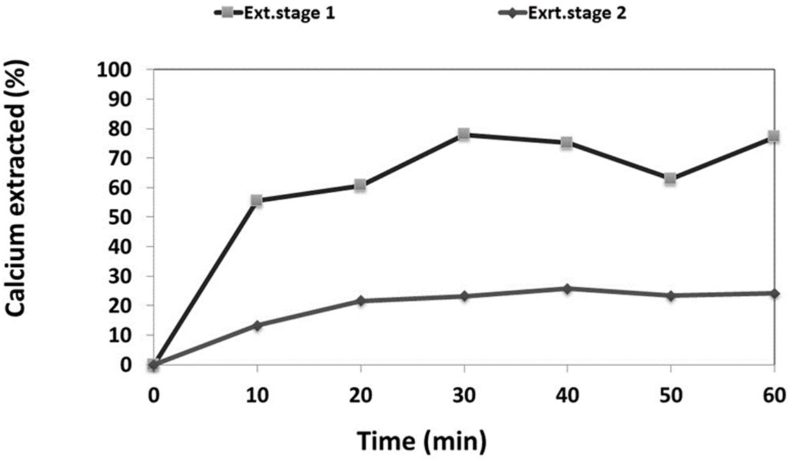

Figure 64. Two stages extraction calcium tests

6.2.2.3. Extraction with low solvent concentration test

Solvent concentration in the extraction stage is critical for maximizing the Ca extraction efficiency. On the other hand, H-P Mattila, proposed using very low concentrations of NH_4Cl (0.01M) to reduce the need for PCC washing, which however would have an adverse effect on the calcium extraction efficiency and necessitate a multi-stage extraction process. Figure 65 shows a comparison of Ca extraction efficiency by 1M and 0.01 M NH 4 Cl: extraction efficiency drops from 78% to 4% when going from 1M and 0.01MNH_4Cl.

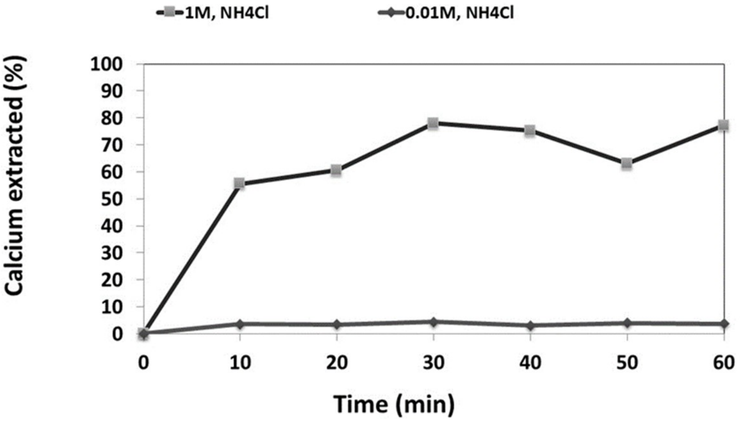

Figure 65. Comparison of calcium extraction efficiency with high and low solvent concentration

8.1.3 Carbonation stage

The Ca-rich solution from the extraction stage was reacted with pure CO_2 in the carbonation reactor resulting in precipitated calcium carbonate (PCC) production.). A precise control over the precipitation conditions is important to ensure a high quality PCC product. In conventional PCC production, aragonite PCC is produced at higher temperatures (> 55°C), but in the Slag2PCC method, such a high temperature carbonation process will result an evaporation of the NH_3 from the ammonium chloride solution. This in turn lowers the solution strength as shown in chapter 6.2.2.

Figure 66 shows the composition of the NH_3 in the flue gas from the carbonation process at 45°C and 60°C measured using FTIR. At 60°C, 20355 ppm, i.e.

more than 2 vol-% of NH_3, was detected in the flue gas. At 45°C only 1137 ppm, ~ 0.11%-vol, of NH_3 was detected.

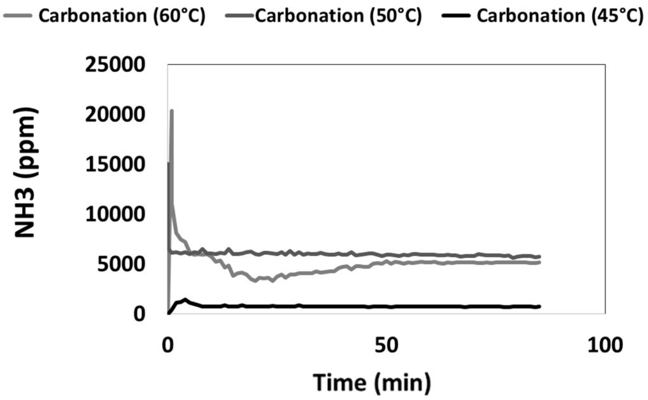

Figure 66. The concentration of ammonia in the flue gas during the carbonation stage (Reactor 2)

To minimize the ammonium evaporation at high temperature, a number of experiments was conducted at 45°C aiming at producing produce aragonite PCC by varying the CO_2 flow rate. According to the XRD analysis (Figure 67), aragonite PCC production is a very sensitive to the CO_2 flow rate. If the CO_2 flow rate is at 14 L/min, the aragonite volume fraction in the product is only 25 %, and if the CO_2 flow rate is 10 L/min, the aragonite fraction is 80 %. Thus it is possible to maximise the aragonite composition at 45°C, although it puts a limit to the CO_2 throughput.

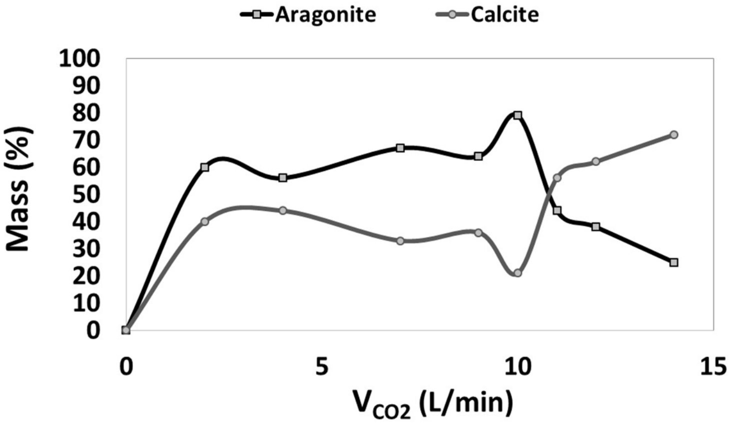

Figure 67. The content of aragonite and calcite in PCC precipitated at 45°C by XRD analysis.

When the CO_2 feeding rate was 10 L/min, the calcium concentration in the solution after the carbonation was 5730 mg/L, while the initial calcium concentration was 19600 mg/L, resulting in a calcium conversion of 71%. The Ca conversion could be maximized by increasing the CO_2 flow rate, but an excess amount of CO_2 will have a direct effect on the PCC quality either by 1) losing its homogeneous crystal shape or 2) increasing particle agglomeration. Therefore, there is a need for process optimization to maximize the Ca conversion and while guaranteeing PCC quality.

XRF was used to analyse the purity of the PCC produced from the pilot plant. Table 11 summarizes the major components detected in the PCC samples when either fresh or recycled solvent was used in the Ca extraction process. After the solvent was recycled many times, samples were not washed but only dried before the XRF analysis, and therefore the concentration of all other species increased except for chloride which was decreased due to the weakening of the solvent strength. However, the purity of the PCC produced from the pilot plant was higher than 99.5% and it can be further improved by washing

Table 11. XRF analysis of the PCC samples produced from the pilot plant.

Element	Fresh solvent	Recycled solvent (recycled 10–20 times)	Differences (ppm)
$CaCO_3$ (%)	99.53	99.76	2300
Si (ppm)	1473	2710	1237
V (ppm)	801	936	135
Mg (ppm)	1392	1450	58
Cl (ppm)	7963	5267	-2696

8.1.4 Development of product quality and the lab-scale continuous process setup

As discussed also above, one of the main challenges of the concept is to guarantee a commercial quality of the produced PCC. This problem can be addressed based on the finding that the process can be operated following different approaches (D532). Maximum utilization of steel slag (i.e. calcium extraction) is achieved by using a solvent concentration exceeding the stoichiometric limitations defined by the calcium extraction reaction; i.e. when ammonium salt is used in concentrations exceeding twice the amount of reactive calcium in the slag. Higher solvent concentrations result in quicker calcium extraction, but too high levels (>1 mol/L) extract also other elements (Mg, Fe, Mn, V, Na, P). These elements may accumulate in the process solutions, eventually precipitating with the calcium carbonate and leading into reduced product purity. Also, at high calcium concentrations the precipitated calcium carbonate tends to form clusters of sizes 10-20 µm, being large in comparison to the commercial PCC particles of < 2 µm.

Alternatively, the process can be run with a much lower ammonium salt solvent concentration. In this way the carbonate precipitation conditions mimic the currently used industrial practices for PCC production. Experimental work with an initial NH_4Cl concentration of 0.01 mol/L produced non-agglomerated rhombohedral calcium carbonate particles (diameter <1 µm, see Figure 68. However, only a small fraction (<5 wt.-%) of the calcium present in steel slag is utilized in one extraction-carbonation cycle. Thus, obtaining the same calcium conversion as in the high molarity process (20-40 wt.-% depending on the slag) requires several extraction cycles using the same slag, which obviously increases the total processing time.

Figure 68 also shows submicron-scale calcium carbonate as well as aragonite and scalenohedral calcite produced with the Slag2PCC process. These samples share similar properties with commercial products, showing that the Slag2PCC process can produce (near-) commercial quality PCC, even if this requires the process parameters to be chosen and controlled carefully. (D532, D541)

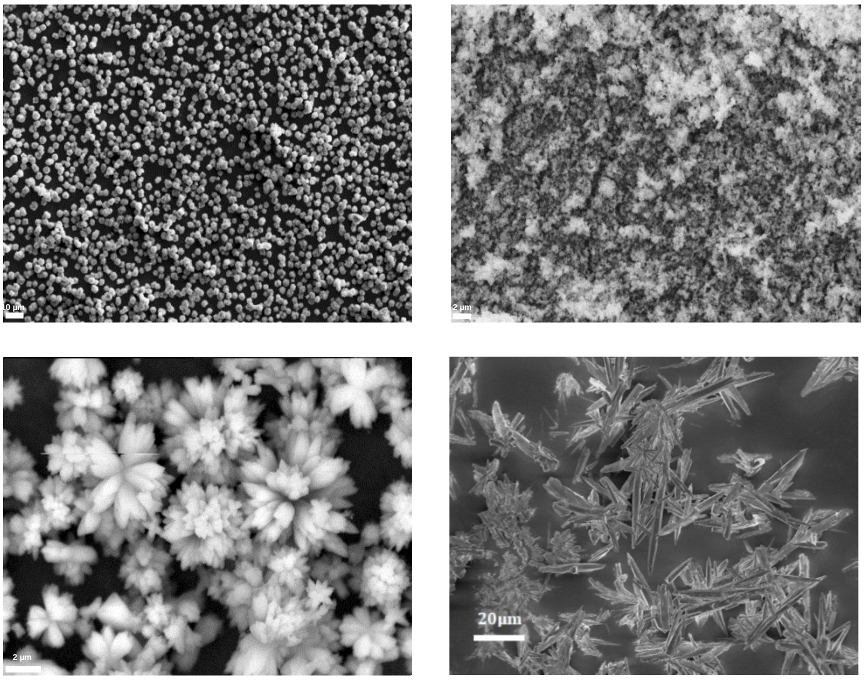

Figure 68. SEM pictures of rhombo- (up left) and scalenohedral (down left) calcite, nano-PCC (up right) and aragonite (down right) particles produced with the Slag2PCC process. Scale bars 10, 2, 2, and 20 µm, respectively (D532).

Certain types of particle morphologies have been obtained only when conducting the reaction steps on continuous basis on lab-scale. In addition, integration of the solids separation and washing units into the process setup could be more straightforward if batch operation was avoided. For this purpose a setup of two reactors with a volume of 28 L, including possibilities to test different separation units such as hydrocyclones or inclined settlers in combination with traditional barrier filters was designed for both continuous and batch operation and has been constructed and taken into use at Åbo Akademi University in 2013. The modelling work and experimentation to study the performance of the separation units is largely completed.Pre-separation efficiencies of up to 99 %-wt have been obtained even using only the inclined settlers, as reported in deliverable D542.

8.1.5 Detailed bubble reactor modelling and experimenting

Besides the extraction and carbonatíon work mentioned above, attempts are made to optimise the dissolution of CO_2 in the carbonation (bubble) reactor, which is a mass transfer-limited process,using CFD-based models. A lab-scale test set-up has been built at Åbo Akademi University too, for visual analysis and model verification. A mathematical description of CO_2 bubbles dissolving while rising through and aqueous solution has been produced which was combined with CFD model for a 2 m height, 0.13 m diameter water-filled column with mixers (Legendre and Zevenhoven, 2016, 2017). An impression of the results obtained is given in Figure 69 (left). This can be used to determine the carbonator height needed for complete CO_2 bubble dissolution. The model will be expanded with NH_3 transport into the bubble, and finally flue gas vs. CO_2 bubbles will be compared.

In parallel with the modelling work, experimental work was carried out using bubble tower with dimensions mentioned above, using high-speed video for bubble size and rise velocity measurement for model verification. The dissolution of CO_2 bubbles in (tap-)water followed the earlier calculations, while air bubbles showed a negligible dissolution in comparison. The results without the mixers present (these were implemented in September 2016) were recently published (Legendre and Zevenhoven, 2017) – see Figure 69 (right). Tests with mixers and calcium salts and/or PCC particles present will be finalised and submitted for publication during winter/spring 2016/2017.

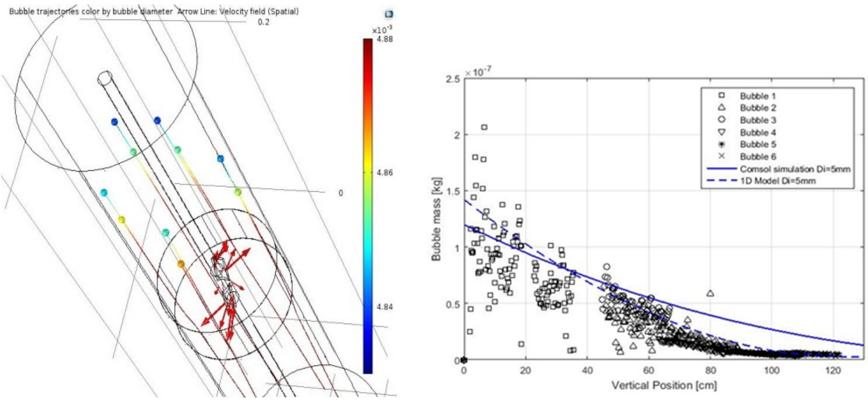

Figure 69. (left) CFD model of a bubble reactor height section with rising bubbles (bubble diameter in mm and velocity vector at the mixer shown) and (right) CO_2 bubble dissolution: mass reduction vs. vertical position and comparison with two models. Starting diameter 5 mm (Legendre and Zevenhoven, 2016, 2017)

8.1.6 LCA assessment of the Slag2PCC technology

A life cycle impact assessment (LCA) study was performed on the Slag2PCC concept by using the current estimates of the process properties (Mattila et al., Journal of Cleaner Production, 2014). The results indicate that using high concentrations of ammonium salt solvents has a drawback in form of removal of the chlorine contamination from PCC and from the residual slag. If this is done by washing, including recirculation and reuse of the washing waters, these steps require so much energy that it strongly impairs the process feasibility. Figure 70 presents the sensitivity analysis results of the study; a low solvent concentration Slag2PCC process has the lowest environmental impact in all the studied impact categories, while the high solvent concentration results, depending on the treatment of the washing solutions, have an impact even higher than the traditional PCC manufacturing.

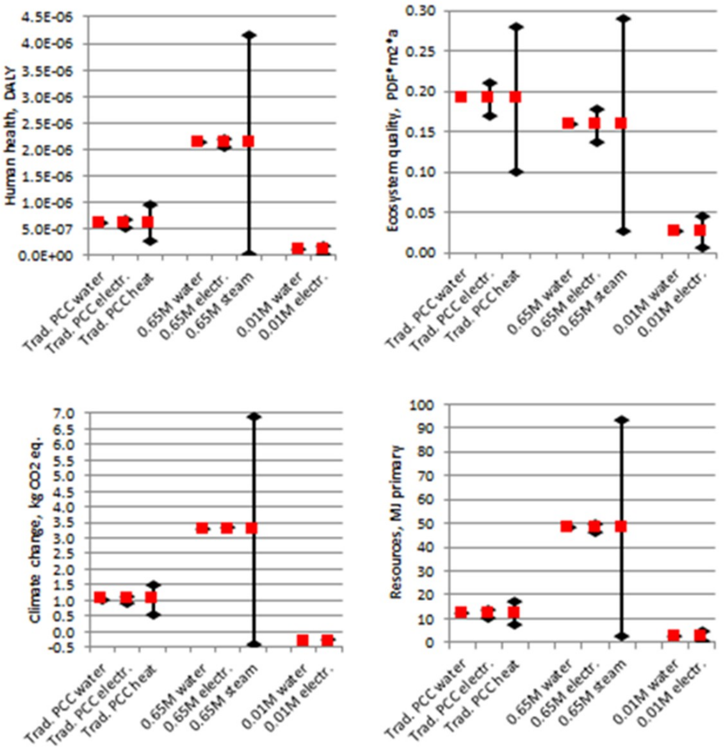

Figure 70. Life cycle impact assessment results per assessed impact category for traditional PCC production and for Slag2PCC with 0.65 and 0.01 mol/L solvent concentrations. Black lines indicate the uncertainty limits for the various commodities used in processes. (D528, Mattila et al., Journal of Cleaner Production, 2014)

8.1.7 Utilisation options for residue

Utilisation options for the process residue (spent steel converter slag) are also needed. One interesting option could be extraction of valuable metals from the residue before its disposal. This might even make it easier to find new utilization options for the spent slag, as leaching of the harmful elements could be reduced.

The research started by investigating porosity of the slag residue of the extraction reactor (where the steel converter slag had reacted with aqueous solution of ammonium salt) (D514). It was found that calcium extraction clearly increases porosity of the slag, likely promoting metal extraction. First a set of the experiments for extraction of valuable metals from the residue were made using the following solvents: sodium chloride (NaCl), sodium hydroxide (NaOH), sodium bicarbonate ($NaHCO_3$) and ammonium sulphate ($(NH4)_2SO_4$). However, none of the elements was dissolved in any significant amount, as the best extraction reached (calcium with 2 M aqueous solution of ammonium sulphate) was less than 20 %.

A literature review focusing on vanadium, one of the most interesting metals in steel converter slag, revealed that global vanadium production grew up to ~74 000 t in 2012 (Polyak, 2013), while the amount of vanadium in disposed of BOF slag in Sweden alone amounts up to 5000 t per year (Ye et al., 2013). In addition, the annual average price for FeV in Europe, ranged from 24.786 to 25.475 $/kg in 2012 (Polyak, 2013). Conventionally vanadium is extracted from its raw material either via alkali leaching, salt roasting or acid (H_2SO_4) leaching (Ye, 2006). Direct alkali or acid leaching generate huge amounts of residues and are hardly used. Acid leaching is effective, but not selective for vanadium, while alkali leaching is less effective, but is selective. Open scientific literature on leaching of vanadium from steelmaking slags was found to be almost non-existent.

None of the solvents represented in the found literature or used in our earlier experiments (Slag2PCC Plus project 2007-2009) show high promise. In addition, although roasted material has been used in many of the experiments reported in the open scientific literature, roasting itself is likely too complicated and energy-intensive for the goals aimed at here. However, several different acids, ammonium dihydrogen phosphate and sodium hydroxide were chosen to be tested. It was found that these solvents are not suitable for dissolving vanadium efficiently and selectively from the residual slag. Nonetheless, if an economic way can be found to recover vanadium selectively from the extraction solutions, the solvents might be useful. (D531) Note, however, that the slag used was a test slag produced by Ruukki Metals, with properties that differed from the slags otherwise used in the experimental work (see Said et al. 2013).

8.1.8 Case study for producing PCC from steelmaking slag

A preliminary assessment for producing PCC from Outokumpu steelmaking slag using the Slag2PCC process for use at Veitsiluoto paper mill was made (D517). The work was performed as a desktop study, using available experimental data. The framework and boundaries for the study were first assessed. It was found that although the current generation of slag suitable for the process is not enough for supplying the amount of PCC needed (130,000 t/a), future expansions are expected to provide enough slag, although the margin will be small. Various alternatives for implementing the process were screened. The option, where PCC is produced at the steel mill site and transported to the paper mill by truck was found to be the cheapest way for implementation, since it had the lowest transportation costs (3-10 euro/t PCC). This option was selected as the base case for concept evaluation to determine a coarse estimation of the investment costs and operational costs for the facility (Figure 71). The feasibility analysis of the case studied showed that the investment costs are relatively high – 76 M€. With an estimated annual revenue of 6.1 M€, the payback time would be 20 years. A large part of the investment costs is due to the demanding washing & filtration requirements. A conventional PCC plant requires only one stage of filtration, while the PCC process evaluated here would require three stages with washing. However, the filtration performance was largely based on assumptions and real experimental data was at the time missing. Therefore, experimental work was carried out to determine the filtration requirements for the process (see below).

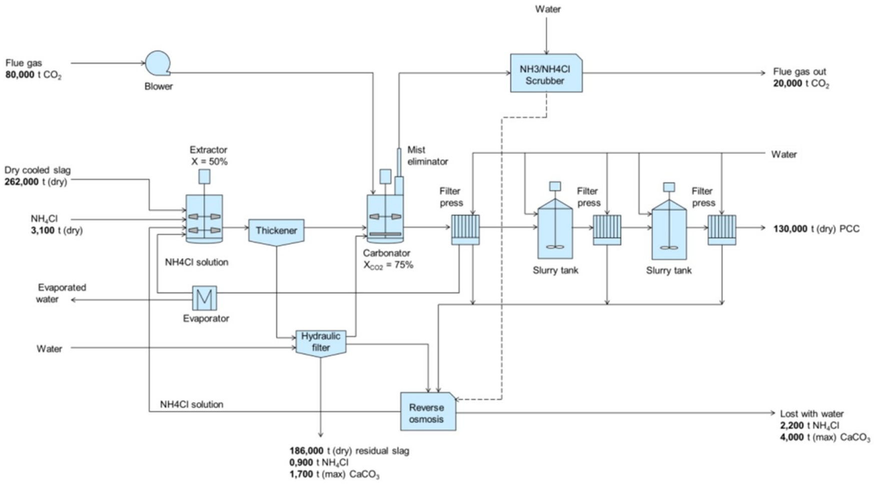

Figure 71. Flow sheet of the case study on the PCC production process for slag (mass flow unit: tonne per year; D517).

As mentioned above, one of the challenges for the Slag2PCC process is the requirements for washing of the PCC. In order to minimize the solvent remnants on fine (1-2 µm diameter) PCC particles, a three-stage washing and filtration equipment setup would be needed. This complex filtration setup would make up a large part of the investment costs for this facility, making a Slag2PCC process 3-4 times more expensive than a similar sized conventional PCC plant. Instead, the Slag2PCC process parameters could be adjusted to produce larger (20-50 µm) particles, to be subsequently ground down to a finer size suitable for paper making purposes. Although this lowers the investment costs significantly, grinding makes the particle size distribution less narrow than that needed for the filler purposes. At the current development stage it seems more economically feasible to aim for a product that can compete with fine-ground aragonite (GCC) instead of fine, scalenohedral PCC.

Therefore, the process simulation was updated for producing GCC (Figure 72). For this case, 60 000 t GCC is required (Teir et al. 2016). The process calculations show that the largest operational cost is expected to be the cost for the slag residue handling (estimated coarsely at 15 €/t), representing 37% of the total operational costs. The largest heat requirements comes from the evaporation (3.6 GWh/a) and the largest power requirements come from PCC grinding (4.7 GWh/a). The total operational costs were 3.8 M€/a. Due to the coarser particles the filtration is much simpler, which is reflected in the much reduced investment costs: the total investment for the new process was estimated to 11 M€. The investment costs were estimated only for the main equipment of the process using in-house process component cost data and experience. Costs for intermediate storage and handling of raw materials and products are excluded. The main equipment prices include the share of construction, piping, automation, etc. The share of main equipment prices is 34% of the total investment price. The filtration investments were estimated on engineering, procurement and construction (EPC) basis by Outotec.

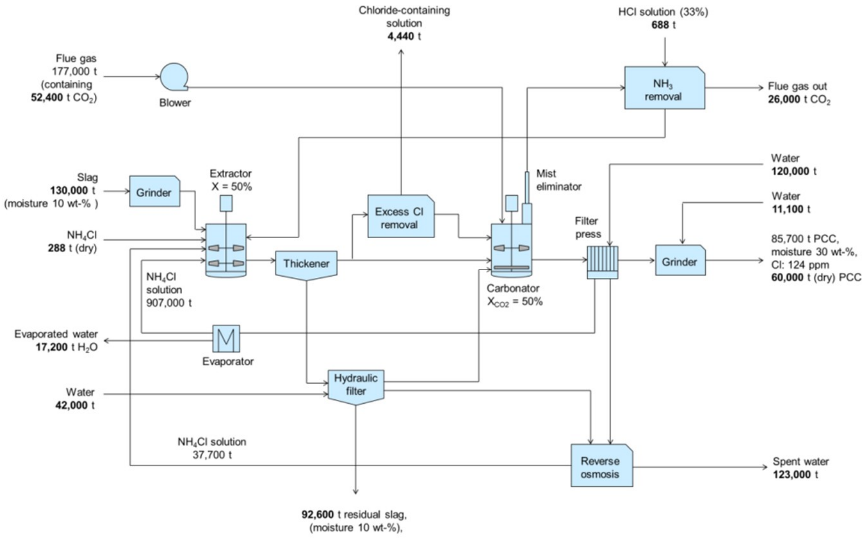

Figure 72. Updated flowsheet for producing PCC to replace GCC in paper applications. Mass flow presented on an annual basis (Teir et al. 2016b)

The economic feasibility of the process is highly dependent on the value of the produced calcium carbonate. If the produced PCC was sold to a price of 150 €/t (the price for paper grade GCC of a similar particle size distribution) the annual revenue would be 5.2 M€ with a turnover of 9.6 M€. Assuming that all the revenue is used for payments of the loan, the investment payback time would be 2 years.

Since the steel mill is part of the EU emissions trading system, it is possible that an economic benefit could be had from the CO2 emissions avoided thanks to the

Slag2PCC process. Currently, emission allowance prices (EUA) have been very low and was 8 €/t CO_2 at the time of writing. At this price, the benefit from emission allowances would only be 0.14 M€ per year.

The environmental footprint of the process was calculated with GaBi software based on the HSC Chemistry model and estimation on the process equipment electricity consumption (D533). In Figure 4 the global warming potential (GWP) per ton of produced PCC is presented. The calculation takes into account CO_2 capture, electricity consumption, process steam consumption and its production, slag residue disposal, waste water treatment, transportation of PCC, fresh water usage and HCl consumption. The main emission source is the electricity production. The electricity consumption in the process is 209 kWh/t PCC. It includes PCC grinding 107 kWh/t PCC, reverse osmosis (RO) electricity consumption 44 kWh/t PCC, general electricity use (stirrers, pumps, etc.) 42 kWh/t PCC and slag grinding 16 kWh/t PCC. The second biggest emission source is the steam consumed in the evaporation unit. It is assumed to be produced with a heavy fuel oil fired unit. The net GWP value was -0.3 tonne CO_2 equivalent per tonne of produced PCC.

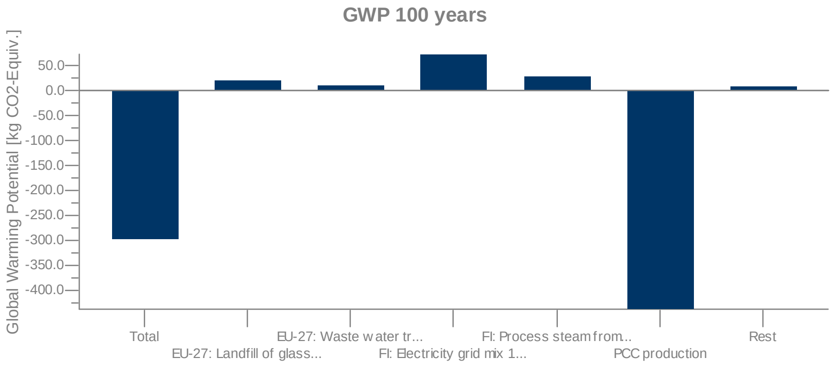

Figure 73. Process environmental footprint per tonne of produced PCC (D533).

8.1.9 Filtration and washing tests

Before the pilot at Aalto was ready, washing and filtration properties of commercial PCC were tested. Experimental work was performed at VTT for comparing the filterability of scalenohedral PCC in ammonium salt solutions to that of pure water. Both the filterability and settling speed of PCC was affected by the ammonium salt. Using experimental data the existing process models were updated and the economic calculations were improved (D517).

Similar experiments were performed at Åbo Akademi University (Hudd MSc thesis, 2014). Using a vacuum filter for $CaCO_3$, particle size <10µm, the dry solids content of the filter cake was measured to be 70-75%. At the same time, the ammonium chloride content of 5 wt.-% was reduced to <0.01 wt.-% in two washing steps using ten times more water compared to the mass of the solid sample. A laboratory scale pressure filter (Labox25) yielded similar results at the filtration pressure of 16 bar, showing that the filter type is not a significant parameter for the overall filtration and washing efficiencies.

When the pilot at Aalto was completed, two calcium carbonate slurries were produced from steel converter slag and CO_2, in order to determine the filterability of PCC produced with the Slag2PCC method (D545). The maximum filtration rate of the calcium carbonate slurries was determined by experimental work, with a focus on minimizing the chloride content in the carbonate by filtration and washing. The tests included pressure filtration and vacuum filtration and the test series contained altogether 21 different filtration cycles with varying combinations of filtering, washing, and drying steps. The filtered cakes were analyzed by their residual moisture content, chloride content and conductivity, and the filtrates by their residual solids content, chloride content and conductivity. The results showed that a residual chloride content as low as 10 ppm of the filtered solids can be achieved with quite a small amount of washing water and the filtration rate is fast. Pressure filtration gave a high capacity (400-460 kg/m2h) and a low cake residual moisture content (12-14 wt-%). Vacuum filtration gave even higher filtration rates (500-610 kg/m^2h at the lowest residual chloride contents of the cakes), but the cake residual moisture also stayed higher (25-26 wt-%).

For the slag residue, small scale filtration tests resulted to a dry solids content of 90 wt.-% (D502). In general, washing the ammonium chloride solvent from the process solids quickly destroys the feasibility of the Slag2PCC technology compared to the traditional PCC manufacturing, and thus it is advisable to use only low solvent concentrations. (Mattila et al. Journal of Cleaner Production, 2014).

8.2 Magnesium silicate rock carbonation for a lime kiln

Driven by a range of well-documented motivations (such as large mineral resources in many locations like Finland, production of useful materials, no need for CO_2 storage monitoring, etc.) CO_2 mineral sequestration is being developed in the CCSP program. This is further supported by the ongoing international R&D efforts to find cost-effective use of CO_2 or other products related to the CCS chain, which can (partly) cover the costs for CCS.

8.2.1 The ÅA route

More than a decade of work that originally started at Aalto University has been further developed in Åbo Akademi to what has become known as “the ÅA route” for stepwise carbonation of serpentinite, a rock composed mainly of magnesium silicate mineral serpentine. Similar to other research groups the chemical reaction kinetics of the process steps have received much attention but the work done in CCSP is unique in having the minimization of energy input and chemicals use as starting points as well. Energy is recovered (as ~500ºC heat) from the carbonation reaction (Fagerlund et al. 2012). Current trends – certainly in part due to Åbo Akademi's work – show several routes that focus on the use of ammonium salts and integration with CO_2 removal from (flue) gases. These salts are relatively cheap and in principle fully recoverable within the process routes that make use of the fact that the sulphate of magnesium, extracted from rock, is water-soluble. Another trend is to apply mineralization on the CO_2-containing gas directly, without the expensive (and for oxygen-containing gases challenging) capture step of a CCS process train.

The "ÅA route", as depicted in Figure 74, comprises extraction of magnesium from rock using ammonium sulphate salt in a 400–450ºC solid/solid reaction followed by precipitation of magnesium hydroxide (besides iron hydroxide) in aqueous solutions, using ammonia vapour from the upstream solid/solid reaction for raising pH levels. Subsequently, the magnesium hydroxide is carbonated within ~10-30 minutes in a pressurized fluidized bed reactor at ~500ºC, 20 bar CO_2 pressure, producing ~1/3 of the heat needed for the magnesium extraction (Fagerlund 2012, Nduagu 2012, Romão et al. 2012). Conversion levels obtained so far are 80% and 70%, respectively, for the production and carbonation of $Mg(OH)_2$ produced from serpentinite.

As addressed below, one challenge to applying this route is that it may have to be operated on other magnesium-containing feedstock rock than serpentinite.

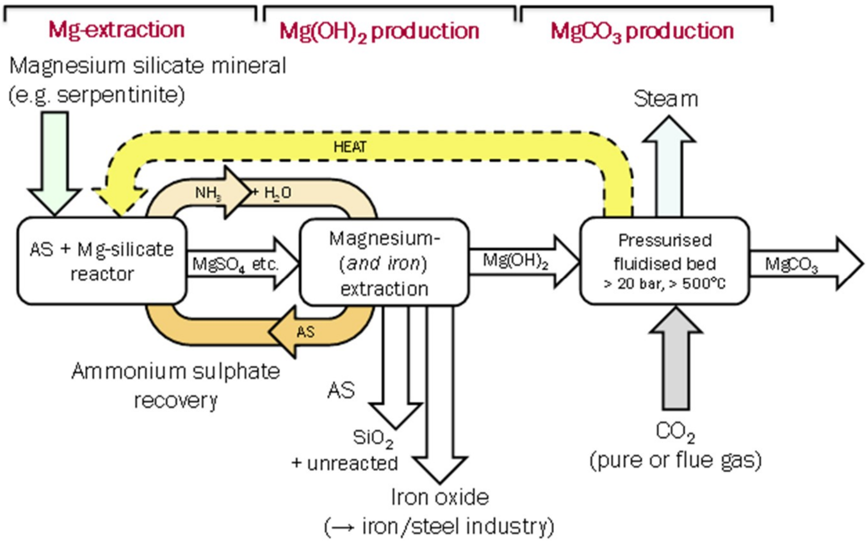

Figure 74. The mineral carbonation process concept ("ÅA route") developed by Åbo Akademi

8.2.2 Application at an industrial lime kiln

Application of the mineral carbonation process at an industrial lime kiln, possibly located in Parainen, is under consideration in CCSP: a recent study shows that operating at 80 bar carbonation pressure with ~22 %-vol CO_2 flue gas without capture, mineral sequestration may be accomplished at an energy penalty of 0.9 GJ/t CO_2 electricity besides 2.6 GJ/tCO_2 heat which can be extracted from the kiln gas (Slotte et al. 2013). Another application that has been considered is the mineralization of CO_2 from the Meri-Pori power plant using rock at Vammala, ~85 kg east of the power plant (Zevenhoven et al. 2012). Specific for application in Parainen, the use of diopside-type material has been suggested instead of a serpentinite, also considering the possible differences of using ammonium sulphate (AS) or ammonium bisulphate (ABS) as the preferable fluxing salt for magnesium extraction. An engineering study by Outotec has given the first suggestions for application of the ÅA route at an industrial lime kiln, using serpentinite, identifying several challenges.

Thus, recent research work involved the upgrading of diopside-based material from the Parainen quarry. Using various solvents and thermal (pre-)treatment, the aim was to produce a serpentine-type material fraction besides quartz and dissolved calcium. Having completed that task it was concluded that this upgrading won’t be feasible, apart from the disadvantage that a separation step is needed to obtain the diopside concentrate in the first place. However, another potential rock materials for magnesium extraction were identified near Suomusjärvi and near Vammala, Southern Finland and are being tested before a final rock material will be selected for the purpose of a more detailed process engineering design. Both thermal and wet chemical extaction methods were applied to obtain a reactive magnesium (or calcium) -based for subsequent carbonation (Deliverable D555). The owner of the lime kiln at Parainen, owning / operating several quarries and kilns in Finland, however, made clear in 2015 that they would have to use both rock material and CO_2 obtained from their own activities. A search for such a suitable rock did not give a result, unfortunately.

For application outside Finland, Åbo Akademi has been cooperating with partners in Singapore (with Tekes co-funding 2010-2014), aiming at large-scale application of CCUS (carbon capture, utilisation and storage) for land reclamation by around year 2020, and in Portugal, where very large resources of mineral are available in the north-east of the country, at a stone-throw from the large-scale oxy-fuel power plant demonstration at Ciuden, Spain. One outcome of that is the “alternative ÅA route” where the carbonation step is done in an aqueous solution, again operated directly on CO_2 containing gas (no separate capture step). Also this “alternative” route has been considered for application at the lime kiln, as recently reported (Zevenhoven et al., 2015, 2016, Deliverable D547). Although less energy efficient, this “alternative” route is technically less complicated while giving similar results (however producing hydromagnesite

$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ instead of magnesite $MgCO_3$). LCA calculations showed that the “alternative” route has a smaller environmental footprint than the “original” route, while it also showed that the transport distance for serpentinite rock to a carbonation process plant (5, 150 or 550 km) had very little impact (Slotte, 2017). This was also considered for the final large-scale application process design and feasibility study aimed at.

No suitable magnesium silicate feedstock could, however, be found or extracted from the wall-rock or other side-stones from limestone quarries at Parainen or other locations in Finland. Therefore, it was concluded in June 2016 that a case study more worthwhile to consider would be the use of Hitura serpentinite at a lime kiln at SSAB Europe in Raahe. Being larger than the kiln in Parainen, it was expected that significant amounts of waste heat are available at the kiln at Raahe as well. Unfortunately, no data on the kiln in Raahe was put forward for an assessment or producing a design for a possibly feasible process (Deliverable D556).

9. CO_2 utilisation

In addition to permanent storage of CO_2 some industrial applications of CO_2 could offer potential to utilise CO_2 as a raw material and this is gaining interest among industry. Examples of industrial utilisation could be the use of CO_2 as a raw material in chemicals and fuels production, as a solvent or in enhanced cultivation of algae. Sustainability assessment analyses and life cycle analyses are needed in order to evaluate real potential and sustainability of these CO_2 utilisation alternatives in connection to CCS besides the estimation of economic boundary conditions.

Carbon dioxide is already used in commercial processes, both in its pure form and as a feedstock in the synthesis of bulk chemicals and fuels. In the pure form CO_2 is presently used in many industrial sectors for several purposes (Figure 75).

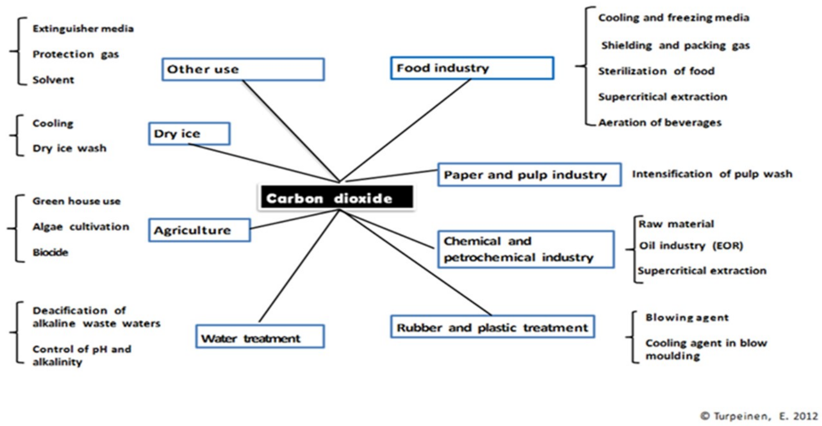

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Figure 75. Sectors where CO_2 is utilized (modified from Miilumäki 2011).

For example, it is used to carbonate drinks in food industry or to accelerate production in greenhouses. As an inert and safe gas it is also used as a protective gas (in chemical or steel industries, in food preservation, in welding etc.) and as a fire extinguisher. Being an acidic compound CO_2 has been used to adjust pH in water treatment. Likewise, large quantities are also used as solvents in processes such as dry cleaning and decaffeination. Carbon dioxide is also used in enhanced oil and gas recovery by pumping it under near critical or supercritical conditions into oil fields where conventional recovery has become uneconomical or impractical.

As an economic, safe, and renewable carbon source, CO_2 turns out to be a tempting carbon-based building block for making chemicals and materials. The utilization of CO_2 as a feedstock for producing chemicals not only contributes to mitigating global climate change caused by the increasing CO_2 emissions, but also provides a grand challenge in exploring new concepts and opportunities for catalytic and industrial development. As a matter of fact, the utilization of CO_2 is the only technology that may produce profit out of the recovered CO_2, while contributing to reducing its global emissions.

Several industrial processes use CO_2 as a feedstock, and R&D is being undertaken to increase such applications. The current industrial use of CO_2 is about 130 Mt/a worldwide, of which the production of urea is the largest consumer of CO_2, accounting for 60% of the total amount (Aresta & Dibenedetto 2007). Other uses include the production of intermediate chemicals required by the chemical industry, such as carbamates, carboxylic acids, inorganic complexes and polymers (Figure 76).

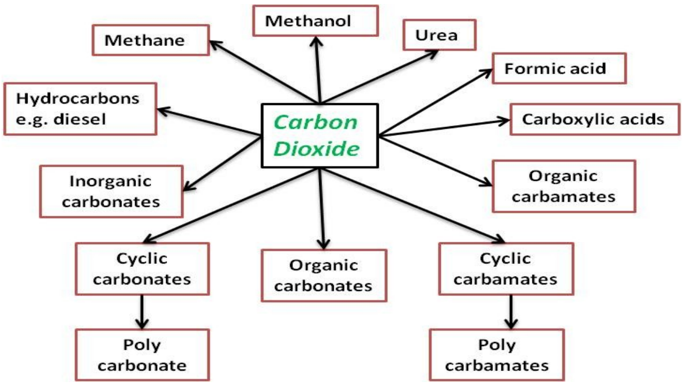

Figure 76. An overview of chemicals production from CO_2 (modified from Styring et al. 2011).

However, in most cases CO_2 is eventually released back to the atmosphere at the end of the life-cycle of the product, which can range from days to decades (and in some cases centuries). Recent estimates of the maximum use of CO_2 as a feedstock for chemical products are 180-230 Mt/a worldwide (VCI & DECHEMA 2009, Styring et al. 2011), which is a small potential contribution in relation to global anthropogenic CO_2 emissions (around 32 Gt in 2012). However, despite the fact that, currently, the usage of CO_2 in the chemical industry cannot reduce significantly the global CO_2 levels, it is believed that the full potential of the fixation of CO_2 into value added products has not yet been completely explored. The further development of industrial processes that are utilizing CO_2 for high-demand products is of importance.

9.1 Use as a reactant (chemical utilization)

CO_2 can also be used as a feedstock for the production of fuels such as methanol and synthetic liquid hydrocarbons. For example, VCI and DECHEMA (2009) estimate that a maximum of 2 Gt/a CO_2 could be used for fuel synthesis. Although the amount of energy required to produce liquid synthetic fuels exceeds the recoverable energy, they allow storage of energy and can easily be used in transport applications. Their production may be supported by renewable energy sources as a way of balancing supply and demand in the future electricity systems dominated by variable renewable energy sources.

In CCSP, various technologies and concepts in which CO_2 can be utilized directly (D201) and chemically (D203, D607) have been screened. The most promising CO_2 based reaction routes have been elaborated and their market potential analysed (D260). Attention has been given also to the sustainability (economic, environmental and social aspects) of the technologies and concepts and their greenhouse gas mitigation effects.

Thermodynamic calculations offer a practical and useful way to observe the effects of process variables, such as temperature and amounts of raw materials, on product composition. Moreover, thermodynamics tells limits of certain reaction (how far the reaction can proceed). The viability of selected CO_2 utilizing reactions was analysed by thermodynamic calculations (effect of temperature, pressure and feed ratio) (D617). Utilization of CO_2 for the production of fine chemicals is, in many cases, severely limited by the reaction equilibrium but there exist reactions that are viable. While CO_2 has low chemical activity, it is possible to activate it towards reaction by using efficient catalysts and proper process conditions. CO_2 conversion into useful chemicals and fuels can be driven by homogeneous, heterogeneous and enzymatic catalytic systems. Typical catalytic systems used in selected reactions were listed (D617).

Several processes were found promising in terms of viable future CO_2 utilisation routes: production of synthesis gas, methanol, formic acid and dimethyl carbonate as well as CO_2 methanation. A preliminary sustainability assessment and comparison against conventional production routes was performed for some of these reaction routes (D202): syngas production via steam methane reforming (SMR) vs. dry reforming (CO_2 reforming), syngas based methanol synthesis vs. methanol synthesis using CO_2 and dimethylcarbonate (DMC) production via oxidative carbonylation vs. direct synthesis of DMC via CO_2. Dry reforming was found to be environmentally a more sound process than SMR but it had a lower economic sustainability/competence. Methanol synthesis via syngas showed slightly better overall sustainability than the CO_2 based reaction. DMC production via oxidative carbonylation was more cost-effective than the CO_2 route but the CO_2 based route was environmentally and socially more sustainable. Morever, a multicriteria based evaluation tool was used to assess the sustainability of three different reaction routes to dimethyl carbonate: direct synthesis from carbon dioxide and methanol, transesterification of methanol and propylene carbonate, and oxidative carbonylation of methanol (D608). The assessment showed that the transesterification route had the best potential toward sustainability. The assessment gave clear understanding of the main benefits of each reaction route, as well as the major challenges to sustainability, which can further aid in orienting development efforts to key issues that need improvement. Direct synthesis of DMC from CO_2 was studied experimentally as well (D247). This work focused on this reaction using calcined hydrotalcite supported on hexagonal mesoporous silica as a catalyst and phosphonium ionic liquid as a promoter.

Sustainability assessment was conducted also for processes producing formic acid, comparing routes using CO_2 with conventional formic acid production routes (D221, D246). The results from the assessment showed that the conventional route was harmful to the environment while the CO_2 utilization routes were beneficial to the environment. The CO_2 utilization route was economically more viable than the conventional, but more development work is needed on the CO_2 utilization route to fulfil its potential.

Recently, a new concept of ‘‘tri-reforming’’ has been launched and experimentally demonstrated for the utilization of power plant flue gases for synthesis gas production, without the need to first separate CO_2. The technical viability to utilize biogas, refinery gas and coke oven gas as a feedstock for synthesis gas production by the reforming process was tested (D247).

Among the catalytic reactions of CO_2, hydrogenation of CO_2, the so called methanation reaction, is a suitable technique for the fixation of CO_2. Methane has proven to be an outstanding energy carrier and is the main component of natural gas and synthetic natural gas (SNG). SNG may be synthesized from the CO_2 and hydrogen available from various sources and may be introduced into the existing infrastructure used by the natural gas sector for transport and distribution to power plants, industry, and households. A literature survey and analysis on potential concepts (chemical, photochemical, electrochemical and membrane-assisted routes) for CO_2 methanation reaction was conducted and the report was drawn up. (D609).

The viability of the CO_2 methanation reaction route was elaborated and assessed experimentally. There are many challenges existing in catalyst development for low temperature (<350^oC) CO_2 methanation. Several typical metal oxide catalysts (e,g, Ni-, Ru- and Rh- based ones) were prepared and tested in the methanation reaction. Commercial Ni/Al_2O_3 and Ru/Al_2O_3 catalysts were used as references. Moreover, the novel catalytic materials were prepared (mostly hydroxyapatite (HAP) and carbon based materials) and tested in CO_2 methanation in order to improve the key properties of the catalysts, i.e. activity, durability and selectivity. The preliminary results shows that Ni (10 wt.%) modified CeO_2/HAP catalyst was found to be most active and selective catalyst and achieves high CO_2 and H_2 conversions already below 350°C.

9.2 Use of CO_2 as a solvent

Supercritical CO_2 is becoming an important commercial and industrial solvent due to its low toxicity and environmental impacts. The use of supercritical CO_2 and its applications were mapped (D223). The impact of the solvent on the catalyst behavior was studied in the dimerization reaction of isobutene wherein CO_2 and propane were comparatively used as a reaction medium (D222). The results showed that carbon dioxide is a potential solvent for industrial purposes as it prolongs the catalyst activity due to a reduced coking tendency.Besides used as a reactant or solvent carbon dioxide can be utilized in other industrial sectors e.g. in mining industry.

Utilization of carbon dioxide in beneficiation of PGE (platinum group elements) minerals was also studied (D220). Carbon dioxide conditioning was not found to have significant effect on the recovery and grade of platinum and palladium minerals.

9.1 Thermo-catalytic decomposition of methane

Methane can be thermo-catalytically decomposed into gaseous hydrogen and solid carbon. The decomposition reaction itself produces no CO_2 and could thus possibly be used to reduce CO_2 emissions in energy production based on natural gas. However, the decomposition reaction requires very high temperatures. In practice, temperatures above 1200 °C are required to achieve relatively high conversions with practical residence times. The temperature needed can be lowered by the use of catalysts. The catalysts suitable to accelerate the methane decomposition can be divided into carbonaceous and metal catalysts. However, the catalysts are easily deactivated due to the carbon formation in the decomposition reaction.

9.1.1 Experimental studies

In CCSP, the literature reviews of thermo-catalytic decomposition were conducted (Fager-Pintilä 2012, Rajamäki 2014). Moreover, a patent review was done (Fager-Pintilä 2012). Thermo-catalytic decomposition of methane was also experimentally tested. Fager-Pintilä (2012) conducted experiments in a stainless tube reactor (I.D. 42.3 mm). The experiments were conducted with a commercial carbon black catalyst in a temperature range of 500–950 °C. Methane conversions up to 0.8 were observed, and temperature and space velocity were found to affect the methane conversion.

Fager-Pintilä (2013) conducted experiments in a quartz tube reactor (I.D. 26 mm) with different catalysts. Quartz sand, pure quartz, biomass-based active carbon and commercial carbon black were tested. One of the objectives of the work was to find cheap catalyst materials. However, quartz sand, quartz, and biomass-based char had very little effect on the decomposition reaction. Moreover, the active surface area of the biomass-based char dramatically reduced in high temperatures needed for the methane decomposition reaction. The high surface area of the commercial carbon black was found to be a critical requirement to achieve even moderate methane decomposition rates.

Rajamäki (2014) conducted experiments on the thermal decomposition and autothermal pyrolysis of methane in a ceramic tube reactor (I.D. 25 mm) in a temperature range of 800–1200 °C. In autothermal pyrolysis of methane, unstoichiometric amount of oxygen or air is added to the methane decomposition process. The combustion of the feedstock or the reaction products provides heat for the process, thus reducing the need for external heat input. The experimental results showed that also the autothermal pyrolysis of methane produced hydrogen and solid carbon. The amount of methane combusted in the process was found to be low, and the autothermal pyrolysis can thus be seen as a feasible option for enhancing the heat input of the methane decomposition process. The elemental analysis of the carbon product showed that it is crystalline and contains over 95% of carbon. The oxygen content varied between 3 and 4.5%. Other minor components, aluminium, silicon, and copper, were assumed to originate from the experimental setup.

Moreover, Keipi (2014) experimentally studied the effect of four metal catalysts on methane decomposition reaction in the ceramic tube reactor. The noble metal catalysts (rhodium and iridium) were not active at the temperature range of 500-1000 °C in the reactor in concern. The zirconium oxide catalyst catalyzed the reaction at 800 °C but a rapid deactivation occurred as the product carbon accumulated on the catalyst surface and sequestered the catalyst pellets from the reaction. The nickel catalyst showed most promising results and methane decomposition occurred at a temperature range of 500–700 °C. The methane decomposition reaction continued during several hours although the solid carbon formation gradually broke down the catalyst pellets. The experimental observations may refer to the production of whisker carbon that breaks down the catalyst into pieces but at the same time remains the catalytic activity of the catalyst.

Due to the several limitations of the previous ceramic reactor related to the heat transfer in the reactor and small amount of produced carbon, a new larger scale test reactor (I.D. 73 mm, length 2500 mm) was built. The flow-through reactor is electrically heated (power 60 kW) and the reactor tube made of high temperature resistant alloy is filled with heat transfer material to stabilize the temperature distribution inside the reactor. The new reactor enables more detailed study of the reaction kinetics of TDM reaction and produces larger amount of carbon to the analysis purposes. This information is required for TDM process design purposes and to scale-up the reactor.

9.1.2 Technical analysis

A market analysis of the carbon product was conducted (Tolvanen 2013). The morphology of the carbon produced by thermo-catalytic decomposition or auto-thermal pyrolysis of methane strongly depends on the temperature and catalyst used. Possible forms include carbon black, carbon nanostructures, graphitic carbon film, and amorphous carbon. The carbon product could be used for example for energy production, soil amendment, in construction industry, and in tire, paint, and rubber industry. Also activated carbon could possibly be produced.

The reaction parameters of TDM and those effect on the process design were analysed in Keipi et al. 2016b. The most important reaction parameters in TDM are temperature and catalyst. These two parameters define the product carbon type and the reactor's heat requirement. Furthermore, these parameters affect the selection of reactor type as well as reactor design. Market potential of the TDM product carbon was evaluated. The product carbon quality and its utilization possibilities needs to be carefully considered if TDM is to be applied in commercial scale.

Two technologies, TDM and Power-to-gas, were studied as potential technologies to be applied for storing renewable energy to chemical energy carriers, hydrogen and synthetic methane (Lappalainen 2016). A literature survey was conducted to compare the utilization possibilities, storage and transportation options as well as the environmental and safety issues of these two technologies. In the Power-to-gas method the energy carrier is synthetic methane, which is a compatible fuel with the currently available natural gas infrastructure. In contrast, the hydrogen produced by TDM is an environmentally friendly fuel but it requires investments in the infrastructure. However, the TDM installation could be located at the point of utilization where extensive transportation of hydrogen would not be needed.

9.1.3 Techno-economic evaluation

A techno-economic concept study on the thermal decomposition of methane (TDM) was conducted by Keipi et al. (2016a). Four concepts with the fuel input capacity of 150 MW and different process characteristics were analysed. Concepts were designed so that those can be installed in front of an existing natural gas fuelled power plant. In TDM process, methane is partially converted to solid carbon and gaseous hydrogen. In this concept study, the product gas was utilised for power generation in a steam turbine cycle and the extracted carbon was sold.

Four concepts applying different technologies to conduct the TDM reaction were sketched. Concept 1 was a non-swirling methane burner reactor where burning methane in one reactor zone produced the heat required to decompose the major methane flow in the other reactor zone. In Concept 2 (power-to-carbon) the heat was produced with electricity. Concept 3 was a catalytic fluidized bed reactor utilising a circulating fluidized bed reactor. Concept 4 was a heat exchanger reactor utilising heat exchange material for pre-heating the methane input. Concept 4 is described more detailed in the invention disclosure made to the Tampere University of Technology (Raiko et al. 2014).

Each concept contained process connections to pre-heat the feedstock methane (and air in Concept 1) with heat transferred from the product gas. Furthermore, there was a cooling system for the product streams to allow them to exit the process at a feasible temperature range. Carbon extraction from product gas was designed with a cyclone and a fabric filter.

The study included mass and energy balance calculation and preliminary techno-economic comparison of the concepts. Calculation was based on TDM reaction stoichiometry assuming certain methane conversion rates and a fixed under-stoichiometric air factor in Concept 1. Input values were selected on the basis of the literature review done earlier and existing experience from experimental tests on a laboratory scale. The most important input values were the methane conversion rates, the reactor temperatures, the reaction enthalpies and the consumption rates of the supply materials. Reactor dimensions were roughly estimated and the resulting residence times were calculated.

Economic evaluation was also conducted. The investment costs were estimated based on similar reactor types and components found in process industry. Moreover, the project costs were added up. Operational costs were estimated based on the calculated internal electricity consumption, fixed operational & maintenance costs and other supply material costs. Annual income consisted of sold product carbon. All costs in each process were divided by the amount of produced electricity. Thus, the outputs of the analysis were the cost of electricity production (€/MWh$_e$) and the cost of avoided CO_2 emissions (€/t$_{CO2}$ avoided). A reference case in the analysis was the electricity production from natural gas in a steam power cycle. The cost of electricity production in the reference case includes the fuel cost and the cost of emission allowances when electricity is produced from natural gas in a steam power cycle with the efficiency of 30% which is the same as in the concepts.

The investment costs were the highest in Concept 3, which also was technically the most complicated process. As a whole, the feasibility of the concepts depended especially on the price of the sold product carbon. A clear result was that the product carbon has to be commercially valuable in order that the concepts appear economically feasible. In Concepts 1 and 3, the net efficiency of electricity production was the highest and the CO_2 emissions were the lowest among all the concepts. With a product carbon price of 600–700 €/t, the cost of electricity production in Concepts 1 and 3 was equal with the reference case. Increasing the price of product carbon to the level of 700–1500 €/t rapidly decreased both the cost of electricity production and the cost of avoided CO_2 emissions. I was found out that with the current assumptions the TDM process can be economically feasible. For example, in Concept 1, a moderate price of product carbon, 500 €/t, and a relatively high conversion, 0.8, resulted in the cost of avoided CO_2 only 51 €/t_{CO2}. In conclusion, the CO_2 emissions decreased compared with the reference when only a part of the carbon was taken out from the feedstock in a solid form.

The study is a preliminary analysis of the full-scale application of TDM, and therefore the results can be primarily utilized to compare the concepts with each other. Furthermore, the study indicates the importance of the quality of the product carbon and gives an approximate value that the product carbon has to meet. Additional evaluation and experimental verification of input values and results is still needed in order to achieve a more detailed analysis results.

9.2 CO_2 capture by algae cultivation

Photosynthesis is known as a means, at least in theory, to capture anthropogenic carbon dioxide. Aquatic microalgae are among the fastest growing photosynthetic organisms, having carbon fixation rates an order of magnitude higher than those of land plants. Thus algal photosynthesis may be a viable option for anthropogenic CO_2 capture and sequestration. While microalgal culturing imply investment and operational costs, microalgal biomass can be utilised as biofuel in various forms or produce a variety of high value compounds that can be used to generate revenues. In our work on CO_2 uptake by microalgae, new methods for sustainable industrial utilisation of CO_2 are studied with the main focus on microalgae research and design of a technical solutions. The ultimate objective is to create technological readiness for a pilot plant utilising microalgae for CO_2 capture and biogas/-fuel production integrated, as a case, into a gas refinery. The target is to reach optimised CO_2 uptake in combination with technically feasible and cost efficient production and utilisation of the algal biomass.

9.2.1 Review of concepts and technologies for capturing CO_2 by algae

The objective of this work (D601) was to identify possible technical solutions for algae uptake of CO_2 from industrial gases such as flue gases and vent gases, with focus on processes that can maximize CO_2 uptake and conversion to organic carbon. An overview of algal cultivation from a CO_2 capture perspective is given, starting with studying how algae assimilate CO_2 to reviewing various large-scale algae cultivation methods with CO_2 supply techniques. Possible restrictions imposed on a CO_2 capture system using algae are reviewed, including CO_2 gas quality and impurities, temperature, pH, light and nutrient requirements. Finally, an overview of important pilot facilities from a CO_2 capture perspective is given.

Using algal cultivation for CO_2 capture is not a straightforward process. The CO_2 feeding to the algae need to be optimised and typically the CO_2 gas loss to the atmosphere from the algal cultivation is relatively high. As algae can thrive using the CO_2 fraction of from desulphurized flue gases injected into the cultivation water, there is no need for using costly CO_2 separation processes, as long as the algae cultivation is built close to a suitable industrial CO_2 source, avoiding costs relating to CO_2 containing gas transport. The most promising systems for CO_2 capture was found to be the use of separate bubbling carbonation columns, both for open ponds and closed photobioreactors. This makes the design of the photobioreactors simpler, as CO_2 is fed readily dissolved by recycling the cultivation water through the bubbling columns. Using separate bubbling columns for open ponds enables a higher CO_2 concentration in the ponds than what can be achieved by direct injection, and reduces the risk for release of gaseous harmful flue gas components into the area surrounding the ponds. The addition of alkaline salts for pH adjustment can significantly improve the CO_2 uptake of water as well without turning the water too acidic for common algal species. Further nutrients addition enhances algal growth and thus also the CO_2 uptake. Nutrients can be provided be using nutrients (P, N, K) containing waste water as cultivation media.

9.2.2 Integration of algae cultivation with a CHP plant

Enhancing the growth of microscopic algae (microalgae) with CO_2 from a flue gas source has been considered a promising approach both in terms of CO_2 capture and utilisation and in renewable energy production. Algae grow quickly when sufficiently CO_2, light, water, and nutrients are available, and therefore produce abundantly biomass which in addition can have high energy content due to the high amount of lipids. Hence, integration of algae cultivation with a CHP plant providing CO_2 and heat, and a municipal waste water source providing water and nutrients, has been suggested as a concept that combines carbon capture, biofuel production, and waste water treatment.

In CCSP, the potential of algae for carbon capture and utilisation was experimentally assessed from the point of view of their tolerance towards potentially toxic substances in unpurified CHP flue gas, such as nitrogen and sulphur oxides. It was concluded, that the tolerance is dependent on the algal species, and there were indications that certain species could even utilize the nitrogen and sulphur in the flue gas as nutrients (D218, D219). Currently, conditions are being identified, in which algal CCS and biofuel production could be feasible from the point of view of energy balance and environmental sustainability, and the most critical phases in microalgae cultivation process in terms of energy consumption and sustainability are being identified.

In CCSP, algae cultivation for carbon capture and utilisation has also been assessed on a concept level (D207, D244). The main purpose in the modelled, hypothetical cultivation plant is to utilize the CO_2 from a nearby district heating power plant, and nutrients from a nearby waste water treatment plant. Based on the reviewed research studies, two different algae cultivation systems were selected for the analysis: open pond, and tube photobioreactor (PBR). The system boundaries of the studied system are presented in (Figure 77). System boundaries were set to include biomass processing until the harvesting and dewatering step, i.e. the final product was not specified.

The main bottlenecks for developing this concept sustainably were identified with the life cycle analysis (LCA) tool SimaPro, by utilizing data from the existing research literature (D244). The system was assessed from the point of view of three elements: energy consumption, other resource requirements (e.g. CO_2, nutrients, water), and construction material requirements.

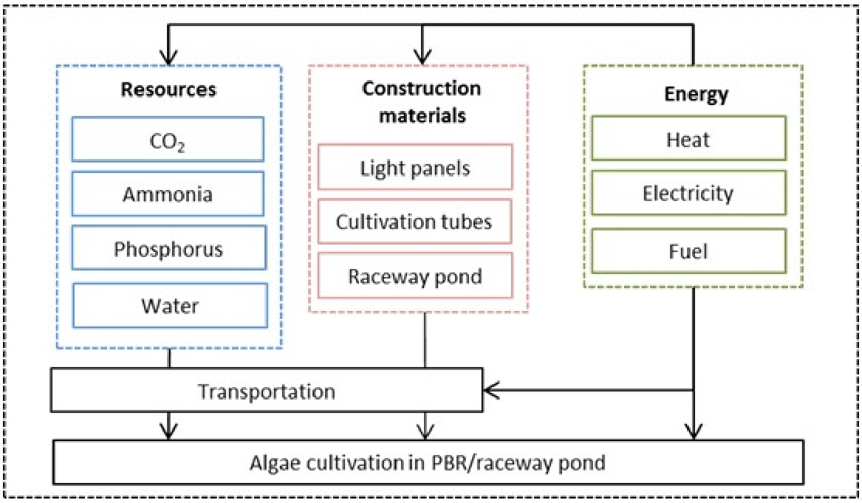

Figure 77. System boundaries in LCA analysis (D603).

The environmental effects were assessed with the aid of several impact categories, among which freshwater eutrophication, terrestrial acidification, and climate change were identified as the most critical. Energy consumption was identified as the most critical element, from two perspectives. Firstly, energy consumption frequently appeared as the major factor in the environmental effects. For this reason, e.g. the selection electricity profile for modelling (e.g. hydro vs. coal) had a significant impact on the overall sustainability. Secondly, assumptions related to the amount of energy required in different process steps need further research – especially related to the provision of light, circulation of water into and within the system, as well harvesting and dewatering of biomass. For the latter point, the possibility of utilizing of waste heat from the CHP plant requires further attention.

We concluded that the availability of land area for the cultivation has a profound impact on the CCS and nutrient removal potential of the system. From dozens to hundreds of hectares of cultivation surface may be required for any considerable portion of CO_2 or nutrients to be fixed. Tubular photobioreactors allow more cultivation surface with smaller land area, but this is partially limited by the energy consumption required for extra lighting for dense cultivations.

9.2.3 Integration of CO_2 capture and waste water utilisation with algae cultivation

Algal based systems hold high potential for secondary and tertiary wastewater treatment in particular for countries at low latitudes with a warm climate and high solar radiance. This low-cost natural system providing efficient nutrient and CO_2 capture opposed to the conventional systems. In addition, these systems offer economic return in the form of algal biomass that can be used for biogas production or as bio-fertilizer. If electrical power is needed for operating the system, like in the case with High Rate Ponds (HRPs), the electricity can be generated from the produced biogas, making these systems self-sustaining with concomitant GHG abatement of fossil fuel derived CO_2. As wastewater is generally carbon-limited, the algal production can be increased markedly by adding CO_2 to these systems. Cost-efficient solutions would be to include flue gas from nearby power plants.

Due to their requirement for land area, their optimal use is as decentralized systems in rural areas and offers a technology based on natural processes. For obtaining sufficient wastewater treatment, algal-based systems are most efficient when it is organized into a series of ponds providing different services like reduction in Biological Oxygen Demand (BOD) and nutrient removal. Different cultivation systems exist, and can broadly be divided into suspended and immobilized systems. Immobilized systems, where the algae grow in a biofilm, could be more cost-effective than suspended systems since harvesting is significantly easier and algal settling ponds are not required. However, immobilized systems have not been developed to the same extent as suspended systems and would require more R&D.

Similarly to all types of wastewater treatment plants, the successful application of algal based systems requires knowledge on the construction, operation and maintenance of these systems. In addition, motivation is a significant factor determining how well these systems will work, as earlier experiences have shown that even very simple systems such as anaerobic/ aerobic ponds and reed beds, will not work when neglected. The economic return might act as incentive for keeping the algal systems functioning. However, the commercialization of the products has to be done considering local communities, e.g. as untreated wastewater has traditionally offered a free fertilizer for poor farmers in developing countries.

- Our literature review (D602) can be summarized in the following recommendations for developing an integrated wastewater treatment and CO_2 capture by microalgal cultivation:Algal based systems have a potential for integrating CO_2 capture with wastewater treatment, but the areal footprint will be large and it will be most suitable for decentralized operation.
- For the purpose of CO_2 uptake, algal cultivation should be integrated with wastewater treatment in open ponds.
- Wastewater with high Biological Oxygen Demand (BOD) should be treated in a facultative pond before the algal cultivation, and a maturation pond might be required to reduce harmful pathogens.
- High BOD provide a lot of CO_2 during oxidation, and would reduce the CO_2 uptake from external CO_2 sources.
- Recycling of process water is needed to some extent, depending on availability of inflowing wastewater sources and loss processes (mainly evaporation).
- The R&D need is lowest for utilizing the algal biomass produced in biogas production as wet biomass can be used directly, i.e. the dewatering needed for most other applications is technically challenging at a large scale.
- Careful planning is needed to accommodate cultivation to the local conditions, key parameters for calculating the CO_2 uptake potential is: light availability, land availability, source and amount of wastewater, chemical composition of the wastewater (nutrient concentration, BOD and presence of toxic compounds).

9.2.4 Feasibility study on the utilisation options of algal biomass

Biological CO_2 capture by microalgae is seen as a promising technology and has the advantage of producing biofuel/biomass simultaneously. The combination of biofuel/biomass production, CO_2 fixation and bio-treatment of wastewater underscore the prospect and potential of microalgae. This work (deliverable D605) concerned the optimal use of microalgal biomass, focusing on carbon capture and economic feasibility. Microalgal products have been reviewed as well as the carbon capture from industrial flue gas. The potential of different microalgal applications is significant. The biochemical composition of microalgae allows their biomass to be utilised in several applications such as nutritional supplements, antioxidants, cosmetics, fertilizers, biomolecules for specific applications, biofuels, natural dyes and colorants, pharmaceuticals and polyunsaturated fatty acids (PUFA). One beneficial feature for possible microalgal application is the combined production of renewable energy or other products with environmental solutions such as carbon dioxide capture and wastewater treatment. Three products were selected for further assessment: biogas, lipids and fertilizers.

To note is that biological mitigation of CO_2 from flue gas combined with microalgal biofuel (lipids and biogas in this study) production does not provide permanent CO_2 sequestration because carbon taken up during photosynthesis is released during biofuel combustion. However, in this case the carbon has been used twice. From the sequestration point of view fertilizer is a good product compared to biofuel production as fixed CO_2 in agriculture is estimated to have a retention time of 50–100 years.

In the study conceptual level techno-economic analyses were performed for four concepts (Figure 78) that produce lipids, biofuels and/or fertilizer. The evaluated processes included open pond cultivation with industrial flue gas, harvesting, drying, cell wall disruption, extraction of lipids and anaerobic digestion. Process parameter and economic evaluation data, such as prices, specific power consumptions and the yields of unit operations, were obtained mainly from literature. The results of this study indicate that microalgae-based production of selected products would be unprofitable with the assumptions used. The most significant factors affecting the profitability were high investment costs and other fixed costs. Energy costs had also a major impact on feasibility, especially in concepts including drying of biomass. Comparing selected product portfolios, the co-production of lipids and biogas was the most promising. That concept benefits from wet extraction, and nutrient recycling from anaerobic digestion compared to other concepts.

Techno-economic studies found from literature showed similar performance. However there is large variety in the results of techno-economic assessments found in literature and comparison of these is difficult. This is due to different assumptions and process technologies used in cultivation system and downstream processes, financial inputs and productivity assumptions.

Based on the literature reviewed in the study and the results of our techno-economic evaluation the key challenge of microalgal based carbon capture targeting primarily bulk products is its low economic feasibility resulting mainly from high capital and operating costs of biomass cultivation and downstream processing. However the economic feasibility of large scale algae cultivation may change significantly in the future. Many techniques, for example for harvesting and extraction, are available but the best available technique is yet to be determined. Moreover, the combined production system of microalgae based low value commodities (biofuels, fertilizers) and high value co-products, with CO_2 capture and waste water utilisation are important topics for the future development efforts. Also the selection the most suitable solution for each individual case, including identification of local opportunities and constraints, systematic analysis for best available technology and specie selection, may affect the feasibility significantly.

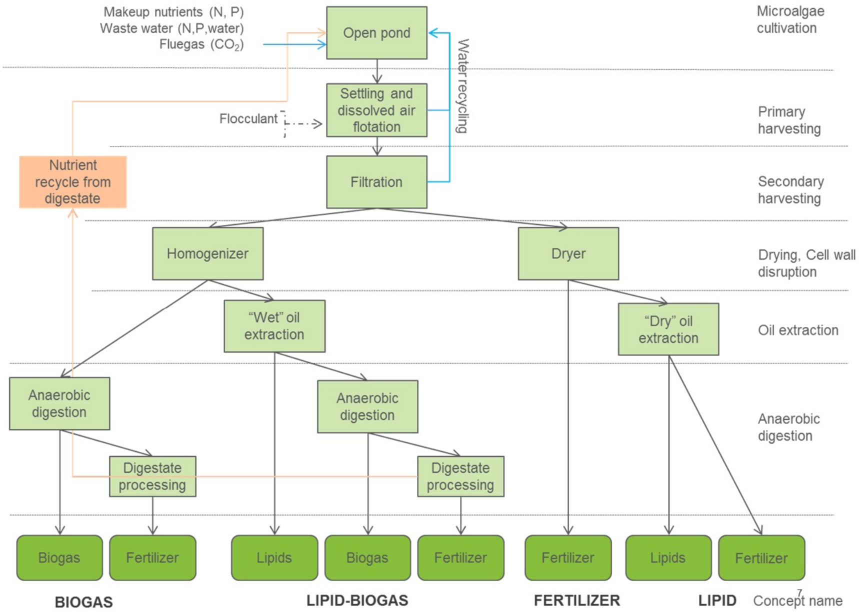

Figure 78. Schematic view of the four studied concepts: Biogas, Lipid-Biogas, Fertilizer and Lipid.

9.2.5 Cultivation of green algae using CO_2 from flue gas – lab scale research (Background material from ONGC)

A lab-scale study was commissioned by ONGC on utilization of CO_2 present in the flue gas for the cultivation of green algae and cyanobacteria using solar energy in a suitable photobioreactor.

Algal cultivation was done mostly using Airlift photobioreactor with artificial light. The amount of H_2S in the flue gas was 120 ppm. Four different approaches was taken for the maximization of the algal cultivation namely

- using diluted flue gas,
- using flue gas after passing through scrubber,
- serial dilution of the flue gas and
- using two different reactors.

From above approaches it was concluded that different approaches of algal cultivation could reduce the negative effect of high percent of CO_2 and presence of H_2S in the flue gas. Highest amount of CO_2 sequestered was 3 g/l after 14 days of batch cultivation of green algae in Airlift photobioreactor.

Maximum of 3 g/L of CO_2 has been sequestered using flue gas from *Chlorella sorokiniana.* This is approximately double of what can be sequestered from the atmospheric air under similar experimental conditions

The conclusion from the lab scale study was that scale up research at industrial or pilot scale will be required in order to improve the productivity. A maximum productivity of 1.2 g/l.day was already obtained at IIT Kharagpur corresponding to 2.2 g CO_2 sequestration per liter per day. Extrapolating only data with air, it can be concluded that 803 kg of CO_2 can be sequestered annually from 1 m^3 of the airlift photobioreactor.

9.2.6 Development of the Process for Mass Cultivation of Selected Microalgae for Hydrocarbon Production (Background material from ONGC)

A three year project on selecting and testing Indian microalgal strains for industrial processes is summarised as follows:

A survey of 186 natural water bodies/habitats of 10 States of India was undertaken for collection of water samples for isolation of algal strains. A total of 41 micro-algal isolates were isolated from the water samples collected from natural water bodies and these microalgae have been purified and are being maintained as monoalgal cultures. Morphological characterization of all the microalgal isolates has been carried out for their identification. Growth characterization of microalgal isolates was completed and their biomass yields (g/L) in growth media were recorded. The lipid content (w/w) of all the microalgal isolates was determined by gravimetry and their fatty acid profile by GC.

Based on the data on lipid content, 12 algal isolates were identified as containing >30% lipid content (w/w) and 9 isolates as containing 20-30% lipid content (w/w). Again, the data on fatty acid profile indicated C-18:1 (Oleic acid), C-16:0 (Palmitic acid), C-16:1 (Palmitoleic acid), C-18:3 (Alpha linolenic acid), C-18:2 (Linoleic acid) to be the major fatty acids present in microalgal isolates. Some microalgal isolates also showed presence of C-12:0 (Lauric acid), C-14:0 (Myristic acid), C-22:0 (Docosanoic acid) and C-24:0 (Tetracosanoic acid).

Laboratory studies showed enhancement in lipid accumulation under nitrogen and salinity stress conditions. This has been validated in outdoor ponds. Ammonium acetate, Ammonium carbonate and Urea were identified as alternate nitrogen source.

Based on data on algal hydrocarbon content (determined by gravimetry and GC), 2 microalgal isolates were identified as containing 40% or above hydrocarbon content (w/w). Six microalgal isolates showed 13% to 20% of hydrocarbon content (w/w) with another 6 microalgal isolates showing 10%-11% hydrocarbon content (w/w). GC analysis of hydrocarbon profile indicated that majority of the peaks occurred in the <C-15 to C-20 carbon chain length followed by C-20 to C-30 region.

Based on the analysis of lipid /hydrocarbon content and the biomass yields, two microalgal isolates were selected for outdoor cultivation studies for hydrocarbon and five isolates for lipid production. Outdoor adaptation studies were carried out for two hydrocarbon and three lipid producing isolates. Studies were also carried out to standardize a staining method for in-situ estimation of lipids in algal isolates.

The study identified certain indigenous microalgae as source of algal lipid and/or hydrocarbon for the first time not reported before. A method to control rotifer (predator) infestation in outdoor algal cultures has been developed and filed for a joint patent. The method is also found to be effective in control of predator ciliates and other protozoans,

Based on these studies, a two stage cultivation method to enhance the lipid and hydrocarbon content of microalgal biomass is recommended.

Further, harvesting of biomass and recycling of media has been studied for outdoor cultivation. CFTRI constructed an exclusive algal R&D facility, including open outdoor raceway ponds and analytical instruments. The analytics included molecular identification of selected isolates (12 isolates) and evaluation of spent biomass for its safety/toxicity in animal model for its possible application as feed. Ten marine microalgal strains were obtained from Central Marine Fisheries Research Institute (CMFRI), Tuticorin and cultures were established in laboratory. These strains have been evaluated for their lipid content and fatty acid profile. Algal mats from salt pans near Puducherry were collected and were analysed for mineral characteristics of water and biochemical constituents of algal mat. A treatment method is evolved to reduce high ash content in the harvested algal biomass. An indicative cost estimate is worked out for a pilot scale production (1.25 MT/Annum) of algal biomass in outdoor ponds based on limited scale trials carried out at CFTRI.

9.2.7 Development of process for methane production and CO_2 capture from vent gases at Hazira plant by algal cultivation (D604)

Microalgae suitable for cultivation using vent gases from a natural gas processing facility were screened by employing a 20 L photobioreactor (PBR). CO_2 tolerance of various species was studied by sparging CO_2 and monitoring pH. Mixtures of species were also tested. Based on these experiments, a certain mixture of microalgae exhibited rapid growth and better tolerance in terms of time taken to reach pH 7. Larger-scale cultivation of the mixture was tested using a 0.3 m^3 CO_2 absorption column for absorbing CO_2 from vent gas in connection to a 0.2 m^3 raceway pond. The produced algae was harvested and sent for anaerobic digestion studies. The experiments were successful, with a microalgae yield of 18 $g/m^2/day$ achieved, which on anaerobic digestion yielded about 0.4 m^3 CH_4/g volatile solids fed.

9.2.8 Energy requirements

The objective of this work was to perform a survey over the energy requirements of various microalgae biomass production units to assist subsequent case studies undertaken in the CCSP program (D606). Processes such as cultivation, harvesting, drying and cell disruption are included, each process step including possible different methods are described shortly and energy consumption of each step is discussed. References for more detailed description of different methods are also given. Energy consumption is divided on the thermal energy and power. In addition the local condition and strain properties and the possible needs which they bring are discussed shortly. The energy consumption numbers of methods described are collected from literature, project partners, and equipment manufacturers and attached to the report. The report gives an overview of the energy requirements assessment done in literature for the various equipment used in cultivation of microalgae. This includes various cultivation systems (raceway ponds and different types of photobioreactors), harvesting methods, drying of algal biomass, and cell disruption methods. In addition, the effect of local conditions is discussed.

9.2.9 Case study

The aim of this study was to evaluate the techno-economic feasibility of large scale microalgae cultivation for production of animal feed with a particular focus on comparing different CO_2 delivery methods and the possible benefit of selected novel cultivation technologies (D613). Microalgae based animal feed is a promising product and it has several benefits over conventional feed, such as addition to potential high protein content, the high contents of omega-3 fatty acid, antioxidants and carotenoids. Also, by using microalgae as animal feed in the future, it is possible to free up remarkable areas currently used for pasture and animal feed crops and use these areas for new forest plantations, which decrease also global atmospheric CO_2 concentrations.

In this study a techno-economic assessment was performed for large-scale (400 ha) production of phototrophic microalgae in envisioned algae facility located in Spain. The technologies in the selected cases were based on literature based and Global Algae Innovations (GAI) novel technologies.GAI develops and uses these technologies in their demonstration facility in Hawaii. All cases included the production of animal feed with *cyanobacteria* cultivation, Three different distribution methods of CO_2 were assessed.

Based on results it seems that with novel technologies and larger facility size the production of biomass for feed purposes may result to positive profit, however 400 ha facility size were too small to make the system viable. All studied CO_2 distribution technologies seemed to be relevant for large scale production. Based on used assumptions the selected reference case harvesting technology (dissolved air flotation with chitosan as flocculent) had very high operating costs, however there are many uncertainties related to functionality and applicability of that harvesting methods. The case based on novel technology of GAI was the most promising case with the lowest variable cost and thus the best opportunities for economic of scale. Drying of algae was the biggest energy consumer in all cases, as it was supposed also before the study. There was very large variation in electric energy consumption between different cases, GAI cases having the lowest electric energy consumption per produced biomass ton. From the variable costs, nutrients share was also considerable high. In these cases all the nutrients were bought and there were no recycle as the whole biomass was utilized as a product. In earlier studies there were also assumed some nutrients from waste water and relative big share of nutrients were recycled from anaerobic digestion, however feed as product this is not possible. promising minimum selling price of 770 €/t, was obtained for algae based animal feed. To be able to gain benefit from algae cultivation as CO_2 utilization method, facility size should be larger than in this study (400 ha). Amount of CO_2 fixed in envisioned algae facility would be only 2% from the CO_2 emissions of a 500 MW power plant. The results of sensitivity analysis showed that with the used assumptions and wet pond area of 3000 ha or larger the feed production would come profitable.

9.2.10 Cultivation of microalgae and cyanobacteria at extreme pH conditions

Most algae grow well at pH values between 6 and 8, in which range bicarbonate concentrations are higher than CO_2 or carbonic acid. Several species also grow in more extreme pH conditions and shifting to more alkali or acidic conditions may be beneficial for CO_2 delivery, for example when using aqueous CO_2 scrubbers to capture CO_2 from flue gas. A review of the literature suggested algae which grow in alkaline and in acidic conditions should be able to take up similar amounts of CO_2 at similar rates, i.e. that both high and low pH CO_2 feeding are valid options (D615). In order to assess the impact of culture pH on the uptake of CO_2, we grew three relatively fast growing acidophilic (Coccomyxa sp., Euglena mutabilis and Euglena gracilis) and three alkaliphilic (Thalassiosira pseudonana, T. oceanica, Phaeodactylum tricornutum) algal species at pH values near neutral and near the extreme of their growth range. Growth was assessed with step-wise increase or decrease of the pH in the relevant range using parallel photobioreactors, with or without supplementation of additional CO_2, either as gas or as bicarbonate (D616).

The cultivations confirmed that acidophilic algae can take up CO_2 equally efficiently at low (3) pH as at neutral (pH 6 to 7.5) pH and that similarly, alkaliphilic algae can take up CO_2 (bicarbonate) as efficiently at pH 9 as at neutral pH. Although the preferred pH of the system will be determined by the choice of alga(e), neither high nor low pH should cause a limitation to the CO_2 uptake potential of the system and both direct injection of flue gas and provision of bicarbonate from CO_2 scrubbers remain valid options.

However, we also observed that the alkaliphilic systems generally removed more CO_2 (i.e. a higher percentage) from the air stream than was observed in acidic systems. Up to 60% of the CO_2 was removed from the air when cultivating alkaliphilic algae, whereas only up to 40% of CO_2 was removed from air by the acidophilic algae, with only up to 15% CO_2 being removed when the gas streams was enriched to ~2.3% CO_2. Thus more CO_2 was lost from the acidic cultivations than from alkaline cultivations. On the other hand, the acidophilic algae still took up more total CO_2 than the alkaliphilic strains included here, since their air could be supplemented with gaseous CO_2. When alkaliphilic algae were fed extra CO_2, precipitates formed in the medium which reduced light penetration into the system and thus limited algal growth and CO_2 uptake. The alkaliphilic algae included in this study also produced less biomass than the acidophilic strains studied, reflecting the fact that they had taken up less total CO_2 than the acidophiles. Thus we observed that acidophiles still have good potential for capturing CO_2, even though they remove a relatively low proportion of CO_2 from the gas stream.

The benefits and disadvantages of direct bicarbonate feeding were demonstrated at pH 7 with an acidophilic alga and at pH 9 with an alkaliphile (Figure 79). When bicarbonate was fed to the alkiliphilic diatom *P. tricornutum*, less than 1% of the CO_2 provided (as bicarbonate) was lost to the atmosphere. More CO_2 could be fed into the system than from air and the CO_2 consumption per unit biomass increased. However, precipitates still formed in the high salt medium and oxygen accumulation limited biomass production. Not all bicarbonate fed into the system will have been consumed by the algae and some was probably converted to insoluble carbonates. However, even at pH 7, at which pH part (~21%) of the bicarbonate will convert to free CO_2, a lower proportion of CO_2 was lost to the atmosphere with bicarbonate feeding than when air was supplemented with gaseous CO_2. Oxygen accumulation limited biomass production, reducing total CO_2 uptake per day and illustrating the choice between removing a high proportion of CO_2 (bicarbonate feeding) and having high total removal of CO_2, with higher throughput of CO_2, but more loss to the atmosphere. Bubbling some air through the liquid to strip oxygen from the solution quickly increases the proportion of CO_2 which is lost to the atmosphere. There is currently considerable interest in cultivation of algae in alkaline pH, and use of alkali scrubbers to provide CO_2 to algal cultures appears to be a sensible option for a wide range of species. The coupling of alkali scrubbers with algal cultivation should be further developed, along with low energy strategies for removing oxygen from the cultures so that higher biomass and growth rates can be obtained without loss of CO_2 to the atmosphere.

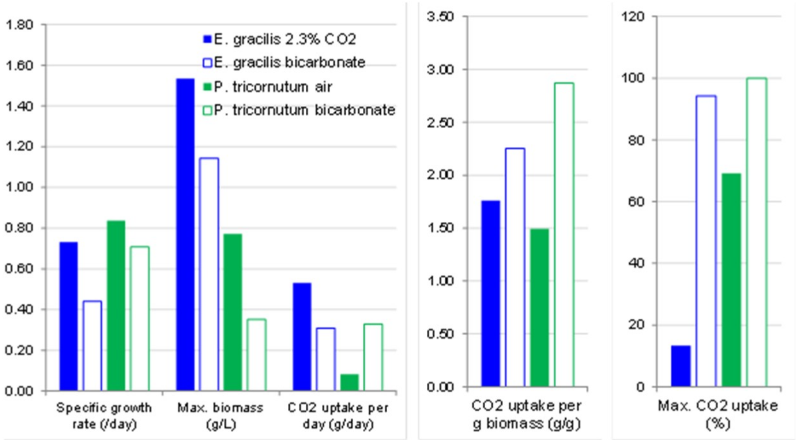

Figure 79. Growth and CO_2 uptake parameters for *E. gracilis* (blue, pH 7.3) and *P. tricornutum* (green, pH 9) grown in photobioreactors fed with either CO_2 in the gas stream (solid bars) or with sodium bicarbonate (open bars).

10. Regulation, legislation and EHS

CCS is still a young and complex group of technologies and applications and thus environmental, regulation as well as safety issues are not fully developed or understood in detail. Many parts of the CCS process are well known and can be considered state-of-the-art but the deployment of complete CCS chains (covering from capture to storage) is so far limited to a handful of demonstration-scale units.

Legal frameworks concerning CCS have been evolving during the past years. They include international treaties, EU regulations and directives and national laws and decrees. One of the objectives in CCSP was to keep track of the evolving regulations affecting the implementation of CCS in Finland. Moreover, the goal was to support the development of the needed regulatory framework by finding its current weaknesses and underlining future work to create a suitable environment for CCS in Finland. The legislative framework for CO_2 transportation is in special focus since it is crucial for a country without known possibilities for geological storage of CO_2. Obviously, also regulatory questions related to bio-CCS are of interest in Finland because “negative” emissions are not recognised in EU ETS.

Also environment, health and safety (EHS) issues of industrial activities and transportation are controlled by international and national regulations and requirements. Prevention of accidents and environmental damages, as well as ensuring safety and well-being of people are among the key objectives of the responsible companies all over the world. The establishments introducing CCS technologies are no exception of the EHS requirements. Therefore, an overview of the EHS-requirements relevant for the various life-cycle phases of establishments introducing CCS technologies and CO_2 transportation was made in CCSP.

Considerable amount of regulatory data was collected and assessed during the work, resulting in a regulatory status reports (D127-D128) and two guidebooks on EHS issues on capture and transportation parts of CCS (D129-D130). Additionally, a report on the monitoring possibilities in the case of CO_2 transportation by ships utilising existing information requirements related to sea traffic was made. The latter discusses the gap between the current monitoring and reporting regulation under the EU’s Emissions Trading System (EU ETS) and possible future ship based transportation of CO_2 for the purposes of CCS. The results include an outline of monitoring procedure for ship transportation.

The results are meant to serve the decision makers as a source of concise information on legal issues concerning CCS, including any regulations still in the preparation. For owners of power plants, industrial plants or for future owners of CO_2 pipelines and intermediate storage facilities it is important to be aware of the upcoming changes in European and Finnish EHS legislation and requirements possibly affecting the CCS process.

10.1 Legal and regulatory framework for CCS

The legal framework enabling the capture, pipeline transport and geological storage of CO_2 is essentially operational across the EU and EEA. The European commission released a communication on February 2014 (COM(2014)99 final), summarizing the member state reports on the implementation of the CCS Directive. Commission noted that the implementation of the directive across the union has been slow. By November 2013 Austria, Cyprus, Hungary, Ireland, Sweden and Slovenia had not notified the Commission complete transposing measures of the directive. Finland, Luxembourg and the Brussels Capital Region of Belgium chose to prohibit geological storage of CO_2, other than for research purposes, due to unsuitable geology. In the Baltic Sea region, Estonia, Latvia, Sweden and Germany have also prohibited or imposed restrictions to the geological storage. In addition, Austria, Ireland and Slovenia have prohibited the geological storage of CO_2 and Czech Republic has restricted it. In the end of 2014, Norway was still undergoing efforts to implement the CCS Directive. Finland has adopted the amendments into existing national legislation required by the CCS Directive (EC 2009) and transposed the remaining requirements of the directive into a new act in July 15th 2012 (FINLEX 2012).

The existing and emerging regulatory framework was tested through comparison to a published model framework (IEA, 2010) to obtain a general qualitative view on the effectiveness and maturity of the legislation concerning CCS implementation. Additionally, possible EU's legal frameworks in preparatory stage were identified. The national legal framework on CCS seems to address most of the key issues identified in the IEA model regulatory framework (IEA 2010) on capture and storage of CO_2. Concerning storage of CO_2, a comparison is not meaningful, as geological storage was prohibited in Finland. The comparison between the enacted legal framework to the key issues or requirements identified and reposted by IEA (2010) pointed out open question mainly on the field of transport of CO_2 and inclusion of the capture of CO_2 from biogenic sources into the EU's Emission Trading Scheme (ETS).

Annex I of the ETS Directive (2003/87/EC) requires monitoring, reporting and verification (MRV) rules only for transport of greenhouse gases by pipelines for geological storage. Consequently, ship transportation of CO_2 is not included in the current MRV regulation issued by the EU Commission, and is not enabled in the

ETS. In other words, ship transportation is so far not a viable solution to transfer captured CO_2 from a capture facility to a geological storage site.

Therefore, the major regulatory barriers relate to the transport of CO_2 from Finland by ships. More accurately, new regulations are needed for MRV of emissions from the specific CO_2 transport processes which differ from processes included in pipeline transport of CO_2. These processes are CO_2 liquefaction and intermediate storage with recirculation loop for boil-off CO_2, loading and unloading facilities, and CO_2 transport and handling during the ship voyage. Inclusion of ship transport of CO_2 for the purpose of CCS under the EU-ETS would likely require addressing and amending the transport network access article of the CCS Directive and the resulting national legislations. Aside from the CCS Directive and the resulting national legislations, an amendment to the monitoring and reporting regulation (MRR) under the EU-ETS will have to be made to enable ship transportation of CO_2 for the purpose of geological storage.

On top of the missing monitoring, reporting and verification rules, ship transport of CO_2 is at the moment hindered also due to the London Protocol. Agreed in 1996, London Protocol is a maritime treaty under the International Maritime Organization (IMO). The Protocol modernizes and eventually replaces the original 1972 Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter.[6] Article 6 of the 1996 Protocol prohibits Contracting Parties to export wastes for dumping off-shore. Although the Article 6 was amended in 2009 to allow off-shore geological storage of exported CO_2, the amendments remain waiting for ratifications. Although a party of the original London Convention, Finland has not signed the 1996 Protocol. Therefore, off-shore storage of CO_2 captured from Finland should not be prohibited.

Capture of CO_2 from biogenic sources is a relevant issue when considering a large-scale implementation of CCS in Finland. Inclusion of Bio-CCS into the emission trading mechanism will hardly happen in the short-term, as this would require more political pressure or interest from the industries. After all, implementation of CCS in Europe has yet to get going as the first call of NER300 funding resulted in withdrawals of all CCS project applications. In the second NER300 call, only one CCS proposal was submitted by the UK.

The EU regulation 2015/757 on the monitoring, reporting and verification of carbon dioxide emissions from maritime transport was adopted in April 2015. Regulation applies to ships above 5 000 gross tonnage in respect of CO_2 emissions released during their voyages. In CCSP an analysis was made on the remaining missing MRV rules and practices that would be needed if ship transportation of CO_2 was included as an activity requiring and emission permit under the ETS Directive. The assessment was based on: (i) definition of CO_2 emissions from

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[6] Finland is a contracting party to the 1972 London Convention, but has not ratified the 1996 agreement.

ship transport of CO_2; (ii) review of EU regulations on MRV of maritime CO_2 emissions; and (iii) review of the MRV regulation on capture, transport and geological storage of CO_2 under the EU ETS. The considered activities related to ship transportation of CO_2 are liquefaction and intermediate storage with recirculation loop for boil-off CO_2, loading and unloading facilities, CO_2 transport and handling during the ship voyage.

The MRR does not produce any lawful excuse why the immobile installations of the ship transportation network at the port of origin, such as liquefaction plant, intermediate storages and loading facilities could not be included in the emission permit of a capture plant. Therefore, the emissions from these facilities can be monitored according to the activity specific rules in the Paragraph 21 under the ANNEX IV of the MRR (Table 12). Similarly, the unloading and intermediate storage facilities at the port of arrival could be included in the emission permit of the storage operator. The related emission would then be monitored and reported according to the Paragraph 23 of ANNEX IV. Alternatively, the stationary installations at the ports could fall under the MRV rules given in Paragraph 22.

Paragraph 22 under the Annex IV of the MRR sets emission monitoring requirements for pipeline transportation of CO_2. The requirements set for pipeline transportation of CO_2 serve as an analogy for how corresponding requirements for ship transportation of CO_2 should look like. The regulation allows the pipeline network operator to choose from mass balance methods to individual emission source monitoring. Both methods consist of quantifying the emissions from combustion processes in the transportation system and direct emissions from the transported CO_2. Since the adoption of the maritime MRV regulation in 2015 (European Commission, 2012), monitoring of CO_2 emissions from combustion of fuels in a ship-specific manner has a corresponding regulation. Therefore, the remaining question is whether any MRV rules exist which could be applied to direct emissions from the ship's cargo.

If emissions from ship transportation of CO_2 were monitored by using a mass balance approach similar to subsection B.1 of MRR Annex IV Paragraph 22, the direct emissions from the ship's cargo would be determined by subtracting the amount of CO_2 unloaded at the port of arrival from the amount loaded at the port of departure. Section 3 and 4 of the MRR sets rules how the transferred amounts of CO_2 are quantified by measure-based methodologies in stationary installations. Considering the port facilities for loading and unloading the cargo are stationary installations, the same monitoring rules could be applied to ship transportation of CO_2.

Monitoring of each emission source from the carried CO_2 individually, similar to subsection B.2 of MRR Annex IV Paragraph 22, calls for emission monitoring rules more adapted to gas tankers. This applies to the fugitive and leakage emissions from the cargo. Although not stationary installations, the ship cargo tanks and possible re-liquefaction systems are analogous to intermediate storages and connected facilities, for which MRV rules are given in MRR Annex IV Paragraphs 21 to 22. Therefore, same methodology could be followed, possibly taking into account existing international standards for gas tankers such as The International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IGC code). The IGC code is a standard to provide safe carriage by sea in bulk of liquefied gases and certain other substances by prescribing the design and construction standards of ships involved in such carriage and the equipment they should carry so as to minimize risk to the environment (IMO, 1982). The code gives details for example on pressure gauges and temperature indicators to be installed in the liquid and vapour piping systems, in cargo refrigerating installations, and in the inert gas systems. Concerning the intentionally vented emissions from the transport network, MRR Annex IV Paragraph 22 essentially only requires the pipeline operator to provide a documented methodology for calculating the amount of CO_2 vented and an analysis of potential situations where venting occurs. These MRV rules could be applied directly to ship operators to quantify the CO_2 vented during the ships' voyages.

Table 12. Summary of needed MRV rules to enable ship transportation of CO_2 for geological storage pursuant to Directive 2009/31/EC.

MRR Annex IV Paragraph	Contents assuming pipeline transportation of CO_2	Applicability to ship transportation of CO_2
Paragraph 21. (subsection A.): Scope	Intermediate storages and compression facilities can be included in the emission permit of the capture installation.	Paragraph 21 can apply to liquefaction, intermediate storage and transfer of CO_2 at the port of departure without any necessary changes. Alternatively, the stationary installations can be monitored by similar rules as given in Paragraph 22.
Paragraph 22. (subsection B.1): monitoring of emissions using the overall mass balance approach	$E_{own\ activity}$= Emissions from the transport network's own activity, meaning not emissions stemming from the CO_2 transported, but including emissions from fuel used in booster stations. $\sum_i \boldsymbol{T}_{IN,i}$ = Amount of CO_2 transferred to the transport network at entry point i and $\sum_j T_{OUT,j}$ = Amount of CO_2 transferred out of the transport network at exit point j, determined in accordance with Articles 40 to 46 and Article 49.	Emissions from ship's own activity is monitored according to Regulation 2015/757. MRR Articles 40 to 46 on measurement-based methodologies and article 49 on transferred CO_2, although meant for stationary installations, would in principle be valid for determining the amount of CO_2 loaded to and unloaded from a ship.
Paragraph 22. (subsection B.2.): monitoring of emission sources individually	$CO_{2\,installations}$= Amount of CO_2 (t CO_2) being emitted from combustion or other processes functionally connected to the pipeline transportation in the transport network.	Regulation 2015/757 lays out rules how ship's emission sources related to combustion of fuels can be monitored individually.

Paragraph 22. (subsection B.2.1): Fugitive emissions from the transport network	$CO_{2\,fugitive}$ = Amount of fugitive emissions (t CO_2) from CO_2 transported in the transport network, including from seals, valves, measurement devices, intermediate compressor stations and intermediate storage facilities. The operator shall determine average emission factors EF (expressed in g CO_2/unit time) per piece of equipment per occurrence where fugitive emissions can be anticipated.	New monitoring rules are needed.
Paragraph 22. (subsection B.2.2): Emissions from leakage events	$CO_{2\,leakage\ events}$ = Amount of CO_2 (t CO_2) transported in the transport network, which is emitted as the result of the failure of one or more components of the transport network The operator shall provide evidence of the network integrity (or leaked quantity of CO_2) by using representative (spatial and time-related) temperature and pressure data.	New monitoring rules are needed.
Paragraph 22. (subsection B.2.3) – Vented emissions	$CO_{2\,vented}$ = Amount of vented emissions (t CO_2) from CO_2 transported in the transport network, The operator shall provide in the monitoring plan an analysis regarding potential situations of venting emissions, including for maintenance or emergency reasons, and provide a suitable documented methodology for calculating the amount of CO_2 vented, based on industry best practice guidelines	Could be applied directly as an MRV rule for ship operators concerning vented CO_2 during ship's voyages.
Paragraph 23. (subsection A): Scope	The boundaries for monitoring and reporting of emissions from geological storage of CO_2 are decided by the competent authority based on the delimitation of the storage site and storage complex.	Paragraph 23 can apply to installations at the port of arrival, given the port is located at the injection site. Alternatively, the stationary installations can be monitored by similar rules as given in Paragraph 22.

The new maritime MRV regulation improves significantly the position from where ship transportation of CO_2 could be included as an option within CCS in the EU's Emission Trading Scheme. Based on the results, the missing MRV rules for emissions from ship transportation of CO_2 using overall mass balance approach could be written almost word for word based on the current MRR under the EU emission trading scheme and the MRV regulation for maritime transportation.

Monitoring and verification of the cargo carried is a key issue in determining possible fugitive and leaked emissions during a ship's voyage. Upon the publication of the maritime MRV regulation, a subgroup of experts was established under the European Sustainable Shipping Forum (ESSF) responsible for proposing the Commission monitoring methods and implementing acts on monitoring of cargo carried (European Commission, 2015). These upcoming technical rules may have further implications on the remaining gaps in needed MRV rules for ship transportation of CO_2.

A possible trade-off of using the MRR for pipeline transportation of CO_2 as a basis for monitoring rules for ship transportation of CO_2 comes from the MRR Annex IV Paragraph 22 requirement that the end and start points of the network have to be determined in the emission permit. If same rules were applied to shipping of CO_2, the routes and function of the ships would then also have to be predetermined and fixed during the period of validity of the emission permit. This would limit any flexible use of the gas tankers. Similarly, using the gas carriers for any other purpose than CO_2 transportations during the validity of the emission permits could rule out time-based monitoring methods of ship emissions, such as relying on the BDN in calculating the emissions from fuel combusted.

10.2 CCS from an EHS perspective

The implementation of various technological options for carbon capture and transport can due to environmental, safety and health (EHS) issues be a lengthy procedure, which has to be started several years before the installation is taken into use. Also after commissioning, the lifespan of the installation is likely to include several points, where the EHS issues have to be revisited, related documents updated, and training courses and dissemination schemes repeated.

In CCSP, two guidebooks have been made that review the current legal EHS requirements for carbon capture and transfer in Finland. The first guidebook (internal deliverable number D129) covers the requirements related to the capture, transfer and intermediate storage of carbon dioxide. The second guidebook (D130) concerns the EHSrequirements for ships and seafaring (carrying CO_2) within Finnish territorial waters. These guidebooks form the basis for future environmental, health and safety (EHS) assessments in CCSP.

The guidebook on EHS requirements related to the capture, transfer and intermediate storage of CO_2 in Finland (D129) covers the EHS issues relevant for the various life-cycle phases of establishments introducing some of the best documented CCS technologies like post-combustion, pre-combustion and oxy-fuel combustion. EHS issues of CO_2 pipeline transportation from a power plant or an industrial source to a Finnish harbour and intermediate storage of CO_2 in the harbour are also considered. In addition to carbon dioxide, there are several other chemicals involved in the various carbon capture technologies. The data package covers EHS issues related to the handling and storage of six common chemicals present in the various CCS reference technologies. These chemicals are carbon dioxide, carbon monoxide, hydrogen, monoethanolamine, oxygen, Selexol^{TM} solvent. In addition to these chemicals, EHS issues related to solid oxygen carriers used in chemical-looping-combustion technology are also described.

The focus of the work has been on what current legal environmental, health, and safety requirements an operating company must fulfil, when introducing various technologies for carbon capture in Finland. Although CO_2 is generally not classified as a hazardous substance, various sections in the Finnish legislation will apply when carbon capture technologies are introduced at power plants and other industrial establishments in Finland. Emphasis is put on those obligations, which, when carbon capture technologies are employed, will be different from those of conventional installations.

The study comprises the following three types of onshore facilities: industrial facilities (including power plants) in which CO_2 is formed, pipelines for carbon dioxide transfer to Finnish harbours, harbour facilities including intermediate storage tank(s) and ship loading facilities. As capture, transfer and intermediate storage of carbon dioxide can be carried out in many different ways, there has been a need to restrict the discussion to a limited amount of technology options. Representative cases for post-combustion and pre-combustion carbon capture are used as reference. Also an oxy-fuel case study is presented. In addition, a pipeline case and an intermediate storage and harbour facility are used as examples.

Each topic starts with a General Requirements section. In this section the basis of a law is explained as are those requirements in the legislation that concerncarbon dioxide sources (power plants and other industrial installations), transfer lines as well as intermediate storage facilities. The General Requirements section is followed by Case Specific Requirements sections, in which additional specific requirements concerning each of the various types of installations are described.

As one of the outcomes, a road map presenting the milestones of CCS project from an environmental and legal perspective has been created (Figure 80). It includes the EHS requirements and licensing procedures for capture, transfer and intermediate storage of CO_2. The road map is presented as a web based demonstration tool in which the main topics are further discussed via hyperlinks. The road map is made easy to use in which the user finds the needed information of a particular step with the least effort. The road map gives also the overview of the whole regulatory process for implementing a CCS project.

Several steps are included, which need to be considered when initiating a CCS project in order to find out the social and environmental impacts. The significance of each step has been evaluated and the possible risk stages for the project have been identified. Figure 80 gives an overview of the main EHS steps during the entire life cycle of installations designed to enable carbon capture and transfer within Finland. Along the CCS project timeline, the relevant legislation and general description is given on each of the phases and milestones. Additionally, time estimate needed for the stage is given and responsibilities and the decision makers are identified. Other addressed issues are:

- Impacts of CCS on the current protocol
- Hearing/Interaction requirements
- Appeal procedures
- Connection to other stages
- Expenses.

The second guidebook (D130) contains description of the current national and international requirements of EHS issues in terminal operations and marine transportation. It also includes descriptions of temporary storage, loading process, and ship transportation of carbon dioxide. In addition to that the most potential hazards of CO_2 in terminal loading and marine transportation are considered. Marine transportation of CO_2 is relatively safe compared to the other hazardous substances transported at sea, and the most potential risks are already well-known. However, the cooling substances as well as the cooling and capturing processes of CO_2 during loading and transporting are issues which require special attention.

Main EHS-concern for CO_2 capture in power plants is related to the very large quantities of CO_2 which need to be handled and stored (before transportation to permanent storage place). In a commercial-scale plant CO_2 would be present in volumes not previously handled. Whereas in conventional CO_2 handling facilities an inadvertent release of CO_2 may have created a small-scale hazard, potentially only affecting those in the local vicinity, a very large release of CO_2 from a CCS scale of operation has the potential to produce a harmful effect over a significantly greater area and as such it would be likely to affect a significant number of people. (Harper 2011). Carbon dioxide is not classified as a hazardous substance, but at high inhalation levels it is lethal. A major release of CO_2 has a potential to endanger a large number of people and also vegetation.

To ensure and develop safety of CO_2 capture, there is need to identify and analyse the major accident risks of capture and intermediate storage, assess the consequences of CO_2 leaks, provide training and to develop good safety management practices. Challenges related to EHS risk management of the CCS-chain are e.g. (DNV 2012):

- Lack of experience handling very large quantities of liquid phase CO_2
- Absence of CCS-specific or CCS-validated reference material and tools
- Need to integrate hazard management across the whole CCS chain
- Lack of maturity in CCS personnel competency development
- Rapid technology development and innovation
- Trans geographic, legislative and national nature of CCS
- Political pressures (e.g. for rapid implementation, scale-up, cost reduction)

- High impact of an actual or perceived major incident or event (e.g. a large leak from a CO_2 pipeline)
- Lack of stakeholder awareness and understanding.

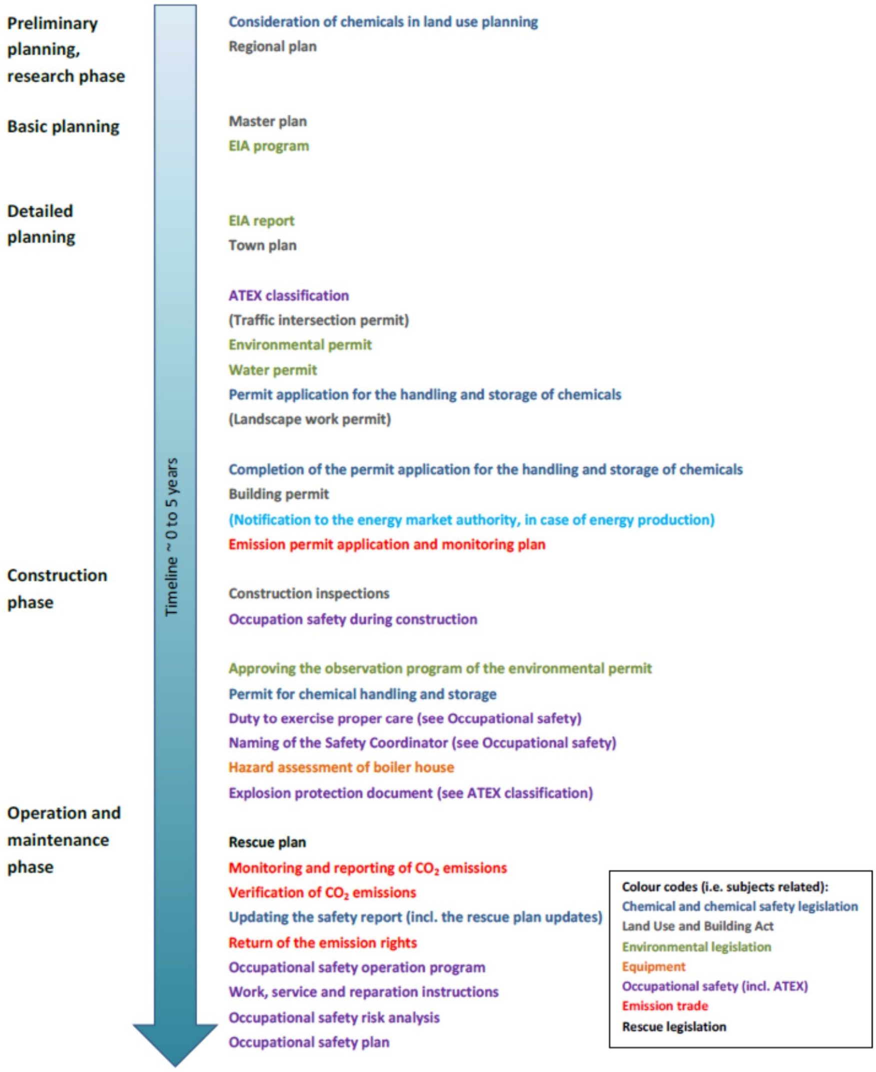

Figure 80. CCS project timeline, as presented in the web-based road map tool (D129).

10.3 Sustainability

Sustainability science aims to respond to the challenge of solving severe global environmental and social problems, such as climate change. Essential elements of sustainability are interactions between industrial and ecological systems (Seager 2008; Pope et al. 2004), and the orientation towards problem solving (Sala et al. 2012).

While there is no commonly agreed definition of sustainability, it is typically considered to include three dimensions: environment, economy and society. When assessing sustainability of a technology, the potential environmental, economic and social impacts of the technology are considered. The assessment should take into account potential positive and negative impacts, direct and indirect impacts, and apply a life cycle perspective.

A qualitative sustainability assessment of CCS technologies was conducted by integrating the findings of EHS risk assessment, economic assessment, analysis of legal and regulatory framework, environmental life cycle assessment and public acceptability, and reflecting the findings with relevant international publications from the field. The findings of these assessments were further analysed and integrated using the PESTEL framework, in which most important drivers and barriers having an impact on the general environment and on the potential implementation of CCS technologies in Finland were analysed. PESTEL stands for Political, Economic, Social, Technological, Environmental and Legal factors. The aim of the assessment was to highlight the interlinkages between different aspects of sustainability, to discuss challenges for sustainable technology implementation, and to consider means for improving the sustainability of CCS in Finland.

Since the main findings from the other tasks are discussed elsewhere in this report, the following paragraphs will mainly focus on the environmental aspects of sustainability, assessed based on life cycle assessment (LCA), and on the integration of results using the PESTEL framework.

10.3.1 Environmental aspects

Life cycle assessment (LCA) was applied to assess the potential environmental impacts of different carbon capture technologies in the context of energy production in Finland. LCA is a technique in which potential environmental impacts occurring during a life cycle of a product are quantitatively and systematically assessed (ISO 14040:2016). Within the assessed case studies, life cycle was studied from raw material acquisition until the ship transport of captured CO_2 to the storage site. Assessed environmental impacts were climate change, terrestrial acidification, marine eutrophication, photochemical oxidant formation, particulate matter formation and fossil resource depletion. Assessed case studies included:

1) Retrofit of post combustion CO_2 capture to a coal fired condensing power plant

2) Retrofit of post combustion CO_2 capture on natural gas combined cycle (NGCC), combined heat and power (CHP) plant
3) Greenfield oxy-CFB CHP plant (using coal and forest residues as fuels).

Detailed results from the case studies are reported in CCSP D142. In short, the findings of the case studies show that CO_2 emissions can be significantly and efficiently reduced with CCS. In all the assessed cases, CCS implementation led to overall reduced climate change impact over the life cycle, even though more fuels were required to cover for the energy penalty, and ship transport of captured CO_2 was added as an additional life cycle stage.

In addition to CO_2, also the SO_2, NOx and N_2O emissions from the assessed power plants decrease remarkably due to efficient purification methods that have to be applied in the context of CO_2 capture. As a consequence, impacts related to terrestrial acidification, marine eutrophication, photochemical oxidant formation and particulate matter formation from the assessed power plants decreased. However, the need for compensating energy due to efficiency loss related to CCS implementation, and the need for ship transport of captured CO_2 cause an increase in upstream and downstream emissions, when the whole life cycle is considered. Thus a change in the distribution of emissions and related impacts occurs: from power plant to upstream and downstream in the life cycle.

Based on the case results, CCS would be an effective means for reducing GHG emissions, but we should also be aware of the potentially increasing other environmental impacts that might take place in geographically distinct locations, for example due to increasing need for fuels and transport. Depending on the case specific conditions, CCS might provide possibilities for reducing other than climate change impacts as well, especially if ship transport of CO_2 and fuel sourcing are optimised. Thus the results clearly underline the need for life cycle based evaluation, to understand potential changes between different life cycle stages and environmental impact categories, and to avoid burden shifting.

The findings of the case studies highlight that the results are sensitive to the applied assumptions. In the assessed cases, especially the assumptions related to compensating energy production and ship transport proved to be of importance for the overall results. The case studies were based on theoretic cases that showed both potentially positive and negative overall impacts due to CCS implementations. In case concrete investment plans for CCS technologies would be made, comprehensive case specific studies would be needed. This is important since the severity of different environmental impacts depends of local characteristics. Site specific assessment would be required in order to asses and weight the importance of different impact categories within the affected locations.

For improving the environmental sustainability of CCS, improving efficiency of the CO_2 capture technologies, and minimizing the emissions both at the beginning and the end of the life cycle, would be important. Importance of optimizing both upstream and downstream emissions has been highlighted also by Corsten et al. (2013) in their review of several published LCA studies of CCS technologies.

However, there might be limited ability of the CCS implementer to have an impact on the preceding or following phases of the life cycle, which might be operated by several different actors, as pointed out by both, the assessment of EHS questions and the assessment of the regulatory framework concerning CCS.

In Finland, one potential hot spot could be ship transport of captured CO_2, from which the potential impacts would need to be carefully assessed and optimized. Due to lack of accurate life cycle inventory data of the impacts of the recent EU Sulphur Directive on ship transport and production of marine fuels, some uncertainty is related to these findings, and more research regarding the environmental impacts of ship transport would be needed in future.

The evaluated LCA cases were simplified assessments that were focused on air emissions and related environmental impacts. As a consequence, not all potential environmental impacts have been considered in this case. In future, it would be important to look at other potential impacts, that would include for example toxicity, water use and water quality (so called water footprint).

10.3.2 Integration of different aspects and identification of potential drivers and barriers

Findings from different studies related to framework for CCS and representing different aspects of sustainability were analysed and integrated using the PESTEL framework. PESTEL-framework is a tool that can be applied for analysing the macro-environment in which the companies operate. The macro-environment consists of factors that have an impact on almost all organizations. PESTEL framework categorizes environmental influences of the operational environment into six main categories: Political, Economic, Social, Technological, Environmental and Legal. PESTEL can be used to provide an overview of most important factors, and to identify key drivers of change. Key drivers of change can be defined as high-impact factors that are likely to impact significantly the success or failure of a strategy of an organization. (Johnson et al. 2008)

While PESTEL analysis is commonly applied for strategic analysis within a company, it is often applied for a more general analysis of the business environment, as part of future studies (see e.g. Auvinen et al. 2012; Näyhä & Pesonen 2012). In this case, PESTEL framework was applied for summarising results discussing different aspects of sustainability, for highlighting interlinkages and for identifying key drivers and potential barriers for implementation of CCS technologies in Finland. Within strategic management literature, barriers are considered as factors that need to be overcome by new entrants if they are to compete successfully (Johnson et al. 2008). In this study, barriers were defined as factors that might prevent or significantly slow-down implementation of CCS in Finland.

The PESTEL analysis was based on the outcome of several different studies discussed elsewhere in this report. These include techno-economic assessment, regulatory assessment, environmental, health and safety (EHS) assessment, sustainability assessment and public acceptance. In addition, an additional literature review regarding potential drivers and barriers was conducted. Detailed findings from the PESTEL analysis are presented in CCSP D 146.

The results of the PESTEL analysis indicate that significant barriers at the moment lie in the economic and legal categories. From economic point of view, the estimated high investment costs combined with estimated low profitability of CCS are among the key barriers in current situation. Low profitability is especially due to combination of increasing operational costs which are due to the energy penalty caused by CCS, and the estimated high transport and storage costs, due to lack of storage sites in Finland.

Instead of fossil energy production, carbon capture in industry, carbon capture and utilisation, or bio-CCS could perhaps be more viable solutions in Finnish conditions. However, barriers related to price and legal framework would need to be overcome also in these cases. According to EU emissions trading scheme (EU-ETS), ship transport is not a viable solution to transfer captured CO_2 to a geological storage site. Since geological storage is not possible in Finland, this barrier would practically prevent any CCS activities to take place in Finland. A barrier for bio-CCS is that only CO_2 originating from fossil carbon is included in EU-ETS. Possibilities for including it in the current legal frameworks and market mechanisms include open questions that would require more research. To overcome these barriers, clear policy drivers could act as motivators for the industry and for the academia to continue development of the most potential and promising solutions, and would require ensuring availability of funding for pilot scale demonstrations.

From environmental and social point of view, the key driver for CCS implementation is the need to reduce greenhouse gas emissions. Based on the case results, CCS would be an effective means for this purpose, but we should also be aware of the potential risks related to handling large amounts of CO_2, and of the potentially increasing environmental impacts that might take place locally, for example due to increasing need for fuels and transport, or the substances handled and emitted as part of CCS process.

Many of the potential economic, environmental and social impacts are case specific, and depend on the context, location, system and neighbouring communities in which CCS would be implemented to. As a consequence, economic, environmental and social impacts would need to be carefully assessed in case any decisions to implement CCS in Finland would be made. Until now, stakeholder attitudes towards CCS in Finland have been rather neutral, but situation might change in case concrete implementation plans would be made. A thorough impact assessment together with active stakeholder consultation would be required in order to identify potential future barriers and avoid conflicts. This is important since decision to invest in CCS is not only a technological, economical or legal question, but also an environmental, social, and even ethical question that relates to public acceptance and on the principles of sustainable development.

A summary of the results from the PESTEL analysis is presented in Figure 81. In the figure, green boxes describe potential drivers, while orange boxes describe potential barriers. White boxes represent factors that could have an impact or that could become either drivers or barriers, depending of the circumstances and future developments.

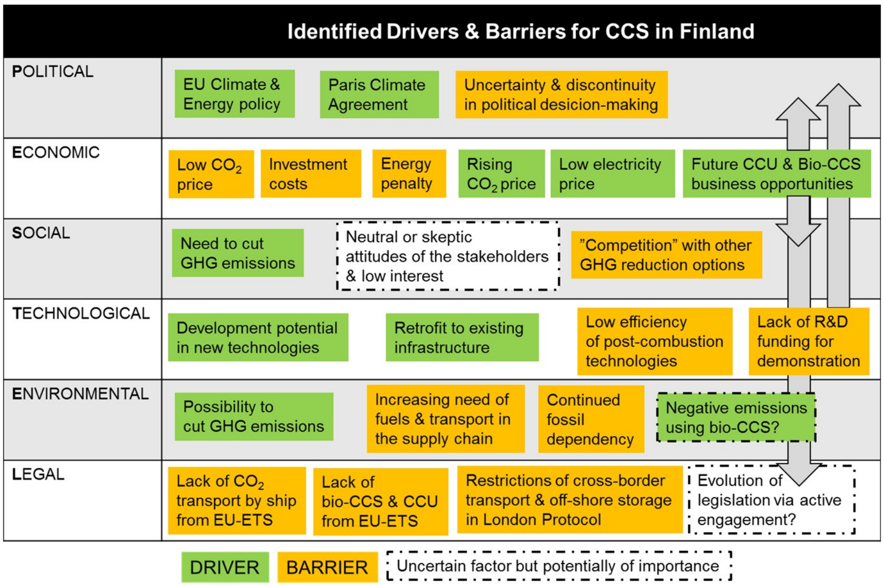

Figure 81 Summary of the results from the PESTEL analysis

Although the barriers and drivers have been categorized as political, economic, social, technological, environmental and legal, it is important to note that many of them are in fact interlinked, and could be included in several of these categories, depending of the applied point of view.

For example, the development of new business opportunities related to bio-CCS and CCU would be dependent on the evolution of the regulatory framework that would need to develop in favour of these new applications. Most likely it would also require dedicated R&D funding for demonstration purposes. In the end, all these aspects would require public acceptance and political engagement, including willingness to support development of these technologies and taking an active role in developing the legal framework. In Figure 81 these interlinkages are illustrated with top-down arrows crossing the PESTEL categories. In future more attention should be paid to interrelatedness of social and technical aspects of CCS technologies.

11. Public acceptability of CCS

This study focuses on public acceptability of CCS in Finland. The study was conducted by analysing (1) Finnish stakeholders' opinions regarding CCS technology (D103; Kojo and Nurmi, 2012a; 2012b) and (2) the public debate about CCS technology in the Finnish print media (Kojo and Innola, 2017; D123; D137). The main research questions were as follows: What are the stakeholders' concerns related to CCS technology in the context of Finnish climate and energy policy? Which actors are taking part in the CCS-discussion in the Finnish print media? How CCS is framed in the Finnish print media?

Public acceptance and acceptability have been actively discussed in relation to different controversial technologies such as CCS (e.g. Huijts et al., 2007; van Alphen et al., 2007; Shackley et al., 2009; Terwel et al., 2011; Bradbury, 2012). One reason for being in the focus of attention is seen to be the lack of progress in the commercialization of technologies. The negative consequences have served to emphasize the importance of public acceptance in the strategic development, application and commercialization of technologies. (Gupta et al., 2011, p.2.) Lack of progress and public opposition can also be seen as a result of biased approaches applied in planning and implementation. Participatory approaches and understanding of technologies as socio-technical combinations have emphasized the role of stakeholder engagement in planning and decision-making.

According to van Alphen et al. (2007, p.4369) stakeholders can play a double role in the development of CCS technology, i.e. (1) a direct influence on the implementation of CCS projects and presumably also much better chances to influence policymaking compared to lay people and (2) indirect influence on the deployment of CCS because of their ability to shape the public opinion. This raises the question how the Finnish stakeholders perceive CCS. Do they accept CCS technology?

Debate in the mass media influences public perception of new technologies such as CCS technology. A survey (Special Eurobarometer, 2011) indicated that CCS is fairly unknown technology in Finland. The low awareness calls for analyzing to what extend CCS technology has been discussed in the Finnish media. Media studies have been conducted at the national level for example in Australia, the Netherlands and in Sweden (van Alphen et al., 2007; Ashworth & Quezada, 2011; Buhr & Buhr, 2011), but not so far in the large extend in Finland (cf. Mikkola, 2012).

11.1 Stakeholders' opinions to CCS

The study is based on interviews with twelve Finnish stakeholders representing industry, the authorities, non-governmental organisations and a research organization. The interviewees were selected based on (1) stakeholders' statements on the national implementation of the CCS Directive (2009/31/EY) collected by the Ministry of the Environment in 2011, (2) researcher's own consideration and (3) interview feedback. Interview feedback, i.e. a snow-ball method, was applied to make sure that all potential stakeholders were identified (See D103, p.21–22). The interviews were conducted between November 2011 and January 2012. The length of an interview varied a quite lot, as the shortest one lasted about 45 minutes and the longest one almost one hour and 40 minutes. The method of the interview was based on semi-structured interview. The request for an interview was attached with the Factsheet of the Carbon Capture and Storage Program. The sheet was the only piece of advance information on CCS technology the interviewees were provided with by the researchers.

Currently CCS technology is not a burning issue in Finland. The stakeholders interviewed stated that they followed the development of the technology at some level, but their main interests are elsewhere. Due to the current energy production mix in Finland, the absence of storage sites in Finland, the high costs and impaired energy efficiency, the deployment of CCS technology was seen as unrealistic in the near future. Hence we argue that deployment of CCS technology in Finland is framed with low expectations at the moment. However, there are differences in ways of framing the CCS issue in Finland.

Two frames were identified. When the concerns of the stakeholders with a positive position on CCS were compared to the concerns of those with critical views, it seemed that the former are more concerned with issues related to costs, storage of CO_2 (absence of storage site) and policy and regulation issues, whereas the latter were concerned with environmental and health issues, investments (reduced investments in renewables due to CCS), public subsidies and technology issues (immaturity of CCS technology). We call the former as the 'CCS development oriented' frame and the latter as the 'CCS sceptical' frame. These frames, although general, could help one to better understand different views on CCS e.g. in preparing CCS policy or project measures.

11.2 CCS in the Finnish print media

The study is based on print data set comprised of 282 articles providing a comprehensive view over the CCS debate in the Finnish print media. The study covered the time period from the 1st of January 1996 to the 31st of December 2015 (Kojo & Innola, 2017).

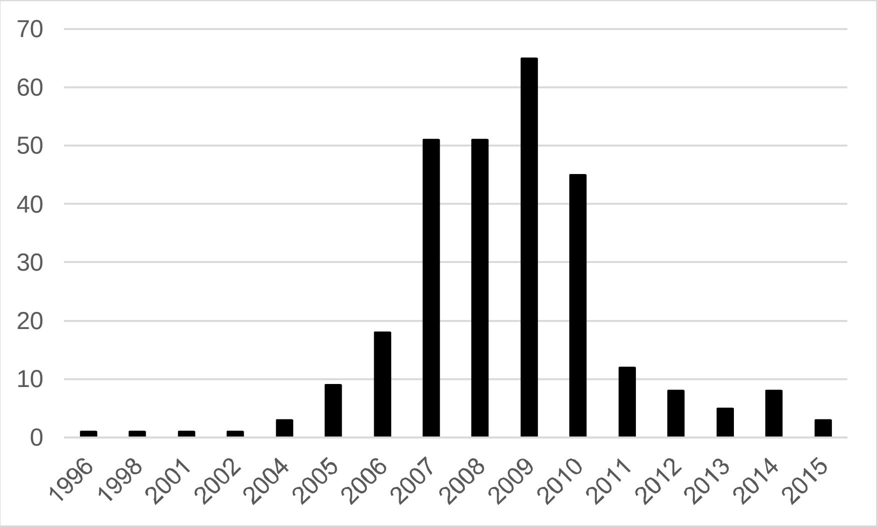

Figure 82. The number of articles with a reference to CCS published in the chosen Finnish daily newspapers in the period 1996–2015 (Kojo & Innola, 2017).

Data covered only Finnish-language print media. Data was retrieved from two newspaper databases Media-arkisto and Sanomat-arkisto. The former provided access to the six major provincial daily newspapers Aamulehti, Kainuun Sanomat, Lapin Kansa, Satakunnan Kansa and Pohjolan Sanomat. Aamulehti was the third largest newspaper in Finland in 2011. Furthermore, Media-arkisto included the commerce-oriented weekday-paper Kauppalehti which was the eighth largest newspaper in Finland in 2011. The latter database, Sanomat-arkisto, covered Helsingin Sanomat, the most circulated newspaper in Finland in 2011 and the business daily newspaper Taloussanomat. Taloussanomat has been published only as online newspaper since the beginning of 2008. The database covered also the tabloids Ilta-Sanomat, the second largest newspaper in 2011, and Iltalehti, the fifth largest newspaper, but the tabloids included only a few articles focused on carbon capture and storage issue.

Altogether ten actor groups were identified as contributors to the public debate in this study (Table 13). Industry was distinctly the most frequent speaker in the CCS related news items. Industry was given a voice in three out of five items (63%) in the print media news items investigated. Administration and experts were the second frequent speakers.

Table 13. Extent which a voice was given (Yes/No) to certain actor groups in all news items related to CCS (N=171) (Kojo & Innola, 2017)

	Yes	No	Yes (%)
Industry	107	64	63
Administration	36	135	21
Experts	36	135	21
Politicians	22	149	13
Int Org	21	150	12
NGO	16	155	9
Academia	13	158	8
Journalists	4	167	2
Public	1	170	1

In the study four temporal periods were identified based on the frequency of CCS-references in the Finnish press. The periods were as follows: (1) the period of nearly non-existent visibility (1996–2003), (2) the period of rising awareness (2004–2006), (3) the peak of attention (2007–2010) and (4) the period of decreasing interest (2011–2015).

In the first period (1996–2003) CCS was mentioned only few times in the Finnish press. First reference to CO_2 capture in the daily newspaper media was made in 1996 by the Finnish MEP Satu Hassi (the Green League) in her anti-nuclear energy tinged article. She described how some expenses of electricity production are omitted. Hassi noted that the price of electricity produced by coal would double if carbon dioxide capture were to be required in coal power plants.

During the second period (2004–2006) awareness concerning CCS in the Finnish press was raised. As CCS was discussed in the international arenas the technology was also noticed in Finland. However, the terminology used about this particular topic is somewhat tenuous and unsystematic. The abbreviation CCS is yet nearly non-existent. Triggering events that spurred the articles around this topic include the Vattenfall Schwarze Pumpe CCS-plant investment in Germany and the UN climate conference in Montreal, the COP 11, in the end of 2005.

In the third period (2007–2010), the peak of attention, CCS-related discussion is substantial, summing to over 40 articles each year. The amount of articles published is multiple compared to previous years. Discussion is more vivid also in arguments and has more diverse portfolio of actors. International climate politics steps in with a bigger influence to the Finnish discussion as CCS finds its place in EU climate and energy policy. The growth in released articles can be explained by the increasing number of CCS-related events also in Finland. In 2008 the energy companies Fortum and Teollisuuden Voima announced their plan to build a retrofit CCS-plant in Meri-Pori in Western Finland. Due to the plan several purely explanatory articles were released to explain and summarize the key points of yet widely unknown CCS-technology. Before 2007 CCS references in the Finnish press were short comments in wider climate political context, whereas from 2007 onwards articles solely concentrating to CCS technology start to appear in the newspapers. The abbreviation CCS is used in the Helsingin Sanomat, the largest newspaper in Finland, for the first time in January 2007. During the peak period attitudes towards CCS are mainly positive. Press attention forecast hope in the fight against climate change and new possibilities for coal energy. The German example of a carbon neutral coal plant and the Swedish and Norwegian announcements concerning future plans for carbon neutrality in their energy sectors are often referred to in the Finnish press.

However, it should be noted that even during the “peak” the total annual number of articles mentioning CCS was very low in the Finnish data compared to some other countries such as Canada and the UK. The attention peak itself, the meteoric rise in media attention as Shackley and Evar (2009, 157) noted it, can also be identified in other countries although the last few years have not so far been studied (Nerlich & Jaspal, 2013; Boyd & Paveglio, 2014).

The fourth period (2011–2015) characterized by decreasing interest towards CCS. The number of articles is remarkably lower compared to the peak years (2007–2010). The obvious explanation to this is the discontinuation of the Meri-Pori plan. After this industry output for the Finnish CCS debate was diminished a lot.

11.3 Bio-CCS in the Finnish print media

The aim is to study arguments regarding bio-CCS in the Finnish print media. The starting point for this study was introduced in the CCSP research plan (DoW, FP3) as follows: “the need for carbon-negative solutions – i.e. systems that withdraw more CO_2 from the atmosphere than they emit – as safeguards against irreversible climate change is increasingly being recognized on an international level”. As the most frequent positive argument for CCS technology in the Finnish print media was the statement that “CCS reduces emissions/slows down climate change” (D123, p. 17; Kojo, 2013) it was interesting to study from the viewpoint of acceptability how bio-CCS was perceived by different actors.

The print media data gathered earlier in the CCSP from ten Finnish newspapers (see D123, p. 4–6) was applied as a basic data. However, this data consisting of 226 CCS related articles contained only eight articles with a more or less direct reference to bio-CCS (such as “double catching”, kaksoissieppaaminen in Finnish). Thus bio-CCS or reference to it was mentioned only very rarely and therefore it can be argued that there is almost no existent public debate regarding bio-CCS in Finnish print media. This is not a surprise taking into account the decreasing trend of overall CCS attention in the Finnish print media (Kojo and Innola, 2017).In the newspaper articles bio-CCS was referred to by a researcher, a private person and general news items. These happened most often during the period of ’peak of press media attention’ (i.e. 2007–2010). Bio-ccs was perceived neutrally or very positively, even too optimistically. The advantages of bio-CCS according to these actors were the ability to capture of old emissions, cleaning of the atmosphere and support for wood and other bioenergy sector. The only disadvantages which was referred to, was that there were no explicit plans of implementation of CCS in Finland.

11.4 Public engagement in CCS

Lack of public acceptance is often deemed as one crucial barrier in deploying CCS technologies. As a result of controversies due to CCS projects different kinds of reports, guidelines, and recommendations focused on building public acceptance for CCS have been published in recent years. Authorities, international corporations and organisations, but also NGOs have published these documents which aim at rising awareness and fostering public involvement in related CCS projects.

In this study selected documents are analysed to gather lessons learned regarding public engagement (D141; D146). The guiding principle is to consider how public engagement in the case of CCS technologies could be applied in Finland. Three guideline reports for engagement in CCS project were chosen for a short review (D146). The reports were published by different kinds of organisations. One was published by Bellona which is a NGO engaged in environmental issues, one by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) which is the federal government agency for scientific research in Australia, and one by the Global CCS Institute (GCCSI) which is an international membership organization supported by governments, global corporations, small companies, research bodies and non-government organisations.

Extent and specificity of the reports varyed. Bellona’s compact report emphasized interaction between the social and technical processes of a CCS project at a general level. CSIRO’s report consisted of many practical-oriented and informative data gathering advices and forms. GCCSI’s report was the most comprehensive including also detailed analysis of one CCS project.

The target audience of all three reports is more or less project developer, although also other actors less familiar with stakeholder and public engagement issues could find these useful in planning and implementing their CCS policy or project. CSIRO's report emphasised that it aimed at designing a universal guide particularly.

All reports underlined that stakeholders of a CCS project should be understood broadly. For instance Bellona (2009, p2) noted that "[a] CCS project is a local project but is carried out within the context of national and even international debate. This means that the group of stakeholders or potentially interested parties is considerably broad." Diversity of stakeholders has also effects on applied engagement methods. CSIRO (2011, p36) point out that as the range of stakeholders is broad and diverse it is required "to employ a combination of engagement processes both formal and informal, that will encourage particular stakeholder groups to engage in ways that are conducive to both your project and the individual group needs". CSIRO and GCCSI also underlined importance of studying societal context of a project before stakeholder engagement phase. GCCSI (2013) referred to this phase as a three-step social site characterization and CSIRO (2011) as gathering social data, which aims at learning and understanding about "the consequences of the proposed CCS project on the population and community".

Although the level of details of the guidelines and recommendations varyed all these organisations spoke for a proactive engagement approach. According to Bellona (2009, p2) "public consultation and participation is based on consultation, public involvement and information sharing procedures which allow stakeholders to have an input into the decisionmaking process". Thus effectiveness of participation was underlined. According to GCCSI (2013, p98, p100) the main challenge is to ensure that three basic rules are followed. These are as follows: "(1) Everyone has the right to be heard. (2) Any expressed concern must be noted down and considered, even though it may seem irrational or unfeasible. Therefore do not disregard any comment before it has been discussed any further with the audience. (3) There should be no ostentatious display of a final project design that has not yet been endorsed." Furthermore, GCCSI stated that "limiting the engagement strategy only to communication will, most likely, exacerbate a projects failure to maintain stakeholder engagement". GCSCSI (2013, p124) also warned about shortcuts as it noted that

> "*Real stakeholder engagement is required to obtain support for the project or, at minimum, to avoid blockage. Indeed, it is assumed that the exercise of authority or persuasive communication are no longer appropriate in our societies, where stakeholders are increasingly asking to be involved in important decision-making processes, especially when these decisions have an impact on their environment, interests, safety or welfare.*"

What are the lessons learned for the Finnish CCS policy? It seems that recent Finnish engagement activities related to CCS technologies have been based mainly on public communication, i.e. one-way communication (education). Although confidence in institutions and representative democracy in Finland is relatively high (Melin 2009) and as there are no CCS projects on the planning board, organisations possibly interested in implementation of CCS in the long-term in Finland should consider whether joint communication and engagement guidelines to be applied in the Finnish context are needed. It is recommendable that the guidelines would be planned in collaboration with potential CCS stakeholders. Guidelines should pay attention to legal requirements and formal phases related to planning and decision-making of a single CCS project (Figure 80), but at the same time it would be important to propose a policy for developing and taking voluntary activities regarding engagement in the field of CCS. These kind of recommendations could take into account both different levels of decision-making (i.e. policy, local/project) and different phases of a programme or a project.

Currently the most urgent issue would be to consider how broader variety of stakeholders could be involved in a R&D programme of CCS technologies. This would underline engagement on early lifecycle phases and therefore help to assess various impacts and implications of technological choices.

12. International collaboration in CCSP

A specific feature of the CCSP program was an active international networking and collaboration. One significant task of the programme was information transmission and collaboration between national and international actors. Participation and work in several international networks was funded via CCSP, such as IEAGHG (The IEA Greenhouse Gas R&D Programme), ZEP (The European Technology Platform for Zero Emission Fossil Fuel Power Plants), EERA (European Energy Research Alliance, CCS programme), networks of geological surveys (CGS Europe and ENeRG), IGU (International Gas Union) and EASAC (The European Academies Science Advisory Council).

CCSP had an active collaboration with the Swedish CCS project, in particular regarding the mutual Bastor-project. The Bastor-project was established by the CCSP program and the Swedish CCS project. The implementation of the project was done in tight collaboration between Finland and Sweden and all the results were shared. In addition to Finland and Sweden the Bastor-project established good contacts to several other Baltic Sea countries and thus the project was in practice a multinational activity.

CCSP also collaborated with NORDICCS, a virtual CCS networking platform aiming for increased CCS deployment in the five Nordic countries, by organising joint workshops and seminars.

In addition to the collaboration listed here, the CCSP partners were also involved in other international collaboration activities with significant CCS activities, such as collaboration with the IEA CCS unit, Global CCS Institute, PRISMA, Tekes/A*Star Singapore cooperation, SINTEF and EU projects such as MUSTANG and FLEXIBURN.

12.1 IEA Greenhouse Gas Programme and IEA CCS unit

VTT has been acting as the representative of Finland in the IEA Greenhous Gas R&D Programme Executive Committee (ExCo) and distributed information delivered by IEAGHG in Finland. IEAGHG is an international collaborative research programme established in 1991 as an Implementing Agreement under the International Energy Agency (IEA). The role of the Programme is to evaluate technologies that can reduce greenhouse gas emissions derived from the use of fossil fuels.

IEA GHG ExCo meetings are organised twice a year. An important ExCo activity is to suggest and vote for studies to be funded by IEAGHG. The selected studies, as well as recently published reports, are reported regularly to CCSP partners and other Finnish interest groups. These lists of studies are recommended to follow up by the partners because they represent useful information on CCS and integration of CCS in industry, In addition, it is possible for Finnish research institutes and companies to offer and get contracted with IEAGHG regarding these studies. Furthermore, similar studies published or to be published by IEAGHG should not be conducted in Finland, unless country specific issues are remarkable.

In addition, national priority lists have been prepared with Finnish partners of CCSP concerning project proposals to be funded by IEAGHG programme and new ideas for research topics are submitted to IEAGHG for voting.

The highlights of the co-operation with IEAGHG include:

- International seminars and conferences in conjunction with the meetings
- Visit at several pilot and demonstration sites, including the Boundary Dam power plant (the first full scale integrated CCS project in the world)
- Increased discussion on the importance of CCS in industry
- Increased discussion on the role of CCS in future energy system, including more intermittent energy supply (solar and wind) with low operational expenditures, and unconventional gas. What are the potential CCS applications, what is the utilisation rate and flexibility of these plants and how much does it impact on the economics of CCS, are there any benefits in CCS processes in terms of energy storage (e.g. oxygen or solvent storages) which could be benefits in future energy systems.
- Positive funding decision for the study regarding CCS in pulp and paper industry and execution of the study with CCSP

CCSP has in collaboration with IEAGHG evaluated the techno-economic potential of retrofitting CCS in the pulp and paper industry. The study is presented in section 4.4.1. The comprehensive report will be an addition to the collection of technical reports published by the IEAGHG on implementin$_g$ CO_2 capture in industries. The final report will be available from March 2017 in the IEAGHG web pages.

12.2 Zero Emission Platform (ZEP)

In CCSP Foster Wheeler, Fortum and VTT have participated in the work of ZEP. ZEP is a unique coalition of stakeholders united in their support for CCS as a key technology for combating climate change. Minutes of ZEP meetings are available under the public domain and therefore work of ZEP is not separately reported or minutes uploaded to CCSP portal.

12.3 International collaboration related to utilisation of CO_2 by microalgae cultivation

Oil and Natural Gas Corporation (ONGC) Ltd from India joined CCSP as a full partner for one funding period during 2014-2015. The joint research topic was carbon capture and utilization by microalgae cultivation, and further refining of the algal biomass into biofuels and other commercial products. ONGC performed background research on the use of microalgae and conversion into biogas. As background, extensive work on microalgae species selection was provided. VTT, SYKE and Neste Jacobs were the Finnish research partners performing the R&D work, which was related to technical solutions, experimental research with microalgae at extreme pH conditions, and techno-economic assessments of various process routes for converting CO_2 into various products by microalgea cultivation. Two miniseminars were held – one in Delhi and another one in Espoo. Experts were invited for guest presentations at these miniseminars. The peak of the collaboration was a small pilot experiment run (200 L reactor size) at ONGC's gas processing facility at Hazira, India, cultivating algae in CO_2 captured from offgas from the facility. Experiments were further performed with producing methane from the algal biomass (D612).

A visit to two micro-algae production facilities were organised in the last year of CCSP. These were Global Algae Innovations and Cellana, located in Hawaii, both aiming at large-scale production of microalgae biomass for feed or/and biofuel. Global Algae Innovation provided valuable data of their process and novel technologies applied in microalgae production to the techno-economic case study.

12.4 International collaboration related to oxy-fuel combustion

Amec Foster Wheeler, VTT, and LUT have participated in two EU FP7 projects, in which the objective has been the development of oxygen-fired combustion in CFB. The FLEXI BURN CFB project, which was coordinated by VTT, was carried out in 2009-2012. The O2GEN project was carried out in 2012-2016. The two projects involved collaboration of several universities, research organizations, and industrial partners in Finland, Spain, Portugal, Italy, Poland, Germany, Belgium, and France.

In August 2012 Jarno Parkkinen from LUT visited at 30 MW_{th} oxy-fuel combustion CFB technology development plant (TDP) in Ponferrada, Spain. Visit was hosted by Fundación Ciudad de la Energía (CIUDEN). During the visit he participated data collecting from TDP, which was used for 3D modelling tool development in oxy-fuel combustion environment.

In order to get the most updated knowledge about radiative heat transfer modeling in oxygen fired combustion systems, a research collaboration has been developed with the research group of Professor M. Modest in University of California-Merced. Professor Modest is among the most well-known scientist of the field and author of the most widely used text book of radiative heat transfer. Hadi Bordbar from LUT visited UC-Merced for four months from Jan. 2014 to May.2014. During his visit he learned more about the most recent developments in non-gray gas modeling of combustion gases. The host group was the founder of the state of the art method of full spectrum correlated-k method (FSK) and provided a wide information and knowledge about this method to the visiting researcher.

In 2015, LUT participated in writing of an extensive review article on oxyfuel combustion (Oxyfuel combustion for CO_2 capture in power plants, International Journal of Greenhouse Gas Control 40 (2015) 55–125).

12.5 International collaboration related to hot solid looping processes

LUT's dual fluidized bed model for gaseous fuel CLC has been successfully validated in cooperation with Vienna University of Technology (TUV). The validation of was based on the data obtained from the operation of a 120 kWth CLC pilot unit located at TUV (Peltola et al., 2013a).

The integration of a copper-based CLOU process in a state-of-the-art coal power plant has been investigated by LUT in collaboration with Politecnico di Milano (Polimi). The performance of the proposed CLOU reactor configuration was evaluated by the LUT 1-D model and the overall power plant performance was computed with the Politecnico di Milano GS® code, a modular code widely used to assess a number of complex energy systems (Peltola et al., 2015b; Spinelli et al., 2016).

Related to calcium looping (CaL) process research, LUT has participated in two EU projects. In EU FP7 project Caoling (2009-2013) world's largest 1,7 MW carbonate looping pilot plant was built in the Hunosa 50 Mwe CFB coal power plant of "La Pereda", using a side stream of flue gases of the commercial plant. In CaO2 project (2014-2017) the aim is to demonstrate CaL process operation in high O_2 content environment utilizing La Pereda CaL pilot plant.

At the end of 2015 started a Nordic Flagship Project called "Negative CO_2 emissions in the Nordic energy system". This 5 years project is funded by Nordic Energy Research and partners are leading research organizations in Chemical Looping Combustion: Chalmers University of Technology, VTT, SINTEF, Åbo Akademi and Bellona. In addition, in steering group there are 12 companies interested in development of chemical looping technology for biomass. The ultimate goal of the Negative CO_2 project is the development of new competitive technology that:

- enables CO_2 capture and negative CO_2 emissions with the lowest possible cost and energy penalty
- is able to produce power and/or steam for industrial and other applications
- utilizes Nordic expertise and competence in fluidized bed technology
- eliminates thermal NOx emissions and has potential to achieve more efficient fuel utilization compared to ordinary biomass combustion.

VTT's bio-CLC PDU construction works and the first test campaign were done in co-operation with Negative CO_2 project.

12.6 NORDICCS

The Nordic CCS Competence Centre (NORDICCS) was established in 2011 as a joint programme between R&D, academia and industry from all the Nordic countries. The main objective of the project was to act as a networking platform for Nordic CCS stakeholders by concentrating CCS expertise and boost CCS deployment in the Nordic region. NORDICCS was funded by the Top-level Research Initiative (TRI) and coordinated by Sintef. The NORDICCS project ended in 2015. Finland was represented by VTT in NORDICCS.

The main activity areas of NORDICCS were related to implementation of CCS in typical Nordic industries with high CO_2 emissions and the assessment of feasibility for entire Nordic CCS chains including transportation and storage. Also communication with different stakeholders was addressed. Main results from the NORDICCS project include techno-economic assessments of implementation of CCS in oil and gas activities, pulp and paper industry, iron and steel industry, cement production and geothermal power production. Various scenarios were laid out for potential CCS chains, including regional CO_2 capture clusters with intermediate storage hubs and joint Nordic transportation and storage of CO_2. A detailed storage atlas for the Nordic region was also developed.

The CCSP and NORDICCS projects were ongoing during the same time period and involved in active cooperation such as joint workshops, meetings, seminars and conferences.

12.7 Networks of geological surveys

GTK has participated in the CGS Europe and ENeRG networks and transferred information from meetings and seminars to CCSP in the form of memorandums and short meeting reports that can be found in the CCSP portal. The highlight of this period was the organisation of the CGS Europe workshop 23.5.2013 in Espoo (in cooperation by GTK, CGS Europe and CCSP) that focused on international cooperation in the Baltic Sea region. More than 50 participants all over the Baltic

Sea area attended the one-day workshop. A pre-meeting and dinner was also organised 22.5.2013 for participants of the pre-meeting and the invited speakers of the workshop. Participation in this network was discontinued from 2014 onwards.

12.8 Bastor projects

The Bastor projects was a joint initiative funded in its first stage by CCSP and in the second stage[7] by the Swedish Energy Agency. The projects were carried out together Elforsk, OPAB, SSAB, MinFo, Nordkalk, Cementa, SMA Mineral, Preem, Vattenfall, Fortum, Jernkontoret, Swedish Energy Agency and Global CCS Institute (GCCSI). The focus of the work was the estimate the geological storage potential for CO_2 in the bedrock of the Baltic Sea. The actual evaluation of the suitability of the geology in Baltic Sea region for storage of CO_2 was subcontracted to geological consultant (SLR, Ireland) who is an expert in this field of research. The basic data required to carry out the assessment was received from the Swedish enterprise OPAB, searched from open data sources and purchased from Latvia (Latvian Environment, Geology and Metereology Centre). The results are presented in section 7.1.1.

12.9 BASREC network

The Baltic Sea Region Energy Cooperation (BASREC) has identified environmental care and safe CO2 transport and storage solutions as key areas of common, regional interest. As part of a BASREC initiative, a CCS network was formed in 2014, for strengthening and accelerating the regional CCS cooperation. The network arranged two seminars during 2015, one organized in Tallinn in April and another in Warsaw in October. VTT and GTK have participated in the network core group. Nicklas Nordbäck (GTK) also chaired the network Storage Task Force during 2015. As a result of the storage task force work, the CGS Baltic seed project will in 2016-2017 be working on developing a regional CO2 geological storage project.

12.10 EERA Joint Program on CCS

VTT and LUT have participated in the work of EERA CCS programme in Oxyfuel, CLC and Industrial CCS topics. Marie Bysvein from Sintef Energy is the new manager of the CCS joint program and the program is structured in two sub-programs.

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[7] The second stage was named “Bastor 2”

Subprogramme 1, CO_2 capture, is led by Sven van der Gijp (TNO) and organised in four areas (Post-combustion, Pre-combustion, Oxyfuel, Cross-cutting issues). Subprogramme 2, CO_2 storage, is led by Jonathan Pearce (BGS) and organised in three areas (Monitoring, Static modelling, Dynamic modelling).

12.11 International gas union

Recent experiences from CCS implementation in the gas industry were shared in this study group. The group was gathering information on the technology, costs, benefits, legal framework and public acceptance of CCS. The target was to create a CCS roadmap including an estimation about when and how the gas industry should develop and deploy CCS in the future. The report was finalized in the beginning of 2015 and presented at World Gas Conference in Paris in June, 2015. Participation in this network was discontinued from 2015 onwards.

12.12 EASAC

CCSP's program manager participated in a work group formed by EASAC (European Academies Science Advisory Council) for producing an overview and recommendation report on CCS. EASAC presented the report on 22 May 2013 at the Royal Academies' Palace in Brussels.

The report (EASAC, 2013) considers the main components of CCS – capture, transport and storage. It also presents an evaluation of alternatives to mainstream CCS technologies and reviews the important overarching issue of public engagement. The report finds that at present CCS is not economically viable and strong policy action will be essential to creating CCS demonstration plants and the first generation of commercial facilities.

Drawing these strands together, the report evaluates the prospects for CCS in Europe from now until 2050 and makes recommendations on the policy initiatives that will be necessary to enable CCS to contribute to climate change mitigation in Europe. Financial viability of CCS, storage issues, CCS technology development, CO transport and public engagement are analysed and discussed.

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List of deliverables from CCSP

(Travel reports and intermediate reports has been removed with the approval of the Program Steering Group from the list of final public deliverables)

Deliverable number	Authors	Title
D101	Salokannel, Kimmo: Sokka, Laura; Sorsa, Reetta; Tsupari, Eemeli	Milestones of a CCS project from an environmental and legal perspective
D103	Kojo, Matti; Nurmi, Anna	A report on the acceptability of CCS in Finland
D108	Salokannel, Kimmo: Sokka, Laura; Sorsa, Reetta; Tsupari, Eemeli	Determination of emissions related to CCS by LCA
D109	Sorsa, Reetta	Transportation of CO2 by ship: Monitoring of greenhouse gas emissions
D115		ZEP Taskforce Technology meeting TFT22-TFT25
D122	Kojo, Matti; Nurmi, Anna	Low expectations and remarkable opportunities of CCS technology in Finland
D123	Innola, Eeva; Kojo, Matti	CCS in the Finnish print media
D124	Pihkola, Hanna; Behm, Katri; Tsupari, Eemeli; Sokka, Laura	LCA case results - Overview & summary
D125	Hakkarainen, Elina; Tsupari, Eemeli; Kärki, Janne	Updated figures about CCS investments and costs per avoided CO2 emissions
D127, D128	Kujanpää, Lauri	Summary report on regulatory status of CCS
D129, D102	Malmén, Yngve; Nissilä, Minna; Luste, Sari; Tammivuori, Riikka	Data package about environmental, health and safety requirements related to the capture, transfer and intermediate storage of carbon dioxide in Finland
D130, D112	Askola, Hanna	Guidebook on environmental, health and safety requirements when transporting carbon dioxide by ships within Finnish territorial waters
D132		ZEP Taskforce Technology meeting TFT26-TFT30
D137	Kojo, Matti	Bio-CCS argumentation in the Finnish print media
D138	Pihkola, Hanna; Kojo, Matti; Kujanpää, Lauri; Luste, Sari; Nissilä, Minna; Saavalainen, Paula, Salokannel, Kimmo; Sokka, Laura; Tsupari, Eemeli	Assessing the sustainability of CCS technologies in Finland – Highlighting future potential, uncertainties and challenges for technology implementation
D138	Pihkola, Hanna; Kojo, Matti; Kujanpää, Lauri; Luste, Sari; Nissilä, Minna; Saavalainen, Paula; Salokannel, Kimmo; Sokka, Laura; Tsupari, Eemeli	Assessing the sustainability Assessing the sustainability of CCS technologies in Finland – Highlighting future potential, uncertainties and challenges for technology implementation
D140	Kujanpää, Lauri; Teir, Sebastian	Implications of the new EU maritime emission monitoring regulation on ship transportation of CO2
D141	Kojo, Matti	Public engagement in developing CCS technologies in Finland
D142	Pihkola, Hanna; Behm, Katri; Tsupari, Eemeli; Sokka, Laura	Life cycle assessment of CCS in the context of energy production – case report
D143	Hongisto, Mikko; Tsupari, Eemeli	Options to create incentives for negative emission sources in the EU-ETS
D144	Pihkola, Hanna; Tsupari, Eemeli; Kojo, Matti; Kujanpää, Lauri; Nissilä, Minna; Sokka, Laura; Behm Katri	Integrated sustainability assessment of CCS - Identifying non-technical barriers and drivers for CCS implementation in Finland
D144	Pihkola, Hanna; Tsupari Eemeli; Kojo, Matti; Kujanpää, Lauri; Nissilä, Minna; Behm, Katri; Sokka, Laura	Integrated sustainability assessment - Identifying non-technical barriers and drivers for CCS implementation in Finland
D145	Salokannel, Kimmo; Luste, Sari; Järvinen, Eerik	Graphical tool for industrial risk identification and general evaluation (Ramboll)
D146	Pihkola, Hanna; Tsupari, Eemeli; Kojo, Matti; Kujanpää, Lauri; Nissilä, Minna; Behm, Katri	Overcoming non-technical barriers, summary
D147	Lehtilä, Antti; Koljonen, Tiina	Potential deployment of CCS in Finland under low carbon scenarios
D201	Rajamäki, Jaana	Evaluation of a method for “Carbon Capture and Neutralization”
D201, M201	Miilumäki, Noora	Hiilidioksidin suora teollinen hyödyntäminen
D202	Kinnula, Matti	Feasibility study and sustainability assessment for selected CO2 utilizing reaction routes
D203	Turpeinen, Esa; Koskinen, Rauli; Huuhtanen, Mika; Keiski, Riitta	Roadmap for CO2 Utilization - Evaluation of the CO2 Use as a Solvent - INTERMEDIATE REPORT

D204	Kärki, Janne; Tsupari, Eemeli; Arasto, Antti	CCS feasibility improvement in industrial and municipal applications by heat utilisation
D204	Kärki, Janne; Tsupari, Eemeli; Arasto, Antti	CCS Feasibility Improvement in Industrial and Municipal Applications by Heat Utilisation
D205	Pirhonen, Leena	Effects of Carbon Capture on Combined Cycle Gas Turbine
D206	Keskitalo, Esa	Savukaasujen hiilidioksidin talteenottoprosessin vaikutukset olemassa olevaan monipolttoaine-CHP-voimalaitokseen
D207	Manninen, Kaisa; Spilling, Kristian	Growing algae for carbon capture: a review of available technologies and life cycle analyses
D209	Lampinen, Isa	Carbon Capture From Oil Refineries - A Concept Study
D210	Arasto, Antti	IGCC with CCS
D211	Arasto, Antti; Tsupari, Eemeli; Kärki, Janne; Sormunen Risto; Korpinen, Timo; Hujanen, Sari	Feasibility of significant CO2 emission reductions in thermal power plants – comparison of biomass and CCS
D212	Helen	Conceptual Study on Post Combustion CCS Technology for "Vuosaari C" Multifuel Power Plant
D213	Hujanen, S; Kankkunen, K	Technical pre-feasibility study of South-West Finland´s district heating system´s multifuel CHP plant based on oxy-fuel fired circulating fluidized bed (CFB) boiler
D214	Laine, Melina	Effects of carbon capture on an existing combined cycle gas turbine power plant
D215	Kärki, Janne; Tsupari, Eemeli; Arasto, Antti	Web based cost estimation tool
D216	Andtsjö, Janne	Comparison of Carbon Capture Methods in Hydrogen Production by Steam Methane Reforming
D217	Tsupari, Eemeli; Kärki, Janne	Cost estimation toolkit (steel industry)
D218, D219	Sonck, Matti	Cultivation of Microalgae for the Fixation of Carbon Dioxide from Power Plant Flue Gas
D220, D245	Kumar, Haresh	Utilization of Carbon dioxide in Beneficiation of PGE minerals
D221	Juntunen, Terhi; Ojeiduma Linda	Hydrogenation of CO2 to formic acid and methanol
D222	Koskinen, Rauli; Turunen, Helka; Tiitta, Marja; Keiski, Riitta	Extended activity of zeolite catalysts with CO2 as reaction medium
D223	Pulkkinen, Iiris	Ylikriittinen hiilidioksidi ja sen käyttö
D225	Raiko, Markku	Paineistettuun happipolttoon perustuva CHP-voimalaitos
D226	Fager-Pintilä, Markus	Thermo-catalytic Decomposition of Methane - Annual Report
D227	Keipi, Tiina; Hankalin Ville; Nummelin, Jaakko; Raiko, Risto	Techno-economic analysis of four concepts for thermal decomposition of methane: Reduction of CO2 emissions in natural gas combustion
D228	Teir, Sebastian	Evaluation of concepts for CO2 neutralisation using feldspar
D229	Suomalainen, Marjut; Arasto, Antti	Optimisation of Partial Oxygen Combustion
D230	Merikoski, R.; Linjamaa, A.; Paavola, M.; Raiko, R.	Comparison between two oxygen production methods for power plants capturing carbon dioxide
D231	Raiko, Markku	Hiilitalteenoton kannattavuusarvio
D232	Tolvanen, Katariina	Thermo-catalytic decomposition of methane-carbon product utilization and market analysis
D233	Niskanen, Tuomas	Biogas with CCS
D234	Sipilä, Kai; Arasto, Antti	Longer term R&D needs and priorities on Bioenergy
D235	Kärki Janne, Tsupari Eemeli	Cost analysis tools on case studies (bio-CCS)
D236	Teir, Sebastian; Aarlien, Rune	CCSP & NORDICCS Joint seminar & workshop 2013 summary
D237	Tähtinen, Matti; Tsupari, Eemeli; Kärki, Janne	Feasibility and sensitivity of solid fuel CLC plant investment with oxygen carrier recovery
D238	Kujanpää, Lauri	Evaluation of flexible CCS-CHP concepts and systems - status report
D240	Hujanen, S.; Korpinen, T.; Salmensaari, I.; Kankkunen, K.; Dernjatin, P.; Nyberg, K.; Sormunen, R.	Technical pre-feasibility of a multifuel CHP plant based on oxy-fuel fired circulating fluidized bed boiler
D241	Sormunen, Risto; Korpinen, Timo; Hujanen, Sari	Design criteria and feasibility of a multi-fuel CHP plant based on oxy-fuel fired CFB
D242	Kärki, Janne; Tsupari, Eemeli; Hurskainen, Markus	Cost and CO2 evaluation toolkit for PCC in multi-fuel CHP plant
D243	Arasto, Antti; Tsupari, Eemeli; Kärki, Janne; Lilja, Jarmo; Sihvonen, Miika	Oxygen blast furnace with CO2 capture and storage at an integrated steel mill—Part I: Technical concept analysis
D244	Manninen, Kaisa; Sonck, Matti; Spilling, Kristian	ENVIRONMENTAL IMPACT ASSESSMENT OF ALGAE CULTIVATION UNDER FINNISH CONDITIONS
D246	Omodara, Linda	Sustainability assessment of formic acid production: Comparison of CO2 based and conventional processes
D247	Kabra, Satish K.; Turpeinen, Esa; Keiski, Riitta L.; Yadav, Ganapati D.	Direct synthesis of dimethyl carbonate from methanol and carbon dioxide: A thermodynamic and experimental study
D248		Innovation workshop memo 15082013
D248		Innovation workshop memo 20121211

D249	Teir, Sebastian; Suomalainen, Marjut; Onarheim, Kristin	Pre-evaluation of a new process for capture of CO2 using water
D250	Keipi, Tiina	Catalytic decomposition of methane -Experiments with metal catalysts
D251	Teir, Sebastian	Utilisation of industrial alkaline streams for capture of CO2
D252	Arasto, Antti; Onarheim, Kristin; Tsupari, Eemeli; Kärki, Janne	Bio-CCS: Feasibility comparison of large scale carbon-negative solutions
D253	Kujanpää, Lauri; Pursiheimo, Esa	Report on flexible CCS in a CHP system
D254	Suomalainen, Marjut; Onarheim, Kristin	Flue gas recirculation in gas turbine for CO2 post-combustion capture
D256	Nummelin, Jaakko; Hankalin, Ville; Pirhonen, Leena	Energy storage systems and CCS
D257	Rajamäki, Jaana	Thermal Decomposition and Autothermal Pyrolysis of Methane
D258	Tsupari, Eemeli; Kärki, Janne	Flash-based toolkit of the most promising business case for bio-CCS in CHP production
D259	Tsupari, Eemeli; Arasto, Antti; Kärki, Janne; Tähtinen, Matti	The most promising business case for bio-CCS in power and CHP production
D259	Tsupari, Eemeli; Arasto, Antti; Kärki, Janne; Tähtinen, Matti	The most promising business case for bio-CCS in power and CHP production
D260	Hannula, Ilkka; Arpiainen, Vesa; Tuomaala, Mari	Identification of best options for CO2 utilisation for biorefineries (Vesa Arpiainen, Ilkka Hannula / VTT – Comment: Mari Tuomaala / Gasum)
D260	Arpiainen, Vesa; Turpeinen, Esa-Matti	CO2 to chemicals and market study
D260	Hannula, Ilkka; Kurkela, Esa	Doubling of synthetic biofuel production with hydrogen from renewable energy
D260	Hannula, Ilkka	Hydrogen enhancement potential of synthetic biofuels manufacture in the European context
D261	Kujanpää, Lauri; Pursiheimo, Esa	Techno-economic evaluation of flexible CCS concepts in a CHP system
D262	Keipi, Tiina; Tolvanen, Katariina E.S.; Tolvanen, Henrik; Konttinen, Jukka	Thermo-catalytic decomposition of methane: The effect of reaction parameters on process design and the utilization possibilities of the produced carbon
D263	Keipi, Tiina	Summary report: Thermo-catalytic decomposition of methane applied to reduce CO2 emissions in natural gas utilization
D264	Kouri, Sampo	Feasibility of Carbon Capture in Kraft Pulp Mills
D265	Kouri, Sampo; Tsupari, Eemeli; Kärki, Janne; Teir, Sebastian; Sormunen, Risto; Arponen, Timo; Tuomaala, Mari	The potential for CCUS in selected industrial sectors – summary of concept evaluations in Finland
D301	Pekkanen, Martti	CO2-MEA simulation with Aspen Plus
D302	Tähtinen, Matti; Pikkarainen, Toni; Paakkinen, Kari	CLC cold model testing and design development
D303	Laukkanen, Timo	Aspen Dynamics as a dynamic simulation tool for oxyfuel power plants
D305	Savolainen, Jouni; Lappalainen, Jari, Mikkonen, Hannu; Jegoroff, Mikko	Methods to link the sub-models between Aspen and Apros dynamic simulation softwares
D306	Mohammad Hadi Bordbar, Timo Hyppänen	The Effect of Combustion Type on the Radiation Heat Transfer in Back Pass Channel of a CFB Boiler
D307	Bordbar, M.H., Wecel, G., Hyppänen, T	New line by line based weighted sum of gray gases model for inhomogeneous CO2-H2O mixture in oxy-fired combustion
D308	Rahiala, Sirpa; Hyppänen, Timo; Pikkarainen, Toni	Bench-Scale and Modeling Study of Sulfur Capture by Limestone in Typical CO2 Concentrations and Temperatures of Fluidized-Bed Air and Oxy-fuel Combustion
D309	Jukola, Perttu; Kallio, Sirpa	CFD simulations of air and oxy-fuel firing with several fuels in a large scale CFB furnace
D310	Laukkanen, Timo	Submodel for Calculating Exergy Linked to AspenPlus
D311	Mustonen, Silja	Carbon dioxide recovery with activated methyldiethanolamine
D312	Vaittinen, Johanna; Björklöf, Thomas; Nyman, Timo	CFD and kinetic modelling of postcombustion CO2 absorber
D313	Uusi-Kyyny, Petri; Dell'Era, Claudia; Penttilä, Anne; Pakkanen, Minna; Alopaeus, Ville	Measurements of H2S solubility in aqueous diisopropanolamine solutions and vapour pressure of diisopropanolamine
D315	Tähtinen, Matti	Studies of CLC hydrodynamics and test rig design
D316	Kärki, Janne; Tsupari, Eemeli; Tähtinen, Matti	Techno-economical studies about performance of industrial scale CLC power plant
D317	Tähtinen, Matti; Lagerbom, Juha; Pikkarainen, Toni	Development of oxygen carrier synthesis methods and characterization of oxygen carriers applicable for solid fuels
D318	Peltola, Petteri; Ritvanen, Jouni; Tynjälä, Tero; Pröll, Tobias; Hyppänen, Timo	One-dimensional modelling of chemical looping combustion in dual fluidized bed reactor system

D319	Peltola, Petteri; Tynjälä, Tero; Ritvanen, Jouni; Hyppänen, Timo	Mass, energy, and exergy balance analysis of chemical looping with oxygen uncoupling (CLOU) process
D320	Vepsäläinen, Ari; Shah, Srujal; Peltola, Petteri; Hyppänen, Timo	Bed Sherwood Number and Chemical Kinetic Coefficient in a Fuel Reactor of Chemical Loopling Combustion by Eulerian CFD Modeling
D322	Meriläinen, Tuomas	Evaluation of Blast Furnace gas cleaning efficiency
D323	Laukkanen, Timo	A model for simultaneous synthesis of flexible heat exchanger networks with heat storage - CASE: Oxyfuel power production
D324	Rahiala, Sirpa; Myöhänen, Kari; Hyppänen, Timo	Modeling the behavior of limestone particles in oxy-fuel CFB processes
D325	Bordbar, M.H.; Myöhänen, K.; Hyppänen, T.	Coupling of a radiative heat transfer model and a three-dimensional combustion model for a circulating fluidized bed furnace
D325	Bordbar, M.H.; Hyppänen, T.	The correlation based zonal method and its application to the back pass channel of oxy/air-fired CFB boiler
D326	Penttilä, Anne; Uusi-Kyyny, Petri; Salminen, Arto; Seppälä, Jukka; Alopaeus, Ville	A comprehensive thermodynamic study of heat stable acetic acid salt of monoethano-lamine
D327	Penttilä, Anne; Uusi-Kyyny, Petri; Alopaeus, Ville	Distillable Protic Ionic Liquid 2-(Hydroxy)ethylammonium Acetate (2-HEAA): Density, Vapor Pressure, Vapor–Liquid Equilibrium, and Solid–Liquid Equilibrium
D328	Lahti, Tytti	Phase Change Solvents in Carbon Dioxide Capture
D329	Jäntti, Niina	Analysis of a gas flow in structured packed bed columns using computational fluid dynamics
D331	Pikkarainen, Toni; Hiltunen, Ilkka	Hot test rig design - CLC PDU
D332	Lagerbom, Juha	Laboratory scale oxygen carrier characterisation - test rig design, construction and test procedure
D333	Tsupari, Eemeli; Tähtinen, Matti; Kärki, Janne	Feasibility of Solid Fuel CLC Plant Investment in the Future Energy Systems Including High Share of Solar and Wind
D334	Pikkarainen, Toni; Teir, Sebastian; Hiltunen, Ilkka	Piloting of bio-CLC for BECCS
D335	Peltola, Petteri; Ritvanen, Jouni; Tynjälä, Tero; Hyppänen, Timo	Model-based evaluation of a chemical looping combustion plant for energy generation at a pre-commercial scale of 100 MWth
D336	Peltola, Petteri; Ritvanen, Jouni; Tynjälä, Tero; Hyppänen, Timo	Fuel reactor modelling in chemical looping with oxygen uncoupling process
D337	Ylätalo, Jaakko; Tynjälä, Tero	CaL model development_Modelling CO2 carrying capacity of lime particles over time
D338	Ylätalo, Jaakko; Tynjälä, Tero	Calcium looping process design and retrofitting
D339	Myöhänen, Kari; Bordbar, Mohammad Hadi; Hyppänen, Timo	Modelling of radiative heat transfer in oxygen-fired CFB at various process conditions
D340	Ostonen, Alexandr; Ojala, Leo; Uusi-Kyyny, Petri; Penttilä, Anne; Alopaeus, Ville	A comprehensive study of CO2 solubility in aqueous 2-HEAA and MEA + 2-HEAA solutions – Measurements and modeling
D341	Jäntti, Niina; Vaittinen, Johanna; Keskitalo, Tuomo; Keskinen, Kari; Siikonen, Timo	Analysis of a gas flow in structured packed bed columns using CFD
D342	Keskinen, Kari	
D343	Peltola, Petteri; Ritvanen, Jouni; Tynjälä, Tero; Hyppänen, Timo	Investigation on feasible solids flow arrangements in a dual fluidized bed reactor system for the CLOU process
D343	Peltola, Petteri; Ritvanen, Jouni; Tynjälä, Tero; Hyppänen, Timo	Investigation on feasible solids flow arrangements in a dual fluidized bed reactor system for the CLOU process
D344	Lagerbom, Juha	Characterization of oxygen carriers performance – procedures and results
D345	Spinelli, Maurizio; Peltola, Petteri; Bischi, Aldo; Ritvanen, Jouni; Hyppänen, Timo; Romano, Matteo C.	Process integration of chemical looping combustion with oxygen uncoupling in a coal-fired power plant
D346	Peltola, Petteri	Analysis and modelling of chemical looping combustion process with and without oxygen uncoupling
D347	Parkkinen, Jarmo; Korpinen, Timo; Tynjälä, Tero; Sormunen, Risto; Hyppänen, Timo	The post-combustion calcium looping process integrated with CHP plant
D348	Chechurin, Yegor; Tynjälä, Tero	Hydrodynamic fluidization properties of limestone particles
D349	Martínez, Isabel; Grasa, Gemma; Parkkinen, Jarno; Tynjälä, Tero; Hyppänen, Timo; Murillo, Ramón; Romano, Matteo C.	Review and research needs of Ca-Looping systems modelling for post-combustion CO2 capture applications
D350	Myöhänen, Kari; Bordbar, Mohammad Hadi; Błaszczuk, Artur; Hyppänen, Timo	Optically thick radiation heat transfer in CFB boilers
D351	Myöhänen, Kari; Hyppänen, Timo	Limestone reactions in oxy-CFB conditions based on 3D CFB calculations

D352	Penttilä, Anne	Phase Equilibrium Measurements and Modeling for Alkanolamine Systems
D353	Ostonen, Alexandr	Solubility of hydrogen sulphide in aqueous solution of MAPA + DEEA - extended abstract
D354	Ostonen, Alexandr	Solubility of hydrogen sulphide in aqueous solution of MAPA + DEEA
D355	Honkanen, Elina	Thermodynamical models for electrolyte solutions
D356	Pikkarainen, Toni; Hiltunen, Ilkka; Teir, Sebastian	Piloting of bio-CLC for BECCS
D357	Peltola, Petteri; Ritvanen, Jouni; Hyppänen, Timo	1D bubbling fluidized bed model for in-situ gasification-chemical looping combustion of biomass
D358	Parkkinen, Jarno; Tynjälä, Tero; Hyppänen, Timo	Mass and energy balance analysis of a calcium looping process with solid heat carrier
D359	Tynjälä, Tero; Parkkinen, Jarno; Peltola, Petteri; Spinelli, Maurizio; Matinez, Isabel; Romano, Matteo C.	Advanced calcium looping process - effect of particle segregation efficiency on process parameters
D360	Peltola, Petteri; Parkkinen, Jarno; Tynjälä, Tero; Korpinen, Timo; Sormunen, Risto;Hyppänen, Timo	Performance comparison of calcium looping chemical looping and oxycombustion processes for CO2 capture in a CHP plant
D401	Suominen, Sarianna; Pehkonen, Antero	High pressure CO2 pipelines and equipment
D403	Suvanto, Juha	Emissions of carbon dioxide capture in power generation when using precombustion capture or oxyfuel combustion methods
D404	Fraboulet et al.	Round Robin Tests on Nitrosamines Analysis in the Effluents of a CO2 Capture Pilot Plant
D406	Ritola, Jouko; Kujanpää, Lauri; Lindberg, Antero; Nordbäck, Nicklas	Economy of intermediate storage a as part of CO2 terminal
D407, D411	Kujanpää, Lauri	North European infrastructure for transporting CO2 in 2050 – Scenario results and cost sensitivity analysis
D410	Ritola, Jouko; Kujanpää, Lauri; Lindberg, Antero; Nordbäck, Nicklas	CO2 - Terminals and Intermediate storage
D412	Järvinen, Eerik	Description of general sampling system
D413	Korhonen, Kimmo; Ahonen, Lasse; Nordbäck, Nicklas	Investigation of geological and geothermal considerations related to geological intermediate storage of CO2
D414	Kujanpää Lauri, Ritola Jouko, Nordbäck Nicklas, Teir Sebastian	Scenarios and new technologies for a North-European CO2 transport
D415	Järvinen, Eerik	Final report on sampling and analysis methods developed for carbon capture from flue gas
D416	Korhonen, Kimmo; Ahonen, Lasse; Nordbäck, Nicklas	Geothermal and geochemical constraints of liquid CO2 storage in rock
D417	Malm, Marianne; Saari Jouni	Seismic monitoring applications and possible regulations for seismic hazard
D501	Nordbäck, Nicklas	Status report and analysis of global storage situation
D502	Kotiranta, Tuukka	Modeling of the Slag2PCC process
D503	Zevenhoven, R.; Björklöf, T.; Grigaliunaite, I.; Romão, I.; Fagerlund, J.; Mattila, H.-P.	Assessment of options and a most feasible design of serpentinite carbonation applied to a lime kiln
D504	Zevenhoven, R.; Fagerlund, J.; Romão, I.; Nduagu, E.	A technology survey report on the feasibility of large-scale CO2 mineralisation in Finland
D506	Nordbäck, Nicklas	Situation of CCS in Russia
D507	SLR	Screening level assessment for the identification of prospective sites for the geological storage of CO2 in the Baltic Sea area
D508	SLR	Final report on the screening of prospective sites for the geological storage of CO2 in the southern Baltic Sea
D509	Cosma, Calin; Enescu, Nicoleta	Report on the reprocessing of the borehole seismic data collected at Ketzin in 2007-2011
D510	Romão, I.; Eriksson, M.; Nduagu, E.; Fagerlund, J.; Gando-Ferreira, L.M.; Zevenhoven R	D510 Carbon dioxide storage by mineralisation applied to an industrial-scale lime kiln
D510	Slotte, Martin; Romão Inês; Zevenhoven, Ron	Design and technical feasibility study of a magnesium silicate carbonation demo-plant
D511	Mattila, H.-P.; Slotte, M.; Said, A.; Zevenhoven, R.	BOF slag carbonation in aqueous NH4Cl-solutions: steering product quality in continuous process
D511	Filppula, Sami	Continuous separation of steelmaking slag and PCC particles from aqueous streams using an inclined settler
D511	Mattila, H.-P.; Grigaliūnaitė, I.; Zevenhoven, R.; Said, A.; Fogelholm, C.-J.	Production of papermaking grade calcium carbonate from steelmaking slag
D511	Mattila, H.-P.; Zevenhoven, R.	Tests with sub-demo for slag2PCC at Åbo Akademi University

D512	Romao, IS; Grigaliunaite, I; Mattila, H-P; Slotte, M; Zevenhoven, R	Water management and separation technologies for serpentinite carbonation and for PCC production from steelmaking slag
D513	Zevenhoven, Ron, Nduagu, Experience, Romão, Inês S.	Investigation of alternative-silicate raw materials for carbonation
D514	Said, Arshe; Eloneva, Sanni	Assessment of feasibility of extracting different metals from spent steel converter slag
D515	Sais, Arshe; Eloneva, Sanni	Report on results obtained with slag2pcc demo
D517	Teir, Sebastian	PCC from steelmaking slag - case study
D518	Nordbäck, Nicklas; Virtasalo, Joonas	Report on the prospective areas for CO2 storage in Western Russia
D519	SLR Consulting, Uppsala University	Bastor2: WP1 Final report on prospective sites for the geological storage of CO2 in the Southern Baltic Sea - Appendix
D519	SLR Consulting, Uppsala University	Bastor2: WP1 Final report on prospective sites for the geological storage of CO2 in the Southern Baltic Sea
D520	Nieminen, Matti	Report on activities of the Baltic Sea CCS Network
D522	Cosma, Calin; Enescu, Nicoleta	Report on conceptual design for a semipermanently installed shallow seismic source
D523	Cosma, Calin; Enescu, Nicoleta	Report on the realization of the fully built semi-permanent underground seismic source
D524	Stanescu, Traian; Cosma, Calin	Conceptual design of an intelligent wireless surface receivers array
D525	Stanescu, Traian; Cosma, Calin	Report on the full specifications for Intelligent wireless acquisition system
D526	Cosma, Calin; Enescu, Nicoleta	Optimized seismic methodology for CO2 injection monitoring at the Ketzin pilot site, Germany
D526	Cosma, Calin; Enescu, Nicoleta	Optimized seismic methodology for CO2 injection monitoring at the Ketzin pilot site, Germany
D527	Zappa, William	Pilot-scale Experimental Work on the Production of Precipitated Calcium Carbonate (PCC) from Steel Slag for CO2 Fixation
D527	Said, Arshe; Zappa, William; Eloneva, Sanni	Report on results obtained with demo unit at Aalto
D528	Hudd, Hannes	Post-treatment of precipitated calcium carbonate (PCC) produced from steel converter slag
D529	Zevenhoven, Ron; Slotte, Martin; Kotiranta, Tuukka	Report on detailed design features for Mg-silicate carbonation demonstration at a lime kiln
D530	Slotte, Martin; Romão, Inês; Zevenhoven, Ron	Integration of a pilot-scale serpentinite carbonation process with an industrial lime kiln
D530	Slotte, M; Zevenhoven, R	Total lime kiln gas compression for CO2 mineral sequestration
D531	Eloneva, Sanni; Zappa, William; Said, Arshe	Report on progress with extracting vanadium from spent steel converter slag
D532	Mattila, H.-P.; Grigaliūnaitė, I.; Zevenhoven, R.	Chemical kinetics modeling and process parameter sensitivity for precipitated calcium carbonate production from steelmaking slags.
D532	Mattila, H.-P.; Hudd, H.; Zevenhoven, R.	Cradle-to-gate life cycle assessment of precipitated calcium carbonate production from steel converter slag.
D532	Mattila, H.-P.; Zevenhoven, R.	Design of a continuous process setup for precipitated calcium carbonate production from steel converter slag.
D532	Mattila, H.-P.; Grigaliūnaitė, I.; Said, A.; Filppula, S.; Fogelholm, C.-J.; Zevenhoven, R.	Process efficiency and optimization of precipitated calcium carbonate (PCC) production from steel converter slag
D532	Mattila, Hannu-Petteri; Zevenhoven, Ron	Producing precipitated calcium carbonate (PCC) from steelmaking slags using the slag2pcc concept
D532	Mattila, H.-P.; Zevenhoven, R.	Production of precipitated calcium carbonate from steel converter slag and other calcium-containing industrial wastes and residues.
D532	Mattila, Hannu-Petteri; Hudd, Hannes; Zevenhoven, Ron	Studies on the Slag2PCC process at ÅA
D532	Mattila, Hannu-Petteri	Utilization of steelmaking waste materials for production of calcium carbonate (CaCO3)
D533	Teir, Sebastian; Kotiranta, Tuukka; Parviainen, Timo; Mattila, Hannu-Petteri	Case study for utilisation of CO2 from flue gases in PCC production from steelmaking slag
D533 (appendix)	Pirkonen, Pentti	Filtration of S-PCC slurry
D533 (appendix)	Kotiranta, Tuukka	PCC production from steel mill slag - update
D534	Nordbäck, Nicklas	Report on status and capacities of geological CO2 storage in the surrounding regions to Finland
D535	Nilson, Per Arne	Bastor2: Final Summary Report
D536	Nieminen, Matti	Report on promotion activities of the Baltic Sea CCS Network
D537	Cosma, Calin; Enescu, Nicoleta	Report on construction and deployment of 60 near-surface digital sensors at Heletz CO2 storage test site
D539	Cosma, Calin; Enescu, Nicoleta	Report on Concept of quasi on-line processing and interpretation protocols and

		equipment
D541	Mattila, Hannu-Petteri; Said, Arshe; Zappa, William; Eloneva, Sanni; Zevenhoven, Ron	Steering particle morphology in the Slag2PCC process
D542	Mattila, Hannu-Petteri; Zevenhoven, Ron	Solid-liquid separations in the Slag2PCC process
D543	Koskinen, Juha	Recover of valuable metals from residual slag
D544	Gunning, Peter	Treatment of Steel Slag Residues using Accelerated Carbonation
D545	Kotiranta, Tuukka; Peltola, Heljä; Auvinen, Toni	Filtration tests of Slag2PCC slurries manufactured at the Aalto pilot
D545	Teir, Sebastian; Auvinen, Toni; Said, Arshe; Kotiranta, Tuukka; Peltola, Heljä	Performance of separation processes for precipitated calcium carbonate produced with an innovative method from steelmaking slag and carbon dioxide
D546	Said, A; Järvinen, M	Demonstration pilot plant for the production of precipitated calcium carbonate (PCC) from steelmaking slag and carbon dioxide
D546	Said, Arshe; Järvinen, Mika	Reporting of results obtained from the pilot plant Aalto
D547	Zevenhoven, Ron; Slotte, Martin; Åbacka, Jacob; Highfield, James	Mg-silicate rock carbonation for a lime kiln
D547	Zevenhoven, Ron; Slotte, M	Selection of dry gas/solid (Mg(OH)2) or wet aqueous ($MgSO_4$) carbonation of lime kiln gas CO2
D548	Erlund, Rickard; Koivisto, Evelina; Mattila, Hannu-Petteri; Zevenhoven, Ron; Fagerholm, Mats	Process for upgrading diopside-based rock for lime kiln gas CO_2 carbonation
D549	Nordbäck; Nicklas	
D552	Puotinen, Tiina	The chemical and mineralogical character and the utilization potential of the slag residue
D553	Said, Arshe; Järvinen, Mika	Report on practice observations from pilot-scale test facility unit at Aalto
D554	Said, Arshe; Koskinen, Juha; Kotiranta, Tuukka; Teir, Sebastian; Zevenhoven, Ron	Fixation of CO2 by producing PCC from steelmaking slags – Summary report
D555	Koivisto, Evelina; Erlund, Rickard; Zevenhoven, Ron; Fagerholm, Mats	Extraction of magnesium from four Finnish magnesium silicate rocks for CO2 mineralisation
D556	Zevenhoven, Ron; Koivisto, Evelina; Erlund, Rickard; Slotte, Martin; Fagerholm, Mats	Updated cost evaluation including a feasible plant design for large-scale magnesium silicate carbonation at a lime kiln
D601	Teir, Sebastian	Review of concepts and technologies for capturing CO2 by algae
D602	Piiparinen, Jonna; Spilling, Kristian	Wastewater treatment by algal in developing Asian countries: an integrated approach to carbon capture
D603	Spilling, Kristian; Seppälä, Jukka; Manninen, Kaisa; Tamminen, Timo	The potential of using algae as feedstock for biofuel, a Nordic perspective
D604		Report on lab-scale experiments on CO2 uptake by microalgae cultivation for CO2 capture at Hazira plant
D605	Nappa, Marja; Karinen, Pertti; Hytönen, Eemeli	Producing lipids, biogas and fertilizer from microalgae - conceptual design and techno-economic analysis
D607	Norrena, Tomas	Hiilidioksidin kemiallinen hyötykäyttö
D608	Saavalainen, Paula; Kabra, Satish; Turpeinen, Esa; Oravisjärvi, Kati; Yadav, Ganapati; Keiski, Riitta; Pongrácz, Eva	Sustainability Assessment of Chemical Processes: Evaluation of Three Synthesis Routes of DMC
D609	Turpeinen, Esa; Seelam, Prem; Huuhtanen, Mika; Pitkäaho, Satu; Koskinen, Rauli; Keiski, Riitta	CO2 Conversion to Synthetic Natural Gas (SNG)
D610	Raunio, Jukka; Karinen, Pertti; Laitio, Jussi	Recovery of CO2 from industrial low pressure vent and flue gases using algae cultivation processes
D612	Teir, Sebastian; Mutnuri, Srikanth; Sonck, Matti; Spilling, Kristian; Atri, Neelam; Yadav, Anant; Choudhary, Piyush	CO2 from industrial off-gases for algae cultivation
D612	Yadav, Anant; Choudhary, Piyush; Atri, Neelam; Teir, Sebastian; Mutnuri, Srikanth	Pilot project at Hazira, India, for capture of carbon dioxide and its biofixation using microalgae
D612	Teir, Sebastian; Sonck, Matti; Spilling, Kristian; Choudhary, Piyush; Mutnuri, Srikanth; Atri, Neelam; Yadav, Anant	Qualitative assessment of CO2 capture from industrial flue gases by algal cultivation
D613	Nappa, Marja; Hakala, Juha; Sorsamäki, Lotta; Teir, Sebastian	Microalgae cultivation for animal feed for large scale production
D614	Pathak, S K; Choudhary, Piyush; Kapoor, N K; Singh, Sudhir Kumar	Carbon uptake by algae - Results from pilot tests on vent gas sequestration with algae at a gas refinery plant
D614	Teir, Sebastian	CO2 from flue gas to cultivation media
D614	Nappa, Marja; Hytönen, Eemeli; Karinen, Pertti; Arnold, Mona	Conceptual level techno-economic assessment to produce biogas, lipids and fertilizers from microalgae
D614	Spilling, Kristian	Finnish actions in algae cultivation (in CCSP)
D614	Eriksen, Niels	Personal experiences from cultivation and sequestration by algae

D614	Sormunen, Risto; Teir, Sebastian; Arnold, Mona	Welcome and opening - CCSP WP6 mini-seminar 2015 Espoo
D615	Wiebe, Marilyn	Report on literature review on algae growth in extreme pH
D616	Wiebe, Marilyn; Piiparinen, Jonna	Report on growth and CO2 uptake of algae/cyanobacteria in high and low pH conditions and implications for CO2 delivery systems
D617	Turpeinen, Esa	Chemical utilization of CO2 - Thermodynamics and Catalysts