

CO₂ CAPTURE, STORAGE AND UTILISATION IN FINLAND

Authors Tiina Koljonen, VTT Processes
 Hanne Siikavirta, Fortum Engineering
 Ron Zevenhoven, Helsinki University of
 Technology

Publicity: Public



CLIMTECH

Research organisation and address VTT Processes, Systems and Models P.O. Box 1606 FIN-02044 VTT, FINLAND Project manager Tiina Koljonen Diary code (VTT) ENE6-16T-01	Customer Tekes / Climtech P.O. Box 69 FIN-00101 TEKES Contact person Raija Pikku-Pyhältö, TEKES Order reference 40574/01	
Project title and reference code 41CO2SIJOITU C1SU00366	Report identification & Pages PRO4/T7504/02 95 p.	Date 29.08.2002

Report title and author(s) CO ₂ CAPTURE, STORAGE AND UTILISATION IN FINLAND Koljonen, Tiina, Siikavirta Hanne, Zevenhoven, Ron
--

Summary

The report outlines the state of the art of the CO₂ capture technologies, the long-term storage options of CO₂ and possibilities to reuse captured CO₂. Application of CO₂ capture technologies in energy sector and process industries were outlined. The potential to reduce Finland's CO₂ greenhouse gas emissions by CO₂ capture, storage and utilisation was evaluated. Finally, opportunities for Finnish technology were identified.

Several CO₂ separation and capture technologies exist today to produce CO₂ for commercial markets. The main capture technologies are absorption, adsorption, cryogenics and membranes. The capture technologies may be applied before or after combustion of fossil fuel depending on the capture concept. The major barriers for applying CO₂ separation and capture technologies and concepts to power plants are the high capital and operating costs and reduced efficiencies. The cost of avoided emissions for capture stage (including pressurisation for transport) ranges from 30 to 50 US\$ per tonne CO₂.

The main options considered for the long-term storage of CO₂ are underground geologic formations. These include old oil and gas fields, coal formations and saline water aquifers. Deep oceans represent large potential sink for CO₂, but environmental uncertainties make it less feasible in the short term. Today, several demonstration projects are underway to evaluate technical, economical and environmental aspects of CO₂ sequestration. The estimated total cost with current technology for CO₂ sequestration ranges from 40 – 60 US\$ per tonne CO₂ avoided.

Wide range physical and chemical properties of CO₂ make it a key part in countless industrial and chemical applications, either in gaseous, liquid or solid forms. Unfortunately, most of these applications do not offer long term sink of CO₂. Also, the current industrial need is very small compared to the amount of emitted CO₂. In future, CO₂ usage will obviously increase, as environmentally more harmful chemicals would be replaced by CO₂.

The costs of CO₂ sequestration were estimated from Finland's perspective. The production cost of electricity for condensing natural gas power plant was about two times higher than the average electricity market price in Finland. For pulverised coal power plant, the corresponding production cost of electricity was even higher.

Distribution Tekes / Climtech Programme	Publicity Public
---	----------------------------

Project manager Tiina Koljonen	Reviewed and approved by Seppo Kärkkäinen Group Manager	Ritva Hirvonen Research Manager
--	--	------------------------------------

ABSTRACT

The report outlines the state of the art of the CO₂ capture technologies, the long-term storage options of CO₂ and possibilities to reuse captured CO₂. Application of CO₂ capture technologies in energy sector and process industries were outlined. The potential to reduce Finland's CO₂ greenhouse gas emissions by CO₂ capture, storage and utilisation was evaluated. Finally, opportunities for Finnish technology were identified.

Several CO₂ separation and capture technologies exist today to produce CO₂ for commercial markets. The main capture technologies are absorption, adsorption, cryogenics and membranes. The capture technologies may be applied before or after combustion of fossil fuel depending on the capture concept. The major barriers for applying CO₂ separation and capture technologies and concepts to power plants are the high capital and operating costs and reduced efficiencies. The costs of separation and capture of CO₂ including compression to the required pressure for the sequestration option used, are generally estimated to make up about 75% of the total costs when ocean or geologic sequestration is applied. The cost of avoided emissions for capture stage (including pressurisation for transport) ranges from 30 to 50 US\$/t CO₂.

The main options considered for the long-term storage of CO₂ are underground geologic formations. These include old oil and gas fields, coal formations and saline water aquifers. Deep oceans represent large potential sink for CO₂ but environmental uncertainties make it less feasible in the short term. Today, several demonstration projects are underway to evaluate technical, economical and environmental aspects of CO₂ sequestration. The estimated total cost with current technology for CO₂ sequestration ranges from 40 – 60 US\$ per tonne CO₂ avoided.

Wide range physical and chemical properties of CO₂ make it a key part in countless industrial and chemical applications, either in gaseous, liquid or solid forms. Unfortunately, most of these applications do not offer long term sink of CO₂. Also, the current industrial need is very small compared to the amount of emitted CO₂. In future, CO₂ usage will obviously increase, as environmentally more harmful chemicals would be replaced by CO₂.

The costs of CO₂ sequestration were estimated from Finland's perspective. The CO₂ capture process was applied to a condensing power plant. As long term geological storage of CO₂ is not possible in Finland, except in the form of solid mineral carbonate, carbon free energy production would mean that CO₂ should be transported abroad, decarbonised fuel should be imported or electricity should be imported. The production cost of electricity would be approximately doubled if CO₂ capture, 1000 km onshore transmission and offshore storage would be included to the condensing natural gas combined cycle plant. For pulverised coal power plant, the corresponding production cost of electricity would be about three times higher than with conventional coal power plant.



PREFACE

This report is a final report of the Climtech projects 'CO₂ capture technologies and their potential' and 'Carbon dioxide storage and reuse'. Climtech (The technology and climate change programme) is a Tekes (Finnish National Technology Agency) programme, which investigates the development needs and possibilities of the technologies, which can be applied to control greenhouse gas emissions and climate change.

The project 'CO₂ capture technologies and their potential' was managed by Mrs Hanne Siikavirta from Fortum Engineering. The work was carried out in cooperation with Tampere University of Technology, who had a subproject 'Capture of Carbon Dioxide from Power Plants'. The results of the subproject have been published in a separate report by Mrs. Liisa Aarikka. The project was funded by Tekes and Fortum.

The project 'Carbon dioxide storage and reuse' was managed by Mrs Tiina Koljonen from VTT Processes. The work was carried out in cooperation with Helsinki University of Technology and Helsinki University, who had a subproject 'Mineral carbonation for CO₂ removal from flue gases'. The results of that subproject have been published in a separate report by Jens Kohlmann, Ron Zevenhoven, Arun Mukherjee and Tiina Koljonen. The project was funded by Tekes, Nordkalk Oyj Abp and VTT.

The above projects had a common steering group, which chairman was Mrs Jenni Kivivirta of Nordkalk Oyj Abp. The other members were Mrs Raija Pikku-Pyhältö of Tekes, Mr Mats Fagerholm of Nordkalk Oyj Abp, Mrs Hanne Siikavirta and Mrs Helka Turunen of Fortum Engineering, Prof. Risto Raiko of Tampere University of Technology, Dos. Ron Zevenhoven of Helsinki University of Technology, Prof. Ilkka Savolainen of Climtech programme, and Mrs Tiina Koljonen of VTT Processes.

The report was written by Tiina Koljonen (chapters 1, 4 – 12), Hanne Siikavirta (chapters 1 – 3, 7, 11 - 12) and Ron Zevenhoven (chapter 4.3). The authors express warm thanks to the project partners, steering group members and financiers for their efforts and fruitful collaboration during the project.

Espoo, August 2002

Authors

CONTENTS

1	INTRODUCTION.....	9
2	OVERVIEW OF CO₂ CAPTURE TECHNOLOGIES AND NOVEL COMBUSTION CONCEPTS.....	13
2.1	CHEMICAL AND PHYSICAL ABSORPTION.....	13
2.1.1	<i>Absorption and absorbents.....</i>	13
2.1.2	<i>Process and process equipment.....</i>	14
2.1.3	<i>Challenges in development.....</i>	15
2.2	PHYSICAL AND CHEMICAL ADSORPTION.....	16
2.2.1	<i>Adsorption and adsorbents.....</i>	16
2.2.2	<i>Process and process equipment.....</i>	17
2.2.3	<i>Future development.....</i>	18
2.3	LOW TEMPERATURE DISTILLATION.....	19
2.4	GAS SEPARATION MEMBRANES.....	20
2.4.1	<i>Membrane materials.....</i>	20
2.4.2	<i>Modules and processes.....</i>	21
2.4.3	<i>Challenges in development.....</i>	21
2.5	PRE-COMBUSTION AND NOVEL COMBUSTION CONCEPTS.....	21
2.5.1	<i>Pre-combustion concepts.....</i>	21
2.5.2	<i>CO₂/O₂ combustion.....</i>	24
2.5.3	<i>Chemical looping combustion.....</i>	27
2.5.4	<i>Fuel cells.....</i>	27
3	APPLICATION OF CO₂ CAPTURE TECHNOLOGIES AND CONCEPTS.....	28
3.1	ENERGY PRODUCTION.....	29
3.2	OIL REFINING AND PETROCHEMICAL INDUSTRY.....	29
3.3	IRON AND STEEL PRODUCTION.....	33
3.4	CEMENT PRODUCTION.....	34
4	OVERVIEW OF CO₂ STORAGE TECHNOLOGIES.....	36
4.1	UNDERGROUND STORAGE OF CO ₂	36
4.1.1	<i>Oil and gas formations.....</i>	36
4.1.2	<i>Aquifers.....</i>	37
4.1.3	<i>Coal formations.....</i>	38
4.2	OCEAN SEQUESTRATION.....	39
4.2.1	<i>Direct injection of CO₂.....</i>	39
4.2.2	<i>Ocean fertilisation.....</i>	39
4.3	STORING CO ₂ AS INERT SOLIDS.....	40
4.3.1	<i>Mineral carbonation.....</i>	40
4.3.2	<i>CO₂ hydrates.....</i>	41
4.4	FUTURE PROSPECTS.....	41
5	DIRECT UTILISATION OF CO₂.....	42
5.1	PROPERTIES OF CO ₂ AND ITS REACTIONS.....	42
5.2	MARKET SEGMENTS.....	43
5.2.1	<i>Food Processing Industry.....</i>	44
5.2.2	<i>Carbonated beverages.....</i>	46
5.2.3	<i>Chemical industry.....</i>	47
5.2.4	<i>Metal fabrication.....</i>	48
5.2.5	<i>Agriculture.....</i>	48
5.2.6	<i>Rubber and plastics processing.....</i>	49

5.2.7	<i>Other uses as solvent</i>	50
5.2.8	<i>Water treatment</i>	51
5.2.9	<i>Well reinjection</i>	51
5.2.10	<i>Dry ice production</i>	52
5.2.11	<i>Fire fighting</i>	53
5.2.12	<i>Other applications (not using large quantities of CO₂)</i>	53
5.3	EVOLUTION OF THE MERCHANT MARKET OF CO ₂	53
5.4	CHEMICAL CONVERSION TO FUELS	54
6	CO₂ TRANSPORT	55
7	PROGRAMMES, PROJECTS AND ACTIVITIES IN SELECTED COUNTRIES	57
7.1	JOINT INDUSTRY CARBON CAPTURE PROJECT (CCP)	57
7.2	IEA GHG R&D PROGRAMME	58
7.3	PROJECTS FUNDED BY EU	59
7.4	USA	60
7.5	CANADA	68
7.6	JAPAN	68
7.7	NORWAY	69
8	CO₂ PRODUCTION AND UTILISATION IN FINLAND	70
8.1	CO ₂ PRODUCTION IN FINLAND	70
8.2	CO ₂ UTILISATION IN FINLAND	70
8.2.1	<i>Pulp and paper industry</i>	70
8.2.2	<i>Beverage carbonation</i>	71
8.2.3	<i>Water treatment plants</i>	72
8.2.4	<i>Agriculture</i>	72
9	POTENTIAL TO REDUCE FINLAND'S GHG EMISSIONS	73
9.1	CO ₂ EMISSIONS AND EMISSION SCENARIOS FOR FINLAND	73
9.2	THE LARGEST CO ₂ EMITTING POINT SOURCES	75
9.3	SELECTION OF CONCEPTS AND BASIS FOR ECONOMIC EVALUATION	78
9.3.1	<i>Power production with CO₂ capture</i>	78
9.3.2	<i>CO₂ transport</i>	79
9.3.3	<i>CO₂ storage</i>	80
9.4	RESULTS OF THE ECONOMIC EVALUATION	80
9.5	POTENTIAL TO REDUCE FINLAND'S CO ₂ EMISSIONS	81
9.5.1	<i>Three alternative scenarios for 2020</i>	82
10	SAFETY AND ENVIRONMENTAL ASPECTS	86
11	OPPORTUNITIES FOR FINNISH TECHNOLOGY	87
11.1	CO ₂ CAPTURE TECHNOLOGY STUDIED IN THE PROJECT	87
11.2	MINERAL CARBONATION STUDIED IN THE PROJECT	88
11.3	OPPORTUNITIES FOR FINNISH TECHNOLOGY	88
12	CONCLUSIONS AND SUGGESTIONS FOR THE NEXT STEPS	89
13	LIST OF PUBLICATIONS	91
14	REFERENCES	92

1 INTRODUCTION

The concentration of greenhouse gases in the atmosphere is expected to grow rapidly in the 21st century, resulting in global warming, a rise in sea level and changes in rainfall. It has been estimated that to stabilise the atmospheric concentration of CO₂ at a level no more than 50% above its current level (i.e. from 360 to 550 ppm), emissions would need to be reduced by more than 60% during the first decades of this century. Achieving such large reductions will require deployment of new and improved technology [1].

Worldwide emissions from fossil fuel combustion are about 25 Gt of CO₂ per year. Approximately one third of all CO₂ emissions due to human activity come from using fossil fuels for generating electricity. Several industrial processes also emit large amounts of CO₂, like oil refineries, cement works, and iron and steel production. To make deep reductions in global emissions, for example, CO₂ emissions from power production should be reduced by 90% [1]. Fossil fuels may continue to be used if the CO₂ produced was captured and put into long-term storage. CO₂ capture and storage is already possible and currently several demonstration projects are underway. Capturing and storing CO₂ would not need major changes to processes, and widespread use of this technique could be achieved without the need for rapid change in the energy supply infrastructure.

Presently, the main drawback regarding CO₂ sequestration is high energy and capital cost requirements as shown in the Figure 1. Also, uncertainties exist regarding long-term integrity of possible CO₂ storage. The cost of avoided emissions for capture stage (including pressurisation for transport) is 30 – 50 US\$/t CO₂ and the total cost (including also CO₂ storage and transport) 40 – 60 US\$/t CO₂ [2]. However, opportunities exist for significant reductions in costs and energy requirement, and there appear to be niches wherein CO₂ sequestration may be competitive among other long-term mitigation technologies, like large-scale renewable energy production.

Wide range of CO₂ separation and capture technologies exist today to produce CO₂ for commercial markets. The capture technologies may be applied before or after combustion depending on the capture concept. Concepts for capturing CO₂ can be divided into three main categories (Figure 2).

1. Post-combustion decarbonisation (Flue Gas Scrubbing)
2. Pre-combustion decarbonisation
3. Novel combustion concepts (Oxygen Combustion)

The main CO₂ capture technologies are:

1. Absorption
2. Adsorption
3. Cryogenics
4. Membranes

Capture of CO₂ is best carried out at large point sources, such as power stations, oil refineries, petrochemical, fertiliser and gas processing plants, steel works and pulp and paper mills. More than 70 oil fields worldwide use chemical absorption with monoethanolamine (MEA) solvent for enhanced oil recovery (EOR). MEA absorption is also used in natural gas production, where CO₂ is generated as a by-product, and has to be removed to produce pipeline-quality gas.

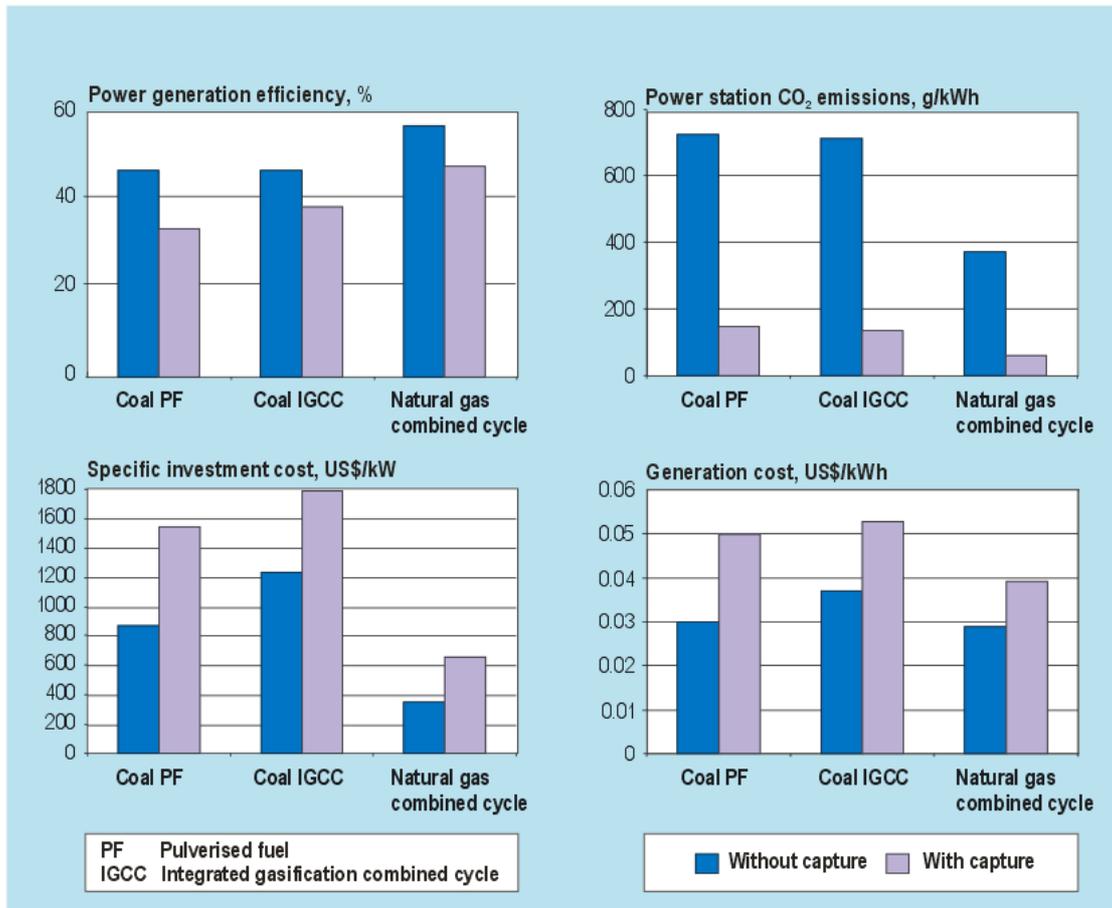


Figure 1. Comparison of the efficiencies, emissions, specific investments and electricity production costs of power plants with and without CO₂ capture assuming a 5% discount rate, a natural gas price of 3.5 US\$/GJ and a coal price of 1.5 US\$/GJ [2, 3].

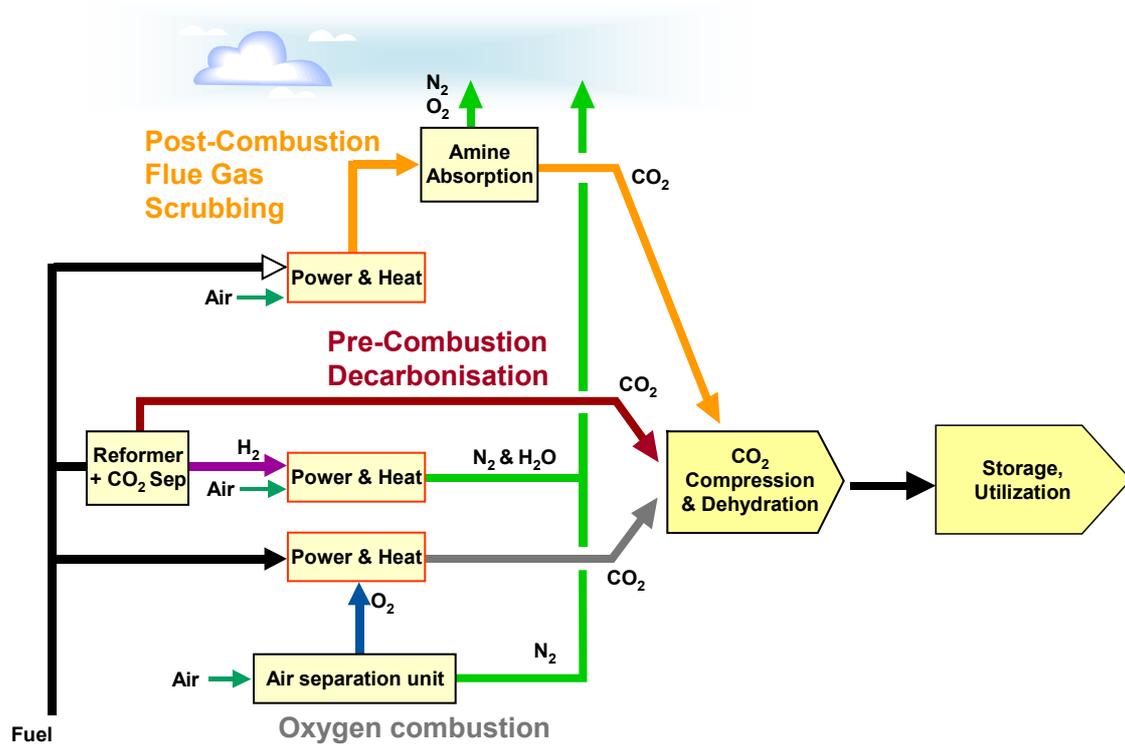


Figure 2. CO₂ capture in power generation [4]

The captured CO₂ should be concentrated and pressurised into a liquid or gas stream suitable for transportation and sequestration. Major options considered for the final storage of CO₂ are deep underground geological formations, such as oil and gas fields, deep coal seams, salt domes, rock caverns, and deep aqueous formations including saline formations (see Figure 3). The geologic formations are widespread and have large potential for CO₂ sequestration, which is shown in the Table 1. Also, deep oceans represent a large potential sink for anthropogenic CO₂ storage. CO₂ storage in hydrocarbon reservoirs should have economical advantages over storage in aquifers or ocean. Enhanced oil (EOR) has the commercial benefit of sequestering CO₂ while increasing production from active oil field. Deep, unmineable coal beds provide an opportunity to simultaneously sequester CO₂ and increase the production of natural gas. Recently, mineral carbonation of CO₂ has been studied to sequester CO₂ as a solid carbonate.

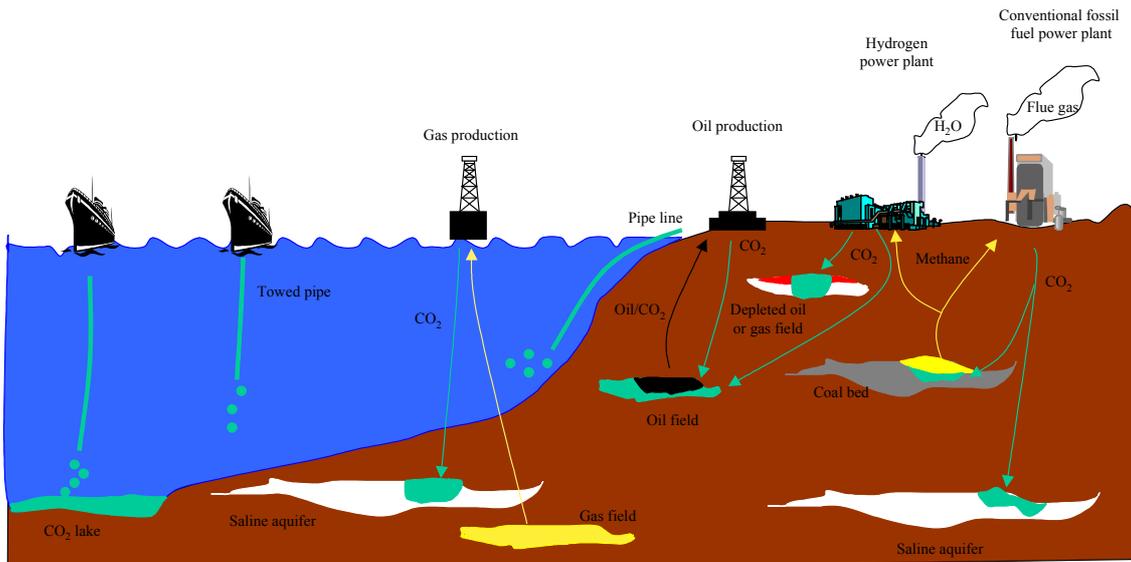


Figure 3. Illustration of major options considered for the final storage of CO₂.

Table 1. Estimates of global capacity of CO₂ storage reservoirs compared with projected total emissions between 2000 and 2050, according to 'business as usual scenario' [2, 5, 6].

Carbon storage reservoir	Range, Gt CO ₂	% of emissions to 2050
Deep ocean	5 000 – 100 000	250 - 5000
Deep saline reservoirs	400 – 10 000	20 - 500
Depleted gas reservoirs	800	40
Depleted oil reservoirs	120	5
Unmineable coal seams	> 15	> 1

Reuse of captured CO₂ in industry is another way to prevent the release of CO₂ to the atmosphere. The lifetime of the product determines the mitigation benefit. Unfortunately, industrial utilisation of CO₂ is very small compared to the total CO₂ emissions from heat and power production and most of the CO₂ products have relatively short lifetimes (carbonate drinks, cooling applications, etc.). This means that CO₂ utilisation can only be a minor part of a mitigation strategy.

2 OVERVIEW OF CO₂ CAPTURE TECHNOLOGIES AND NOVEL COMBUSTION CONCEPTS

The information in chapter 2.2 is mainly from reports prepared for U.S. Carbon Sequestration programme [7, 8] and the EU funded RUCADI- project [9].

2.1 CHEMICAL AND PHYSICAL ABSORPTION

2.1.1 Absorption and absorbents

Absorption processes can be classified as chemical and physical absorption processes depending on whether or not a chemical reaction takes place after dissolution of the substance into the liquid absorbent. In the desorption stage the substance is transferred from liquid to vapor phase.

Chemical absorption of CO₂ from gaseous streams depends on acid-base neutralisation reactions using basic solvents. Most common among the solvents in commercial use are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). Other chemical solvents in use are ammonia and hot potassium carbonate. Flue gases are typically at atmospheric pressure and the partial pressure of CO₂ varies between 3.5 - 21 kPa. Under these conditions alkanolamines are the most suitable chemical solvents to enable good CO₂ recovery levels. The use of these solvents must be balanced against the high energy penalty of regenerating them using steam-stripping.

The presence of impurities can reduce the absorption capacity of amines as well as create operational difficulties such as corrosion. The impurities must be often reduced to acceptable levels through pre-treatment methods. Another possibility is to use chemical inhibitors.

Physical absorption processes are governed by Henry's law. The absorbents, which are used for absorption of CO₂, have been selected to offer high CO₂ solubility. Commercial physical absorption processes e.g. Rectisol and Selexol use methanol and dimethyl ether, polyethylene and glycol.

Physical absorption is mainly used in high-pressure CO₂ separation processes in where high CO₂ partial pressure leads to high solubility.

2.1.2 Process and process equipment

The absorption stage takes place normally in a packed or tray column (see Figure 4). The equipment used for desorption will depend on whether the absorption process is based on chemical reaction or physical dissolution.

The physical absorption takes place at low temperature, most often at -5 to -10 °C. There is a lower limit for the temperature due to the fact that the viscosity of the absorbent will increase with decreasing temperature resulting in poor mass transfer. Regeneration of a physical absorbent can be done by lowering the pressure and separating the gaseous CO_2 and liquid.

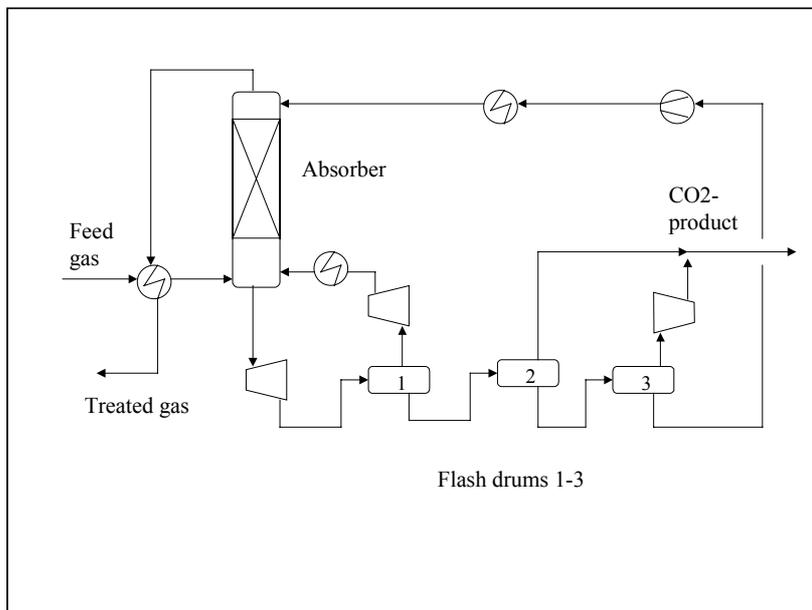


Figure 4. Physical absorption process [9].

Chemical absorption takes place in the absorber at 20 to 50 °C. The stripper column is typically a packed column with a steam reboiler for heating of the absorbent (see Figure 5). In the stripper the absorbent is heated to 100 °C in order to strip off the CO_2 . The CO_2 leaves the stripper column at the top together with the steam. It is cooled in a heat exchanger and most of the steam is condensed. The regenerated absorbent is cooled and pumped back to the absorber.

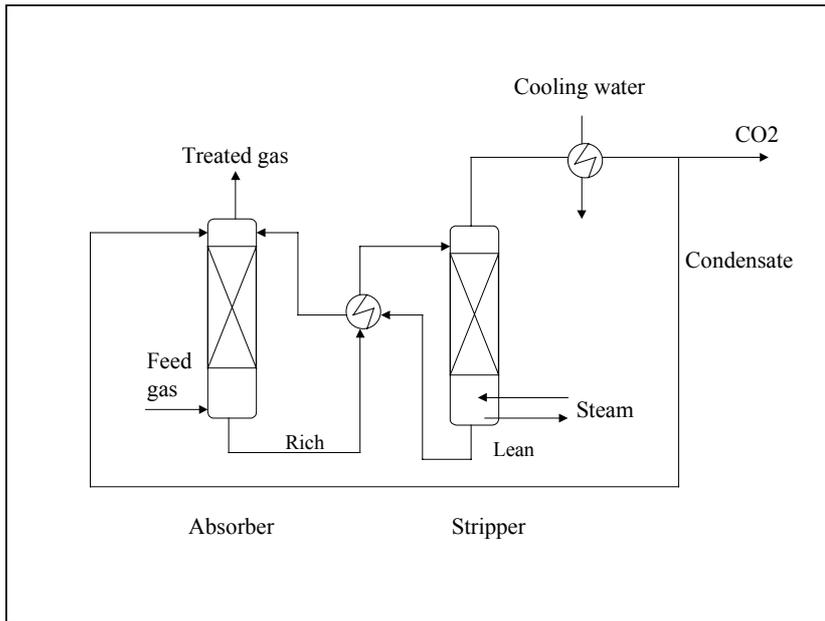


Figure 5. Chemical absorption process [9].

2.1.3 Challenges in development

Some problems related to absorption of CO₂ are:

- Foaming
- Impurities in flue gas (particulate, SO₂, H₂S)
- Other flue gas components (O₂)
- Corrosion
- High investment costs and energy consumption

Formation of foam may cause flooding of the column. Formation of foam may result from the characteristics of the process equipment (type of column), type of absorbent and impurities in the process. Particulates may cause foaming and lead to higher pressure drop and lower efficiency. SO₂ forms stable salts with alkanolamines and thus causes serious problems in chemical absorption processes. Also oxygen may form stable salts with amines if its partial pressure is too high.

Membrane contactors can offer some advantages over conventional trayed or packed columns. Potential benefits include the elimination of foaming and vapor entrainment, ability to maintain liquid and gas flow rates independently and reduce the size and cost of the equipment. The removal of particulates and SO₂ before CO₂ removal requires efficient pretreatment. The selection of solvent and use of inhibitors can be applied to problems resulting from H₂S and excess oxygen.

Kvaerner Oil & Gas started in 1992 development of membrane gas/liquid contactors for exhaust gas CO₂ removal. The advantages of using gas absorption membranes compared to conventional technology (columns) are:

- capital costs 35 - 40% lower
- operating costs 38 - 42% lower
- 60 - 75% reduction in size and weight
- footprint reduced to 40%
- less operating problems like foaming and corrosion

The technology has been developed for the exhaust gas from a gas turbine but it can be used also for capturing CO₂ from coal fired power plants. This would need however testing and further R&D [10].

Mitsubishi Heavy Industries has developed absorbents that consume less energy in regeneration process and are more stable in flue gas environment. The first commercial plant using absorbent named KS-1 has been constructed and operated since October 1999 in Malaysia. New absorbents are under development and also tests with SO₂ containing flue gas simulating flue gas from coal-fired power plant are being carried out [11].

2.2 PHYSICAL AND CHEMICAL ADSORPTION

2.2.1 Adsorption and adsorbents

The process of separation by physical adsorption is based on the ability of porous solids to reversibly adsorb large quantities of certain components in a mixture. It can be used to separate components in liquid or gaseous mixtures. Adsorption capacities and kinetics are governed by numerous factors including adsorbent pore size, pore volume, surface area, and affinity of the adsorbed gas for the adsorbent. Rates of adsorption and desorption are controlled by diffusion within the pore network rather than by the kinetics of surface adsorption. The mechanism of pore diffusion depends on the type of adsorbent used.

Adsorbents can be divided into two categories. The first comprises adsorbents having a distribution of pore size and a mean pore diameter, which are controlled by the manufacturing process. Typical for this group are silica gel, alumina and activated carbon. The second group is the zeolites where the micropore size is determined by the crystal structure.

Chemisorbents can be used for separation of CO₂ at high temperatures such as 300°C to 500°C. A typical example is a potassium carbonate promoted hydrotalcite in pelleted form, which reversibly chemisorbs CO₂ in the presence of high partial pressures of water vapour.

2.2.2 Process and process equipment

Most adsorption processes take place in beds of adsorbent pellets where they are contacted by fluids flowing during the adsorption and regeneration phases. Important variables are particle size, fluid velocity and bed dimensions which determine the pressure drop, axial mixing and heat transfer properties which are important factors in the economics of the process. The bed shape is either cylindrical or annular, a shape which in general is gaining increasing favour as a means of limiting bed pressure drop.

The regeneration of the adsorbent i.e. desorption can be done by reducing the pressure or increasing the temperature. The former is called pressure swing adsorption (PSA) and latter thermal, or temperature swing adsorption (TSA) mode. Typical flowdiagrams of PSA and TSA processes are shown in Figure 6 and Figure 7.

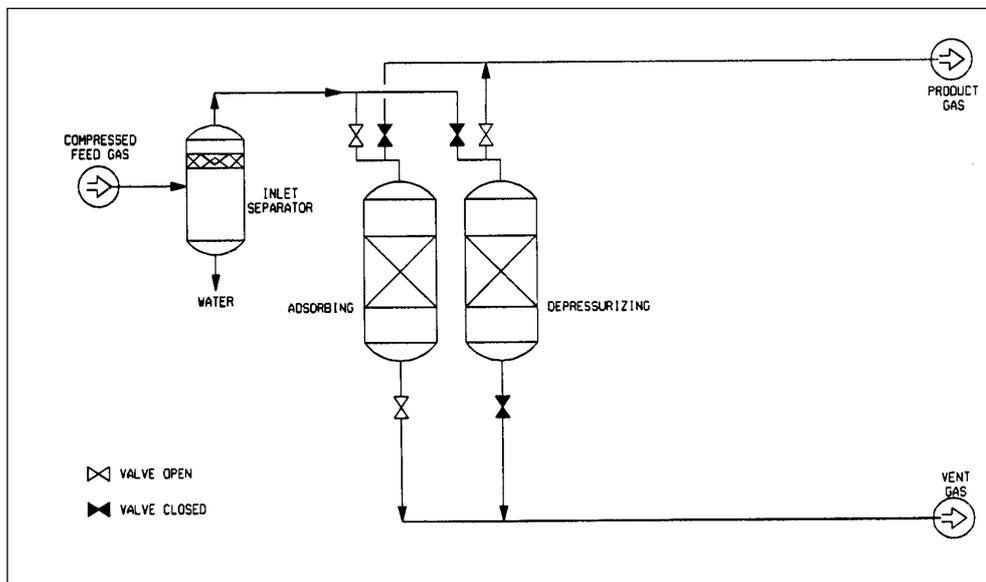


Figure 6. Pressure swing adsorption (PSA) process [9].

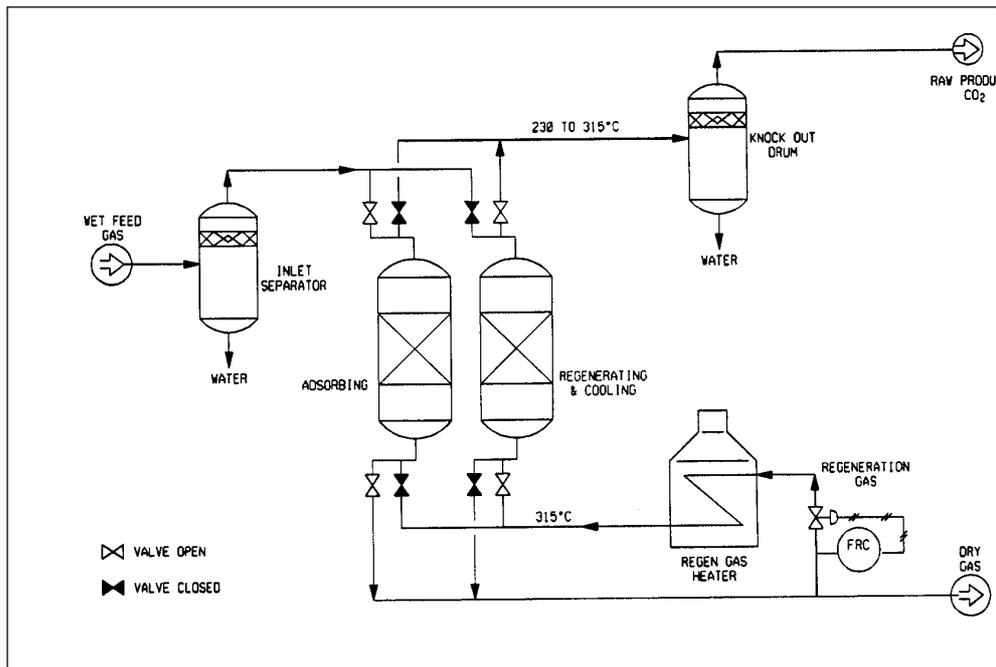


Figure 7. Temperature swing adsorption (TSA) process [9].

Most practical systems operate in a cyclic manner in which the beds are alternately saturated with the adsorbed component, then regenerated.

One disadvantage of the thermal swing system is the cost of regeneration heat. Another is the relatively long cycle time required, usually from one to eight hours. Thermal swing systems are generally only used for trace component removal such as drying and not for bulk separations such as CO₂ removal.

The pressure swing system is well suited to rapid cycling with typical cycle times of from 30 seconds to 10 minutes. This maximises the productivity of the system and bulk separations can be achieved. The right design of regeneration system is a key for obtaining over 90% of the adsorbed CO₂ at reasonable purity (> 97%) in PSA mode.

2.2.3 Future development

Several studies have concluded that adsorption is not a feasible carbon capture technology in post-combustion concepts. Application of adsorption technologies in pre-combustion concepts is regarded more promising. Future coal or oil fired stations may be based on IGCC systems with good prospects for development of hot gas sulphur cleanup systems based on chemisorption. Another approach is to convert the natural gas fuel for a conventional gas turbine combined cycle system to hydrogen and CO₂ and remove the CO₂ by adsorption.

An advanced adsorption concept is electrical swing absorption (ESA). It uses novel carbon-bonded activated carbon fibre as the adsorption medium. Activation conditions for these adsorbents may be varied to increase or decrease pore size, pore volume and

surface area to improve the effectiveness of the carbon fibre. The material is also highly conductive electrically so adsorbed gases can be efficiently desorbed by passing a low-voltage electrical current through the material. The adsorption-desorption process may be used with no variation of system pressure and with minimal variation in system temperature. The electrical energy required for desorption is approximately equal to the heat of adsorption of the adsorbed gas. Thus ESA is a promising energy efficient and economical CO₂ capture method.

2.3 LOW TEMPERATURE DISTILLATION

The triple point of CO₂ is -56.6 °C at a pressure of 5.18 bar abs. Below this temperature and pressure no liquid phase forms when CO₂ is cooled and purification based on phase separation or distillation cannot be achieved. Above this temperature and pressure, carbon dioxide can be separated in a pure form by partially liquefying the mixture of CO₂ and other inert gases followed by a distillation step if very pure CO₂ is required.

The separation can be done in a simple CO₂ condenser, which will allow for a few separation stages. The condenser is normally operated at constant pressure and the flash to vapor and liquid is achieved by lowering the temperature. More separation stages can be obtained with a multistage distillation column. The column will be equipped with a reboiler and a condenser. The column internal can contain either trays, random or structured packings. Depending on the level of impurities and the carbon dioxide purity required a condensator or a multistage distillation column could be chosen.

Low temperature distillation is commercially used for the liquefaction and purification of CO₂ from high purity sources (> 90% CO₂). Distillation is most cost effective when the feed gas is available at high pressure. Components that have freezing points above operating temperature must be removed before the gas stream is cooled to avoid freezing and blockage of process equipment. The process of liquefaction and purification of CO₂ is energy-intensive due to multistage compression and cooling.

Most CO₂ emissions being considered for CO₂ capture are produced in combustion processes. The streams contain compounds that must be removed before the stream is introduced into the low temperature process. The streams are usually near atmospheric pressure. These characteristics together with the energy intensity of low-temperature refrigeration tend to make distillation less economical capture technology compared with other options. The application of low-temperature distillation is expected to be confined to feed sources at high pressure and with high CO₂ concentrations.

A typical application would be a novel oxygen combustion system. The low temperature CO₂ separation process can be used for reducing the content of inerts in case this is needed.

2.4 GAS SEPARATION MEMBRANES

2.4.1 Membrane materials

A membrane is a barrier between two homogeneous phases capable of being selectively permeated by some components of a mixture.

Diffusion mechanisms in membranes are numerous and differ greatly depending on the type of membrane used. The main types of synthetic membranes are:

- Organic (of semicrystalline or amorphous polymers)
 - Rubbery/Glassy
 - Symmetric/Asymmetric

- Inorganic
 - Nonporous (Pd- alloys, oxides)
 - Porous (binary metal oxides, zeolites, glasses and carbon)
 - Structured
 - Unstructured

Polymeric membranes transport gases by a solution-diffusion mechanism (i.e. the gas is dissolved in the membrane and transported through the membrane by a diffusion process). Polymeric membranes are effective but typically achieve only a low gas transport flux and are subject to degradation. They are inexpensive and can achieve large ratios of membrane area to module volume.

Palladium membranes are effective in separating H_2 from CO_2 . Gas fluxes are typically very low and palladium is subject to degradation in sulfur-containing environments.

Porous inorganic membranes are attractive because of the many transport mechanisms that can be used to maximise the separation factor for various gas separations. They have several advantages compared with polymer membranes. Porous inorganic membranes can be 100 to 10 000 times more permeable (volume of gas transported through a membrane per unit of surface area per unit of time per unit of differential pressure). The costs for inorganic membranes are high but the ratio of membrane area to module volume is 100 to 1000 times smaller than that for polymer membranes. The inorganic membrane lifetime is expected to be much longer and they can be operated at high pressures and temperatures and in corrosive environments. They are also less prone to fouling.

Considerable effort is being focused on zeolite-type materials to achieve a membrane with molecular sieving type characteristics. However, the permeance of such membranes tends to be too low. The methods used for fabricating these membranes make them expensive.

2.4.2 Modules and processes

A module is the unit in which membranes are assembled. In the module the feed is divided into the permeate part, which passes through the membrane, and the retentate part, which is the remaining of the feed after separation. The main purposes and requirements to the module are:

- to provide a housing for the membranes that separates the gas/liquid streams
- to provide a mechanical support for the membranes,
- to provide an efficient packing density of membrane area per unit volume,
- to permit an easy cleaning of the membranes,
- to facilitate their maintenance and replacement.

A gas separation plant may require several stages of separation to obtain the desired purity of the permeate. In the design of the complete gas separation system, each stage must be considered in terms of pressure drops, flow rates, selectivity, and recycling of gas streams in order to obtain the highest possible cost efficiency. Different types of modules may therefore be used in series and parallel in an optimised system.

2.4.3 Challenges in development

The potential of gas separation membranes, as CO₂ capture technology in various concepts, is generally viewed as very good.

For all membrane types the main challenge is to lower the ratio of cost/m³ gas separated. Increased cost efficiency may be obtained by developing advanced membrane materials and shaping the membranes to give a high surface area/volume ratio. Many applications are at elevated temperatures, so improved materials stability and module technology are also important challenges.

2.5 PRE-COMBUSTION AND NOVEL COMBUSTION CONCEPTS

2.5.1 Pre-combustion concepts

Pre-combustion or decarbonisation is a concept in which the carbon of fuel is removed prior to combustion. The concept can be applied to natural gas by combining e.g. steam reforming, a water gas shift reaction and a CO₂ removal process. In case of solid fuel e.g. coal, gasification replaces the reforming process.

Natural gas

The main reforming reactions involve the decomposition of the hydrocarbon by means of steam, oxygen/air or by a mixture of both. The product mixture, synthesis gas, contains mainly H₂, CO, CO₂, H₂O, N₂ (if air is used) and unreacted hydrocarbon. The synthesis gas might be used for production of ammonia, methanol, phosgene, polycarbonates, formic acid, acetic acid and oxo-alcohols. With increased focus on

"zero-emission" power plants, the use of H₂ from synthesis gas as a fuel in these plants has emerged. In this case CO₂ and shifted CO has to be removed before combustion.

The most relevant technologies for production of synthesis gas are:

- conventional steam reforming,
- partial oxidation of natural gas with oxygen or air,
- auto-thermal reforming,
- variations of gas heated reforming.

In most of the cases in which fuel contains high amount of hydrogen (refinery gas, coal gas, coke oven gas) diffusion combustor burners are used. Low-NO_x burners for large and modern gas turbines are typically designed for narrow range of fuel properties. In the study made by IEA hydrogen concentrations in the feed stream to gas turbine were 50 - 95% [12]. Problems that high hydrogen concentration may cause are increased NO_x formation, increased combustor wall temperatures, reduced flame stability and combustion induced pulsations. It is probable that some modifications are needed in large modern gas turbines before they can be used in pre-combustion concepts. The CO₂ can be captured by commercial absorption technology.

The production of electricity from decarbonised hydrogen is unlikely to be competitive compared with post-combustion concept unless some synergy effect can be achieved by integration between the different process steps [13].

Membrane technology can be applied in pre-combustion concepts. In conventional steam reformers, high conversions of natural gas in the order of 85 - 90% or even higher, are obtained at reformer outlet temperatures around 850 - 900 °C. The energy efficiency of steam reforming processes is relatively high, but the investments are substantial. Pure hydrogen can be produced at significantly lower temperatures by integrating a membrane in the reactor that selectively removes hydrogen during conversion. Potential savings in membrane reformer and downstream processing costs compared to conventional steam reforming must in many cases to be weighted against additional costs associated with recompression of the hydrogen permeate stream.

A relevant example is a new power generation system for CO₂ recovery based on a gas turbine combined cycle, Hydrogen Decomposed Turbine Systems/HYDET. In this application the natural gas is reformed with simultaneous hydrogen removal using a high-temperature inorganic membrane. The residual gas, containing CH₄ and CO, is burnt in an afterburner using pure oxygen, with exhaust flue gas high concentrations of CO₂ directly available for recovery.

Solid fuels

Integrated gasification combined cycle (IGCC) with CO₂ removal was studied in EU funded project JOU2-CT92-0185 [14]. The focus was on investigation of CO₂ capture concepts for coal-based power plants. The advantage of integration of CO₂ capture with IGCC technology is that the volume of the gas to be treated is small and the pressure

and CO₂ partial pressure are high. The high pressure of removed CO₂ decreases also the costs related to compression and transportation.

Physical absorption (combined H₂S-CO₂-Rectisol) wash is a CO₂ capture technology, that is based on proven components. The block diagram of the Rectisol process is shown in Figure 8.

H₂S is removed, after which the CO₂ concentration is increased in a shift- reactor. After the shift- reactor the CO₂ is removed in a Rectisol wash and the gas from absorber is led to gas turbine. The removed CO₂ is either utilised or stored.

The other CO₂ capture technologies and concepts evaluated in the study were:

- Membrane technology for H₂/CO₂ separation
 - high temperature gas separation membranes
 - low temperature gas separation membranes
 - gas absorption membranes
- CO₂ separation by CaO adsorption (integration with high-temperature gas cleaning technology)
- WIHYS (Water gas shift with integrated hydrogen carbon dioxide separation)
- CO₂ recycling (CO₂/O₂ combustion)
- Coproduction of electricity and gasoline

It was concluded that:

- Proven technology (Rectisol- wash) exists and is feasible for removing CO₂ from IGCC plant.
- CO₂ removal decreases the efficiency of IGCC plant from 46 to 40%.
- The capital investment due to CO₂ removal is 10% higher for a commercial 300 MW IGCC.
- The electricity generating costs are increased by 18% compared to IGCC without CO₂ removal. If CO₂ is extracted as a liquid, the electricity costs are 50% higher compared to the conventional power plant.

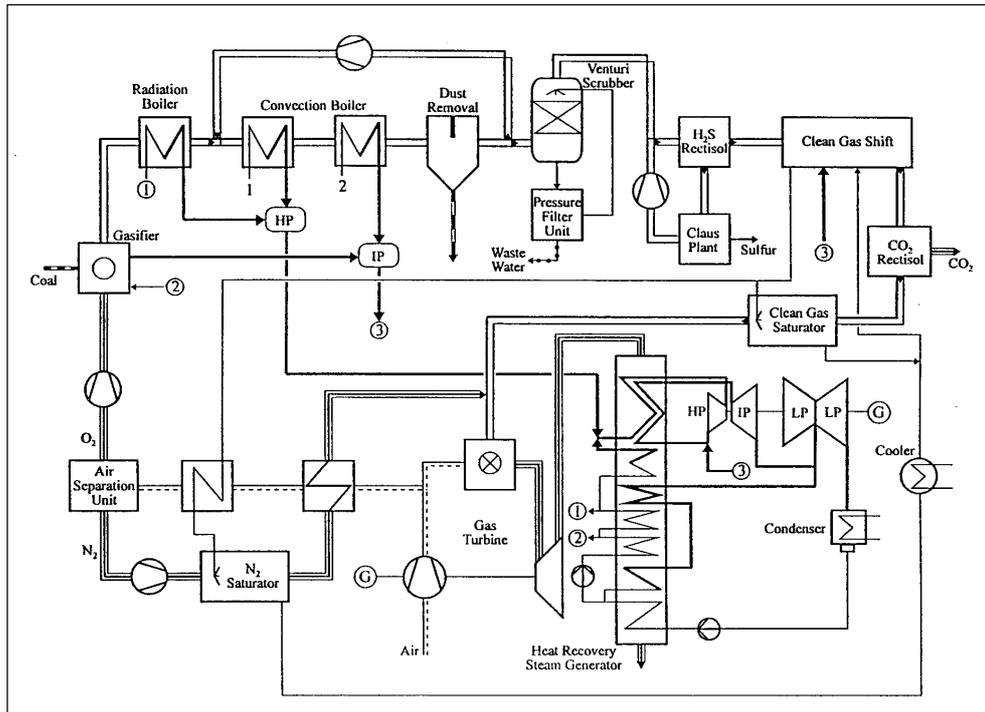


Figure 8. Rectisol process for combined H_2S and CO_2 removal [14].

2.5.2 CO_2/O_2 combustion

In novel combustion concepts oxygen is used instead of air. In order to control the combustion temperature part of the flue gases is recycled back to boiler. In CO_2/O_2 combustion concepts it is possible to increase the CO_2 concentration in flue gases to over 90%, which makes separation of CO_2 unnecessary or much cheaper than in conventional power plants.

The oxygen combustion concept consists of four main processes: oxygen production, CO_2/O_2 combustion, flue gas cleaning (when needed), CO_2 capture and transport. CO_2/O_2 combustion concepts for coal and natural gas are shown in Figure 9 and Figure 10.

Implementation of a CO_2/O_2 combustion concept requires modifications to burners and boiler or gas turbine. Some studies have been made on the conversion of existing power plants into CO_2/O_2 combustion [15, 16]. It has been concluded that this is possible, however CO_2/O_2 combustion is regarded mainly as an option for new power plants. Oxygen production is expensive and energy consuming process in the oxygen combustion concept. There is a need to develop more cost-effective oxygen production technologies.

economically without atmospheric emissions of regulated (SO_x , NO_x) or greenhouse gases. A proposed 5 MW experimental zero emission electric power generating plant burns any gaseous fuel with oxygen. Combustion of natural gas with oxygen produces a mixture of steam and carbon dioxide, which drives series of turbines to produce electricity. After leaving the low-pressure turbine, the gaseous mixture is cooled in a condenser where the carbon dioxide is separated from the condensed stream. In the first phase of the project commercially available steam turbines will be used. In a second phase the high- and low-pressure turbines will be replaced with turbines using uncooled blade technology developed by US DOE. Later on, advanced oxygen production technology using ceramic membranes can be applied. With the second phase technology the cost penalty for sequestration at a 5 MW research plant would be approximately 4%, making it the lowest known cost option for sequestration of CO_2 . A similar cost penalty applies to plants with outputs ranging from 10 to 400 MW [20].

Mixed conductors with high electronic and oxygen ion conductivity can be used as an alternative membrane to solid electrolytes for large-scale oxygen production. Integrated oxygen and gas turbine electricity production is a promising application of mixed conductor membranes. Such a process is schematically shown in Figure 11.

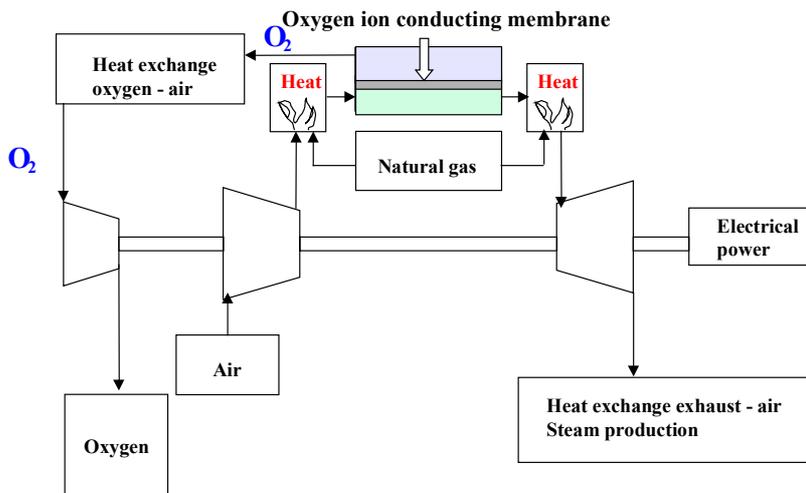


Figure 11. Integrated oxygen and power production [9].

Compressed air is heated and a portion of the oxygen is extracted in the membrane unit, before the oxygen-lean air is heated again and injected into the combustion side of the gas turbine. Produced oxygen can be utilised for partial combustion of coal or hydrocarbons in a conventional IGCC plant. The syngas produced is then combusted for production of electricity. The heat contained in the high temperature combustion gases is recovered in a heat recovery steam generator to produce steam for the production of additional electricity in a steam turbine/generator.

2.5.3 Chemical looping combustion

The main idea of chemical looping combustion (CLC) or sorbent energy transfer system (SETS) is to split combustion of natural gas into separate oxidation and reduction reactions by circulating a suitable metal oxide as an oxygen carrier between two reactors.

The metal oxide is reduced to methane in reactions with hydrocarbon and reformed by oxidation with air. The oxidation is exothermic and provides high temperature exhaust gas for power production or heat. Metal oxide supplies heat to the exhaust stream from the reduction reactor in a gas-solid heat exchange reactor. This increases the power generation potential of exhaust and supplies heat to the endothermic reduction reaction.

CLC is a method for reducing the exergy loss associated with the highly irreversible combustion of a fuel. The possibility to separate CO₂ without severe energy penalties has drawn increased attention. Also formation of NO_x is very low because the temperature in the reactors is too low for NO_x formation. The research has concentrated on reaction kinetics/oxygen carrier tests, reactor design and exergy analysis.

Crucial issues in practical implementation of the method are oxygen carrier durability, chemical performance and mechanical properties. Brandvoll et al. studied the power and heat production efficiency of CLC and concluded that it is a promising CO₂ capture concept. Oxygen carriers must be studied in more detail and long term operation must be demonstrated [21].

2.5.4 Fuel cells

CO₂ capture technology or concepts related to fuel cell technology are being studied or developed in some projects.

Shell develops new technology that allows for the generation of electricity from natural gas or other hydrogen-rich fuels without carbon dioxide emissions into the atmosphere. It involves tubular solid-oxide fuel cells (SOFC) in an integrated carbon dioxide recovery configuration that uses a solid-state afterburner to complete the oxidation of the fuel without introducing air into the exhaust stream. The exhaust is high purity CO₂ at about 5 bar pressure, which is advantageous over technologies that recover CO₂ at atmospheric pressure. The advantages of the technology compared to conventional power plants with CO₂ capture is its high efficiency, which is up to 70%.

Norske Shell will demonstrate the CO₂ separating SOFC in co-operation with Siemens-Westinghouse Power Corporation. The demonstration unit will be located in Norway and will be fuelled with natural gas. It will output 250 kW of electric power, which will be converted to 415 V 3-phase AC. The electricity, heat and CO₂ will be utilised by a fish farm located nearby. The unit is expected to become operative in 2003 [22].

3 APPLICATION OF CO₂ CAPTURE TECHNOLOGIES AND CONCEPTS

The major barriers for applying CO₂ separation and capture technologies and concepts are, in addition to issues related to storage or utilisation of CO₂, the high capital and operating costs as well as reduced efficiencies. The costs of separation and capture of CO₂ including compression to the required pressure for the sequestration option used, are generally estimated to make up about 75% of the total costs when ocean or geologic sequestration is applied.

The technology and concept selected for CO₂ capture depends on the nature of the CO₂ source, chemical and physical characteristics of the feed stream to the capture process and the requirements to the end product.

Sources that appear to lend themselves best to separation and capture technologies include large point sources of CO₂ such as:

- conventional coal fired power plants
- natural gas fired combined cycle plants
- advanced power generation systems
 - coal or natural gas combustion plants employing enriched air or oxygen to support combustion with CO₂ recycling
 - integrated coal gasification (especially oxygen based) combined cycles
 - hydrogen turbines
 - fuel cells.

In addition to power plants numerous other high CO₂ emitting industrial sources are being considered for application of capture and sequestration technologies such as:

- natural gas production
- oil refineries
- iron and steel plants
- cement and lime producers
- pulp and paper mills.

Dispersed sources of CO₂ emissions like residential buildings and mobile engines are challenging sources for applying cost-effective separation and capture methods. Advanced power systems that would use hydrogen as the fuel induce the need for central H₂ production facilities in which separation and capture of CO₂ could be possible. Introduction of electric vehicles combined with CO₂ capture at the central power stations would also indirectly reduce CO₂ emissions from the transportation sector.

The introduction of distributed power supply may have a negative impact on the ability to separate and capture CO₂ depending on the size and nature of power generation plants.

3.1 ENERGY PRODUCTION

The leading options for the capture of CO₂ emissions at power stations were evaluated by IEA GHG R&D programme [23]. The reference case without CO₂ capture for natural gas was a natural gas combined cycle (NGCC). For coal two reference cases were assessed: a power station with a pulverised fuel in which electricity is generated by a steam turbine operating in a supercritical steam cycle (supercritical p/f) and an integrated gasification combined cycle (IGCC). The assessments were done for new power plants built on green-field sites and assuming state-of-the art technology for construction starting in year 2000.

The CO₂ capture options were as follows:

- NGCC + CO₂ capture (MEA absorption)
- NGCC + CO₂ capture (MEA absorption) + CO₂ recycle
- POCC (Partial oxidation combined cycle) + CO₂ capture (physical absorption)
- Supercritical p/f + CO₂ capture (MEA absorption)
- IGCC + CO₂ capture (physical absorption)

MEA absorption was selected as a leading option for NGCC. There were however marginal differences between the three capture options studied for natural gas fired power plants. CO₂ capture is more cost efficient from IGCC compared with supercritical p/f power plant. Because the IGCC process is more expensive the cost of electricity is more expensive from IGCC with CO₂ capture compared with supercritical p/f power plant with CO₂ capture. The key results are presented in Figure 1.

The post-combustion decarbonisation approach is most suitable for reducing emissions from existing energy production facilities and industrial complexes. Post combustion solutions can be considered as a leading approach in the near term. The incentive for pre-combustion decarbonisation could be the combination with large-scale production of alternative energy carriers such as methanol or hydrogen. The commercial competitiveness of oxygen-combustion is that it is a "zero-emission" option, and is more amenable to extended EOR and less dependent on economies of scale.

3.2 OIL REFINING AND PETROCHEMICAL INDUSTRY

Many changes have occurred in the refining business. The demand for heavy fuel oil has decreased and the demand for lighter transportation fuels has increased. There are increasing pressures to produce greener products and improve the environmental performance of refineries.

Large refineries produce full range of products while smaller refineries make only gasoline, diesel and heating fuels. Refining process can be grouped into three classes:

- separation (usually distillation)
- conversion (usually thermal, catalytic or hydrocracking)
- upgrading (hydro-desulphurisation, demetallisation, hydrocracking, catalytic cracking, coking)

A refinery is a highly complex and integrated installation requiring many auxiliary facilities e.g. on site services such as electricity, heat and cooling. Heat is used in many distillation, conversion, reforming and finishing processes in the refinery, with considerable attention paid to heat integration. Motive power to turn pumps and other equipment is normally provided by electricity, often generated on site. Refineries are typically fuelled by crude oil or by waste products from the conversion processes, but sometimes use coal or natural gas as well, depending on local supplies.

The greenhouse gas emissions of refineries and petrochemical plants are associated to great extent with energy use.

Table 2. CO₂ emissions of refineries.

Source	Percent of refinery CO ₂ emissions
Oil and gas fuel firing of furnaces and boilers	65
Regeneration of cat cracker catalyst	16
Flares	< 3
Methane steam reforming to make hydrogen	2
Incineration and effluent processes	1
Power (55 % imported)	13

Typical CO₂ concentrations in refinery vent gases are:

- from combustion plant, furnaces, boilers, flares, and fluid bed catalytic crackers; about 13%
- from gas turbine power generators, or machine drives: about 3%
- from steam reforming process for H₂ generation: up to 100% CO₂

One of the options for reducing greenhouse gas emissions from refineries is CO₂ capture and storage.

CO₂ capture using an absorption-based technique appears to be a viable option for refinery exhaust streams from an on-site power generation, from process furnaces and boilers, and from catalyst regeneration. In addition to amine absorption, oxygen combustion has been studied by IEA and BP and using of hydrogen rich fuel, from which CO₂ has been captured before combustion by IEA.

The costs for CO₂ abatement using alternative technologies are presented in Table 3. A 10% discount rate is used and fuel price of natural gas is 2 US\$/GJ.

Table 3. The costs for CO₂ abatement using alternative technologies.

	MEA Absorption	Oxyfuel	H₂- rich fuel
Installed cost, million US\$	146	137	203
Cost of CO ₂ avoided, US\$/t CO ₂	18	20	22
Net cost of CO ₂ avoided, US\$/t CO ₂ (imported utilities taken into account)	27	28	42

The CO₂ abatement from oil refinery fired heaters can reduce overall emissions from the refining process by 40 - 70%. The cost of CO₂ abatement lies in the range 20 - 40 US\$/tCO₂ emission avoided for reduction in refinery emission of about 40%.

High concentrations of CO₂ are found in the off-gases from the steam reforming process and from some petrochemical streams, such as ethylene oxide manufacture. For these relatively small, high concentration emission sources, cryogenic separation is a promising option.

CO₂ can be used for enhanced oil recovery in case refinery is located near an oil production area. The same criterion is valid also for geological or deep ocean storage.

The CO₂ emission reduction options for refineries are summarised in Table 4. To put the CO₂ capture and storage option into perspective also other CO₂ emission reduction options are included [24, 25].



Table 4. The CO₂ emission reduction options for refineries.

Source	Percent of sector CO ₂ emissions associated with source	CO ₂ reduction technique	CO ₂ reduction efficiency	Maximum CO ₂ reduction potential for whole sector	Cost, US\$/t CO ₂
Power generation	13	Cogeneration	21% relative to on-site oil fired generation	1.2% taking into account that 55% of power is imported	-6.5 relative to onsite generation -48 relative to purchased power
		Fuel cells	25%	1.5% taking into account that 55% of power is imported	Not known
Process furnaces and boilers	65	Dividing wall distillation technology	30% reduction on energy used in distillation processes	Not known	Capital savings of 25%
		Compact heat exchangers	Not known	Not known	Capital savings of 69 - 84%
		Waste heat boilers	14%	11%	Not known
		Miscellaneous energy efficiency measures	10 - 20%	8 - 16%	-20 to -50
Power generation, process furnaces and boilers, FCC catalyst regeneration, incineration processes	95	CO₂ capture and storage	80 - 99%	76 - 94%	20 - 90 (capture by absorption) 2 - 11 (ocean/ geological storage)
Methane steam reforming	2	Cryogenic CO₂ capture	High	2%	10's
Flares	<3	Reduced flaring	50%	1.5%	Savings
Entire refinery plus petrochemicals sector	100	"Energyplex" concept	100%	100%	Not known

3.3 IRON AND STEEL PRODUCTION

The two principal types of steelmaking technology in use today are the primary integrated steel mills and the scrap based mini-mill. Integrated steel plants typically consist of a coke making facility, ore agglomeration plants, blast furnace(s), basic oxygen furnace plants, and continuous casting, rolling and finishing operations. In the scrap based mini-mills, steel production consists of one or more electric arc furnaces and casting, rolling and finishing operations.

The iron and steel industry is the largest energy consuming manufacturing sector in the world. The principal greenhouse gas emitted from iron and steel production is CO₂. The CO₂ emissions associated with the production of one tonne of steel varies depending on the production route. The CO₂ emissions from steelmaking processes are shown in Table 5 [26].

Table 5. The CO₂ emissions of steelmaking processes.

Production Process	CO₂ emission (tonnes/tonne product)
Integrated steel mill	1.6 - 2.2
Scrap based production in a mini-mill	0.6 - 0.9
Scrap substitutes (DRI) in a mini mill	1.4 - 2.0

In integrated steel plants, the majority of CO₂ emissions (70%) arise from iron production in the blast furnace. Smaller CO₂ emissions come from rolling and finishing of products (12%), ore preparation (12%) and oxygen and power production (7%). In scrap based mini-mills the main emissions are from the electric arc furnace (45%), finishing and rolling (36%) and oxygen/power production (16%).

There are several options for reducing the greenhouse gas emissions, including CO₂ capture from blast furnace gas (CO₂ 20% by volume, CO 21% by volume).

It would be technically feasible using available capture technology to decarbonise the blast furnace gas before it is used as a fuel. Due to low partial pressure of CO₂ in the blast furnace gas chemical absorption technology is the most suitable. It has been estimated that the costs are 35 US\$ per t CO₂ abated (based on 8350 operating hours per year). Applying CO₂ capture could add some 15 - 20% to the cost of steel production. The captured CO₂ could not be utilised within the steel process and would need to be transported away for utilisation or storage.

The CO₂ recovery can be further enhanced if carbon monoxide is converted to CO₂ in a two-stage water gas shift reaction. It is estimated that this would result in higher costs per tonne of CO₂ recovered, because of the extra investment costs and the heat requirement for the shift reaction.

Mini-mills were not considered since they use electricity for the electric arc furnaces and the CO₂ emitted would be generated outside the steel plants boundary.

3.4 CEMENT PRODUCTION

There are three main production steps in the production of cement:

- preparing raw materials,
- burning of feed materials to form cement clinker in the kiln,
- finish grinding of clinker and mixing with additives.

There are two types of kiln: rotary and shaft. The former is suitable for large-scale production and used in most industrialised countries. Shaft kilns are suitable for small-scale production and used e.g. in China and India.

CO₂ emissions in cement manufacturing originate mainly from combustion of fossil fuels and from calcining of the limestone. The total emissions during the cement production process depends mainly on:

- type of production process (efficiency of the process and the sub-processes),
- fuel used (coal, fuel oil, natural gas, petroleum coke, alternative fuels),
- clinker/cement ratio (percentage additives).

The formed CO₂ originating from the calcination process as well as from the combustion processes leaves the process via the flue gases. Typical CO₂ concentrations in the flue gases range from 14 to 33%.

Emissions of CO₂ can be reduced by:

- improvement of the energy efficiency of the process,
- shifting to a more energy efficient process (e.g. from wet to dry process),
- replacing high carbon fossil fuels by low carbon fossil fuels,
- replacing fossil fuels by alternative fuels, e.g. waste-derived fuels,
- applying lower clinker/cement ratio (increasing the ratio additives/cement):blended cements,
- application of alternative cements (mineral polymers),
- removal of CO₂ from the flue gas.

According to an IEA study the most suitable CO₂ capture concept for cement production is CO₂/O₂ combustion. The disadvantages of the precombustion CO₂ capture concept are that there are little opportunities to integrate the fuel conversion process into the cement production and that only fuel-related CO₂ can be captured. The problem with application of the post-combustion concept (chemical absorption) is that there is not enough waste heat available for the CO₂ removal process.

In CO₂/O₂ combustion a mixture of oxygen and CO₂ is fed to the burner of the kiln. The oxygen is produced in separate air separation unit and CO₂ is recycled from the exhaust of the kiln. In cement production application considerably less oxygen is required for the recovery of one tonne CO₂, than for a similar process in e.g. power generation plant, because only half of the emissions originate from fuel combustion.

In comparison with the original/reference process without recovery of CO₂, a number of process conditions change. These are: cooling of the cement product by the combustion air, leakage of gases, influence of different CO₂ partial pressure in the cement production process, start-up of the cement production process, application of pre-calciner and other pollutants in exhaust gas.

It was estimated that CO₂ emission reduction potential of a cement production plant by using CO₂ removal technology is 60 - 65% and the cost vary between 50 – 250 US\$/t CO₂ avoided [27].

4 OVERVIEW OF CO₂ STORAGE TECHNOLOGIES

4.1 UNDERGROUND STORAGE OF CO₂

Tackling climate change would mean that CO₂ must be stored for several hundreds or even thousands of years. The other requirements include low environmental impact, low cost and conformation to national and international laws. Geologic formations, like oil and gas fields, coal beds, and aquifers are the most likely options for the large-scale sequestration of CO₂ in the short term. The first commercial scale storage of CO₂ underground is now being undertaken in the North Sea, where Statoil Ltd has injected nearly a million tonnes per year of CO₂ into a deep saline aquifer (about 800 m under the seabed) since 1996 as a part of its natural gas production. The project was marked as the first CO₂ storage in geologic formations driven by climate change considerations. Recently, more demonstration projects have commenced to sequester CO₂ because of environmental reasons, as described below.

CO₂ can be sequestered in geologic formations by three principal mechanisms.

1. Gaseous or supercritical CO₂ can be trapped under a low permeability caprock, which is called hydrodynamic trapping. This mechanism will likely be the most important in the short term for sequestration.
2. In solubility trapping, gaseous CO₂ can dissolve into the fluid phase, such as petroleum. In EOR, dissolved CO₂ lowers the viscosity of the residual oil so it flows more readily.
3. CO₂ can react in geologic formations with the calcium, magnesium and iron minerals as well as with organic matter to become part of the solid mineral matrix. The formation of these stable mineral carbonates is relatively slow process.

4.1.1 Oil and gas formations

About 33 million t/a of CO₂ is used in the USA at more than 74 EOR projects [2]. Commercial EOR operations are also underway in Turkey, Trinidad and Canada. In Turkey, 6 million t/a of CO₂ has been injected. These projects account for only 0.3% of the worldwide crude oil production. However, EOR operations use about 80% of commercially utilised CO₂, which usually is extracted from naturally occurring CO₂-filled reservoirs [6]. In the USA, only 4 currently active projects use CO₂ (about 3 million t/a), which is extracted from ammonia production or from natural gas plants. None of these projects has been established in order to sequester CO₂. No EGR projects with CO₂ storage has been pursued yet. An example of a CO₂-EOR project using anthropogenic CO₂ is the Weyburn project in Canada. The CO₂ will be supplied through a 330 km pipeline from coal gasification plant in North Dakota. The CO₂ is 95% pure and its initial injection rate is 5000 t/day. Some 20 million tonnes of CO₂ is expected to be injected into the reservoir over the project life. The primary objective of the project is

to understand geo-sequestration of greenhouse gases, particularly CO₂. The scope of work includes understanding mechanisms of sequestration and the degree to which carbon dioxide can be permanently sequestered in geological formations [19, 28].

In EOR operations, injected CO₂ enhances oil production through two processes, miscible and immiscible displacement. In miscible displacement, injected CO₂ mixes with the crude oil, causing it to swell and thereby reduce its viscosity. The CO₂ injection also helps to maintain or increase the pressure in the reservoir. In immiscible displacement the injected CO₂ remains physically distinct from the oil but causes the oil to swell, reducing the oil's density and improving mobility. Miscible processes are more efficient and most common in active EOR projects, but immiscible flooding is likely to be increasingly important in CO₂ sequestration. About half of the injected CO₂ is stored in the reservoir. The rest is captured and re-circulated back to injection wells. The CO₂ purchase/preparation accounts for 50% to 80% of total capital and operating costs and therefore detecting and avoiding unnecessary venting of CO₂ is a constant concern in the EOR. However, it has been estimated that about 10% of net CO₂ purchases are lost to the atmosphere due to intentional and unintentional venting. The total cost of capturing the CO₂, transporting it 300 km and storing it in oil field has been estimated to be between 30 – 50 US\$/t CO₂ [2, 6, 29, 30].

In contrast to EOR, injecting CO₂ into depleted gas fields generates little or no offsetting benefit and therefore CO₂ sequestration will apparently be more costly. However, further research into EGR is required. The cost of capturing the CO₂, transporting it 300 km and storing it in depleted gas fields has been estimated to be 40 - 60 US\$/t CO₂. In depleted gas field the CO₂ would occupy some of the void space that had been occupied by the natural gas. In nearly depleted gas fields, it is possible that CO₂ injection can prolong the life of the field by maintaining reservoir pressures longer. For EGR, the reported CO₂ concentrations in produced gas were below 0.5%, which indicated that CO₂ breakthrough was very low [2, 31].

4.1.2 Aquifers

Aquifers are geographically more widespread than oil and gas fields. Most countries have aquifers, which are more likely than other geologic formations to situate close to a CO₂ source. The estimates of worldwide storage potential of CO₂ in deep aquifers range from 400 to 10 000 Gt of CO₂ [2]. It has been estimated that the capacity to store CO₂ underground in Europe, particularly under the North Sea, can be more than 800 Gt of CO₂ [19]. That capacity is enough to store all the CO₂ from Europe's current power stations for 800 years. However, more research is needed to identify the worldwide potential. Research activities are underway in Europe, Australia, Canada and USA to map and assess the storage capacities of onshore and offshore salt-water reservoirs.

If CO₂ is injected into saline aquifer some will dissolve in the saline water. CO₂ may also react with the minerals and form stable carbonate compounds. The most suitable reservoirs are those at depths greater than 800 m, because under these conditions CO₂ will behave more like a liquid than a gas, enabling much more CO₂ to be stored. An aquifer is a commercially non-productive stratum and usually poorly surveyed by well

and seismic data. This increases cost and risk of CO₂ sequestration. Due to the missing infrastructure (pipelines, wells, offshore platforms, etc.), capital costs of CO₂ sequestration in aquifers may be higher than in the case of EOR. Operational experience from aquifer gas storage indicates that the main uncertainties for CO₂ disposal in aquifers relate to the disposal rate of CO₂, available storage capacity, identification and characterisation of suitable aquifer formations and caprock structures, and potential of CO₂ leakage through imperfect confinement. Injection of CO₂ into an aquifer is unlikely to be accompanied by removal of water, which will lead to an increase of pressure over a large area of formation. However, it has been suggested, that even if the reservoir was not fully sealed, the time required for CO₂ to diffuse to the edge would be hundreds or thousands of years.

Since 1994, acid gases (containing both CO₂ and H₂S) from natural gas processing plants have been injected into onshore salt-water reservoirs in Alberta, Canada. In the North Sea a commercial project is underway in the Sleipner West natural gas offshore field. The aim is to monitor the stability of the reservoir and to observe the development of the expanding CO₂ bubble. Reservoir simulation models will be validated with seismic data, which will be essential for planning future geologic CO₂ storage projects.

4.1.3 Coal formations

Natural coal formations contain gases, like methane, in pores of coal matrix and fractures in the seams. A number of patents have been issued during the past twenty years relating to the methane recovery from deep unmineable coal beds by CO₂. Injected CO₂ adsorbs more easily onto the coal structure than methane, which is desorbed from the coal matrix. CO₂ remains sequestered within the seam and desorbed methane can be recovered as free gas. The amount of methane in the coal varies depending on the depth of the coal and its history. The estimated ratio of CO₂ molecules adsorbed for each methane molecule released is around two or even higher. This CO₂ enhanced coal bed methane recovery (CO₂-ECBM) process has the potential to economically sequester large volumes of CO₂ providing the coal is never mined. In the most favourable (with high permeability) coal basins the estimated storing capacity is about 15 Gt CO₂. The storing capacity in less favourable coal basins could be up to 50 times more. The cost of capturing CO₂, transporting it 300 km and storing it in high permeability coal seam has been estimated to be between 30 – 50 US\$/t CO₂ avoided.

Even though a substantial amount of coal bed methane is already produced, there are only two CO₂-ECBM pilot projects. In the San Juan Basin in the southwestern United States, over 100 000 tonnes of CO₂ has been injected to the coal bed through 13 injection wells during three years. The San Juan Basin is a high permeability coal bed. Preliminary results indicate that about 75% recovery of coal bed methane may be achieved. The reported CO₂ levels in produced gas have been as low as 0.4%, which indicates that CO₂ breakthrough has not occurred [2, 31].

The second ECBM demonstration project is being carried out in Alberta, Canada. CO₂ and CO₂/N₂ mixtures are used in low permeability coal bed. The project aims at to pilot

and complete specifications of the technology required performing large-scale ECBM projects [19].

4.2 OCEAN SEQUESTRATION

Two methods are proposed for the ocean sequestration: (1) Relatively pure CO₂ could be injected directly into deep ocean water and become trapped in sediments or ice-like solids called hydrates. (2) The net oceanic uptake from the atmosphere could be enhanced through iron fertilisation. Both of these approaches will require improvements in understanding marine systems before large-scale implementation.

Ocean contains about 146 000 Gt of CO₂, mostly in the form of bicarbonate. Currently, the net oceanic uptake of 2 ± 0.8 GtC/year results from the growth of anthropogenic CO₂ in the atmosphere. It has been estimated that about 90% of today's CO₂ emissions will be transferred to the ocean on a time scale of 1000 years.

4.2.1 Direct injection of CO₂

Several methods have been introduced for CO₂ injection into the deep ocean:

1. CO₂ dispersal in very dilute form at depths of 1000 – 2000 m.
2. Discharge at 3000 m to form a lake of liquid CO₂ on the seabed.
3. Formation of a sinking plume to carry most of the CO₂ into deeper water.
4. Release of solid CO₂ at depth.

The most likely option in the short term is thought to be the first one. However, further research is required to investigate the overall effect of storing CO₂ in the ocean. Questions and uncertainties linked to storage times, technical feasibility, environmental impacts and costs make CO₂ storage more unlikely option compared to geological storage in the short term. Also, legal and public opinion aspects should be considered [2, 32].

4.2.2 Ocean fertilisation

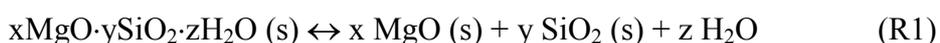
Natural process of carbon fixation by phytoplankton may be enhanced by ocean fertilisation with micronutrients, like iron, and macronutrients, like nitrogen and phosphorus. Short-term field experiments showed an increase in the partial pressure of CO₂, increased chlorophyll concentrations, and a considerable change in species composition. It is not known today, how long-term fertilisation would affect ecosystem structure, transport of carbon to the deep sea, and fluxes of CO₂. With current knowledge the ocean fertilisation may not be recommended for CO₂ storage.

4.3 STORING CO₂ AS INERT SOLIDS

4.3.1 Mineral carbonation

Advanced chemical approaches to CO₂ sequestration could allow gaseous CO₂ to be transferred into inert, stable and long-lived solid materials. A suggestion of an aboveground process that would bind anthropogenic CO₂ is to convert naturally occurring mineral oxides to carbonates, such as magnesium carbonate (MgCO₃) or calcium carbonate (CaCO₃).

For mineral carbonation the use of magnesium based silicates, xMgO·ySiO₂·zH₂O is favoured, because they are worldwide available in huge amounts. These natural resources may be capable of binding all fossil fuel-bound carbon [33, 34]. Magnesium silicates can be divided into several subgroups. The largest quantities are olivine, (Mg,Fe)SiO₄, and serpentine, Mg₃Si₂O₅(OH)₄. Some other suitable minerals exist in smaller amounts. The chemistry for this CO₂ fixation can be summarised as



The overall carbonation reaction (R1+R2) is exothermal: the heat effect is +64 kJ/mol and +90 kJ/mol MgCO₃, for serpentine and olivine, respectively. Large-scale flue gas CO₂ sequestration as mineral carbonates would, however, require enormous amounts of mineral. For a typical power plant, the mass flows of fuel and carbonated mineral will be of the same order of magnitude: 1 kg of CO₂ may require 2 kg of serpentine for disposal.

Only a few laboratories are looking into technical solutions to perform the carbonization of magnesium with carbon dioxide on a large scale. Most important results are reported from the USA, *i.e.* Columbia University, New York (NY), Los Alamos National Laboratory (NM), Albany Research Center at Albany (OR) and Arizona State University at Tempe (AZ) [33, 34, 35, 36]. A wet process using hydrochloric acid, with MgCl₂ as reaction intermediate that was initially studied in the USA [33, 37] is very energy intensive. After that, in 1998 the team from the USA reported conversion rates such as 40 - 50% conversion of MgO to MgCO₃ after 24 h at 150 – 250 °C, 85 – 125 bar, with olivine particles of 75 - 100 μm [35]. More recent achievements using wet systems report 65% conversion after 1 hour [35, 36], followed later by 80% conversion within 30 minutes [38] mainly as a result of careful control of solution chemistry, heat treatment and attrition grinding.

Whilst the research in the USA is concentrating increasingly on wet methods using aqueous solutions, the research started in August 2000 at Helsinki University of Technology [39, 40] (still) aims at dry methods. Finnish serpentine deposits suitable for carbonation appear to enormous.

4.3.2 CO₂ hydrates

Another option is the formation of CO₂ hydrates, an ice-like material (CO₂·nH₂O), which may be sequestered on the ocean floor. Methane hydrates are known to have existed for thousands of years in many parts of the world as finely dispersed particles in the sea floor or as hydrate capped gas reservoirs. It has been suggested, that CO₂ hydrates form similar stable molecules as methane hydrates. If CO₂ could be stored in a similar manner, considerable quantities of CO₂ could be sequestered. The storage of hydrates could take place on the ocean floor or more likely by combining CO₂ storage with release of methane from hydrate deposits. Hydrate reservoirs are found in permafrost areas, but also subsea reservoirs have been observed. Compared to other sequestration options, knowledge on the potential for storing CO₂ as hydrates is at an early stage. However, interesting options could be man-made systems that mimic required conditions (high pressure and low temperature) for storage as hydrate deposits. CO₂ hydrates could be used in CO₂ separation from high-pressure systems, like IGCC, with very low energy penalty (3 – 4%) [41].

4.4 FUTURE PROSPECTS

Capture and storage of CO₂ could enable relatively large reductions in the CO₂ emissions with little impact on the global energy infrastructure and economy. CO₂ sequestration could give a new chance for fossil energy sources in energy production, especially for large-scale centralised power production from coal.

The most potential stores seem to be underground geological formations. Structural or stratigraphic traps, where oil and gas have been present over a geological time, offer a reliable disposal site for CO₂. Similarly, methane has been trapped in coal seams since the coal was formed and deep saline aquifers in sedimentary basins have held water for thousands of years.

The geologic structure and physical properties of most of the oil and gas fields have been characterised extensively and wide experience has been gained in EOR. Particularly in Europe and North America, thousands of oil and gas fields are approaching the end of their economically productive life. Underground storage of natural gas has been an integral part of gas production for many decades. These depleted gas fields could be adapted readily for storage of CO₂. The properties and storage capacities of unmineable coal seams and aquifers are more poorly investigated than oil and gas fields.

The possibility of underground storage of CO₂ to become a commercial technology has evidently good possibilities. There may be concerns about the safety for human health and environment. More research is needed especially before land based schemes could be adopted. Recently, the focus of the research and development work has been on monitoring and simulation techniques for CO₂ in underground strata. Also long-term interaction of CO₂ with potential host rocks has been identified. In the future, clear understanding of legal matters, like questions of ownership of storage sites, will have to be addressed.

5 DIRECT UTILISATION OF CO₂

Although direct utilisation of CO₂ would not solve the problem of global warming, the potential income that it might generate would reduce the burden of disposal. Also, in many applications, like in conversion to fuels, CO₂ is finally released meaning that no net sink of CO₂ is created. CO₂ emissions would be reduced only if captured CO₂ would replace CO₂ that is at present produced from fossil fuel.

The goal of recycling or reuse of anthropogenic CO₂ is to develop processes that can convert separated and captured CO₂ to durable products having commercial value. The most examined alternatives of direct utilisation fall into three categories: industrial uses, chemical conversion to fuels, and biological conversion to fuels. The problem is to create enough applications to sequester large amount of CO₂ generated from fossil fuels.

In the USA, the industrial need of CO₂ is only about 2% of the emitted CO₂ and about 80% of this amount are used in EOR. As mentioned above, CO₂ in EOR is mostly provided by cheap CO₂ from natural gas wells. In countries, which do not have oil production, the industrial usage of CO₂ is usually considerably lower.

Potential commercial products that could utilise CO₂ are polymers, aromatic compounds and dimethyl carbonate (DMC). All of these require metal-based catalysts, which would make the products too expensive at current prices. However, due to increased interest for the use of environmentally sound DMC as an octane booster in motor fuels, commercial operation of CO₂ based catalytic synthesis has been started. Acceptance of DMC as a more attractive gasoline additive than MTBE (methyl tertiary-butyl ether) would create CO₂ demand. Globally one million tonnes of CO₂ per year might be used in DMC production [42]. With the above mentioned hydrocarbon products the fate of net CO₂ emission is case specific and depends on several factors. For example, the net greenhouse gas balance of DMC and MTBE production should be compared and the amount of emitted greenhouse gases by cars should be measured before appraisal of potential positive effects on net greenhouse gas balance.

5.1 PROPERTIES OF CO₂ AND ITS REACTIONS

CO₂ is thermodynamically very stable at normal temperatures, except with water, which means that significant energy source is usually required for CO₂ reactions. Salts and esters are formed in aqueous solution from carbonic acid, which is a product of CO₂ and water. A solid hydrate is separated at low temperatures (below 277 K) and at elevated pressures, as discussed in Chapter 4.3. To reduce energy requirements, advanced techniques like microwave induced reactions, ultrasound initiated redox reactions, and chemically catalysed reactions may offer thermodynamically more favourable reaction pathways. Table 6 lists some key chemical reactions involving CO₂ and their reaction enthalpy (ΔH). Some of the reactions have already been discussed in the previous sections.

Table 6. Thermodynamics of chemical/physical transformations involving CO₂.

	Chemical / physical reaction	$\Delta H_{298\text{ K}}$, kJ/mol
Energy production		
Coal combustion	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	-393,8
Natural gas combustion	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	-802,9
Sequestration		
Carbonate formation	$\text{CO}_2 + 1/3\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \rightarrow \text{MgCO}_3 + 2/3\text{SiO}_2 + 2/3\text{H}_2\text{O}$	-65,73
Bicarbonate formation	$\text{CO}_2 + 1/2\text{CaSiO}_3 + 1/2\text{H}_2\text{O} \rightarrow 1/2\text{Ca}^{2+} + \text{HCO}_3^- + 1/2\text{SiO}_2$	-14,4
Oxalate formation	$\text{CO}_2 + \text{CO} + \text{CaSiO}_3 \rightarrow \text{CaC}_2\text{O}_4 + \text{SiO}_2$	-131,2
Hydrate formation	$\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{CO}_2 \cdot 6\text{H}_2\text{O}$	-23,8 ¹⁾
Liquefaction	$\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{l})$	-5,32 ²⁾
Utilisation		
Methanol synthesis	$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-131,0
(Hydrogen production)	$(3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + 3/2\text{O}_2)$	(+858,5)

¹⁾ at 121 K

²⁾ at 298 K

Wide range physical and chemical properties of CO₂ make it a key part in countless industrial and chemical applications, either in gaseous, liquid or solid forms. Properties of CO₂ important for its industrial applications include:

- fizz
- inert
- nonflammable
- non toxic
- chemical
- acid
- critical pressure
- coolant
- high density
- electrically non-conducting
- solvent
- bacteriostatic
- photosynthesis
- pesticide
- sublimation (not melting)

5.2 MARKET SEGMENTS

CO₂ is widely used in industrial applications, which seldom offers long-term sink for CO₂. For example, in inerting applications, like in fire extinguishing and welding, CO₂ inhibits the reactions with atmospheric oxygen. In refrigeration, solid CO₂ is melted and evaporated while the material to be cooled supplies heat. All of these applications are

CO₂ emitting sources if the used CO₂ is produced from fossil fuel. Otherwise the overall CO₂ greenhouse gas balance is zero. In some applications, CO₂ could be processed in a closed loop, like in refrigeration, but the net reduction of CO₂ in the atmosphere would be negligible. The different industrial applications for CO₂ are described below according to the main markets segments. Most of the information was recovered from progress reports of EU Rucadi project (BRRT-CT98-5089) [9] and from the reference [43].

5.2.1 Food Processing Industry

Five main applications constitute this market segment, which in the USA accounts for more than 44% of the merchant CO₂ market (excluding captive on-site productions such as urea production and re-injection in oil wells):

1. Refrigeration: Chilling food products during transportation
2. Modified Atmosphere Packaging (MAP/CAP)
3. Freezing: Chilling food products during processing
4. Supercritical fluid extraction
5. Stunning: Slaughter of swine, stunning of poultry.
6. Sterilisation: Decontamination of foodstuff.

Most of the above applications are for food safety, which is an area of increasing importance for liquid CO₂ customers. Innovative CO₂-based cooling technologies are focused to solve critical points in food processing chain.

In refrigeration, freezing and packaging applications, CO₂ competes with nitrogen. Both gases are non-toxic and leave no residue on the product, so the choice between the two is based upon cost and availability.

REFRIGERATION: maintaining the “cold chain” for food products during transportation

Liquid carbon dioxide is used to refrigerate food both prior to shipment and during the trip. It is sometimes used to pre-cool trailers equipped with conventional refrigeration systems. It is also used in complete carbon dioxide portable refrigeration systems. The modest equipment costs associated with the use of carbon dioxide chilling and its rapid effect are the main factors behind carbon dioxide's popularity in this use.

Complete carbon dioxide refrigeration systems are gaining market share at the expense of mechanical refrigeration systems due to both environmental and cost considerations. Carbon dioxide systems do not employ chlorofluorocarbon (CFC) refrigerants, which are being phased out because of environmental considerations. These systems also eliminate the emissions associated with the diesel fuel used to operate mechanical systems. Additionally, carbon dioxide systems are silent and require little maintenance. Finally, carbon dioxide systems reach the target temperature more rapidly and hold it longer.



Although the general trend over the last decade has been toward the use of liquid carbon dioxide in food refrigeration, solid carbon dioxide (dry ice) has retained some applications in the food industry. Advantages of dry ice refrigeration include the fact that it leaves no residue upon evaporation, is non-toxic (which permits direct contact with food), and is relatively light.

Modified Atmosphere Packaging (MAP/CAP)

In packaging uses, carbon dioxide gas, generated from liquid, is used as an inerting medium to prevent flavour loss, deterioration by oxidation, and bacterial growth in food. Examples of applications are packaging of coffee as well as processing and transporting of fruits, vegetables and cereals. Carbon dioxide competes with nitrogen in this application, with the choice of gas determined by costs and regional availability.

A potentially growing area in the food processing industry is modified or controlled atmosphere packaging (MAP/CAP). This technology centers on the absolute control over processing and packaging conditions, and employs breathable flexible film in combination with gas flushing (carbon dioxide, nitrogen, or blends of the two) to significantly extend the shelf life of packaged foods. By using gas flushing, MAP/CAP reduces the need for preservatives and additives, making the foods more attractive and healthy.

Freezing: Chilling food products during processing

In freezing uses, large quantities of liquid carbon dioxide are used to "flash freeze" or "tunnel freeze" a variety of food products including fresh vegetables, poultry, sea food and bakery products. Foods are flash frozen by transporting them on a conveyor belt through a tunnel where they are exposed to an atmosphere of "flashing" liquid carbon dioxide, which produces the low temperature required.

Even more CO₂ technologies may move from field testing to food processing plants if governments mandate changes to avoid E. coli and other bacteria. Suppliers of CO₂ are making "substantial" investments in their own processing facilities to ensure that ingredient grade gas meets strict specifications.

Supercritical Fluid Extractions:

The newest application for carbon dioxide in the food industry is supercritical fluid extraction (SFE) processes, which can be used in the decaffeination of coffee and the production of flavours, natural colours and essential oils. This method is gaining favour in coffee decaffeination because it is non-toxic, does not employ solvents such as methylene chloride, and leaves no trace in the final product. Carbon dioxide SFE is also gaining favour for other food extraction applications.

Stunning: Slaughter of swine, stunning of poultry:

Since many years, CO₂ has been used in slaughterhouses for stunning of pigs instead of using conventional electrical stunning. The use of CO₂ offers a wide variety of

advantages, such as reduced animal stress, less injuries, etc., with a better meat quality and yield as result. For poultry, gas mixtures are used.

Decontamination of foodstuff

In a new process liquid foods and liquid medicines are sterilised and preserved by contact with compressed CO₂ at room temperature. The process uses membrane technology, which is the most effective way to bring CO₂ into contact with the liquids to be sterilised. Microbes such as infectious bacteria, spores and viruses (e.g. E. coli, salmonella, and polio virus) are killed as effectively as with heat pasteurisation. For example, apple juice and orange juice contacted with liquid CO₂ at room temperature are as sterile as if they had been heat pasteurised, and there is no settling out of the pulp on storage. In addition to retaining their full nutritional value, juices and other liquids sterilised in this manner are preserved against spoilage. The process is especially attractive for juices where flavour is easily degraded, and for biological therapeutic fluids, which are inactivated by heat processing.

5.2.2 Carbonated beverages

By far the dominant use of CO₂ is in carbonated soft drinks, although carbon dioxide is also used in the production of some types of sparkling wines and other carbonated beverages. Growth in carbon dioxide basically follows soft drink consumption, although the introduction of new carbonated beverages, such as carbonated fruit juices and artificially carbonated sparkling wine, also contributes to market growth. Soft drink consumption is expected to moderate somewhat after a strong growth over the last decade. Bottled water demand is expected to increase favourably. Liquid carbon dioxide used in beverages must be odorless and as pure as possible, as impurities may affect the taste of the beverage. Supply of consistently high quality carbon dioxide to beverage producers is therefore critical.

In addition to providing the effervescence and characteristic bite of soft drinks and other carbonated beverages, carbon dioxide acts as a preservative by preventing fermentation and inhibiting the growth of mold and bacteria. As citric acid or phosphoric acid is typically used with carbon dioxide, bacteria will not survive more than a few hours in an acidified carbonated beverage.

Carbon dioxide requirements for soft drinks range from about 2.5 to 4.5 volumes of gas per volume of liquid. The total CO₂ volumes consumed by this industry is higher because of CO₂ losses, use of carbon dioxide for non-carbonation operations (cleaning, water treatment, propellant gas), and the use of carbon dioxide for carbonating non-soft drink beverages such as wines and fruit juices not included in soft drink consumption figures.

Production of beers and ales, does not require external carbon dioxide injection because, especially in large breweries, the brewing process generates adequate quantities of carbon dioxide and this is recovered and purified on-site for further use.

5.2.3 Chemical industry

CO₂ as Feedstock

As a feedstock, carbon dioxide is used for the production of:

- basic lead carbonate (white lead);
- urea;
- sodium, potassium, ammonium and hydrogen carbonates and bicarbonates;
- methionine;
- sodium salicylate (an intermediate in the manufacture of aspirin) is produced by the reaction of carbon dioxide with sodium phenolate.

Some sectors of the chemical industry are already trying to develop new chemical and biochemical processes, which use carbon dioxide in the production of high-value chemicals. Such processes have the added benefit of avoiding potential environmental penalties for carbon dioxide emissions. If new or improved processes could be developed, carbon dioxide usage by the chemical industry could be increased by a factor of ten or more. New approaches presently under development for using carbon dioxide include: pigment production with reduced toxic by-products; polycarbonate production from supercritical carbon dioxide; urethane production using carbon dioxide instead of phosgene; and the direct synthesis of gasolines from carbon dioxide.

Supercritical Fluid Extraction (SFE):

As in the food industry, carbon dioxide has an emerging use in the chemical industry for supercritical fluid distillation and the extraction of heat sensitive products. Carbon dioxide SFE is especially attractive for pharmaceutical production because of the lack of solvent residues in the product and the low temperature of the process. It can also be used to remove contaminants from chemical process streams. Supercritical carbon dioxide can be used to extract nonvolatile substances at moderate temperatures, at which they are normally non-distillable. The ability of supercritical carbon dioxide to extract nonvolatile compounds at moderate temperatures reduces the energy requirements relative to conventional extraction and distillation.

Pulp and paper industry

Within the last few years, pulp and paper mills have begun to use a CO₂-based technology for washing brownstock. Patented by AGA Ab, the technology sparkles CO₂ into the pulp slurry. As the gas reacts with water, carbonates form and liberate natural calcium-containing compounds in the fibers. As a result, a cleaner pulp goes on to the bleaching phase. In addition, the CO₂ reduces the solution's pH, which keeps the fibers from swelling as much. The application is presently used in more than 40 fiber lines - both unbleached and bleached kraft and sulphite lines.

Other applications:

Liquid and solid carbon dioxides are also used for direct injection into chemical reaction systems to control temperature.

The high chemical stability of CO₂ makes it an inert gas. It is therefore ideally suitable for inerting atmospheres, such as tanks containing combustible gas mixtures, powdered coal, and other products that may cause dust explosions. As an inerting gas, carbon dioxide is also used in the chemical industry to purge and fill reaction vessels, storage tanks and other equipment to prevent the formation of explosive gas mixtures and to protect easily oxidised chemicals from contact with air.

5.2.4 Metal fabrication

Shielding gas for welding

The major use for carbon dioxide in the metals industry is for welding operations in private ships, on construction sites and in numerous types of manufacturing operations. Used either alone or with other gases, carbon dioxide is used in the gas shielded arc as a shielding gas to protect the welding zone from the deleterious effects of oxygen, nitrogen and hydrogen. Carbon dioxide used for welding must be in gaseous form. However, some large welding operations may purchase bulk liquid and convert it to gas at the point of use.

Foundries:

For the production of sand moulds and cores for casting iron and other metals, CO₂ can be used in combination with other additives to form the binding agent between the sand grains.

Separating waste:

Messer Griesheim GmbH plans to commercialise a CO₂ process for recycling sludge generated during metalworking. The waste consists of lubricant oil used for machining and metal fillings. When mixed with CO₂, the oil dissolves into the supercritical gas leaving behind clean metal particles. Both oil and metal are suitable for reuse, and the CO₂ itself is recaptured. Also contaminated soils can be cleaned this way.

5.2.5 Agriculture

Fumigate grain silos

Carbon dioxide is used as a nontoxic pesticide in grain silos. As a fumigant or insecticide, carbon dioxide kills insects by desiccation, and offers significant advantages over competitive chemical pesticides such as phosphine or methyl bromide. In this use, liquid carbon dioxide is converted to a gas onsite, then injected into the silo, where the gas displaces the existing atmosphere with one fatal during all stages of insect life.

Additive to irrigation water

Carbon dioxide may be added to irrigation water to enhance the absorption of nutrients by plants. CO₂ is effective because, although it has weak nutrient properties of its own, it acts as an adjunct to other nutrients by changing the pH of the soil, which can increase the nutrient absorption of plants.

Additive to greenhouse atmosphere for additional plant productivity and consistent quality

By increasing the CO₂ level in the greenhouse atmosphere (typical to 600 ppm instead of normal 400 ppm value), the growth for some plants can be stimulated. The yield increases up to 20%, especially for tomato, cucumber, strawberry, etc. but also for potted plants and cut flowers.

Production and processing of algae for industrial applications

The food, pharmaceutical and other sectors show an increasing demand for fine chemicals that have a renewable origin and natural character. At the same time, the agri-sector in the EU faces small margins on production and tightened rules to reduce the environmental impact. Based on a feasibility study, algae and especially the Spirulina species (a natural source for fine chemicals like phycocyanin, carotene, etc) appear to be a very promising link between fine chemical demand and changes for the agri-sector. Products to be extracted are among other pigments (applications in food, pharmaceuticals, polymers) and vitamins (applications in food, cosmetics and pharmaceuticals). Additionally, algae cultivation has a positive environmental impact when waste heat of a power plant is used and because of CO₂ fixation. However, in the moderate climate areas of the EU large-scale production of high quality algae derivatives is hardly developed. Therefore, a new concept is outlined, in which technologies are developed for algae cultivation, integrated in a greenhouse with supply of waste streams, such as waste heat from power plants and waste nutrients from green houses. Simultaneously, processes and procedures will be developed to extract various high selling additives from algae, particularly from Spirulina. A consortium is formed that consists of partners providing know how on algal cultivation, fine chemical extraction and application development, as well as end user organisation.

5.2.6 Rubber and plastics processing

Blowing Agent

The primary challenge for the 100 kt/a foam blowing industry has been to find suitable alternatives to chlorofluorocarbon (CFC) blowing agents. About 90% of the market is currently being handled by hydrochlorofluorocarbon 141b (HCFC 141b) and HCFC 142b. CO₂ is an environmentally acceptable alternative to chlorofluorocarbon (CFC) blowing agents, which are being phased out because of their allegedly detrimental effect on the Earth's ozone layer. Therefore, an emerging application for carbon dioxide is its use as a blowing agent. CO₂ can also be used in place of hydrocarbon blowing agents, such as butane and pentane, which are also coming under increasing environmental

restrictions due to the emission of volatile organic compounds (VOCs) associated with their use.

The foam blowing industry is divided into two markets, thermoplastics and thermosets. Thermoplastics, which are used in residential housing as sheeting and roofing, as well as in commercial roofing applications, are the smaller of the two. Thermosets are a much larger market, taking about four times as much business as thermoplastics. This industry closely follows the plastics market. Polyurethane agents go into residential sheeting, refrigerator doors, insulating foam for pipes, spray foam for electrical outlets, and sandwich panels - the thin layer of foam which is placed between layers of metal in walk-in refrigerators, storage trucks and other larger refrigerating devices.

Blow Moulding:

By injecting liquid CO₂ into the moulded product immediately after the blowing, the cooling time can be reduced and therefore capacity increased.

5.2.7 Other uses as solvent

Spray Painting:

In spray painting, supercritical carbon dioxide is emerging as a functional alternative to VOCs. Although other gases could be used for this application, carbon dioxide is used because it mixes well with many paint polymers.

Aerosols

CO₂ has since long been used as a propellant in many aerosol applications, as a replacement of conventional propellants, which are known to damage the earth's ozone layer.

Cleaning parts using ultrapure CO₂.

Supercritical carbon dioxide is being used for cleaning precision parts, electronic components, as well as for the removal of hydrocarbon machine coolants from metal parts. Specifically, supercritical fluid technology is currently being investigated for possible application in a vast range of cleaning, extraction and thin metal film deposition applications for semiconductors and electronics. In particular, the future of supercritical fluid technology to precision clean semiconductor substrates and electronic boards and parts is promising with potential commercial applications in the areas of information storage devices, semiconductor devices, electrical and electronic components, inertial guidance systems, precision optical devices, medical equipment and devices, and metal finishings.

Recent work on supercritical fluids indicates that as well as successively removing organic contaminants, the technology may also be used to remove or extract metals by using metal complexing ligands. These discoveries open the potential for a multipurpose (organic and metallic or ionic contaminant removal) clean compatible with

environmentally conscious manufacturing and the process requirements of contaminant-sensitive materials.

Dry Cleaning:

Dry cleaning of clothes is a large industrial activity in Europe. The dry cleaning sector currently has approximately 75 000 cleaning machines using perchloroethylene (PERC) or CFC 113 as cleaning solvents. CFC 113 has been phased out already and PERC has risks to human health and shows toxic effects. As the industry has to meet very stringent low environmental levels for PERC in the near future, the industry needs to look now for new and cleaner technologies with less environmental and economical risks. A major portion of the PERC and CFC 113 might be replaced by SCDC (super critical dry cleaning) with CO₂ if the right technology, apparatuses and detergents are developed.

Production of fine particles

Several companies, such as Separex in France and Messer have developed a number of technologies that use supercritical CO₂ in the production of extremely fine particles. One recently commercialised process dissolves compounds ranging from pharmaceuticals to paint pigments in supercritical CO₂. When the pressure is suddenly released, the material precipitates as particles smaller than 10 µm with a very homogeneous size distribution.

5.2.8 Water treatment

Re-carbonation of sweet surface waters to be used as tap water.

Modern water works use CO₂ together with lime to raise the hardness of drinking water, especially with soft surface waters. At the right pH-level, the mentioned treatment allows the formation of a protective surface layer in water-mains pipes, thus avoiding corrosion and improving water quality.

Water treatment in chemical industry

The chemical industry also uses carbon dioxide for water treatment. Carbon dioxide is non-toxic and leaves no residues upon evaporation. Lowering the pH of alkaline water with CO₂ is becoming more important. Due to the natural buffering capacity of bicarbonate, which neutralising with the gas lowers corrosivity and makes overshooting the pH range difficult. This method offers thus many advantages towards the use of classical acids, such as less reagent, less equipment and monitoring devices, less downtime and increased safety, equipment life, etc. CO₂ used in H₂O system is known to also dissolve CaCO₃ deposit from the pipes. This is commercially not used yet.

5.2.9 Well reinjection

CO₂ enhanced oil and gas recoveries are described in the Section 4.1.1 and enhanced coal bed methane recovery in the Section 4.1.3.

5.2.10 Dry ice production

Dry ice (Carboglance™), or CO₂ in its solid form, is produced by expanding liquid CO₂ at atmospheric pressure. The expansion results in the formation of equal portions of gas and CO₂ snow. The CO₂ snow formed is compressed in extruders or presses at high pressure, resulting in the manufacture of blocks or pellets.

Dry ice is used in practically all type of industries, mainly because of its cooling properties. It is particularly interesting for application where “spot cooling” is needed.

Dry Ice as a cooling medium:

Dry ice is an excellent alternative to water ice for most cooling applications because dry ice sublimates directly into the atmosphere, and because of its higher cooling capacity and lower temperature. Examples are:

- cooling of foodstuffs, meals, ice-products, etc., during transport or when taking frozen food back home from the supermarkets store;
- cooling of catering products in aeroplanes, trains;
- cryogenic transport of pharmaceutical products;
- cooling of moulds, cores, shrink-fitting of metal parts;
- experiments in labs.

CO₂ pellet blasting for paint stripping and other surface cleaning:

This technique, which was originally developed to remove paint from the outer body parts of aeroplanes, has only recently started to gain industrial acceptance in a much broader field. Currently this technique is being used for removing coatings and paints, removing residues from moulds, cleaning production machinery, food processing lines, printing equipment and welding spots in automotive assembly lines.

The principle of surface cleaning using dry ice is based on the projection of dry ice particles at high speed (usually using a flow of dry compressed air) onto the surface to be cleaned. These particles are usually 3 mm diameter pellets, but can also be small crystals scraped off from large blocks of dry ice. When hitting the surface to be cleaned, these particles will explode. The thermal shock (dry ice at -78°C) associated with the sudden expansion of solid CO₂ to gas, effectively remove contaminants of all sorts from the substrate.

The most important advantages of dry ice blasting vs. water cleaning or sand blasting are:

- ✓ only removed substance as waste (dry ice sublimates to gas);
- ✓ not as abrasive as sand: will not damage softer substrates;
- ✓ electrically non-conducting, so even electrical cabinets can be cleaned;
- ✓ food-grade abrasive, so food production lines can be cleaned on the spot.

5.2.11 Fire fighting

In fire fighting cylinders filled with either pure carbon dioxide or blends with other gases for consumer use and industrial applications. CO₂ smothers fires without damaging or contaminating materials and is used especially when water is ineffective or undesirable.

5.2.12 Other applications (not using large quantities of CO₂)

Norsk Hydro ASA (Oslo) and a Norwegian university have developed a CO₂-based cooling system for automobiles. Daimler Chrysler AG (Stuttgart) is testing the Mobile air Conditioning 2000, and Norsk claims the technology competes favourably in price, weight, space and energy efficiency. Likewise, Sanyo Electric Co. (Tokyo) recently developed a closed-type rotary compressor that uses CO₂ as the coolant.

The medical market is a fast growing consumer of industrial gases, with the primary gases used being oxygen (for respiratory therapy, CAT scans and numerous other uses), carbon dioxide (laser surgery), helium (magnetic resonance imaging), and small volume speciality gases (laser surgery).

5.3 EVOLUTION OF THE MERCHANT MARKET OF CO₂

The commercial use of CO₂ in the world is given in Table 7. It has been estimated that CO₂ market is less than 10% of the 28 billion US\$ industrial gases market. High consumption per capita is noticed in countries with high degree of industrialisation, high standard of living, availability of low cost CO₂, R&D dedication and new applications. Table 8 shows worldwide demand of liquified CO₂ in 1998. CO₂ merchant market in Europe is given in Table 9. The installed (nominal) production capacity in Europe is about 3 280 000 t/a and the merchant market has been estimated at 2 120 000 t/a.

Table 7. Commercial use of CO₂ in the world.

	% of Value	% of volume	Consumption/capita	Cost: US\$/t
Total	2 700 US\$	13 500 kt/a	Average 2.4 kg/a	
America's	37%	57%	9.6 - 25	130
Asia	31%	21%	0.8 - 10	326
Europe	26%	19%	5 - 10	248
Others	6%	3%	0.15 - 6	400

Table 8. 1998 demand for liquified CO₂ [43].

Market	USA, kt/a	Europe, kt/a	Japan, kt/a
Food industry	3 248	360	*
Beverage carbonation	1070	1 050	163
Welding	*	90	346
Others**	2 304	450	287
Total	6 622	1 950	796

* Included in 'Others'

** Includes use in aerosols, foundry, firefighting, medical, rubber and plastics

Table 9. CO₂ merchant market in Europe.

Application	Northern Europe: (kg/person & year)	Southern Europe: (kg/person & year)
Soft drinks & mineral waters	1.4	1.3
Breweries	1.5	1.1
Chemical Ind. (inerting, reactive)	1.0	0.12
Refrigeration	1.0	0.20
Freezing	0.4	0.1
Nuclear power stations	0.4	N/A
Greenhouses	0.2	N/A
Water neutralisation	0.2	0.1
Welding + foundries	0.15	0.37
Slaughterhouses (pigs, poultry)	0.1	0.05
Blow moulding + foaming	0.06	0.08
Fire extinguishers	0.05	0.07
Supercritical extraction	0.05	0
Total	6.51	3.49

5.4 CHEMICAL CONVERSION TO FUELS

Chemical conversion of CO₂ to a transportation fuel, methanol (CH₃OH), has gained much interest. The hydrogenation of CO₂ is not a problem, but production of hydrogen, which requires much energy. Currently, hydrogen is mainly produced through steam reforming of methane, which efficiency is about 80%. The main reactions of methanol synthesis are:



Schemes have been proposed to split water to produce H₂, but this is currently far from being economically feasible. On the other hand, if cheap H₂ is available, the most energy efficient technologies, like fuel cells, will probably involve its direct use [44].

6 CO₂ TRANSPORT

The presence of moisture may cause corrosion in carbon steel lines, as dissolved CO₂ forms carbonic acid. CO₂ corrosion has been studied extensively and precautions needed to transport CO₂ in carbon steel lines have been satisfactorily investigated. Without free water in gas, no corrosion problems would occur. However, hydrogen sulfide H₂S may cause sulphide stress cracking and hydrogen induced cracking. This should be taken into account in material specification [45].

Molecular hydrogen (H₂) may be transported without problems in standard low-alloy carbon steel lines. Problems with transportation of hydrogen only occur if there is a mechanism that produces atomic hydrogen (H⁺). This may cause hydrogen induced cracking or hydrogen embrittlement [45].

The transmission distance from Finland to the North Sea or the Barents Sea would range from 800 km to 1500 km depending on the location of the CO₂ emitting plant. If the captured CO₂ were stored onground as a mineral carbonate, the transmission distance would be less than 1000 km.

TRANSMISSION COST FOR 500 MW_e GAS FIRED POWER PLANT

Let us assume a 500 MW_e gas fired combined cycle (NGCC) power plant producing about 1.6 million tonnes of CO₂ per year. Figure 12 shows that offshore CO₂ is the most expensive to transport and electricity is more expensive to transmit than natural gas to the plant. The situation would be different for plants with CO₂ capture, depending on the location of the CO₂ store. The cost of transporting both natural gas and CO₂ onshore is approximately similar to or higher than the cost of transmitting electricity over a distance less than 500 km. With such short distances the only option for Finland is to store CO₂ as solid mineral carbonate. If possible, electricity should be produced near the sequestration site. The cost of transporting captured CO₂ over a distance of 300 km onshore would be about 7 US\$/t CO₂, equivalent to 0.27 USc/kWh. The cost of offshore transportation for 300 km would be 13 US\$/t CO₂, equivalent to 0.5 USc/kWh [45].

TRANSMISSION COST FOR 5000 MW_e

The specific cost of CO₂ transport in larger pipelines and 5000 MW_e electricity transmission by AC and high voltage DC (HVDC) is shown in Figure 13 [45]. For short transmission distances, HVDC is more expensive than AC transmission because of the high cost of AC/DC converters at the ends of the transmission line. The figure shows that if CO₂ has to be stored in an underground storage it may be cheaper to locate the power station close to the gas/storage field, rather than the electricity consumers. As a result, it seems that electricity transmission option would be the most feasible option for Finland, if the transmission distance is more than 1000 km. If CO₂ transport is considered, it would be worthwhile to build trunk pipelines for long distance transmission of CO₂, as is the case for natural gas.

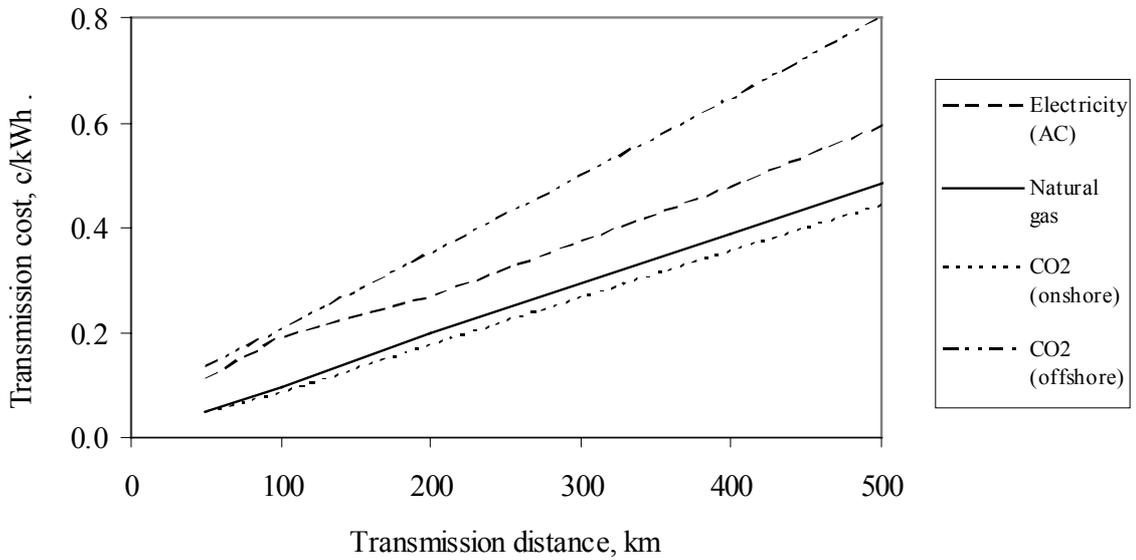


Figure 12. Costs of natural gas and CO₂ pipelines and electricity transmission lines – 500 MWe plant (annual discount rate 10%, a plant life 25 years, and an operating load factor of 90%) [45].

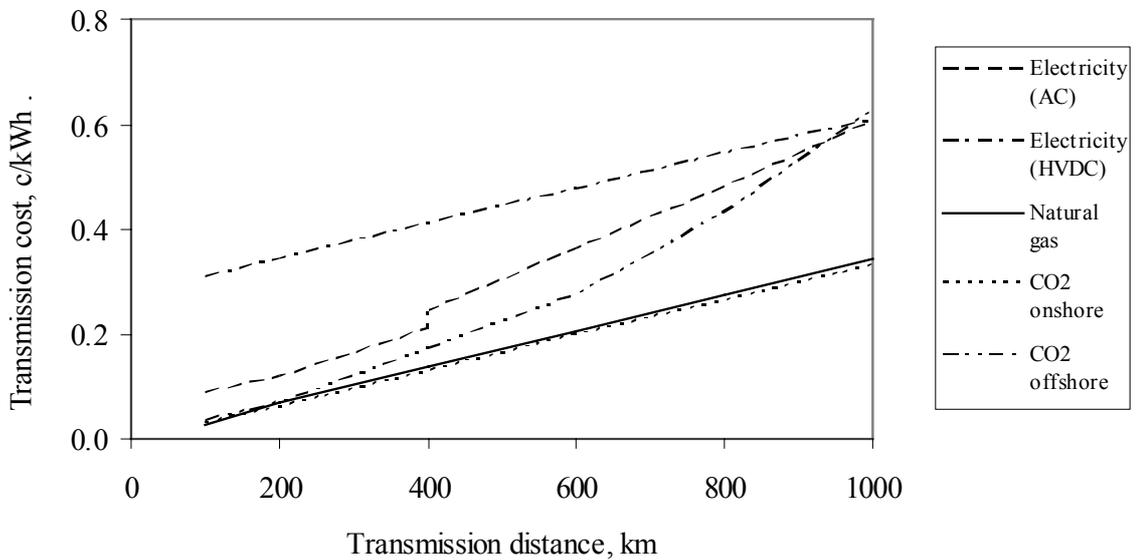


Figure 13. Costs of natural gas, CO₂ pipelines and electricity transmission lines – 5000 MWe (annual discount rate 10%, a plant life 25 years, and an operating load factor of 90%) [45].

7 PROGRAMMES, PROJECTS AND ACTIVITIES IN SELECTED COUNTRIES

CO₂ capture and storage technologies and concepts are mainly being developed in the following programmes and countries:

- Joint Industry Carbon Capture Project
- IEA GHG R&D Programme
- EU funded projects
- USA (DOE, NETL, MIT)
- Japan (NEDO, RITE)
- Norway (Klimatek, Sintef, NTNU)

7.1 JOINT INDUSTRY CARBON CAPTURE PROJECT (CCP)

The Joint Industry Carbon Capture Project is formed by BP together with several large energy companies. The goal of the project is to develop breakthrough technologies that enable cost effective CO₂ capture from large combustion sources and safe storage of CO₂ in geological formations. The goal is to reduce the costs for CO₂ capture and storage in geological formations by 50% when applied to retrofit and 75% when applied to new build applications compared with current best available technology.

The technology development program focuses on the following areas:

- CO₂ capture - pre-combustion, post-combustion and oxyfuels. This area will account for approx. 70% of the project budget.
- Sequestration - measurement and verification of CO₂ injected, and principles and risks of maximising the volume of CO₂ stored in geological formations. This area will account for approx. 20% of the project budget.
- Economic model - can be applied to compare the different technologies. This area will account for approx. 10% of the project budget.

The project budget is 28 million US\$ over 3 years. Funding is provided by participating companies, EU (0.41 million US\$), US DOE (5 million US\$) and the Norwegian government (under discussion).

The technologies will be evaluated and the most promising ones will be developed to the "proof of concept" stage by 2003. At completion of the R&D phase at the end of 2003, the decision will be made to proceed to demonstration of the most promising technologies. Following demonstration phase large-scale implementation could begin in 2006 after confirmation of the cost and operating performance.

By beginning of 2002 following contracts with CO₂ capture concept and technology developers have been made [4]:

- Pre-combustion
 - CaO-CaCO₃ Cycle for H₂ fuels
 - Technology provider is Institute for Energy Technology (IFE)
 - Cofunded with Norway
 - Work location is Norway/UK
- Post combustion
 - MHI Amine Scrubbing/Membrane Contactor
 - Technology providers are Norsk Hydro, MHI and BP
 - Cofunded with Norway
 - Work location is Norway

CCP has several contracts for CO₂ geological storage research. Issues under investigation include for example risk assessments, material questions, basin modelling and monitoring, geochemistry and legal aspects.

7.2 IEA GHG R&D PROGRAMME

IEA GHG was established in 1991 and, since then, its main focus has been on capture and storage of CO₂. It is an international collaboration of governments and industries from many countries, with the following objectives:

- To identify and evaluate technologies that could be used to reduce the emissions of greenhouse gases arising from the use of fossil fuels
- To disseminate the results of evaluations
- To identify targets for research, development and demonstration, and promote the appropriate work.

IEA GHG programme has produced numerous reports on CO₂ capture and storage concepts and technologies during its first three completed phases and additional studies are planned in the ongoing fourth phase.

IEA GHG Programme participates also to other demonstration and information dissemination activities. The ones related to CO₂ capture and storage concepts and technologies are:

- O₂/CO₂- recycle combustion project (Canada)
- CO₂ Capture network
- Precombustion Decarbonisation (PCDC) power generation
- NGGAS (a European part of CCP)
- Sleipner Aquifer CO₂ Storage Project SACS (see chapter 7.3).
- NASCENT – Natural Analogs for the Geological Storage of CO₂ (see chapter 7.3)
- Enhancement recovery of coal bed methane with CO₂ sequestration, Alberta project (see chapter 7.5)
- CO₂ used for enhanced oil recovery (EOR) in the Weyburn field (see chapter 7.5)

Every second year the GHGT conference is organised by the IEA GHG Programme. GHGT-5 was held in Cairns, Australia, in 2000 and GHGT-6 will be held in 2002 in Kyoto, Japan. The proceedings of the GHGT conferences are one of the main sources of information on advances in the field of CO₂ capture and storage concepts and technologies.

In addition to CO₂ capture and storage technologies IEA GHG Programme examines a wide range of other technologies, which makes it possible to put into perspective the potential of capture and storage of CO₂ [46].

7.3 PROJECTS FUNDED BY EU

In the 6th framework of EU, fossil fuels are considered only with respect to GHG emissions, i.e. applying CO₂ capture to a power plant. CO₂/O₂ concepts and integration of CO₂ capture with IGCC technology was studied in EU's Joule Programme 1992 - 1995. CO₂ capture technologies and CO₂ utilisation have been recently evaluated in the RUCADI- project [9]. The EU funds also BP's Carbon Capture Project (NGGAS). NGGAS focuses on geological storage of CO₂. Some technology development projects such as AZEP (Advanced Zero Emission Power Plant) and development of chemical looping combustion technology are also funded in the 5th Framework Programme [47].

SACS 1 & 2 (Saline Aquifer CO₂ Storage) are EU funded projects managed by Statoil. The other industrial partners are BP Amoco, Mobil, Norsk Hydro, Saga and Vattenfall. SACS 1 was completed in 1999 and SACS II will end in 2005. The project cost of SACS II is 3.03 million €. Beginning in 1996, 1 million tonnes of CO₂ per year has been stored at the Statoil operated Sleipner Field in the North Sea. This is the first case of industrial scale CO₂ storage in the world. Being the first case, careful monitoring is necessary of the behaviour of the CO₂ storage facility - a thick saltwater-bearing sandstone at a depth of approximately 1 kilometer, called the "Utsira" formation, of Miocene age. Data will be collected to model and verify the distribution of the CO₂ 'bubble' for three years, and demonstrate prediction methods for the destiny of the CO₂ for many years into the future. The new seismic survey of the Utsira formation after 5 years of injection of CO₂ was successfully completed in September 2001. The seismic survey was undertaken by the "GECO Diamond" survey. The project will also provide scientific documentation of CO₂ storage as a method, which may be applied in other geographical areas and by other industries such as power generation. With national resource authorities, the project will develop a first draft of a "Best Practice Manual" [48].

The NASCENT project will study natural occurrences of CO₂ within Europe to assist in developing knowledge of the long-term fate of CO₂ in geological reservoirs. NASCENT will focus on the safety and stability of CO₂ storage as well as identifying possible environmental affects should leakage occur. The project co-ordinator is the British Geological Survey. The project partners come from Germany, France, Greece, Hungary, The Netherlands, and Italy. The project budget is 3.29 million euros and it will expire in 2005 [49].

GESTCO (GEological STorage of CO₂) is a joint research project conducted by 8 national geological surveys (Denmark, The Netherlands, Belgium, Germany, Norway, France, Greece, and UK). The prime contractor is Geological Survey of Denmark and Greenland. The project will study the distribution and coincidence of thermal CO₂ emission sources and location/quality of geological storage capacity in Europe. The geological storage potential will be studied in selected areas:

1. Onshore/offshore saline aquifers with or without lateral seal.
2. Low enthalpy geothermal reservoirs.
3. Deep methane-bearing coal beds, and abandoned coal and salt mines.
4. Exhausted or near exhausted hydrocarbon structures.

The project cost is 3.8 million euros and it will expire at the end of 2002.

7.4 USA

In the USA, carbon capture and storage technologies and concepts are developed in U.S Carbon Sequestration programme managed by the DOE's Office of Fossil Energy (FE). In FY 2001 the budget of Carbon Sequestration program was 18.7 million US\$ and in 2002 32.2 million US\$. For FY 2003 it was proposed to increase funding to 54.0 million US\$. The Carbon Sequestration programme is implemented by the National Energy Technology Laboratory (NETL).

One of the five R&D pathways of the programme is CO₂ separation and capture. There are two primary goals: 1) reduce CO₂ capture costs for existing plants by 75%; and 2) reduce CO₂ capture costs from new plants by 90%. There are five major research thrusts [7]:

- Pre-Combustion Decarbonisation
- Oxygen-Fired Combustion
- Post-Combustion CO₂ Capture
- Advanced Integrated Capture Systems
- Crosscutting Science and Technology.

Some projects related to CO₂ separation and capture in the Carbon Sequestration Program are [50, 51]:

- ***A Novel CO₂ Separation System:*** The aim is to develop the Sorbent Energy Transfer System (SETS (= CLC)) in which gasified coal or natural gas is used to reduce a metal-oxide sorbent, thereby producing steam and high-pressure CO₂. The steam condenses in a heat-recovery steam generator, and the CO₂ is compressed and sequestered. The metal oxide sorbent is treated in a secondary reactor, where the reduced metal is oxidised in air and recycled. Sorbent materials with desirable properties will be developed and tested, and the economics and emissions performance of integrated electricity generation systems based on the various sorbents will be estimated. The project schedule was 9/1998-3/2001 and budget

550 000 US\$ (100 % DOE funding). [TDA Research, Inc. Louisiana State University]

- **Research Needs for CO₂ Capture from Flue Gas by Aqueous Absorption/Stripping:** The aim of the study is to identify research needs for technology to capture CO₂ from conventional coal-fired power plants. The focus is on alkanolamine absorbents. The promoted carbonate scrubbing is included, but physical absorption excluded. The project schedule was 9/1999-9/2000 and budget 49 000 US\$ (100 % DOE funding). [University of Texas at Austin]
- **Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents:** The aim is to develop a CO₂ separation technology that uses a regenerable, sodium-based sorbent to capture CO₂ from flue gas. Thermodynamic analysis and preliminary laboratory tests indicate that the technology is viable. Process data will be collected to assess the technical and economic feasibility of various process configurations. This retrofit process is amenable to all conventional steam-generating power plants. The project schedule is 8/2000-2/2003 and budget 1 050 900 US\$ (DOE's share 812 300 US\$) [Research Triangle Institute, Church and Dwight, Inc.]
- **Recovery and Sequestration of CO₂ from Stationary Combustion Systems by Photosynthesis of Microalgae:** The project studies the characteristics of CO₂ supply from fuel combustion systems, selection of microalgae, optimisation and demonstration of industrial scale photobioreactor, carbon sequestration system design and performs economic analysis for the proposed process. The project schedule is 9/2000-10/2003 and budget 2 360 000 US\$ (DOE's share 1 680 000 US\$) [Physical Sciences, Inc.]
- **CO₂ Capture Project:** This integrated collaborative technology development project aims at proving the feasibility of advanced CO₂ separation and capture technologies. The team will develop an economic model to compare different approaches and will also develop guidelines for safe CO₂ storage in underground formations. The project schedule is 7/2001-11/2004 and budget 9 994 000 US\$ (DOE's Share 4 995 000 US\$) [BP, Anchorage, AK]
- **Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers:** The goal is to determine if CO₂ can be recovered at a cost of \$10/t CO₂ avoided in existing or newly constructed CFB combustor while burning petroleum coke, coal or biomass fuels with a mixture of oxygen and recycled flue gas. Seven cases including one baseline case for CFB combustion will be evaluated. The project schedule is 9/2001-10/2004 and budget is 1 996 500 US\$ (DOE's share 1 598 000 US\$) [ABB Power Plant Laboratory]
- **Engineering Feasibility and Economics of CO₂ Sequestration/Use on an Existing Coal Fired Power:** In this study technical and economic assessment of retrofitting an existing coal fired power plant with systems capable of significant CO₂ reduction is made. Three options (CO₂ separation, O₂/CO₂ combustion and Oxygen Removal and CO₂ Separation by tertiary amines) will be studied. The project schedule was 8/1999-6/2001 and budget 649 000 US\$ (DOE's share 250 000 US\$) [Alstom Power, Inc.]
- **CANMET CO₂ Consortium- O₂/CO₂ Recycle Combustion:** The aim is to conduct pilot-scale tests of oxygen enhanced coal combustion with the objective of lowering the cost of retrofit systems. [CanMet Energy Technology Center, and a consortia of

industrial companies including McDermott Technology, Trans Alta Corp., Saskatchewan Power, Air Liquide Canada, Nova Scotia Power, Ontario Power Generation, and Edmonton Power]

- **Thermally Optimized Membranes:** Manufacture a high-temperature polymer membrane with better separation capabilities than current polymer membranes. The project focuses on the separation of CO₂, methane, and nitrogen gases in the range of 100 to 400 °C. [*Los Alamos National Laboratory, University of Colorado, Idaho National Energy and Environmental Laboratory, Pall Corporation, and Shell Oil*]
- **CO₂ Selective Ceramic Membrane for Water-Gas-Shift Reaction with Simultaneous CO₂ Recovery:** Develop a high temperature CO₂-selective membrane to enhance the water-gas-shift reaction efficiency, while recovering CO₂ for sequestration. The improved membrane is ideally suited to integrated gasification combined-cycle power generation systems. [*Media and Process Technology Inc., University of Southern California*]
- **Vortex Tube:** Conduct a laboratory scale study of CO₂-liquid absorption kinetics, solvent-regeneration requirements, and scale-up parameters for vortex contactors. In a vortex contactor, solvent and gas are injected under high pressure into a tubular reactor. They expand and accelerate to create a cylindrical flow of fine mist down the tube, enhancing capture of the gas in the solvent. [*Idaho National Engineering and Energy Laboratory, Pacific Gas & Electric, Southern California Gas, BP, and Purdue University*]
- **CO₂ Hydrates:** Develop a process that captures CO₂ by combining it with water at low temperature and high pressure, thus forming CO₂/water hydrates, ice-like macromolecular structures of CO₂ and water. Laboratory experiments seek to determine the level of CO₂ removal achievable, measure energy requirements, and assess any negative effects attributable to hydrogen sulfide and methane gases. [*Los Alamos National Laboratory, Nexant, Inc. (A Bechtel Technology and Consulting Firm), Simteche*]
- **Recovery of CO₂ in Advanced Fossil Processes Using a Membrane Reactor:** Construct an inorganic, palladium-based membrane device that reforms hydrocarbon fuels to mixtures of hydrogen and CO₂ and separates high-value hydrogen. The hydrogen can be used to power fuel cell systems or advanced turbine power systems. The remaining gas, predominantly CO₂, can be recovered in compressed form. [*Research Triangle Institute*]
- **Advanced Oxy-fuel Boilers and Process Heaters:** Develop a novel oxy-fuel boiler to reduce the complexity of CO₂ capture. [*Praxair, Inc., Tonawanda, NY*]

There are four primary goals for U.S. R&D in geological storage of CO₂: 1) develop reliable monitoring, verification and mitigation technology for geologic formations; 2) demonstrate the environmental acceptability of underground storage in diverse geologic settings; 3) understand the behaviour and assure the predictability of CO₂ in geologic storage; and 4) develop field practices that lower the cost of storage and ensure formation integrity [7].

The GEO-SEQ Project is a public-private R&D partnership sponsored by the U.S. DOE and will take place from 2000 - 2003. The overall goals of the project are to lower the cost of geologic sequestration, lower the risk of geologic sequestration; and decrease the

time of implementation. The GEO-SEQ- project team is carrying out the four coordinated and inter-related applied R&D tasks, which include 1) development of co-optimisation techniques for value-added sequestration technologies, 2) identification and evaluation of monitoring technologies and approaches, 3) improvement of reservoir models for prediction the performance of sequestration, and 4) improvement of the methodology and information available for capacity assessment. The technologies for monitoring sequestration of CO₂ in geologic formations will be evaluated in three pilot test sites of industry partners. These include the Lost Hills Oil Field (Chevron) in the Central Valley, California, the Vacuum Oil Field (Texaco) near Hobbs, New Mexico, and the Weyburn Field (Pan Canadian Resources) near Regina, Saskatchewan. The research is carried out by three of U.S. DOE's national laboratories (Lawrence Berkley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL) and Oak Ridge National Laboratory (ORNL)), Stanford University, Texas Bureau of Economic Geology (TBEG), Alberta Research Council (ARC), and TNO Institute of Applied Geosciences [52].

In addition to GEO-SEQ project there are several active projects on CO₂ storage. Some of them are listed below [53].

- **Large Scale CO₂ Transportation and Deep Ocean Sequestration:** To demonstrate the techno-economic viability of large-scale carbon dioxide transportation and deep ocean sequestration. [*McDermott Technology, Inc. (MTI-OH)*]
- **Geologic Sequestration of CO₂ in Deep, Unmineable Coalbeds:** Demonstrate N₂/CO₂ - ECBM and CO₂ sequestration process in deep, unmineable coalbeds on a commercial scale using existing recovery technology to evaluate the viability of storing CO₂ in the San Juan Basin. [*Advanced Resources Internaitonal, B-P Amoco, and Shell Oil*]
- **Maximizing Storage Rate and Capacity and Insuring the Environmental Integrity of Carbon Dioxide:** Develop a methodology to determine the suitability of a particular geologic formation with a novel well-logging technique using nuclear-magnetic resonance (NMR). [*Texas Tech. University*]
- **Reactive, Multi-phase Behaviour of CO₂ in Saline Aquifers Beneath the Colorado Plateau:** To investigate the chemical behaviour of CO₂ currently stored in saline aquifers beneath the Colorado Plateau. This region contains numerous natural CO₂ fields, which are presently in production, with most CO₂ (25 Mt/year) being piped 800 km to EOR projects in Texas. [*University of Utah*]
- **Geologic Screening Criteria for Sequestration of CO₂ in Coal:** Quantifying Potential of the Black Warrior Coalbed Methane Fairway, Alabama: Develop a screening model that is widely applicable, quantify CO₂ sequestration potential in Black Warrior CBM fairway, and apply screening modeling to identify favourable demonstration sites for CO₂ sequestration. [*Geological Survey of Alabama*]
- **Sequestration of Carbon Dioxide Gas in Coal Seams:** To evaluate the effectiveness and economics of carbon sequestration in an unmineable coal seam. Directional drilling methods will be employed to develop a grid of horizontal holes within an unmineable seam of coal. The project will involve development of a 7 524 000 m² area involving two coal seams. [*CONSOL inc.*]

- **Natural Analogs for Geologic Sequestration:** To document empirically - both to the scientific community and the public at large - the capability of depleted oil and gas fields to technically and economically sequester CO₂ safely and securely. [*Advanced Resources International*]
- **Sequestration of CO₂ in a Depleted Oil Reservoir – LANL:** The use of a comprehensive suite of computer simulations, laboratory tests, field measurements and monitoring to understand, predict and monitor the coupled geomechanical, geochemical and hydrogeologic processes associated with downhole injection of CO₂ into a depleted oil reservoir. [*Los Alamos National Laboratory*]
- **Sequestration of CO₂ in a Depleted Oil Reservoir:** The joint government-industry project is focused on a field/laboratory effort using a comprehensive suite of computer simulations, laboratory tests, field measurements and monitoring to understand, predict, and efficiently monitor the coupled geomechanical, geochemical, and hydrogeologic processes associated with downhole injection of CO₂ into a depleted oil reservoir. [*Sandia National Laboratories*]
- **CO₂ Sequestration by Mineral Carbonation Using a Continuous Flow Reactor:** The development of a continuous reactor for aqueous-based mineral carbonation process. Several different reactor systems will be investigated, such as conventional continuous-flow stirred autoclaves and pipe-line reactors. [*Albany Research Center*]

A carbon separation and capture technology roadmap is presented in Table 10 and a CO₂ geologic sequestration roadmap in Table 11.



Table 10. A carbon separation and capture technology roadmap.

Research Thrust	Barriers and Issues	Technology Opportunity	Technology Targets	Outcomes
Pre-Combustion Decarbonization Capture CO ₂ from the decarbonization processes	<ul style="list-style-type: none"> Existing capture technologies operate at too low a temperature. Syngas must be cooled down and often reheated, increasing cost and reducing efficiency Often more economic to combust syngas before full shift, reducing the portion of CO₂ captured 	<ul style="list-style-type: none"> Chemical sorbents Physical sorbents CO₂-selective membranes Hybrid sorbent/membrane systems Membranes that both shift CO and separate CO₂/H₂ 	<ul style="list-style-type: none"> Establish pilot-scale test capability 2005 Complete pilot-plant testing of promising technologies 2006 Initiate cost-shared precommercial test 	<ul style="list-style-type: none"> Efficient, low-cost electricity and hydrogen production from fossil fuels with low GHG emission
Oxygen-Fired Combustion Burn fuels in enriched air or pure oxygen to produce a concentrated stream of CO ₂	<ul style="list-style-type: none"> Oxygen from cryogenic air separation is expensive and oxygen combustion consumes 4.5 times more oxygen than gasification Combustion temperature is too high for existing boilers of turbine materials. CO₂ recycle increases parasitic load. 	<ul style="list-style-type: none"> O₂- selective membranes Advanced cooling cycles Compact boilers and turbines that operate at high temperature and pressure 	<ul style="list-style-type: none"> 2003 Establish pilot-scale test capability 2002 Complete studies of advanced boiler designs for oxygen-enriched air firing 2005 Complete pilot-plant testing of promising technologies 2006 Initiate cost-shared precommercial scale test 	<ul style="list-style-type: none"> Commercially viable options for retrofit/repower of existing fossil fuel conversion systems to reduce emissions of CO₂ per unit of power or other products by 80 % or more
Post-Combustion Capture Capture CO ₂ from the flue gas of an air combustion system	<ul style="list-style-type: none"> CO₂ is dilute in flue gas, requiring large gas handling systems Non-CO₂ flue gas components adversely affect available separation technologies 	<ul style="list-style-type: none"> Chemical sorbents Physical sorbents CO₂-selective membranes Hybrid sorbent/membrane systems Gas/Liquid contactors 	<ul style="list-style-type: none"> 2003 Establish pilot-scale test capability 2005 Complete pilot-plant testing of promising technologies 2005 Complete proof-of-concept testing of promising technologies 2006 Initiate cost-shared commercial scale power plant testing 2008 Cost-shared power plant retrofit which advanced CO₂ capture technology 	
Advanced Integrated Capture	<ul style="list-style-type: none"> Limited number of promising approaches identified Lack of experimental data 	<ul style="list-style-type: none"> Chemical looping combustion 	<ul style="list-style-type: none"> 2005 Laboratory-scale testing of promising advanced concepts 	<ul style="list-style-type: none"> New concepts to broaden scope of cost-effective CO₂ capture
Crosscutting Science and Technology Enable synergistic advances between CO ₂ control and other systems	<ul style="list-style-type: none"> Available CO₂ capture technologies exhibit poor selectivity and/or cause significant loss of temperature and pressure Decreased efficiency and resulting increase in resource consumption 	<ul style="list-style-type: none"> Heat and pressure integration with other system components Integration/combination with other emission control Hybrid oxyfuel/post combustion capture systems Coordination of R&D efforts with related international activities 	<ul style="list-style-type: none"> 2006, 2008, 2010 Respectively provide enabling science and technology base for the above pathways 2006 Develop analysis and modelling capabilities to enable optimization of integrated systems 	<ul style="list-style-type: none"> Complete integration of CO₂ capture into advanced fossil fuel conversion



Table 11. A geologic sequestration roadmap.

Research Thrust	Barriers and Issues	Technology Opportunity	Technology Targets	Outcomes
1. Monitoring, Verification and Mitigation Technology	<ul style="list-style-type: none"> Monitoring and verification of CO₂ storage with monitor wells is costly Time-lapse seismic approaches cannot detect concentrations of CO₂ Inadequate understanding of equilibria between multi-component gases, oil, and water 	<ul style="list-style-type: none"> Tracers that can be reliably monitored from the subsurface and surface High resolution methods for identifying concentration of CO₂ Development of low-cost, near surface technology for presence of CO₂ Subsurface and near surface geologic models of storage areas Migration and flow modeling of CO₂ in storage reservoir, underlying aquifer, and overlying sediment 	<ul style="list-style-type: none"> Affordable indirect monitoring technology acceptable to permitting agency by 2006 Low-cost, direct CO₂ monitoring technology acceptable to permitting agency by 2008 Reservoir monitoring field test, with modeling plus indirect and direct detection by 2010 	<ul style="list-style-type: none"> Reliable monitoring and verification technology builds confidence in operation of geologic storage
Mitigation Technology	<ul style="list-style-type: none"> Mitigation technology for CO₂ leakage not currently available 	<ul style="list-style-type: none"> Intelligent, self activating control systems Coupled subsurface, land surface, and atmospheric models of CO₂ migration and dispersion 	<ul style="list-style-type: none"> Coupled flow and dispersion models by 2008 Field tested CO₂ leakage mitigation technology by 2012 	<ul style="list-style-type: none"> Real-time mitigation technology reduces risks of geologic storage
2. Health, Safety and Environmental Risk Assessment				
Data and Methodology	<ul style="list-style-type: none"> HSE risk assessment methodology for geologic storage does not exist Database for HSE risk assessment is lacking Natural seismic events with effects on storage integrity are difficult to anticipate 	<ul style="list-style-type: none"> Adaptation of risk assessment methodology from natural gas storage and oilfield waste injection to geologic storage of CO₂ Define performance standards for geologic storage of CO₂ Identify safe and acceptable CO₂ leakage rates appropriate to each geologic setting Comprehensive studies of natural CO₂ reservoirs and gas storage fields Integrated studies of natural seepage of CO₂ with reservoir simulation and basin modeling Safe cost-effective CO₂ storage field development and operating practices 	<ul style="list-style-type: none"> HSE risk assessment methodology for geologic storage acceptable to permitting agency by 2004 National and regional HSE databases by 2006 	<ul style="list-style-type: none"> Risks of geologic storage of CO₂ are well understood
Natural and Operating Analogs	<ul style="list-style-type: none"> Lack of long term data on interactions of CO₂ and storage reservoirs No data on stress related changes to integrity of caprock and reservoir Limited experience with CO₂ storage field operations 		<ul style="list-style-type: none"> 'Best practices' development and operations manual by 2004 Comprehensive study of natural CO₂ fields by 2006 Integrated natural CO₂ seepage and modeling studies by 2007 	<ul style="list-style-type: none"> Public confidence with geologic storage is greatly enhanced



Research Thrust	Barriers and Issues	Technology Opportunities	Technology Targets	Outcomes
3. Knowledge Base and Technology for CO₂ Storage Reservoirs				
Depleted and Near-Depleted Oil and Natural Gas Reservoirs	<ul style="list-style-type: none"> Conflicts between optimizing recovery of oil and maximizing long-term storage of CO₂ Reluctance of industry to consider storage of CO₂ in depleted gas reservoirs Long-term effects of CO₂ on reservoir properties not well understood Natural seepage of gases from reservoirs not quantified 	<ul style="list-style-type: none"> Studies of long-term CO₂ flow and migration in hydrodynamic formations Modeling and testing for maximizing long-term storage of CO₂ with enhanced oil and gas recovery Geochemical research of effects of CO₂ on caprock integrity and reservoir properties Geomechanical research on effects of stress on reservoir seal integrity Geologic database on caprock and overlying strata 	<ul style="list-style-type: none"> Field demos of CO₂ storage in oil reservoirs by 2005 Geologic and reservoir properties database by 2006 Validated geochemical models by 2007 Feasibility of CO₂ storage and enhanced gas recovery by 2008 	<ul style="list-style-type: none"> Technology in place for use of oil and gas reservoirs for long-term storage of CO₂ with incremental production of oil and natural gas
Deep Coal Seams	<ul style="list-style-type: none"> CO₂/N₂ flow and storage in coals not well defined Uncertain effects of CO₂ on coal reservoir permeability Competition from using N₂ rather than CO₂ for ECBM Lack of criteria for identifying favourable coal formations 	<ul style="list-style-type: none"> Laboratory tests and reservoir modeling studies of injection of CO₂/N₂ mixtures Laboratory modeling studies of swelling behaviour in domestic coals Alternative injection well configurations and procedures for maximizing CO₂ injection Screening criteria and models for matching coal storage sites with CO₂ sources 	<ul style="list-style-type: none"> Validated models of CO₂ storage in deep coal reservoirs by 2003 Effects of CO₂ on major coal types by 2004 Site selection criteria and screening models by 2005 Field demos on maximum CO₂ storage in coal seams by 2008 	<ul style="list-style-type: none"> Coal seams established as feasible CO₂ storage reservoir with incremental production of natural gas
Saline Aquifers	<ul style="list-style-type: none"> Limited data on reservoir properties and capacity lack of data on CO₂ vertical and lateral migration Inadequate data on solubility and mineral trapping in brine systems Limited field experience 	<ul style="list-style-type: none"> National geologic and reservoir properties databases for saline aquifers CO₂ flow modeling for diverse brine-chemical-mineral systems Horizontal and multi-lateral wells for improved injectivity of CO₂ 	<ul style="list-style-type: none"> CO₂/fluid interactive studies by 2004 Verified geochemical and flow models by 2005 National database by 2006 Field demos of aquifer storage by 2010 	<ul style="list-style-type: none"> Large, regionally diverse geologic storage capacity becomes available
Novel Storage Reservoirs	<ul style="list-style-type: none"> Limited understanding of feasibility and storage capacity of potential storage reservoirs (e.g., gas shales, below basalt) 	<ul style="list-style-type: none"> Identify, characterize and test novel geologic settings for CO₂ storage and 'value-added' hydrocarbon production 	<ul style="list-style-type: none"> Establish feasibility and capacity of organically rich gas shale reservoirs and other geologic storage options by 2008 	<ul style="list-style-type: none"> Additional CO₂ storage options become available
Crosscutting Research and Technology	<ul style="list-style-type: none"> Data on long-term cement and well completion integrity is lacking Unreliable data on location and integrity of abandoned wells Long-term corrosion effects 	<ul style="list-style-type: none"> Research on long term cement integrity national database of abandoned oil and gas wells Low-cost, reliable well abandonment technology Corrosion control and materials science research 	<ul style="list-style-type: none"> Alternative well cementing materials and procedures by 2006 Database and technology on well abandonment by 2007 Economically feasible corrosion resistant materials and mitigation procedures by 2010 	<ul style="list-style-type: none"> Integrity and safety of CO₂ transportation, injection, and storage is improved

7.5 CANADA

Canada's National Initiative on CO₂ Capture and Storage was established in 1998. It is a voluntary network of power utilities, industry, provincial governments and federal government and universities. The purpose of Initiative is sharing information, encouraging collaboration and identifying a role of CO₂ capture and storage within Canada's GHG reduction actions. One of the three working groups is CO₂ Capture, which focuses on absorption, O₂/CO₂ combustion, and membrane and cryogenic separation. The initiative does not have funding capability [54].

The Alberta Research Council, Inc. (ARC) is testing a novel process of injecting carbon dioxide into Alberta's vast deep unmineable coal beds. The project began in 1999 Phase III-A. Two micro-pilot tests were performed on the new well in the spring of 2000, one by injecting pure nitrogen and the other by injecting the exhaust from a compressor engine used for underbalanced drilling (flue gas composition 13% CO₂, 87% N₂). If Phase III-A is successful, Phase III-B, will be started, which is the implementation of an isolated 5-spot pilot with four injection wells and one production well, sized between 20 and 40 acres. The goal of the large-scale pilot is to visibly demonstrate that carbon dioxide sequestration and enhanced gas recovery is possible. ARC's partners in Phase II included Sproule International Ltd., Canadian Association of Petroleum Producers, IEA Greenhouse Gas R&D Programme, Alberta Department of Energy, Environment Canada, US Department of Energy, UK Department of Trade and Industry, Gulf Canada Resources, Burlington Resources, BP Exploration (Alaska) Inc., Suncor Energy, Canadian Fracmaster, Air Liquide Canada, TransAlta Utilities, EPCOR Utilities, Western Economic Partnership Agreement, PanCanadian Petroleum Limited, Netherlands Institute of Applied Geoscience and Mobil Oil Canada [12, 55].

The Weyburn EOR monitoring project was described in chapter 4.1.1. The Weyburn oil field is operated by PanCanadian Resources.

7.6 JAPAN

CO₂ fixation and utilisation technology is one of the three technical areas, which purpose is to develop a "new industrial technology system" in NEDO's global environment industrial technology R&D [56]. Since 1990 350 million euros governmental funding and a significant amount of private sector funding has been invested in CO₂ sequestration research. The main projects include:

- **Biological CO₂ Fixation and Utilisation Technology:** The goal of this project is to develop environmentally friendly CO₂ fixation and utilisation technology whereby CO₂ discharged into the atmosphere is reduced/controlled using microorganisms (bacteria/algae) which fix CO₂ with greater efficiency than by natural photosynthesis. Furthermore, the fixed micro-organisms will be changed into natural resource alternative materials through the developed technology (1992 - 2001).
- **CO₂ Fixation and Utilization Technology using Catalytic Hydrogenation Reactions:** This project aims at developing technology to continuously separate and

recover a large quantity of carbon dioxide from stationary sources using polymer separation membrane processes, and to produce useful substances such as methanol through hydrogenation of recovered carbon dioxide (1990 - 1999).

- **High Temperature CO₂ Separation, Fixation and Utilization Technology:** The target of this study is to develop a separation system to continuously recover hot and highly concentrated CO₂ from stationary sources in large quantities, using materials such as a ceramics separation membrane, etc. The current focus is on inorganic and composite membranes. At the same time, the study aims at identifying utilization methods for recovered CO₂ (1992 - 1999).
- **Programmed Method CO₂ Fixation and Effective Utilization Technology Development:** Identification of themes based on a survey of national and international technology developments and studies on basic technologies will be conducted (1999 - 2003).

7.7 NORWAY

The Norwegian government invests 95 million NOK and the private sector additional 64 million NOK (total 19.7 million euros) to develop technology to reduce carbon emissions from fossil fuel combustion. The funding is managed by the KLIMATEK Program. In 2001 four projects have been targeted for support [19, 57]:

- **NorCap Project (CO₂ Capture):** The project is a joint venture between Statoil and international partners. The objective is to develop and test promising technologies that can reduce the costs of separating, capturing, transporting, and storing CO₂ from the combustion of fossil fuels. The project will be active until 2003, and has a budget of 72 million NOK (8.9 million euros), of which 40% comes from KLIMATEK.
- **Power Generation with CO₂ Capture:** Project is carried out by Sintef Energiforskning AS. This project aims to improve the energy conversion of natural gas in power cycles that significantly reduce greenhouse gas emissions. The project will run until 2004, and its budget of 28 million NOK (3.5 million euros) is financed fully by KLIMATEK.
- **Future Energy Plants:** The primary objective of the project, based on work by Institute for Energy Technology and the Christian Michelsen Research group (IFE/CMR) is to develop and test a concept for co-production of electrical power and hydrogen from natural gas with integrated CO₂ capture and high overall efficiency. The project will run until 2005, and its budget is 24 million NOK (3 million euros).
- **HiOx:** Aker Technology develops HiOx ("High Oxygen") technology. A feasibility study showed that an emission-free gas fired power plant is realisable. In the next phase of the project, the technology is being further refined through development of gas turbine and a demonstration plant of about 25 - 40 MW is being planned. The project has a total budget of about 35 million NOK (4.3 million euros) and KLIMATEK is donating about 14 million NOK (1.7 million euros). The demonstration plant is expected to be operational around 2005.

8 CO₂ PRODUCTION AND UTILISATION IN FINLAND

8.1 CO₂ PRODUCTION IN FINLAND

In Finland, most of the industrial utilisation of CO₂ is covered by captured CO₂. Those capture plants are owned by Oy AGA Ab and Oy Polargas Ab.

1. In Sköldvik oil refinery of Fortum Oyj CO₂ is produced as a byproduct from hydrogen production. The capacity of the capture plant is about 30 000 tonnes of CO₂ per year.
2. In Koskenkorva plant of Primalco Oy CO₂ produced as a byproduct from alcohol production.
3. In Kokkola calciumchloride plant of Kemira Oyj CO₂ is produced as a byproduct. The capacity of the Kokkola CO₂ plant is 70 t/d.

The total capacity of the above capture plants is about 70 000 t CO₂ per year. In the year 2000, the total CO₂ production was 62 000 t [58]. Oy AGA Ab also produces carbon dioxide dry ice in Riihimäki.

In addition to capture plants, beverage industries capture CO₂ for its own use (see chapter 8.2.2). Some greenhouses produce CO₂ by burning fossil fuel (see chapter 8.2.4).

8.2 CO₂ UTILISATION IN FINLAND

In the end of the year 2000 there were 5.181 million people living in Finland. According to the Table 7 the annual consumption of CO₂ in Finland would therefore be 34 000 t/a. This figure is about half of our annual CO₂ production in capture plants and evidently too low.

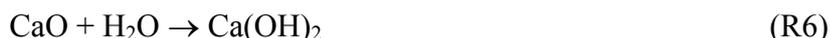
8.2.1 Pulp and paper industry

Polargas has focused on importing new gas applications to Finnish pulp and paper industry. It has been developing CO₂ applications especially for recycled paper processing. Polargas holds several patents, for example for pH control after bleaching of mechanical or deinked pulps and for wet-end pH control. The method is in use at least in Georgia-Pacific tissue paper manufacturing process in Nokia.

Oy AGA Ab has developed ways to exploit the properties of CO₂ in paper machines. UPM-Kymmene Oy has cooperated with AGA to develop a method to replace sulfuric acid by CO₂ to improve runnability of paper machine that uses deinked pulp. An application called CODIP[®] Process Improver is nowadays in use at UPM-Kymmene

Kaipola mill. Another method of AGA to improve paper machines runnability is ADALKA[®] Process Stabilizer. This has been developed in response of efforts to stabilise the pH conditions at the paper machine for optimised runnability [58].

Paper industry uses precipitated calcium carbonate (PCC, CaCO₃) as a paper pigment. In Finland, PCC production is usually integrated to a pulp and paper mill. CO₂ needed in the process is captured from flue gases of an integrate. The chemistry of PCC production may be summarised as follows:



Calcium oxide is produced by calcination of limestone, which produces CO₂. As a result, the net CO₂ balance is zero.

The PCC production plants in Finland are situated in Lappeenranta, Myllykoski, Tervakoski, Äänekoski, Imatra, Kuusankoski and Kemi. About 400 000 – 500 000 tonnes annual production of PCC in Finland utilises approximately 200 000 tonnes of CO₂ per year [59, 60].

8.2.2 Beverage carbonation

Finland's beer and soft drinks are mostly produced by three companies: Oyj Hartwall Abp, Oy Sinebrykoff Ab and Olvi Oyj. Beverages are produced in Helsinki, Lahti, Tornio and Karijoki by Hartwall, in Kerava and Pori by Sinebrykoff, and in Iisalmi by Olvi. Table 12 shows the market shares of the above companies.

Table 12. Market shares of brewery products and soft drinks in Finland in 2001 (million liters) [61].

Company	Beer	Cider	Long drink	Soft drinks	Mineral waters	Total
Oyj Hartwall Abp	182.2	27.8	11.2	141.3	30.5	376.2
Oy Sinebrykoff Ab	174.8	17.1	5.2	135.3	15.7	363.2
Olvi	50.7	6.3	0.5	20.5	13.0	93.7
PUP	0.7	0.2		0.1	0.3	1.3
Total	408.4	51.4	16.9	297.2	59.5	833.4

In the 1990's beverage sales in Finland increased from 200 million to 300 million litres. The sales of mineral waters increased from 30 million litres to 60 million litres. The maximum was reached in 1999 and in 2000 the sales had decreased a little. It may be assumed that the usage of beverages could increase to some degree, but not in the same extent as in the 1990's.

Some of the production units capture the CO₂ produced during fermentation. For example, Oy Hartwall Ab has capture plants in Lahti and Tornio. The CO₂ production capacities of these plants are 350 kg/h and 400 kg/h respectively. In 2000, the total amount of purchased CO₂ for beverage carbonation was 14 600 t [62, 63].

8.2.3 Water treatment plants

The biggest water treatment plant in Finland is the Viikki plant owned by Helsingin Vesi. It produced 85.1 mill m³ of water in 2000 and its CO₂ usage was 1768 tonnes. The second biggest water treatment plants are in Tampere and Turku, which produced 18 - 19 million m³ of water in 2000 and their CO₂ usage was about 300 tonnes. In Oulu, Jyväskylä, Pori and Kuopio the annual CO₂ usage in water treatment plants is 100 – 200 tonnes. It should be noted that CO₂ is needed only if pumped water is sweet surface water. All together, the annual CO₂ consumption of water treatment plants in Finland may be approximated to less than 4000 t/a.

8.2.4 Agriculture

In Finland, greenhouse vegetable production accounts for 60% of the cultivation area and the share of production of ornamental plants is about 40%. More than half of the vegetable production is located in Ostrobothnia (central and northern part of Finland). Ornamental plant production is more evenly distributed over the whole country. In Finland, the average size of a greenhouse company is about 1800 square metres [64].

Growing tomato utilises approximately 3 – 5 kg/h CO₂ per 1000 m² for photosynthesis [65]. However, the latest installations have CO₂ capacities up to 10 – 12 kg/h per 1000 m². For cucumber, CO₂ concentration of air should be higher (i.e. 1000 – 1200 ppm) compared to other vegetables (600 – 800 ppm). Therefore CO₂ capacities may be more than 20 kg/h CO₂ per 1000 m². Table 13 shows the cultivation area of greenhouse vegetables and ornamental plants. The total annual CO₂ usage in greenhouses is not known.

Table 13. Greenhouse cultivation area in 2000.

	Number of companies	Cultivation area, 1000 m ²
Tomato	865	1273
Cucumber	557	786
Outdoor cucumber	150	65
Head lettuce	113	321
Other vegetables ¹⁾	551	508
Rose	162	369
Other cut flowers	141	130
Others ²⁾	975	1438
Total	2695	4890

¹⁾ Without potted vegetables

²⁾ Includes potted plants and bulbous flowers

9 POTENTIAL TO REDUCE FINLAND'S GHG EMISSIONS

9.1 CO₂ EMISSIONS AND EMISSION SCENARIOS FOR FINLAND

Most of the greenhouse gas (GHG) emissions in Finland are formed from fossil fuels utilisation. The annual GHG emissions are, for example, dependent on hydro power production in the Nordic countries, demand of heating energy and the degree of economic growth. On the average, in the 1990's the total GHG emissions have grown slightly, but the annual variation has been quite large due to variation in hydro power production and imported electricity. In the year 2000, the net amount of imported electricity was 15% (12.2 TWh) of which 63% came from Sweden and 37% from Russia. In the 1996, the hydro power production was exceptionally low in Norway and Sweden. Finland became electricity exporter and therefore the GHG emissions were at its highest. Table 14 shows the variation in GHG emissions in Finland in the 1990's. In Figure 14 the variation in total hydropower production in Norway, Finland and Sweden are plotted against Finland's CO₂ emissions in power production. Figure 15 shows the amount of imported electricity to Finland and exported electricity from Finland as well as the specific CO₂ emissions from electricity production in Finland.

Table 14. Greenhouse gas emissions in Finland in 1990, 1996, 1998 and 1999, Mt CO₂-eq [66].

Mt CO₂-eq.	1990	1996	1998	1999
CO ₂				
- fuel combustion	53.9	61.2	57.4	56.8
- losses	3.5	3.5	3.5	3.5
- industrial processes	1.2	0.9	0.9	1.1
- agricultural soils	3.2	1.8	2.0	2.0
- others	0.6	0.7	0.7	0.8
Methane (CH ₄)	6.1	4.5	4.1	3.9
Nitrous oxide (N ₂ O)	8.4	7.8	7.9	7.7
Fluorinated gases (HFCs, PFCs, SF ₆)	0.07	0.09	0.26	0.38
Total	77.1	80.5	76.8	76.2
Land-use change and forestry (removals)	-23.8	-21.0	-9.7	-10.8

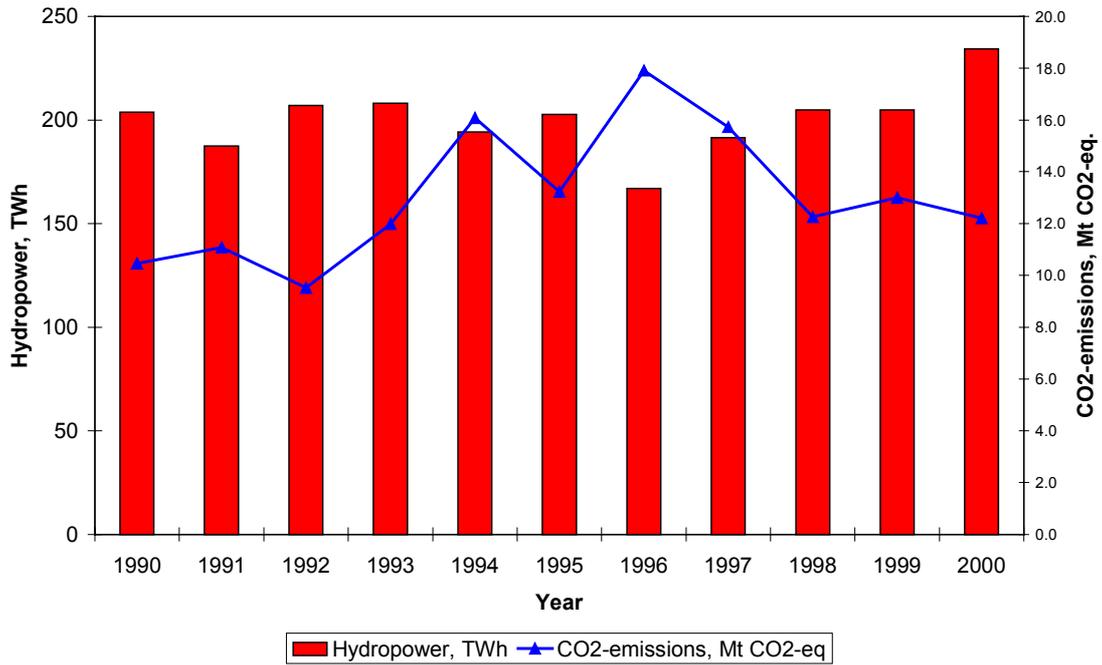


Figure 14. Total hydropower production in from 1995 to 2000 in Norway, Sweden and Finland and Finland's CO₂ emissions in power production, Mt CO₂ [67, 68, 69].

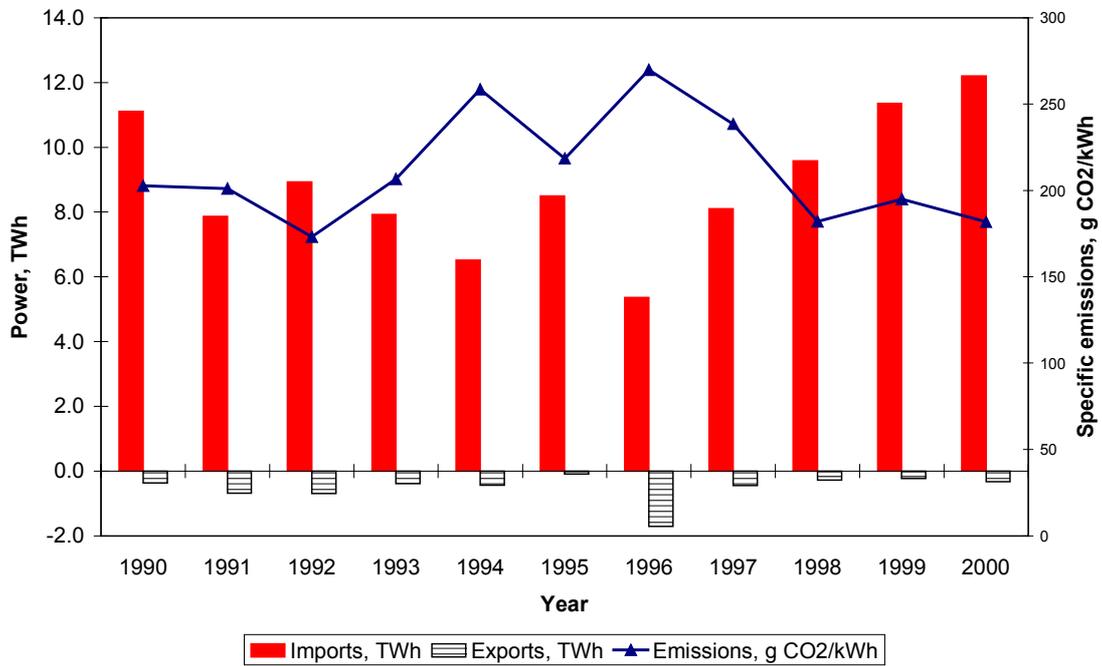


Figure 15. Finland's imports and exports of electricity as well as specific CO₂ emissions in electricity production, g CO₂/kWh [69].

Table 15 shows Finland's CO₂ emissions from fossil fuel and peat combustion without any additional measures to reduce emissions (i.e. the so-called BAU scenario) and sensitivity analyses made in terms of the development. Sensitivity analysis include:

- The growth of energy-intensive industry would be each year higher/lower by one percentage point than in the BAU (Business as Usual) scenario.
- From the year 2010 onwards, net electricity imports would be 0 or 15 TWh, when in the BAU scenario it would be 6 TWh.

Table 15. CO₂ emissions from fossil fuel and peat combustion for Finland in different baseline scenarios, Mt CO₂ [70].

Sensitivity analysis	2010	2020
BAU	69.1	74.2
BAU energy intensive industry -1%/a	73.1	83.0
BAU energy intensive industry +1%/a	65.4	66.8
BAU volume of electricity imports 15 TWh	60.8	66.3
BAU volume of electricity imports 0 TWh	74.6	79.4

9.2 THE LARGEST CO₂ EMITTING POINT SOURCES

The capture of CO₂ would be more economical in large scale. Also, environmental benefit would be bigger if large amounts of CO₂ were sequestered. For that reason, the largest CO₂ emitting point sources were evaluated. Only anthropogenic CO₂ sources have been considered.

The largest CO₂ emitting plants in Finland are oil refineries, coal burning plants for energy production and steel works. In pulp and paper industry, an increased amount of biofuels usage in energy production has decreased CO₂ emissions considerably. A map of the biggest point sources is shown in Figure 16. It should be noted that due to insufficient environmental reporting of many companies, some large CO₂ point sources might be missing. This is especially true for industrial sector. Also, some CO₂ emissions from coal fired plants are calculated and therefore may not be accurate. The data is mainly collected from companies' annual or environmental reports.

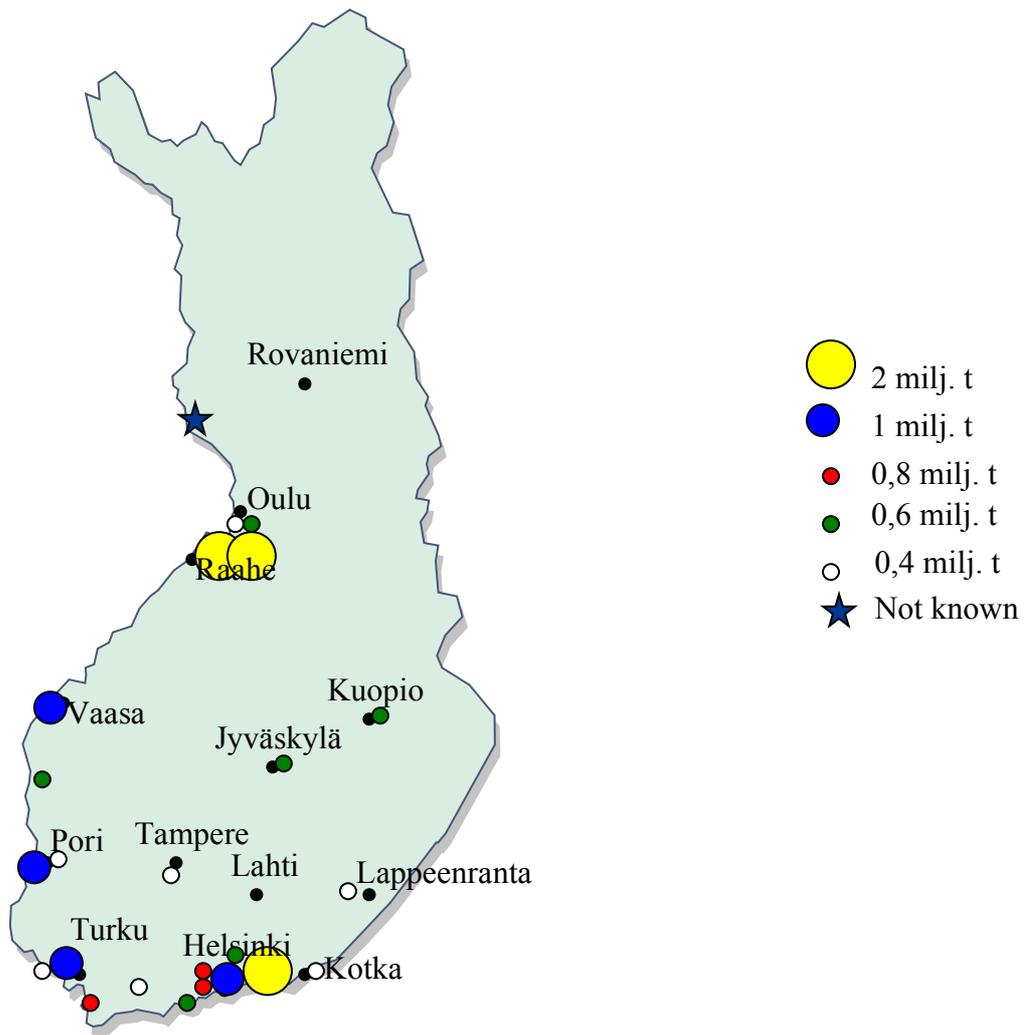


Figure 16. The largest CO₂ emitting point sources.

Table 16. CO₂ emissions from selected plants in 2000.

Plant	City	Company	Fuel	Plant type	CO ₂ , 1000 t
Energy production					
Vuosaari B	Helsinki	Helen	ng ¹⁾	CHP	1340
Vuosaari A	Helsinki	Helen	ng	CHP	321
Salmisaari	Helsinki	Helen	coal	CHP	839
Hanasaari B	Helsinki	Helen	coal	CHP	769
Suomenoja 1	Espoo	Espoon Sähkö	coal	CHP	523
Suomenoja 2	Espoo	Espoon Sähkö	ng	CHP	204
Martinlaakso	Vantaa	Vantaan energia	ng, coal	CHP	613
Naantali	Naantali	Fortum	coal	CHP	1176
Meri-Pori	Pori	Fortum, PVO	coal	cond. ³⁾	1226
Kristiina 2	Kristiina	PVO	coal	cond.	500 ⁴⁾
Vaskiluoto	Vaasa	PVO	coal	cond.	900 ⁴⁾
Tahkoluodon voima	Pori	PVO	coal	cond.	400 ⁴⁾
Toppila 1	Oulu	Oulun Energia	peat	CHP	350
Toppila 2	Oulu	Oulun Energia	peat	CHP	621
Haapaniemi I & II	Kuopio	Kuopion Energia	peat	CHP	593
Plant	City	Company	Raw material	Plant or product	CO ₂ , 1000 t
INDUSTRY					
Sköldvik	Porvoo	Fortum	raw oil	oil refining	2228
Naantali	Naantali	Fortum	raw oil	oil refining	340
Raahe	Raahe	Rautaruukki	iron	steel works	4879
Tornio	Tornio	Avesta Polarit	iron	steel works	not known
Parainen	Parainen	Finnsementti	burnt lime	cement	760 ⁴⁾

¹⁾ natural gas

²⁾ includes Martinlaakso 1, 2 and 3 plants

³⁾ condensing power plant

⁴⁾ estimated

It can be seen that all of the largest point sources are situated on coastal area. This is advantageous if we consider transporting of captured CO₂ abroad.

9.3 SELECTION OF CONCEPTS AND BASIS FOR ECONOMIC EVALUATION

The feasibility of CO₂ sequestration was evaluated for electricity production only. Integration of CO₂ capture plant to an industrial plant is discussed in chapter 3.

In CO₂ sequestration, costs are dominated by the capture of CO₂, although pressurisation for transmission is also a relatively expensive item. In Finland's case, CO₂ transmission cost is relatively high because of long transport distances.

The costs of CO₂ sequestration were estimated from Finland's perspective. As long term geological storage of CO₂ is not possible in Finland, carbon free energy production would mean that something must be transported. Long term options for CO₂ management, which were evaluated in this study, are listed below.

1. Fossil fuel is imported and electricity produced in Finland. The closest known suitable geological formations for sequestration are situated in the North Sea and the Barents Sea. The captured CO₂ must be transported there or be sequestered as a mineral carbonate in Finland. Some of the captured CO₂ may be processed into long-lived end products.
2. Carbon-free fuel, i.e. hydrogen, is imported into Finland. In this scenario, fuel is decarbonised near the storage site.
3. Electricity is produced near the sequestration place and imported into Finland. In this case, cross-border electricity transmission capacity was increased.

For comparison, the total cost of CO₂ capture, transmission and storage were included also for those cases, where CO₂ would be captured and stored abroad.

9.3.1 Power production with CO₂ capture

The starting point was that CO₂ capture would be integrated in the new condensing power plant for two reasons: 1) Existing condensing power plants in Finland would have come to the end of their lifetime before the first power plant with CO₂ capture would be built 2) there is only few data available on CO₂ capture integrated in the existing plant. Conventional natural gas combined cycle (NGCC) and pulverised coal fired once through boiler (PF) concepts were studied with and without CO₂ capture by MEA absorption. The detailed technical and economical description of the concepts are given in the IEA GHG report [23]. The conversion factor from US\$ to € was one. Summary of the results is given in Table 17.

Table 17. Key results for NGCC and PF (at 5% discount rate, natural gas cost 3.5 €/GJ and a coal price of 1.5 €/GJ, 25 a)

Process	Efficiency %(LHV)	Specific Investment (€/kW _e)	Cost of electricity (snt/kWh)	CO ₂ emission (g/kWh)	Cost of CO ₂ avoided (€/t CO ₂)
NGCC (no capture)	56	410	2.9	370	reference
NGCC + CO ₂ capture	47	790	3.9	61	32
PF (no capture)	46	1020	3.0	722	reference
PF + CO ₂ capture	33	1860	4.9	148	33

9.3.2 CO₂ transport

Only pipeline CO₂ transport was considered in this study because of lack of reliable data on ship and railway transports. If power is produced from natural gas, it may be considered that natural gas and CO₂ lines are parallel, i.e. gas goes to the other direction and CO₂ to the other. If the power plant is coal fired, also ship and railway transports could be feasible. In long offshore distances, marine transport is the only solution.

The power plants were assumed to be situated on the coastal site of Finland, like nowadays. The CO₂ trunk pipeline could be routed from south to north collecting CO₂ from several CO₂ emitting point sources. The cheapest way is to use onshore pipelines only. Below, 1000 km onshore CO₂ pipeline is assumed if it is not otherwise mentioned.

Investment and operating costs of CO₂ transmission were calculated with Microsoft Excel-based 'Energy Distribution and CO₂ Capture Cost Estimation Model' recently published by IEA GHG [45]. The model was created by Woodhill Engineering Consultants from UK. In the model, user can choose to size the pipeline and calculate the number of booster stations by using an automatic sizing routine or by setting them manually. Here, automatic sizing routine was used. The power for initial pressure boost facility is taken from power station supply, which will result in additional CO₂ emissions if power plant utilises fossil fuel. The power for booster stations of CO₂ transport is assumed to be provided from off-site (e.g. the local electrical grid) and the impact of additional CO₂ would not be assessed. The inlet pressure in the CO₂ line varied from 60 to 100 bar abs.

9.3.3 CO₂ storage

The investment and operating costs of CO₂ storage were estimated only for offshore final storage. The same calculation routine was used here also. The CO₂ storage facility includes CO₂ storage wells and CO₂ pipeline leading to the well. CO₂ injection is assumed to take place into CO₂ retaining aquifers (saline aquifers). Aquifers were assumed to be approximately 1000 m in depth. The model determines the number of wells required by user input of a ‘CO₂ rate per well’ figure. The pressure required at the top of the injection well was 80 bar abs.

9.4 RESULTS OF THE ECONOMIC EVALUATION

Figure 17 and Figure 18 show that CO₂ capture would be more economical for gas fired power plant than for coal fired power plant. For coal-based power plants the volume of the gas to be treated is higher and therefore the capital investment of the CO₂ capture plant is higher. If CO₂ transmission (1000 km, onshore) and CO₂ offshore storage are included, the production cost of electricity would be about two times higher for NGCC and about three times higher for PF compared to the current market prices of electricity in Finland.

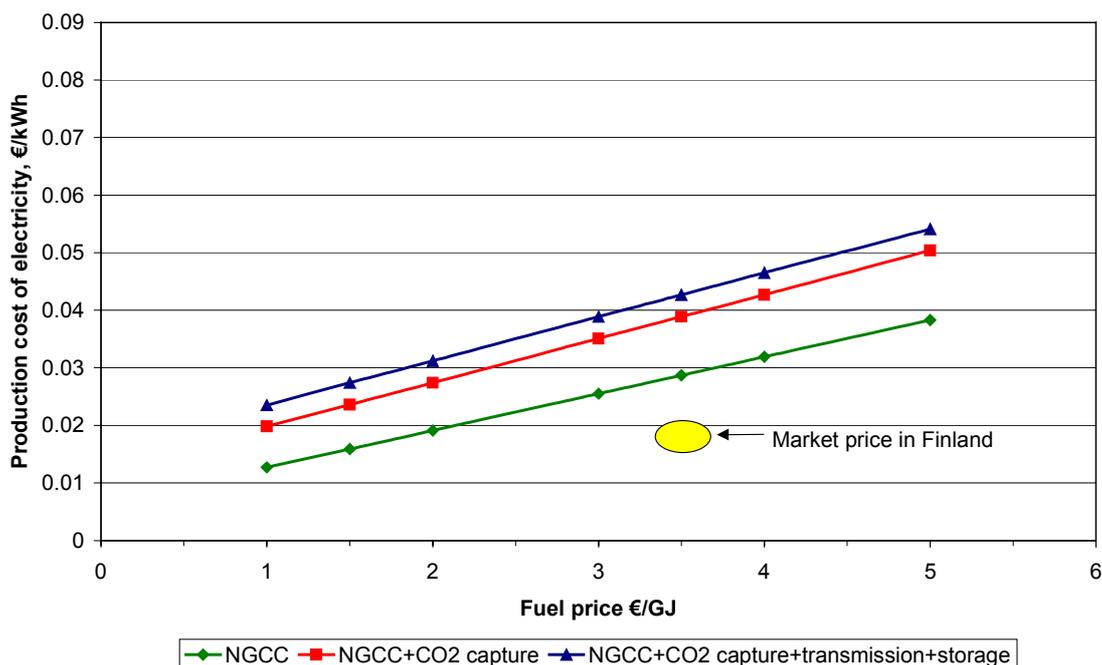


Figure 17. Fuel price sensitivity on the kWh price of gas fired power plants (5% discount rate, annual operating time 8000 h, 25 a).

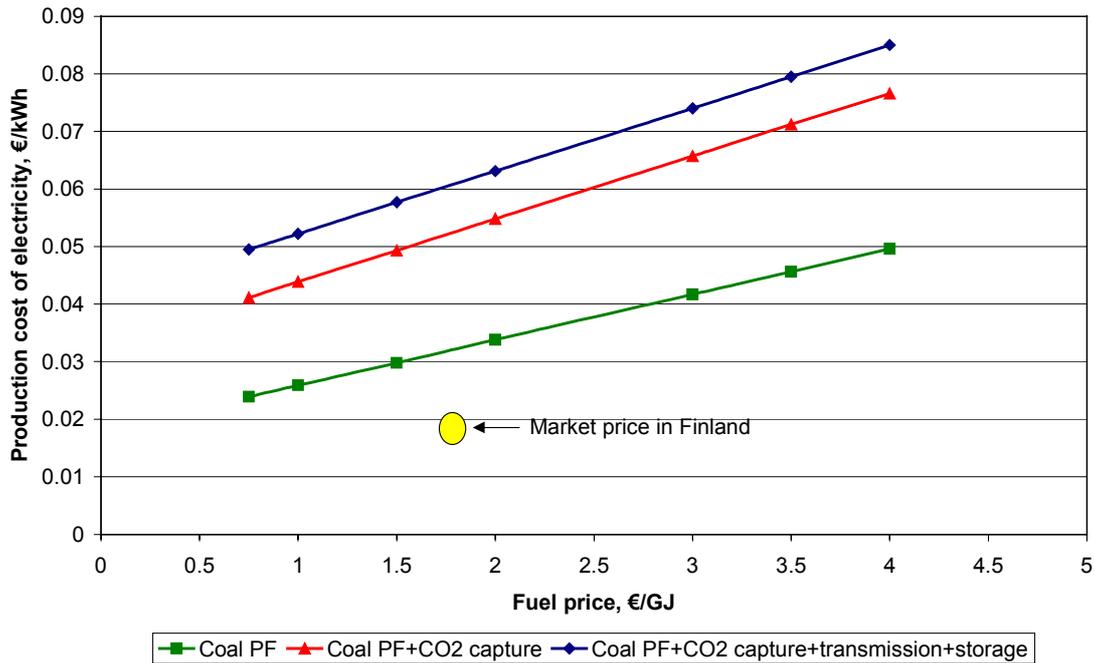


Figure 18. Fuel price sensitivity on the kWh price of coal fired power plants (5% discount rate, annual operating time 8000 h/a, 25 a).

9.5 POTENTIAL TO REDUCE FINLAND'S CO₂ EMISSIONS

Figure 19 shows the estimated CO₂ emissions of condensing coal power plants, which naturally depend on the annual operating time of the power plants. If we assume that one 500 MW_e coal condensing power plant would be replaced with a new one with a CO₂ capture system, the CO₂ reduction potential would be about 2.7 million tonnes of CO₂ with 8000 hours operating time and 80% CO₂ emission reduction. However, the problems related to the missing storage sites in Finland would be the greatest barrier for the implementation CO₂ capture processes in power plants. On the other hand, CO₂ capture from the industrial processes is already in use and new market opportunities could be found for example from the pulp and paper sector, which already uses large amounts of CO₂. Capture process in Finland's iron and steelmaking industries or oil refineries would also be potential targets for consideration.

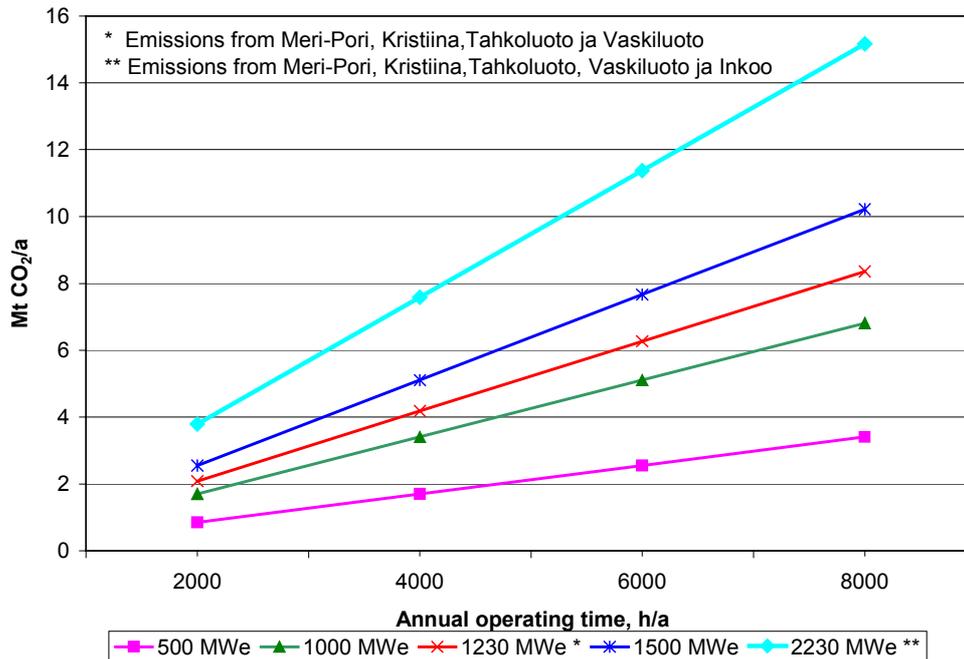


Figure 19. The approximated CO₂ emissions from the existing condensing coal power plants.

9.5.1 Three alternative scenarios for 2020

Cost and performance of the three CO₂ management options described above were calculated with the IEA CO₂ and energy transmission calculator. The model has cost and performance predictions for hydrogen production from natural gas by steam reforming and for hydrogen transport by a pipeline. Electricity production module includes combined cycle gas turbine plant with CO₂ recovery (MEA absorption, 85% CO₂ recovery). Electrical transmission system alternative included DC transmission and converter stations. Table 18 gives some input data for the three cases. The cases were calculated for 500 MW_e, 1000 MW_e and 1500 MW_e electricity use in Finland. This means that the thermal capacity of production is increased to cover losses in transmission. In all the cases, offshore pipelines and overhead electrical lines were assumed.

The results are shown in and Figure 21. The cost predictions indicate that the hydrogen scenario would be the most expensive. This is mainly due to investment cost of steam reforming unit and the cost of hydrogen transport. Compression of hydrogen has low efficiency compared to compression of CO₂ or natural gas. Investment costs of gas lines are usually expected to be two times higher for hydrogen than for natural gas (or CO₂). With 1000 km transmission distances, imported electricity seems a feasible option. Costs of electricity transmission lines might be overestimated especially for 1000 MW_e and 1500 MW_e, which would make that alternative even more feasible.

Table 18. Input data of the performance and cost predictions.

	NGCC in Finland & NG and CO₂ transmission	H₂ production abroad & H₂ transmission	NGCC abroad & electricity transmission
Technical data			
Fuel	NG	NG / H ₂	NG
Power plant - Electrical eff., %	50	50	50
NG transmission - offshore, km - onshore, km	50 1000	50 50	50 50
CO ₂ transmission - offshore, km - onshore, km	50 1000	50 50	50 50
H ₂ transmission - onshore, km		1000	
Electricity transmission - DC onshore, km - losses, %	2	2	1000 2
CO ₂ storage - well depth, m	1000	1000	1000

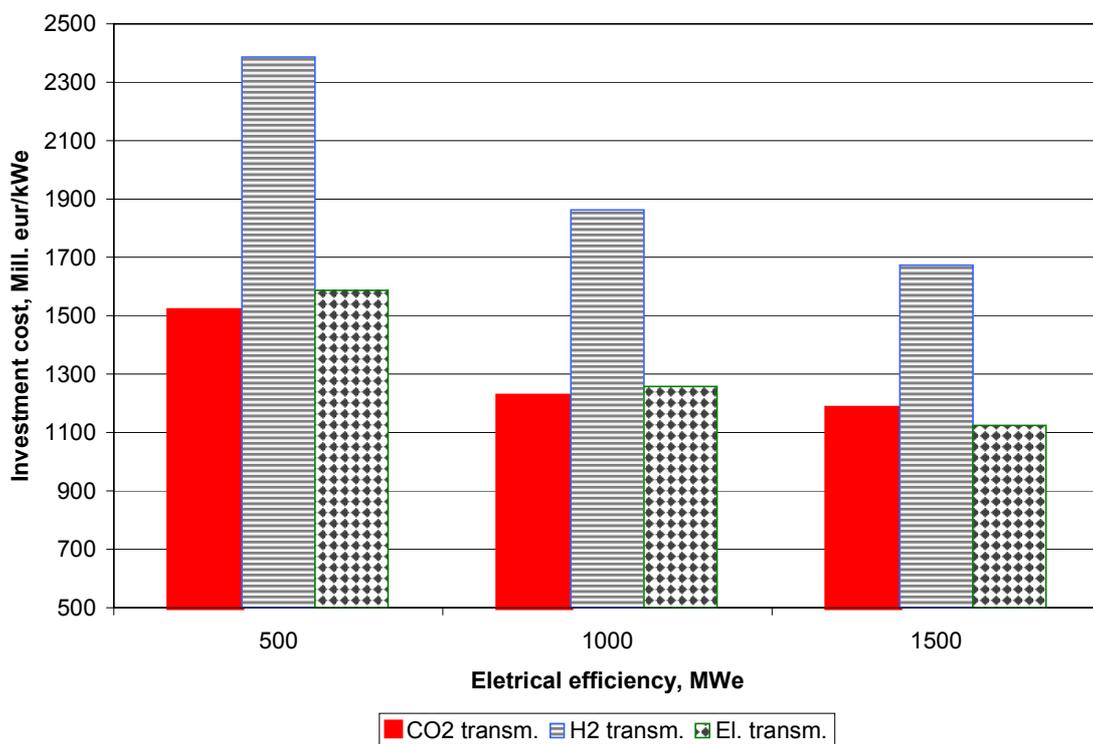


Figure 20. Specific capital investments of the three CO₂ management options for Finland.

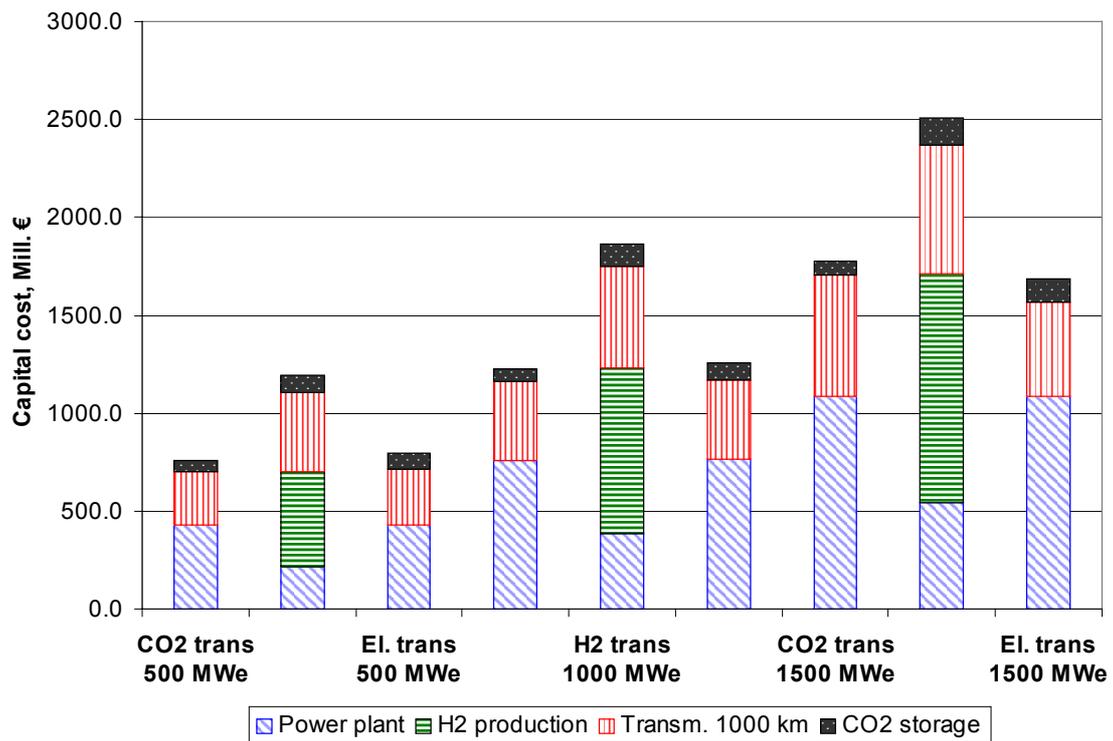


Figure 21. Capital costs of the three CO₂ management options for Finland.

10 SAFETY AND ENVIRONMENTAL ASPECTS

To build confidence in the CO₂ sequestration technology, there is a need to demonstrate safe and reliable long-term storage in full-scale installations. Currently, there are several ongoing projects, which aim at proving the safety of CO₂ sequestration to the environment and human health. However, safety and environmental aspects should be considered carefully from the construction until several hundreds or even thousands of years to minimise CO₂ leakages impact.

Solvents used for CO₂ capture gradually degrade in use. It has been estimated that the CO₂ capture at a 500 MW gas fired power plant could produce about 2000 t/year of sludge from decomposed amines, and about 10 t/year of carry-over in the flue gas. Both of these factors should be minimised not only for environmental reasons but also to reduce capture costs [2].

Large quantities of CO₂ are routinely transported in pipelines and tankers. Nevertheless, as CO₂ is an asphyxiant and heavier than air, elevated concentrations of CO₂ can cause concerns. A level of 6 – 7% CO₂ (normal CO₂ concentration in atmosphere is 0.04%) is considered to be the threshold limit where harmful effects become noticeable in human beings. At CO₂ concentrations over 9%, most people lose consciousness within a short time and over 25 – 30% concentrations narcotic effect occurs whereby breathing may stop immediately. The amount of CO₂ that may escape to atmosphere in a pipeline rupture may be limited with stop valves. The occurrence of incident should be carefully considered in designing pipeline locations and damages may be protected by burying the line. Appropriate monitoring facilities and safety should be included also [45].

In CO₂ underground storage, there may be concerns about either possible slow leakage or sudden large-scale emission resulting from seismic activity. In slow leakage of CO₂ the concerns are more environmental than safety risks. The risk of sudden release of CO₂ would have to be eliminated by avoiding unsuitable, seismic active sites. Chemical interactions between injected CO₂ and geological minerals could sequester CO₂ permanently but there is also a possibility that those reactions could impact the integrity of the cap rock. As mentioned before, deep saline aquifers are less well characterised than oil and gas fields and more information is needed to prove their ability to contain injected CO₂ for the necessary time scales [2].

Naturally occurring geologic gaseous CO₂ deposits have been considered to provide insight into safety and security of geologic sequestration, the long-term impact of CO₂ on reservoirs as well as field operating and monitoring technologies. McElmo Dome field in southwest Colorado is the largest developed natural CO₂ deposit. At discovery, the field contained about 1.6 Gt of 98% pure CO₂, which had been stored for millions of years. The field currently produces about 14.6 million t/year of CO₂, which is transported over 800 km via a dedicated CO₂ pipeline to the oil field in West Texas. At present, total of six natural CO₂ fields sell supplies of injectant to EOR projects in the USA and Turkey. The dedicated CO₂ pipelines total more than 2000 line km and the amount of injected CO₂ in 1998 was about 25 million tonnes [71].

11 OPPORTUNITIES FOR FINNISH TECHNOLOGY

11.1 CO₂ CAPTURE TECHNOLOGY STUDIED IN THE PROJECT

New physical absorption technology for capturing CO₂ from flue gas of power plants developed by Dr. Nurmi was studied in the project. Usually, physical absorption techniques are based on solubility of CO₂ into solvent according to Henry's law. The Nurmi technique employs solvent, which behaviour deviates from Henry's law in certain temperature and pressure range.

A model was created and used to simulate three power plant concepts in connection with Nurmi technique for capturing CO₂. These power plant concepts were conventional pulverised coal fired power plant (PF), pressurised fluidised bed combustion (PFBC) and coal based combustion with oxygen feed and CO₂ recycle (CO₂-recycle).

Table 19 compares recovery percentage of CO₂ and efficiency of reference cases, simulated cases and cases studied in IEA GHG Programme.

Table 19. Comparison of CO₂ capture processes.

	PF		PFBC		CO₂ Recycle	
	<i>Efficiency</i>	<i>Recovery of CO₂</i>	<i>Efficiency</i>	<i>Recovery of CO₂</i>	<i>Efficiency</i>	<i>Recovery of CO₂</i>
Reference Case	40%	0	45%	0	33%	0
Nurmi Technique	30%	83%	34%	37%	31%	94%
Absorption	¹⁾ 29%	90%	-	-	²⁾ 30%	99%
Adsorption	29%	95%	-	-	29%	95%
PSA						
Adsorption	30%	70%	-	-	-	-
TSA						
Cryogenics	-	-	-	-	27%	95%
Membrane	31%	80%	-	-	32%	80%

1) MEA

2) Selexol

In conclusion, the technique of Nurmia is best suited for flue gas streams with high or moderate concentration of CO₂. In addition, pressurisation of flue gas to level, where solubility of CO₂ deviates from Henry's law, is essential in the Nurmia technique. It is clearly seen that results obtained by the technique of Nurmia do not differ significantly from results of current techniques for capturing CO₂ [72]. It is possible that the very low operating temperatures required by the process cause high investment costs and operating problems. It is therefore concluded that there is no need to develop the process further.

11.2 MINERAL CARBONATION STUDIED IN THE PROJECT

The sequestration of CO₂ using magnesium oxide based carbonation seems to suit best for integration with other existing processes, mainly of the mining and metal industry, like ore processes for nickel, chrome, etc. The transport of mineral to/from the CO₂ sources is not reasonable due to high amount magnesium oxide needed (3.5 times the mass of consumed fuel).

The reaction kinetics of carbonation process still has to be investigated before the feasibility of the processes could be evaluated. The most important positive feature, which justifies further work on improvement of this technology, is that CO₂ as MgCO₃ is a stable compound and environmentally acceptable solution for a long term storage of CO₂. It is also the only currently known alternative for Finland to store CO₂.

11.3 OPPORTUNITIES FOR FINNISH TECHNOLOGY

Because of the relatively short history of the development of CO₂ capture technologies and concepts, there is still room for new ideas and improvements of existing concepts. Opportunities exist e.g. in

- Developing Finnish power plant technologies into zero or low-CO₂ emitting direction
- Developing CO₂ capture technologies and concepts that can be integrated to various industrial processes, especially processes that employ Finnish technology.

Capturing CO₂ from flue gases would mean that energy production from fossil fuels would be feasible option also in the future. In the new high efficiency power plant concepts the CO₂ concentration in flue gases is higher, which makes the capture process more cost efficient. Capture integration to industrial process could offer niches, wherein CO₂ capture would become economical. On the other hand, the possible increasing industrial need of CO₂ would possibly not be covered by the current CO₂ capture plants. The gas selling and producing companies should therefore look for new CO₂ emitting sources and separation technologies.

12 CONCLUSIONS AND SUGGESTIONS FOR THE NEXT STEPS

The report outlines the state of the art of the CO₂ capture and storage technologies. Application of CO₂ capture technologies and concepts as well as opportunities to reuse CO₂ in industry are also presented. The potential to reduce Finland's greenhouse gas emissions in the energy sector by CO₂ capture and storage was estimated and cost predictions of different alternative CO₂ management options from Finland's perspective was assessed.

The major barriers for applying CO₂ separation and capture technologies and concepts are, in addition to issues related to storage or utilisation of CO₂, the high capital and operating costs and reduced efficiencies. Costs of separation and capture of CO₂ including compression to the required pressure for the sequestration option used, are generally estimated to make up about 75% of the total costs when ocean or geologic sequestration is applied.

Post-combustion technologies like MEA absorption can be considered commercial, although there is still room for improvement. There are several R&D programmes going on that look for possibilities to reduce the costs significantly in the future. Significant cost reductions require radical changes to combustion technologies and it is estimated that it will take 5 to 10 years before these concepts are commercial.

The main options considered for the long-term storage of CO₂ are underground geologic formations. These include old oil and gas fields, coal formations and saline water aquifers. Deep oceans represent large potential sink for CO₂, but environmental uncertainties make it less feasible in the short term. Recently, CO₂ long term storage as a solid mineral carbonate has also been studied. Today, several demonstration projects are underway to evaluate technical, economical and environmental feasibility of CO₂ sequestration. Unfortunately, there are no underground geologic formations in Finland, which are suitable for CO₂ sequestration. This means that captured CO₂ should be transported abroad.

Wide range physical and chemical properties of CO₂ make it a key part in countless industrial and chemical applications, either in gaseous, liquid or solid forms. In Finland CO₂ is mainly used in food processing industries, beverage carbonation, in pulp and paper industries, metal industries and in greenhouses. Unfortunately, most of these applications do not offer long term sink of CO₂. Also, the current industrial need is very small compared to the amount of emitted CO₂. In 2000, the total amount of CO₂ production was 60 000 tonnes of CO₂. However, in future CO₂ usage will obviously increase, as environmentally more harmful chemicals would be replaced by CO₂. Gas producing and selling companies should therefore look for new CO₂ emitting sources and production technologies to cover the possible increasing industrial need of CO₂.

Capture of CO₂ is best carried out at large point sources, such as power stations, oil refineries, petrochemical, fertiliser and gas processing plants, steel works and pulp and paper mills. The biggest anthropogenic CO₂ emitting plants in Finland are oil refineries, coal burning plants for energy production and steel works. Most of these CO₂ emitting point sources are situated on the coastal side.

The costs of CO₂ sequestration were estimated from Finland's perspective. As long term geological storage of CO₂ is not possible in Finland, carbon free energy production would mean that CO₂ should be transported abroad, decarbonised fuel should be imported or electricity should be imported. The price of electricity would be approximately doubled if CO₂ capture, 1000 km transmission and offshore storage would be included to condensing natural gas combined cycle plant. For pulverised coal power plant, the corresponding electricity price would be about three times higher than with conventional coal power plant. With 1000 km transmission distances the scenario with electricity production near the sequestration place and electricity import seems as feasible as the scenario with electricity production near the consumer and CO₂ transmission. Fuel decarbonation and hydrogen import seemed the most expensive option.

Because of the relatively short history of the development of CO₂ capture technologies and concepts there is still room for new ideas and for improvement of existing concepts. Opportunities exist e.g. in developing Finnish power plant technologies into zero or low-CO₂ emitting direction. Also, developing CO₂ capture technologies and concepts that can be integrated to various industrial processes, especially processes that employ Finnish technology, could offer niches, wherein CO₂ capture would become economical.

The reaction kinetics of a magnesium oxide-based mineral carbonation process should be investigated before the feasibility of the processes could be evaluated. The most important positive feature, which justifies further work on improvement of this technology, is that CO₂ as MgCO₃ is a stable compound and environmentally acceptable solution for a long term storage of CO₂. It is also the only currently known alternative for Finland to store CO₂.

13 LIST OF PUBLICATIONS

T. Koljonen, H. Siikavirta, R. Zevenhoven & I. Savolainen. CO₂ capture, storage and reuse potential in Finland. To be presented in the 6th Int. Conf. on Greenhouse Gas Control Technologies (GHGT-6), Kyoto, Japan, September 30 – October 4, 2002

J. Kohlmann, R. Zevenhoven, A.B. Mukherjee, T. Koljonen. Mineral carbonation for long-term storage of CO₂ from flue gases. Espoo: Helsinki University of Technology, 2002. 64 p. (Report TKK-ENY-9)

Jens Kohlmann & Ron Zevenhoven. The removal of CO₂ from flue gases using magnesium silicates, in Finland. In: Proc. of the 11th Int. Conf. on Coal Science, San Francisco (CA), Sept. 30- Oct. 5, 2001 (CD-ROM)

Ron Zevenhoven & Jens Kohlmann. CO₂ storage by mineral carbonation in Finland (CO₂ lagring genom mineral karbonering i Finland), *invited lecture by Ron Zevenhoven*. In: Proc. of the Second Minisymposium on CO₂ Capture and Storage, Gothenburg (Sweden), October 26, 2001 pp. 13-18 (*available at <http://www.entek.chalmers.se/~anly/symp/symp2001.html>*)

Ron Zevenhoven & Jens Kohlmann. CO₂ sequestration by magnesium silicate mineral carbonation in Finland. Proceedings of R'02 Recovery Recycling Re-integration, Geneva (Switzerland) February 12-15, 2002, paper 220 (CD-ROM)

Ron Zevenhoven, Jens Kohlmann & Arun B. Mukherjee. Direct dry mineral carbonation for CO₂ emissions reduction in Finland. Proceedings of the 27th Int. Tech. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 4-7, 2002, pp. 743-745 (CD-ROM)

Jens Kohlmann, Ron Zevenhoven & Arun B. Mukherjee. Carbon dioxide emissions control by mineral carbonation: the option for Finland. Proceedings of INFUB - 6th European Conference on Industrial Furnaces and Boilers, Vol. 2, Estoril (Portugal), April 2-5, 2002.

R. Zevenhoven & J. Kohlmann. Reaction kinetics of magnesium oxide-based mineral carbonation for CO₂ sequestration. *Under preparation, to be submitted to a technical journal.*

Aarikka, L. Capture of carbon Dioxide from Power Plants. Tampere: Tampere University of Technology, 2001. M.Sc Thesis. 91 p. + app. 13 p.

14 REFERENCES

- 1 IEA GHG. 10th Anniversary 1991 – 2001. UK: IEA Greenhouse Gas R&D Programme, 2001. 35 p.
- 2 IEA GHG. Putting Carbon Back in the Ground. UK: IEA Greenhouse Gas R&D Programme, 2001. 26 p.
- 3 VTT Energy. Energy Visions 2030 for Finland. Helsinki: Edita, 2001. 237 p.
- 4 CO₂ Capture Project. Project's www-pages. Referred in January 2002. Available at <http://www.CO2captureproject.com>
- 5 Edmonds, J.A., Freund, P., & Dooley, J.J. The role of carbon management technologies in addressing atmospheric stabilization of greenhouse gases. In: Williams et al. (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 46 – 51.
- 6 IEA GHG. Barriers to overcome in implementation of CO₂ capture and storage (1) Storage in disused oil and gas fields. UK: IEA Greenhouse Gas R&D Programme, 2000. (Report Number PH3/22.) 116 p.
- 7 U.S. Department of Energy Office of Fossil Energy and National Energy Technology Laboratory. Carbon Sequestration Technology Roadmap. Pittsburg: NETL 2002. Referred in January 2002. Available at: http://www.netl.doe.gov/coalpower/sequestration/pubs/CS_roadmap_0115.pdf.
- 8 U.S. Department of Energy. Carbon Sequestration - Research and Development (Chapter 2. Capture and Separation). USA: U.S. Department of Energy, 1999. Referred in January 2002. Available at: http://fossil.energy.gov/coal_power/sequestration/reports/rd/chap2.pdf
- 9 Progress reports of EU Rucadi project (reports restricted to project partners). EU-contract: BRRT-CT98-5089. <http://www.co2rucadi.uniba.it/>
- 10 Falk-Pedersen, O., Dannström, H., Grønvold, M., Stuksrud, D.-B., Rønning, P. Gas Treatment Using Membrane Gas/Liquid Contactors. In: Williams et al. (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 115 – 120.
- 11 Mimura, M., Matsumoto, K., Iijima, M., Mitsuoaka, S., 2000, Development and Application of Flue Gas Carbon Dioxide Recovery Technology. In: Williams et.al (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 138 – 142.
- 12 IEA GHG. Precombustion Decarbonisation. UK: Greenhouse Gas R&D Programme, 1998. (Report Number PH2/19.)
- 13 Andersen, T., Kvamsdal, H.M., & Bolland, O. Gas turbine combined cycle with CO₂ capture using auto-thermal reforming of natural gas. Presented at the ASME Gas Turbine and Aeroengine Congress and Exposition, München, May 8 – 12, 2000.
- 14 European Commission Joule II Clean Coal Technology Programme 1992-95, 1997, Vol III: Combined Cycle Project. Final Reports. ISBN 92-828-0007-5.

15 European Commission Joule II Clean Coal Technology Programme 1992-95, 1997, Vol II: Powder Coal Combustion Project. Final Reports. ISBN 92-828-0006-7

16 Wilkinson, M.B., Boden, J.C., Panesar, R.S., Allam, R.J. A Study on the Capture of Carbon Dioxide from a Large Refinery Power Station Boiler by Conversion to Oxyfuel Operation. In: Williams et.al (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 179 – 184.

17 Okawa M, Kimura N, Kiga T, Takano S, Arai K, Kato M. Trial Design for a CO₂ Recovery Power Plant by Burning Pulverized Coal in O₂/CO₂, Energy Convers. Mgmt, Vol. 38, Suppl., P. 123-127.

18 Thambimuthu K V, Conrad C R, Palmer A, Sellers T J, Nadarajah R. Novel CO₂ Reduction Technology: Fossil Fuel Combustion in O₂/CO₂ Medium. Combustion Canada, 1996, Vol. 2, P. 1-10.

19 Greenhouse Issues. The Newsletter of the IEA GHG Programme. Number 57, November 2001. Available at: <http://www.iaegreen.org.uk/>

20 Smith, J.R., Surlis, T., Marais, B., Brandt, H., Viteri, F. Power Production with Zero Atmospheric Emissions for the 21st Century, In: Williams et.al (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 1289 – 1294.

21 Brandvoll Ø., Bolland O., Vestøl S. Chemical looping combustion – fuel energy conversion with inherent CO₂ capture. Poster, published in the proceedings of the International Conference POWER GENERATION AND SUSTAINABLE DEVELOPMENT, Liège (Belgium), 8 - 9 October, 2001.

22 Heidug, W.K., Haines, M.R. , Li, K. Economical Carbon Dioxide Recovery for Sequestration from a Solid Oxide Fuel Cell Power Plant, In: Williams et.al (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 132 – 137.

23 IEA GHG. Leading Options for the Capture of CO₂ Emissions at Power Stations. UK: IEA Greenhouse Gas R&D Programme, 2000. 34 p. + 12 app. (Report Number PH3/14.)

24 IEA GHG. The Reduction of greenhouse gas emissions from the oil refining and petrochemical industry. UK: IEA Greenhouse Gas R&D Programme 1999. (Report PH3/8.)

25 IEA GHG. CO₂ Abatement in Oil Refineries : Fired Heaters. UK: IEA Greenhouse Gas R&D Programme, 2000. (Report PH3/31.)

26 IEA GHG. Greenhouse gases from major industrial sources - III Iron and Steel Production. UK: Greenhouse Gas R&D Programme, 2000. (Report PH3/30.)

27 IEA GHG. The Reduction of greenhouse gas emissions from the cement industry. UK: IEA Greenhouse Gas R&D Programme, 1999. (Report PH3/7.)

28 CNW-Canada NewsWire. 1999. PanCanadian Petroleum Limited – Field construction begins on Weyburn Carbon Dioxide Miscible Flood Project. Referred in June 2000. Available at: <http://www.newswire.ca/releases/May1999/20/c5969.html>

29 IEA GHG. CO₂ enhanced recovery in the Weyburn oil field: report of a workshop to discuss monitoring. UK: IEA Greenhouse Gas R&D Programme, 1999. 18 p + 3 App. (Report Number PH3/20.)

-
30. U.S. Department of Energy. Carbon Sequestration - Research and Development. USA: U.S. Department of Energy, 1999. Referred in January 2002. Available at: http://www.ornl.gov/carbon_sequestration/
- 31 IEA GHG. Enhanced coal bed methane recovery with CO₂ sequestration. UK: IEA Greenhouse Gas R&D Programme, 1998. 139 p. (Report Number PH3/3.)
- 32 IEA GHG. Advisory group on R&D on ocean sequestration of CO₂. Report of a meeting, 26th – 27th March 1998, Heathrow, UK. UK: IEA Greenhouse Gas R&D Programme, 1998. 139 p. (Report Number PH3/2.)
- 33 Ziock, H. Zero emissions coal to hydrogen. USA: Los Alamos National Laboratory. Referred in June 2002. Available at: <http://www.lanl.gov/energy/est/zec/index.html>
- 34 Lackner, K., Ziock, H. From low to no emissions. *Modern Power Systems*, 2000. Vol. 20, n:o 3, p. 31 - 32.
- 35 Goldberg, P., Chen, Z-Y., O'Connor, W., Walters, R., Ziock, H. CO₂ mineral sequestration studies in US. Proc. of the First National Conf. on Carbon Sequestration, May 14-17, 2001, Washington, DC. Available at: <http://www.fetc.doe.gov/events/01conferences/carbseq/carbseq01.html>
- 36 O'Connor, W.K. *et al.* Carbon dioxide sequestration by direct mineral carbonation: results from recent studies and current status. Proc. of the First National Conf. on Carbon Sequestration, May 14-17, 2001, Washington, DC. Available at: <http://www.fetc.doe.gov/events/01conferences/carbseq/carbseq01.html>
- 37 Newall, P.S., *et al.* CO₂ storage as carbonate minerals. Cornwall, UK: IEA Greenhouse Gas R&D Programme, 2000. (Report Number PH3/17.)
- 38 O'Connor, W.K., *et al.* Continuing studies on direct aqueous mineral carbonation for CO₂ sequestration. Proc. of the 27th Int. Tech. Conf. on Coal Utilization and Fuel Systems, Clearwater (FL), March 4-7, 2002, P. 819-830.
- 39 Kohlmann, J. The removal of CO₂ from flue gases using magnesium silicates, in Finland. Espoo, Finland: Helsinki University of Technology, 2001. (Report TKK-ENY-3.)
- 40 Kohlmann, J., Zevenhoven, R., Mukherjee, A.B., Koljonen, T. Mineral carbonation for long-term storage of CO₂ from flue gases. Espoo, Finland: Helsinki University of Technology, 2002. (Report TKK-ENY-6.)
- 41 IEA GHG. Issues underlying the feasibility of storing CO₂ as hydrate deposits. UK: IEA Greenhouse Gas R&D Programme, 2000. 29 p. (Report Number PH3/25.)
- 42 IEA GHG. Carbon Dioxide Utilisation. UK: IEA Greenhouse Gas R&D Programme, 1995. 28 p.
43. Crabb, C. Versatile CO₂ continues to expand into new geographic markets and industrial applications. *Chemical Engineering*, 2000. Vol. 1 07, no. 7, p. 49 – 52.
- 44 Ohlström, Mikael; Mäkinen, Tuula; Laurikko, Juhani; Pipatti, Riitta. New concepts for biofuels in transportation. Biomass-based methanol production and reduced emissions in advanced vehicles. Espoo, VTT Energy, 2001. 94 p. (VTT Tiedotteita - Meddelanden - Research Notes; 2074.) ISBN 951-38-5780-8; 951-38-5781-6
- 45 Woodhill Engineering Consultants. Pipeline transmission of CO₂ and energy. UK: IEA Greenhouse Gas R&D Programme, 2002. (Report Number PH4/6.)

-
- 46 IEA Greenhouse Gas R&D Programme. Referred in January 2002. <http://www.ieagreen.org.uk/>
- 47 2nd Nordiska minisymposiet om koldioxidrening och lagring, 26.10.2001 Chalmers, Gothenburg, Sweden. Proceedings available at <http://www.entek.chalmers.se/~anly/symp/symp2001.html>
- 48 IEA Greenhouse Gas R&D Programme. Saline Aquifer CO₂ Storage (SACS). Referred in May 2002. <http://www.ieagreen.org.uk/>
- 49 IEA Greenhouse Gas R&D Programme. NACENT – Natural Analogues for the Geological Storage of CO₂. Referred in May 2002. <http://www.ieagreen.org.uk/>
- 50 U.S. Department of Energy Office of Fossil Energy. Carbon Sequestration. Referred in January 2002. http://www.fe.doe.gov/coal_power/sequestration/sequestration_capture.shtml (Project Data Sheets)
- 51 National Energy Technology Laboratory. Carbon Sequestration. Referred in January 2002. <http://www.netl.doe.gov/coalpower/sequestration/capture.html>
- 52 A national Energy Technology Laboratory. Geo-Seq Project. Referred in May 2002. <http://esd.lbl.gov/GEOSEQ/>.
- 53 U.S. Department of Energy Office of Fossil Energy. Carbon Sequestration. Referred in June 2002 http://www.fe.doe.gov/coal_power/sequestration/sequestration_geologic.shtml
- 54 Legg, J., McDonald, M., Wilson, M. Canada's National Initiative on CO₂ Capture and Storage. In: Williams et.al (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P.1056 - 1061.
- 55 Alberta Research Council, Inc. Alberta Field Pilot to Test CO₂ Enhanced Coalbed Methane Recovery. Referred in June 2002. http://www.arc.ab.ca/envir/Coalbed_pilot.asp.
- 56 NEDO. Referred in January 2002. <http://www.nedo.go.jp/GET/e11.html>
- 57 Klimatek. Referred in January 2002. <http://program.forskningsradet.no/klimatek/fs/index.html?kategoriid=2>
- 58 Gustaffson, J. Industrial Gas Suppliers Invest in OSS Technology To Meet Customers' Growing Demand for Gases. Kemia-Kemi, 2001. Vol 28, n:o 6 pp. 472 – 474.
- 59 Jenni Kivivirta 2002. Nordkalk Oyj Abp. Private discussion.
- 60 Hease, A., Koppinen, S., Riistama, K., & Vuori, M. Chemical industry in Finland (Suomen kemianteollisuus). Tampere: Tammer-paino, 1998. 256 p. [in Finnish]
- 61 Panimo – ja virvoitusjuomateollisuus ry 2002. Market shares in 2001 (Markkinaosuudet 2001). Referred in January 2002. Available as PDF in: <http://www.panimoliitto.fi/tiedotteet.htm> [in Finnish].
- 62 Pia Tornikoski 2002. Panimoliitto. Private discussion.
- 63 Ahonen, M 2002. Oy Hartwall Ab. Private discussion.
- 64 Ministry of Agriculture and Forestry. Horticulture. Referred in January 2002. <http://www.mmm.fi/english/agriculture/horticulture/>

-
- 65 Murmann, T 1988. Growing of tomato (Tomaatin viljely). Finland: Kauppapuutarhaliitto r.y. 1988. Tuotanto-osasto, publication n:o 8. [in Finnish]
- 66 Ministry of the Environment. Finland's national greenhouse gas inventory. Referred in August 2001. <http://www.vyh.fi/eng/envirom/state/air/emis/ghg/un/un.htm>.
- 67 Nordpool 2001. Annual reports 1996 – 2000. Referred in April 2001. <http://www.nordpool.no/products/index.html>.
- 68 Lehtilä, A. Efom database. VTT Energy 2001.
- 69 Adato Energia Oy. Electricity netproduction, imports and exports (GWh) in Finland. Referred in April 2001. <http://www.energia.fi/sahko/sahko.html>
- 70 Ministry of Trade and Industry. The Need for and Possibilities of Reducing Greenhousegas Emissions in Finland (Kasvihuonekaasujen vähentämistarpeet ja –mahdollisuudet Suomessa. Kasallisen ilmastostrategian taustaselvitys). Referred in August 2001. Available as PDF in <http://www.vn.fi/ktm/3/ilmasto/index.htm>. (In Finnish)
- 71 Stevens, S., Fox, C., & Melzer, S. McElmo Dome and St. Johns natural CO₂ deposits: analogs for geologic sequestration. In: Williams et.al (eds.). Greenhouse Gas Control Technologies, Proceedings of the Fifth International Conf. on Greenhouse Gas Control Technologies, 14 – 16 August 2000. Cairns, Australia. Australia: CSIRO Publishing 2001. P. 317 – 321.
- 72 Aarikka, L. Capture of carbon Dioxide from Power Plants. Tampere: Tampere University of Technology, 2001. M.Sc Thesis. 91 p. + app. 13 p.