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Matching CO_2 large point sources and potential geological storage sites in mainland Portugal

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Abstract

Fossil fuel combustion is the major source of the increasing atmospheric concentration of carbone dioxide (CO_2) since the pre-industrial period. Combustion systems like power plants, cement, iron and steel production plants and refineries are the main stationary sources of CO_2 emissions. The reduction of greenhouse gas emissions in one of the main climate change mitigation measures. Carbon dioxide capture and storage (CCS) is one of the possible mitigation measures.

The objective of this study was to analyze the hypothesis for the implementation of CCS systems in mainland Portugal based on source-sink matching. The CO_2 large point sources (LPS) considered in mainland Portugal were the largest installations included in the Phase II of the European Emissions Trading Scheme with the highest CO_2 emissions, representing about 90% of the total CO_2 emissions of the Trading Scheme, verified in 2007. The potential geological storage locations considered were the geological formations formerly identified in existing studies.

After the mapping of LPS and potential geological sinks of mainland Portugal, an analysis based on the proximity of the sources and storage sites was performed. From this it was possible to conclude that a large number of LPS are within or near the potential storage areas. An attempt of estimating costs of implementing a CCS system in mainland Portugal was also performed, considering the identified LPS and storage areas. This cost estimate was a very rough exercise but can allow an order of magnitude of the costs of implementing a CCS system in mainland Portugal. Preliminary results suggest that at present CCS systems are not economically interesting in Portugal, but this may change with increasing costs of energy and emission permits.

The present lack of information regarding geological storage sites is an important limitation for the assessment of implementing a CCS system in mainland Portugal. Further detailed studies are required, starting with the characterisation of geological sites and the candidate sources to CCS, from technical aspects to environmental and economical factors.

Resumo

A queima de combustíveis de fósseis, é desde do período pré-industrial, o maior responsável pelo aumento da concentração atmosférica de dióxido de carbono (CO_2). Entre as maiores fontes estacionárias de CO_2 encontram-se centrais termoeléctricas, refinarias, cimenteiras e indústrias de produção de metais ferrosos. A redução das emissões de gases de efeito estufa é uma das principais medidas de mitigação das alterações climáticas. Entre estas medidas encontra-se a captura e o sequestro de CO_2 (CSC). O objectivo deste estudo foi analisar as hipóteses de implementação de um sistema de CSC em Portugal continental, baseada no cruzamento entre as fontes e os locais de sequestro. As grandes fontes de emissão de CO_2 (GFE) consideradas foram o grupo de instalações incluidas na fase II do Comércio Europeu de Licenças de Emissão (CELE), com maior volume anual de emissões de CO_2, representando 90% do total das emissões verificadas em 2007 no conjunto nacional do CELE. As potenciais áreas de sequestro geológico consideradas foram as formações geológicas previamente identificadas em estudos existentes.

Após o mapeamento das GFE e das potenciais áreas de sequestro geológico, foi realizada uma análise baseada na proximidade entre as fontes e os locais de armazenamento. Desta análise foi possível concluir que existem muitas GFE dentro ou na vizinhança das potencias áreas de sequestro. Foi também efectuada uma tentiva para estimar os custos de implementação de um sistema de CSC em Portugal continental, considerando as GFE e as áreas de sequestro identificadas. Esta estimativa de custos, apesar de ser um exercício grosseiro, permite-nos ter uma ideia da ordem de grandeza dos custos de implementação de um sistema de CSC em Portugal continental. Resultados preliminares indicam que neste momento os sistemas CSC não têm interesse económico, mas a situação poderá mudar se os custos da energia e das licenças de emissão aumentarem.

A actual lacuna de informação em relação aos locais de sequestro geológico de CO_2 é uma limitação importante para avaliação da implementação de um sistema de CSC em Portugal continental. Para tal são necessários mais estudos, começando pela caracterização dos locais de sequestro geológico e pela caracterização profunda das fontes candidatas à implementação de CSC, desde aspectos técnicos a aspectos ambientais e económicos.

Acronyms

AGR	Acid gas removal
APA	Portuguese Environmental Agency
CBM	Coal bed methane
CCGT	Combined cycle gas turbine
CCS	Carbone capture and storage
CDM	Clean development mechanism
CER	Certified emission reductions
CIAGEB	Global Change, Energy, Environment and Bioengineering RDID&D Unit, Fernando Pessoa University
COS	Carbonyl sulfide
DPEP	Divisão para a Pesquisa e Exploração de Petróleo
EC	European Commission
ECBMR	Enhanced coal bed methane recovery
EGR	Enhanced gas recovery
EOR	Enhanced oil recovery
ERU	Emission reduction units
ET	Emissions trading
EU-ETS	European Union Emissions Trading Scheme
EU – 15	Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Netherlands, Portugal, Spain, Sweden and United Kingdom
FEP	Features Events and Processes
FGD	Flue gas desulphurisation
GHG	Greenhouse gases
HHV	Higher Heating Value
IEA	International Energy Agency

IEA GHG	International Energy Agency Greenhouse Gas R&D Programme
IGCC	Integrated gasification combined cycles
INETI	National Institute of Engineering, Technology and Innovation
IPCC	Intergovernmental Panel on Climate Change
IPPC	Integrated Pollution Prevention and Control
JI	Joint Implementation
KP	Kyoto Protocol
LHV	Lower Heating Value
LPS	Large Point Sources
MAOTDR	Portuguese Ministry for Environment, Spatial Planning and Regional Development
MDEA	MethylDiEthanolAmine
MEA	Monoethanolamine
MMV	Monitoring, Mitigation and Verification systems
NAP	National Allocation Plan
NGCC	Natural gas combined cycles
NIR	National Inventory Report
OSPAR	Convention for the Protection of the Marine Environment of the North-East Atlantic
PC	Pulverised coal power plants
PF	Pulverised fuel-fired stations
ppm	Parts per million
SCR	Selective catalytic reduction
UNCLOS	United Nations Convention on the Law of the Sea
UNFCCC	United Nations Framework Convention on Climate Change

Table of contents

List of Figures

List of Tables

1 Introduction

In this chapter, an introduction to the dissertation theme as well as the goals of the dissertation and its organisation is presented.

1.1 Background

The first evidences of the increase of carbone dioxide (CO_2) concentration in the atmosphere appeared in the 60’s and 70’s. In 1988, the World Meteorological Organisation and the United Nations Environment Programme created the Intergovernmental Panel on Climate Change (IPCC). The IPCC published its first report on climate change (IPCC *First Assessment Report*) in 1990, stating that global warming is real and that it is urgent to take measures to tackle it.

According to IPCC, climate change “refers to a change in the state of the climate that can be identified (e.g. using statistical tests) by changes in the mean and/or the variability of its properties, and that persists for an extended period, typically decades or longer (…) whether due to natural variability or as a result of human activity” (IPCC, 2007a). The United Nations Framework Convention on Climate Change (UNFCCC) has a different definition of climate change, where “climate change refers to a change of climate that is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and that is in addition to natural climate variability observed over comparable time periods” (IPCC, 2007a). Climate change has anthropogenic and natural drivers, which can be presented in a schematic diagram representing anthropogenic drivers, impacts of and responses to climate change and their linkages (Figure 1.1).

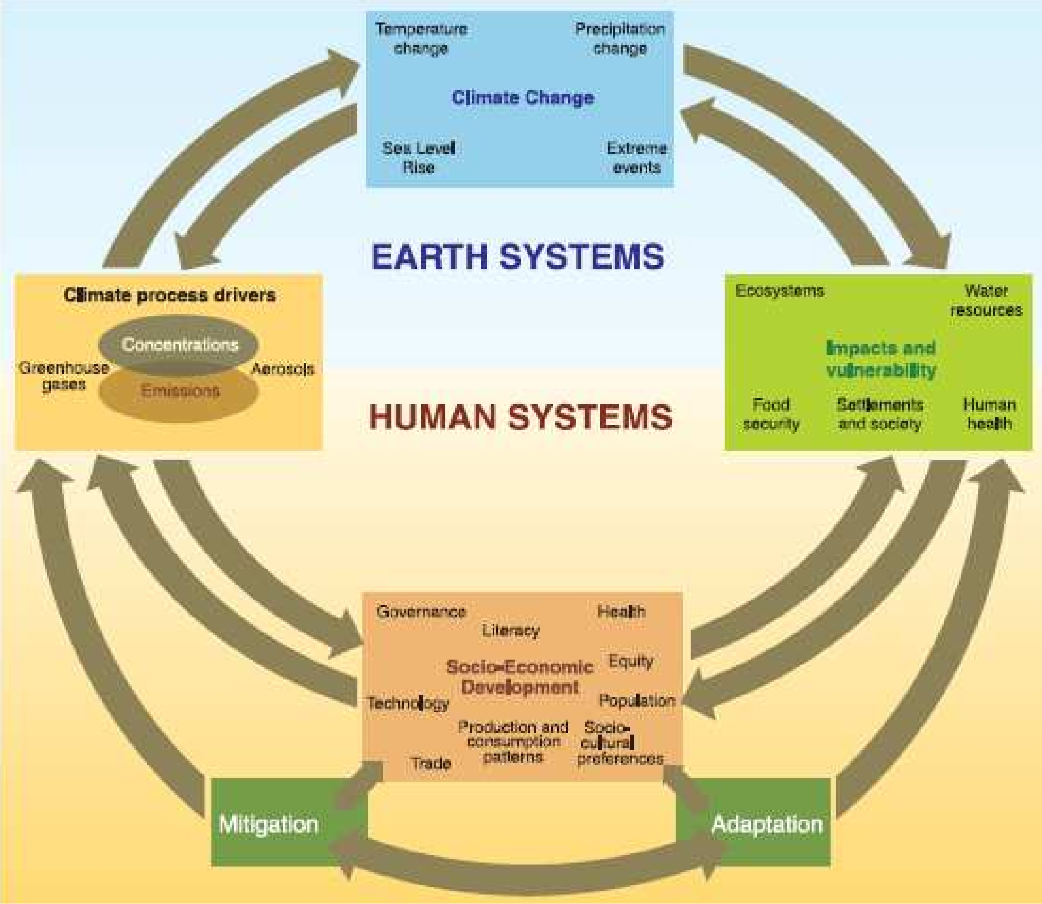

Figure 1.1 - Schematic diagram representing anthropogenic drivers, impacts of and responses to climate change, and their linkages (IPCC, 2007a).

The IPCC fourth assessment report on climate, published in 2007, states that even with emissions restraining within the next few decades climate change consequences are more likely to happen than not to happen. If the emissions remain at 2000 levels, the Earth average temperature is expected to increase 0,1 ºC per decade throughout the next century (IPCC, 2007a).

CO_2 is the most important anthropogenic greenhouse gas (GHG) and its emissions level rose from a pre-industrial level of about 280 ppm to 379 ppm in 2005 (IPCC, 2007b). In the 1995-2005 decade the average annual CO_2 concentration growth rate was 1,9 ppm per year, being higher than the previous verified (1960-2005 average: 1,4 ppm per year). Fossil fuel combustion is the major source of the increasing atmospheric concentration of CO_2 since the pre-industrial period. Land use change is another main source, although smaller than fossil fuel combustion (IPCC, 2007b). In the 1970-2004 period there was an increase of about 70% in the emissions of the GHG covered by the Kyoto Protocol (KP) (CO_2, N_2O, CH_4, SF_6, PFCs, HFCs), CO_2 being the largest source having increased by about 80% (IPCC, 2007c).

The reduction of GHG emissions is one of the main climate change mitigation measures. Carbon capture and storage (CCS) is one of the possible mitigation measures, although it is recognized that no single category of mitigation measures is sufficient. Fossil fuels will continue to play a dominant role in power generation and combustion in industrial processes because they are relatively abundant, cheap, available and globally distributed (Bachu, 2007a). In the particular case of coal, it is abundant in North America, China and India, which are becoming the largest CO_2 emitters in the world (Bachu, 2007b). CO_2 capture and geological storage is considered an option to reduce emissions from the large stationary sources of CO_2.

1.2 Goals

The objective of this study is to analyze the hypotheses for the implementation of CCS systems in mainland Portugal based on source-sink matching. This analysis will consider the CO_2 large point sources (LPS) in mainland Portugal, because they are considered main applicants to CCS.

The identification of CO_2 LPS in mainland Portugal will be based on the installations included in the Phase II of the European Emissions Trading Scheme (EU-ETS) corresponding to the Kyoto Protocol commitment period of 2008-2012, and on the verified annual CO_2 emissions per installation.

The potential geological storage locations that will be considered are the geological formations identified in existing studies. After the mapping of LPS and potential geological sinks of mainland Portugal, an analysis based on the proximity of the sources and storage sites is performed. An estimation of the costs of implementing a CCS system in mainland Portugal is also attempted considering the identified LPS and storage areas.

The adopted method to achieve this dissertation goal involved several research phases that lead to the identification of the criteria to be applied. The main steps are summarized in Figure 1.2.

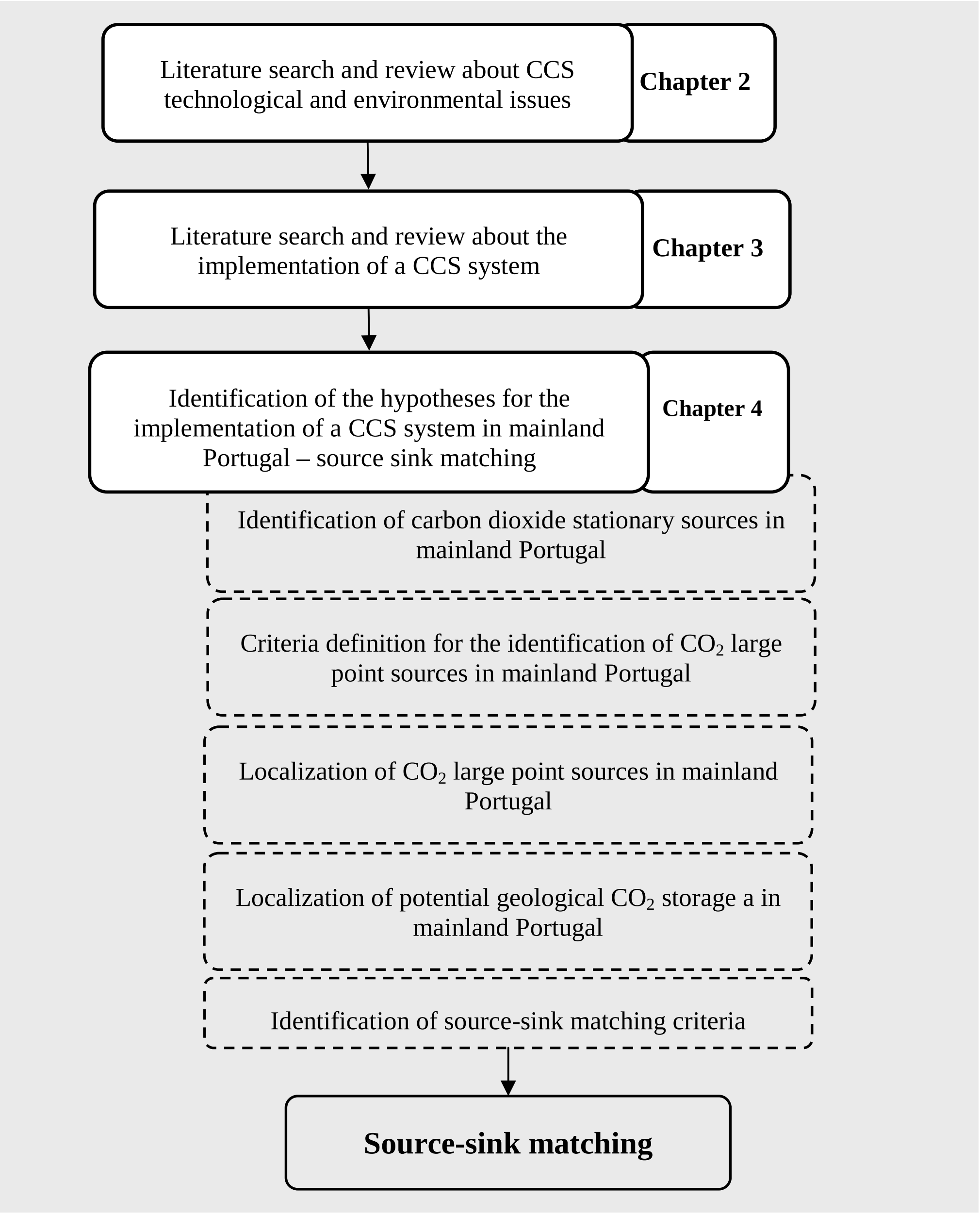

Figure 1.2- Main steps of the method.

1.3 Dissertation organization

The dissertation is organized as follows:

Chapter 2 presents the literature search and review about CCS technological and environmental issues considering CO_2 capture systems and technologies and transport, CO_2 storage, monitoring, mitigation and verification systems, environmental impact assessment and risk evaluation, energy balance and the legal and political aspects related to CCS.

Chapter 3 presents the literature search and review about the selection of CO_2 storage sites, the assessment of CO_2 storage capacity, the process of identification of potential sites for CO_2 geological storage, namely deep saline aquifers and coal beds, CO_2 sources and CCS costs.

Chapter 4 presents the hypotheses for the implementation of a CCS system in mainland Portugal, based on the source-sink matching, considering the proximity of the sources and storage sites. An attempt at estimating costs is also presented.

Chapter 5 presents and discusses the main conclusions of the previous chapters.

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2 State of the art

This chapter intends to give a brief overview of CCS technological and environmental issues considering CO_2 capture systems and technologies and transport, CO_2 storage, monitoring, mitigation and verification systems, environmental impact assessment and risk evaluation and energy balance, as well the legal and political aspects related to CCS.

2.1 Problem definition

From a simple conceptual perspective, a CCS system has three phases: capture, transport and storage. However, in each of these phases not only technological characteristics but also to environmental and safety aspects have to be considered. In the implementation of a CCS system as a mitigation option, costs as well the energy balance and consequently the net GHG emissions are high weighted decision factors. All these technological and environmental issues make CCS a complex system.

Combustion systems like power plants, gas processing, cement, iron and steel production plants and refineries are the main stationary sources of CO_2 emissions. Figure 2.1 shows the share of largest key CO_2 source categories in 2006 for EU-15.

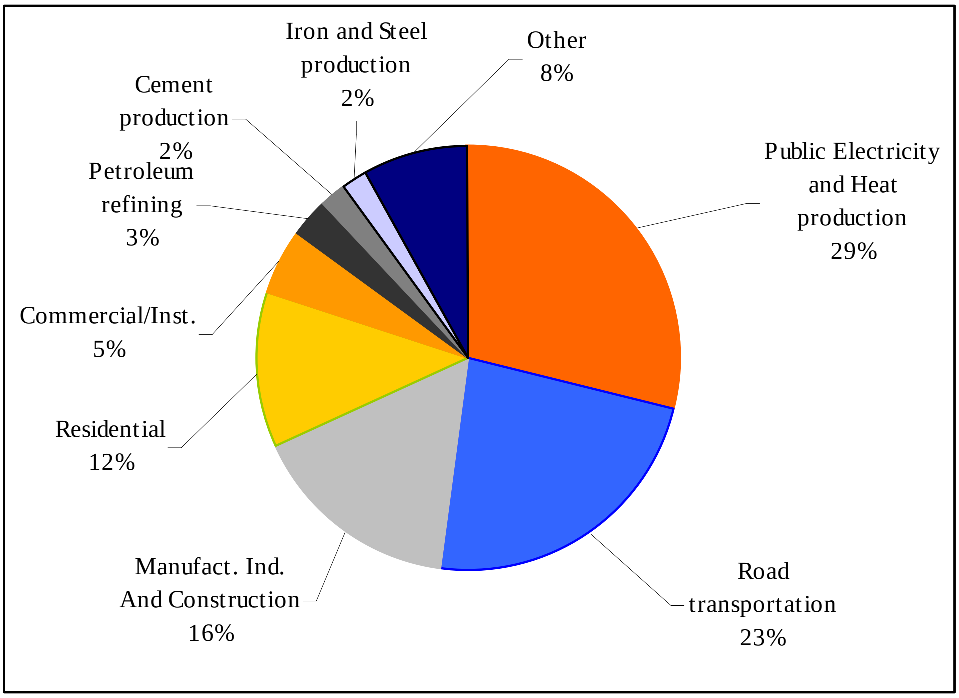


Figure 2.1 – Share of largest CO_2 key sources categories in 2006 for EU-15 (EEA, 2008).

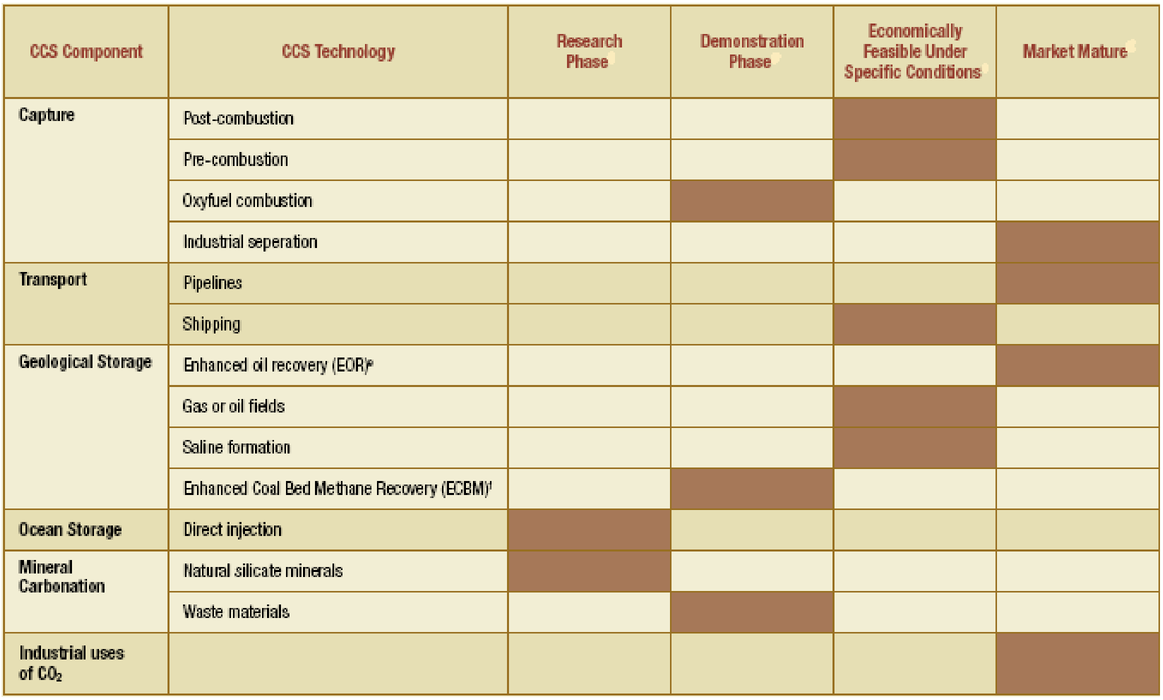
The first international step to tackle climate change happened in 1992 with the establishment of the United Nations Framework Convention on Climate Change (UNFCCC) whose ultimate objective is to achieve "(…) stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system". UNFCCC has been accepted in 1994 and has today been ratified by 192 nations. The international climate negotiations under the UNFCCC lead to the adoption of the Kyoto Protocol in 1997. The Kyoto Protocol entered into force on 2005, and has been ratified until today by 183 Parties of the UNFCCC. The Kyoto Protocol shares the basic principles and institutions of the UNFCCC, but established binding targets of GHG emissions reduction for 37 industrialised countries and the European community. The overall target is a reduction of five per cent of GHG emissions against 1990 levels over the five-year period 2008-2012. In order to meet their targets, Parties must apply national measures and the Kyoto Protocol also established three market-based mechanisms: emissions trading scheme, the clean development mechanism and joint implementation. The EU target is a reduction of eight per cent of GHG emissions against 1990 levels over the first commitment period of the Kyoto Protocol (2008-2012). In this period Portugal is allowed to increase GHG emissions by 27% in relation to 1990 levels.

CO_2 can be captured from installations that use of fossil fuels and/or biomass by four different systems: capture from industrial process streams, post-combustion capture, oxy-fuel combustion capture and pre-combustion capture. CO_2 can be transported in the gas, liquid and solid stage and transported by tanks, pipelines and ships in gaseous and liquid stages. There are three potential CO_2 storage methods: geologic storage, ocean storage (direct release into the ocean water column or onto the deep seafloor) and industrial fixation of CO_2 into inorganic carbonates (IPCC, 2005). Amongst the geological CO_2 storage reservoirs types are deep saline formations, depleted natural gas reservoirs, depleted oil reservoirs, deep unmineable coal seams, deep saline-filled basalt formations and others like salt caverns, organics shales and methane hydratebearing formations (Dooley *et al.*, 2006).

A CCS system has also to be analysed in terms of the environmental impacts and risks, considering the operational, closure and post closure phases. The remediation options in case of CO_2 leakage from the storage location are defined in this stage. For all of the phases of a CCS system there has to be a monitoring, mitigation and verification (MMV) system. These are continuous systems that accompany the transport, injection and storage providing crucial information to the operational system and to environment impact assessment and risk management (NETL, 2008).

As the implementation of a CCS system requires additional energy, an emissions and energy balance is required to assess its mitigation potential. The costs also have to be assessed to all the components of the CCS systems: capture and compression, transport, injection and storage, including monitoring costs and remediation costs if necessary. Another important aspect is how the application of a CCS system will reflect in the cost of the final product, like electricity in the case the system is applied on a power plant.

In Figure 2.2 , the technical components of CCS and the respective state of development are presented.



CCS Component	CCS Technology	Research Phase	Demonstration Phase	Economically Feasible Under Specific Conditions	Market Mature
Capture	Post-combustion			■	
	Pre-combustion			■	
	Oxyfuel combustion		■		
	Industrial seperation				■
Transport	Pipelines				■
	Shipping			■	
Geological Storage	Enhanced oil recovery (EOR)[e]				■
	Gas or oil fields			■	
	Saline formation			■	
	Enhanced Coal Bed Methane Recovery (ECBM)[f]		■		
Ocean Storage	Direct injection	■			
Mineral Carbonation	Natural silicate minerals	■			
	Waste materials		■		
Industrial uses of CO_2					■

Figure 2.2 – Technical components of CCS (Fernando *et al.*, 2008).

The legal and regulatory aspects of CCS are of major importance. However, CCS has not been yet subjected to an effective framework including legal and regulatory templates and guidelines at national or international level, particularly concerning long-term issues. This is a big constraint and until today the regulatory issues have been defined on a case-by-case basis (Robertson *et al.*, 2006). In 2008, the European Commission (EC) published a proposal for a directive[1] on the geological storage of

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[1] COM (2008) 18 final – Proposal for a Directive of the European Parliament and of the Council on the geological storage of carbon dioxide and amending Council Directives 85/337/EEC, 96/61/EC, Directives

CO_2. Part of the existent European legislation can be applied to CCS and the proposal of directive establishes which terms of the existing legislation should apply to which aspects of CCS. With the international climate change negotiations, CCS is not explicitly included in the UNFCCC or the KP.

The criteria for the selection of CO_2 storage sites and matching with CO_2 sources are, according to Bachu, 2007b: “volume, purity and rate of the CO_2 stream; proximity of the source and storage/storage sites; level of infrastructure for CO_2 capture and delivery; existing wells, for injection and for leak prevention; injection and production strategies; terrain and right of way; proximity to population centres; and overall costs, and economics” (Bachu, 2007b). Beyond these technical suitability criteria, further considerations on source-sink matching are controlled by economic, safety and environmental aspects. According to the IPCC Special Report on CCS “assigning technical risks is important for matching of CO_2 sources and storage sites, for five risk factors: storage capacity, injectivity, containment, site and natural resources” (IPCC, 2005).

The analysis that will be performed in this study will be based on the proximity of the CO_2 sources and storage sites. This analysis will consider the CO_2 large point sources in mainland Portugal, because they are considered main applicants to CCS. To classify the mainland Portugal LPS, the chosen criterion is the identification of the group of installations with the highest CO_2 emissions until representing about 90% of the total CO_2 emissions verified in 2007. The potential geological storage locations that will be considered are the prior geological formations identified in a preliminary study of The National Institute of Engineering, Technology and Innovation (INETI – Instituto Nacional de Engenharia, Tecnologia e Inovação) and the Douro coalfield basin, which is being studied for CO_2 sequestration by the Global Change, Energy, Environment and Bioengineering RDID&D Unit (CIAGEB) from the Fernando Pessoa University.

2.2 Carbon dioxide capture systems and technologies

2.2.1 CO_2 capture technologies

CO_2 capture systems use many of the technologies used for gas separation which are integrated into the referred CO_2 capture systems. Among capture technologies are

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2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC and Regulation (EC) No 1013/2006, Brussels, 23.1.2008.

separation with sorbents /solvents, separation with membranes and separation by cryogenic distillation.

In CO_2 separation with sorbents/solvents, the gas contacts with a solid sorbent or a liquid absorbent that has the capacity to capture CO_2. A general scheme of this separation process is presented in Figure 2.3.

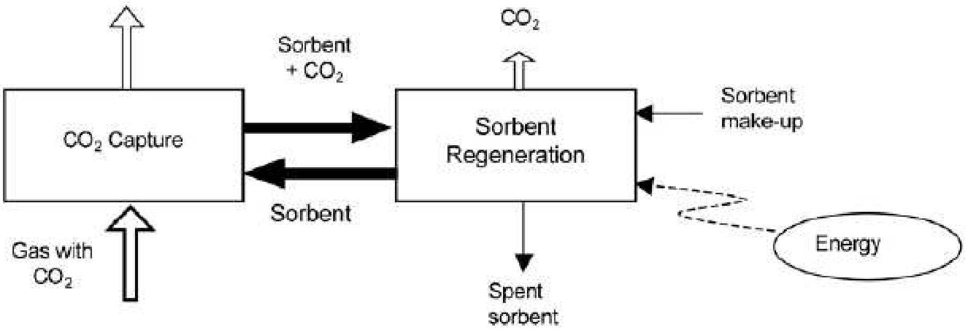

Figure 2.3 - General scheme of separation with sorbents/solvents (IPCC, 2005).

During the process the sorbent within the captured CO_2 is transported to another vessel and the CO_2 is released after a change in the conditions around the sorbent (which can be temperature increase, pressure decrease or other). This process step is called regeneration. Following regeneration, the resultant sorbent is cyclically sent back to capture more CO_2, if the sorbent is liquid. When the sorbents are solid, sorption and regeneration occur by cyclic changes in the vessel where the sorbent is contained. During the process a make-up of fresh sorbent is necessary to compensate the decay of activity or losses. The spent sorbent circulates to another vessel where it is re-oxidized for reuse. This capture technology has a problem: as the flow of sorbent between vessels is large, large size equipment and energy is required, implying added cost and efficiency penalty (IPCC, 2005).

As membranes allow selective permeation, it is possible to use them to separate different gases. Membrane selectivity to different gases depends on the material, but the pressure difference across the membrane drives the flow of gas through it. This technology can have different applications in a CO_2 capture system. It allows separating H_2 from a fuel gas stream, CO_2 from a range of process streams or O_2 from air (to aid the production of a highly concentrated CO_2 stream) (IPCC, 2005). A separation with membranes scheme is showed in Figure 2.4.

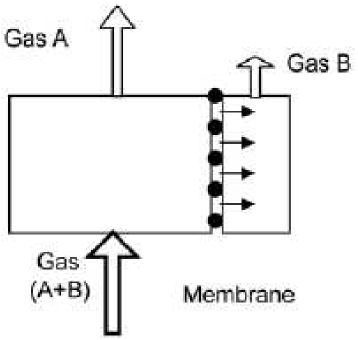

Figure 2.4 - General scheme of separation with a membrane (IPCC, 2005).

In CO_2 separation by cryogenic distillation, after a series of compression, cooling and expansion steps, a gas can become liquid. In the liquid form the gas components can be separated in a distillation column, as demonstrated in Figure 2.5 .

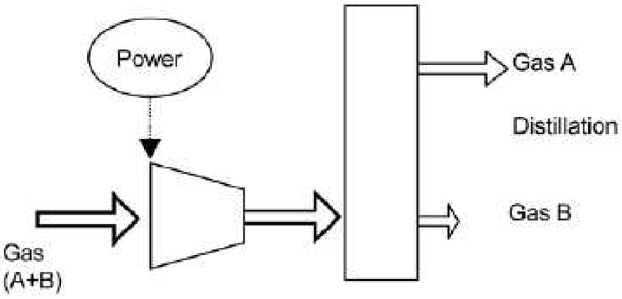

Figure 2.5 - General scheme of separation by cryogenic distillation (IPCC, 2005).

This technology can be applied in different CO_2 capture systems like oxy-fuel combustion and pre-combustion capture (IPCC, 2005).

2.2.2 CO_2 capture systems

CO_2 can be captured from installations that use of fossil fuels and/or biomass by four different systems: capture from industrial process streams, post-combustion capture, oxy-fuel combustion capture and pre-combustion capture. CO_2 is produced in several industrial processes like natural gas sweetening, steel, hydrogen, ethanol, cement and ammonia production, fermentation processes for food and drink processes. As these industrial processes emit large CO_2 quantities, they represent opportunities to capture it. In post-combustion capture, CO_2 from flue gas produced by fossil fuels and/or biomass combustion can be captured. In the oxy-fuel combustion capture, as in combustion, almost pure oxygen is used instead of air, originating a flue gas composed mainly of H_2O and CO_2, being readily captured. In pre-combustion capture[2], a hydrocarbon reacts

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[2] Can also be designated as gasification, partial oxidation or steam reforming.

to produce separate streams of CO_2 for storage and H_2. (IPIECA and API, 2007) (IPCC, 2005). The four capture systems are illustrated in Figure 2.6.

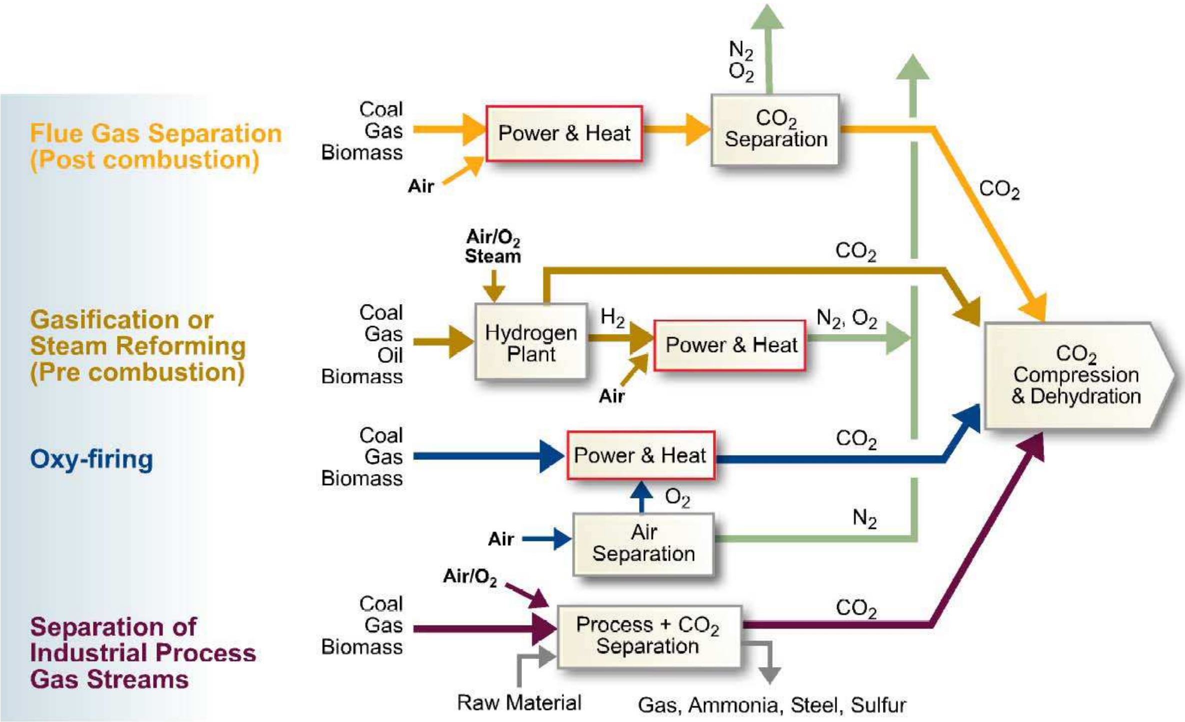

Figure 2.6 - Carbon dioxide capture processes in the four capture systems (IPIECA and API, 2007).

Table 2.1 shows a capture toolbox presented in the IPCC Special Report on Carbon Capture and Storage, with the current and emerging technologies for the different capture systems.

Table 2.1 Capture toolbox (IPCC, 2005).

Separation task	Capture Technologies	**Solvents (Absorption)**	**Membranes**	**Solid sorbents**	**Cryogenic**
Process streams (CO_2/CH_4)	Current	**Physical solvents** **Chemical solvents**	**Polymeric**	Zeolites Activated carbon	Ryan-Holmes process
	Emerging	Improved solvents Novel contacting equipment Improved design of processes	Ceramic Facilitated transport Carbon Contactors		
Post-combustion capture (CO_2/N_2)	Current	**Chemical solvents**	Polymeric	Zeolites Activated carbon	Liquefaction
	Emerging	Improved solvents Novel contacting equipment Improved design of processes	Ceramic Facilitated transport Carbon Contactors	Carbonates Carbon based sorbents	Hybrid processes
Oxy-fuel combustion capture (O_2/N_2)	Current	n. a.	Polymeric	Zeolites Activated carbon	**Distillation**
	Emerging	Biomimetic solvents, e.g. hemoglobinederivatives	Ion transport membranes Facilitated transport	Adsorbents for O2/N2 separation, Perovskites Oxygen chemical looping	Improved distillation
Pre-combustion capture (CO_2/H_2)	Current	**Physical solvents** **Chemical solvents**	Polymeric	Zeolites Activated carbon Alumina	Liquefaction
	Emerging	Improved solvents Novel contacting equipment Improved design of processes	Ceramic Palladium Reactors Contactors	Carbonates Hydrotalcites Silicates	Hybrid processes

Notes: Processes shown in bold are commercial processes that are currently preferred in most circumstances. Some process streams involve CO_2/H_2 or CO_2/N_2 separations but this is covered under pre-combustion capture and post-combustion capture.

Post-combustion capture

Large scale combustion systems fired with fossil fuels generate huge flows of gases due to the high nitrogen concentration in air, the low pressure and the large scale of the units. The CO_2 concentration in flue gas (product of combustion) depends on the type of fuel that is used in combustion. Post-combustion capture systems can be applied to combustion systems with any type of fuel. The fuel impurities are very important for the plant design and costs calculation because the plant may have to have additional units to remove it prior to CO_2 capture, like in absorption-based processes (IPCC, 2005).

Different technologies can be used to capture CO_2 from flue gases, being the most common option to post-combustion capture, the absorption processes based on chemical sorbents, which is commercially available (IPCC, 2005).

The absorption processes in post-combustion capture take advantage of the reversibility of chemical reactions between an aqueous alkaline solvent, normally amine, with an acid or sour gas (IPCC, 2005). Table 2.2 presents the key parameters that determine the technical and economic operation of a CO_2 absorption system.

Table 2.2 - Key parameters that determine the technical and economic operation of a CO_2 absorption system (IPCC, 2005).

Flue gas flow rate	Determines the size of the absorber which represents a substantial contribution to the overall cost.
CO_2 content in flue gas	Flue gas is usually at atmospheric pressure and the partial pressure of CO_2 will be as low as 3-15 kPa – at these conditions, aqueous amines are the most suitable absorption solvents.
CO_2 removal	CO_2 recoveries are in practice between 80% and 95%. “The exact recovery choice is an economic trade-off, a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs” (IPCC, 2005).
Solvent flow rate	Determines the size of most equipment apart from the absorber.
Energy requirement	“The energy consumption of the process is the sum of the thermal energy needed to regenerate the solvents and the electrical energy required to operate liquid pumps and the flue gas blower or fan. Energy is also required to compress the CO_2 recovered to the final pressure required for transport and storage” (IPCC, 2005).
Cooling requirement	“Cooling is needed to bring the flue gas and solvent temperatures down to temperature levels required for efficient absorption of CO_2. Also, the product from the stripper will require cooling to recover steam from the stripping process” (IPCC, 2005).

The post-combustion based on absorption processes has a high energy requirement resulting in a penalty on power cycles efficiency. The high energy requirement of this process is mainly due to “the heat necessary to regenerate the solvent, steam use for stripping and to a lesser extent the electricity required for liquid pumping, the flue gas fan and finally compression of the CO_2 product” (IPCC, 2005). Other solvents for the absorption process are being studied aiming to make it less energy consuming. Other technologies of post-combustion capture like adsorption processes, membranes and solid sorbents are also being developed (IPCC, 2005).

Pre-combustion capture

The pre-combustion capture normally involves a first step that consists of a reaction producing a mixture of hydrogen and carbon monoxide (syngas) from a primary fuel. There are two main ways: to add steam to the primary fuel, in a process called “steam reforming” (1) and to add oxygen to the primary fuel, this process being called “partial oxidation” (when applied to gaseous and liquid fuels) or ‘gasification’ (when applied to a solid fuel) (2). After this step occurs a reaction to convert CO to CO_2 adding steam (3) (IPCC, 2005).

Steam reforming

$C_xH_y + xH_2O \leftrightarrow xCO + (x+y/2)H_2$ ΔH +ve (1)

Partial oxidation

$C_xH_y + x/2O_2 \leftrightarrow xCO + (y/2)H_2$ ΔH –ve (2)

Water Gas Shift Reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$ ΔH -41 kJ mol^{-1} (3)

Then the CO_2 is removed from the mixture produced in reaction 3. “The concentration of CO_2 in the input to the CO_2/H_2 separation stage can be in the range 15-60% (dry basis) and the total pressure is typically 2-7 MPa. The separated CO_2 is then available for storage” (IPCC, 2005).

The pre-combustion capture can have two applications: it can be used in the production of a carbon-free fuel (hydrogen) or to decrease the carbon content of fuels, with the excess carbon (usually removed as CO_2) being made available for storage (IPCC, 2005).

Among the existing technologies for H_2 production with CO_2 capture are: steam reforming of gas and light hydrocarbons, partial oxidation of gas and light hydrocarbons, auto-thermal reforming of gas and light hydrocarbons, gas heated reformer, gasification of coal, petroleum residues, or biomass, integrated gasification combined cycle (IGCC) for power generation, hydrogen from coal with CO_2 capture, carbon-based fuels and multi-products, pressure swing adsorption, chemical solvent processes and physical solvent processes. There are also several emerging technologies in both natural gas reforming and coal gasification like sorption enhanced reaction, membrane reactors for hydrogen production with CO_2 capture, micro channel reformer, conversion to hydrogen and carbon (example: thermal cracking or pyrolysis of methane) and technologies based on calcium oxide (IPCC, 2005).

Oxy-fuel combustion capture systems

In the oxy-fuel combustion process the combustion of a hydrocarbon or a carbonaceous fuel (that can be biomass) in pure oxygen or in a mixture of pure oxygen and a CO_2-rich recycled flue gas eliminates nitrogen from the flue gas. The combustion temperature[3] of fuel combustion with pure oxygen is about 3500°C while in an typical gas turbine cycle it is about 1300-1400°C and in an oxy-fuel coal-fired boiler it is about 1900ºC. The flue gas is constituted mainly of CO_2, water vapour and oxygen in excess, which is necessary to guarantee the complete fuel combustion. The CO_2 content in the net flue gas is about 80-98% depending on the fuel and the oxy-fuel combustion process. The efficiency of oxy-fuel combustion systems to capture CO_2 is very near to 100%. Although is still necessary to develop this technology to a commercial scale (IPCC, 2005).

The oxy-fuel combustion systems can be classified according to “how the heat of combustion is supplied and whether the flue gas is used as a working fluid” (IPCC, 2005) in: oxy-fuel indirect heating – steam cycle, oxy-fuel direct heating – gas turbine cycle and oxy-fuel direct heating – steam turbine cycle. In oxy-fuel combustion systems oxygen is a requisite and the existing large scale production methods are: cryogenic oxygen production and high temperature oxygen ion transport membranes (IPCC, 2005).

2.2.3 CO_2 capture in power plants

A large percentage of the electricity that is produced worldwide has origin in fossil-fuel power plants. According to the International Energy Agency scenarios, fossil fuels will continue to play an important role in electricity production (IEA and OECD, 2003). Fossil-fuel power plants are responsible for about one third of total global CO_2 emissions. So they are major candidates for the application of CCS. There is a variety of techniques that could be applied to various types of large-scale power plant and industrial activities fired on fuels but as originally most of these techniques were not developed for CCS, further research and development is required until they are considered viable IEA and OECD, 2003).

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[3] “The combustion temperature is controlled by the proportion of flue gas and gaseous or liquid-water recycled back to the combustion chamber” (IPCC, 2005).

Post-combustion capture in power plants

Post-combustion capture uses a solvent to capture CO_2 from the flue gas of power plants that is then regenerated. These solvents can be physical, chemical or intermediate. Chemical solvents are less dependent on partial pressure than physical solvents are, and the partial pressure of CO_2 in the flue gas is low (usually 4-14% by volume). On the other hand, chemical solvents require more energy (as steam) to regenerate (to break the relatively strong chemical link between CO_2 and the solvent) (IEA, 2007)[4].

The most mature option for post-combustion capture is the capture by amines absorption, which is a chemical solvent. For this reason amines are the most likely to be used for the first generation of CO_2 post-combustion capture. In this technology the presence of oxygen can be a problem because it causes the degradation of some solvents and the corrosion of equipment. To avoid this problem, inhibitors can be mixed into the solvent to counteract the oxygen activity. The concentration of oxides of nitrogen and sulphur (NO_2 and SO_x) in the flue gas must be very low before it is scrubbed of CO_2 because these two compounds can react with amines to form stable, non-regenerable salts, causing the steady loss of amine (IEA, 2007).

Currently the process of scrubbing CO_2 with amines does not operate on the scale of power plants (IEA, 2007). However, it is referred in (IEA, 2007) that increasing the technology to power plants scale is not considered a major problem. This study also mentioned that for large coal-fired power plants, a demonstration of these technologies is necessary. In these types of power plants the application of post-combustion CO_2 capture requires an upstream de-NO_x and flue gas desulphurisation[5] (FGD) facilities (IEA, 2007).

In a study made by the IEA GHG[6], two post-combustion capture of CO_2 processes were assessed: monoethanolamine[7] (MEA) and hindered amine solvent, concluding that the

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[4] Sterically hindered amines need less steam for regeneration (IEA, 2007). Hindered amines are chemical compounds containing an amine functional group surrounded by a crowded steric environment. They have uses such as gas scrubbing, as stabilizers against light-induced degradation of polymers, and as reagents for organic synthesis (http://en.wikipedia.org/wiki/Hindered_amine).

[5] Flue gas desulfurization (FGD) is the current state-of-the art technology used for removing sulfur dioxide (SO_2) from the exhaust flue gases in power plants that burn coal or oil to produce steam for the steam turbines that drive their electricity generators. (http://en.wikipedia.org/wiki/Flue_gas_desulfurization)

[6] International Energy Agency Greenhouse Gas R&D Programme (http://www.ieagreen.org.uk/).

[7] Monoethanolamine (MEA) is an organic chemical compound that is both a primary amine (due to an amino group in its molecule) and a primary alcohol (due to a hydroxyl group). Like other amines,

hindered amine process loses less energy primarily due to the solvent consuming less heat for regeneration than MEA solvents (IEA, 2007).

Pre-combustion capture in power plants

In the pre-combustion capture process a fuel is reacted with air or oxygen to produce a fuel that contains CO and H_2. Then in a shift reactor this reacts with steam to produce a mixture of CO_2 and H_2. Subsequently the CO_2 is separated and the H_2 is as fuel (IEA, 2007).

This technology can be used for gas turbine combined cycles, in natural gas or coal based plants. The separated H_2 is used as fuel in a gas turbine combined cycle. If coal is the primary fuel and the key process is its gasification[8], it is known as an integrated gasification combined cycle (IGCC) (IEA, 2007).

The IEA GHG assessed IGCC plants based on two types of gasifier: a slurry feed gasifier (in which the gas product is cooled by quenching with water) and a dry feed gasifier (in which the gas product is cooled in a heat recovery boiler). In an IGCC plant without CO_2 capture and with a slurry feed gasifier, “the coal is ground and slurried with water and then pumped to the gasifier vessels where it reacts with oxygen. The products from gasification are quenched with water, the saturated gas is cooled and condensed water and minor impurities are removed. The sulphur compounds are removed from the gas by passing it through a reactor and feeding it to a Selexol[9] acid gas removal (AGR) plant. The clean fuel gas is fed to the gas turbine combined cycle plant” (IEA, 2007). If the IGCC plant has CO_2 capture, “the gas from the gasifier is fed to a CO_2-shift converter prior to cooling and the Selexol unit removes CO_2 as well as sulphur compounds. The Selexol is regenerated to produce separate CO_2 and sulphur compounds steams. The CO_2 stream is compressed and dried for transport by pipeline” (IEA, 2007). In this process the removal rate of CO_2 is 90%, meaning that an overall CO_2 capture rate of 85% can be achieved (IEA, 2007). In an IGCC plant without CO_2

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monoethanolamine acts as a weak base. MEA is used in aqueous solutions for scrubbing certain acidic gases. (http://en.wikipedia.org/wiki/Ethanolamine).

[8] Gasification is the partial oxidation of a fossil fuel to a gas, often known as syngas, which main components are CO and H_2. Gasification acts as a bridge between the fossil fuel and gas turbines with the target of high energy efficiency and minimum emissions to the environment. (IEA, 2007)

[9] Selexol is a physical solvent, unlike amine based acid gas removal solvents that rely on a chemical reaction with the acid gases. Since no chemical reactions are involved, Selexol usually requires less energy than the amine based processes. However, at feed gas pressures below about 300 psia (2.07 MPa), the Selexol solvent capacity (in amount of acid gas absorbed per volume of solvent) is reduced and the amine based processes will usually be superior. (http://en.wikipedia.org/wiki/Selexol)

capture and with a dry feed gasifier, “the coal is dried, ground and then fed to the gasifier vessels. The gasifier product gas is quenched, cooled and then fed to a dry particulate removal unit. Some of the gas is recycled as quench gas and the remainder is scrubbed with water, reheated, the carbonyl sulfide (COS) is removed and it is fed to an MDEA (MethylDiEthanolAmine) solvent acid removal plant. The clean fuel gas is fed to the gas turbine combined cycled plant. The configuration of the plant with CO_2 capture is the same except that the COS removal process is replaced by a two-stage shift converter and H_2S and CO_2 are separated in a Selexol AGR unit” (IEA, 2007).

Oxy-combustion capture in power plants

In the oxy-combustion capture process the fuel is combusted with nearly pure oxygen and recycled flue gas or CO_2 and water/steam to produce a flue gas consisting essentially of CO_2 and water. This technology may have potential as a part of a system for capturing and storing CO_2 because the nitrogen concentration in the flue gas is much lower than when air is used. This means that CO_2 can be stored with less downstream process (IEA, 2007).

The pulverised fuel-fired stations (PF) are a type of coal power station. The PF oxy-combustion plant uses the same steam conditions as the other post-combustion capture plant. This process requires a large amount of oxygen for combustion that is obtained from an air separation unit. The flue gas from oxy-combustion is compressed and cooled to separate nitrogen, oxygen and other impurities, obtaining a CO_2 concentration of about 95mol%. The NO_X and SO_X are converted to acid and condensed from the CO_2 stream, so selective catalytic reduction[10] (SCR) and FGD units may be not needed.

Oxy-combustion capture technology is still in a relatively early stage of development but pilot plants are being built and the plans for the construction of commercial power are at an advanced stage (IEA, 2007).

2.3 CO_2 transport

In comparison to CO_2 capture and storage, the transport technology is considered relatively mature. CO_2 can be transported in the gas, liquid and solid stage and

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[10] Selective catalytic reduction (SCR) is a means of converting nitrogen oxides, also referred to as NOx with the aid of a catalyst into diatomic nitrogen, N_2, and water, H_2O. A gaseous reductant, typically anhydrous ammonia, aqueous ammonia or urea, is added to a stream of flue or exhaust gas and is absorbed onto a catalyst. Carbon dioxide, CO_2 is a reaction product when urea is used as the reductant. (http://en.wikipedia.org/wiki/Selective_catalytic_reduction).

transported by tanks, pipelines and ships for gaseous and liquid stages at a commercial-scale. Dedicated CO_2 pipelines are referred as the most efficient transport mode for shipment (Fernando *et al.*, 2008).

As a gas transported at a pressure close to the atmospheric pressure occupies a large volume, the gas must be compressed before the transport (IPCC, 2005). The compression of CO_2 into a supercritical[11] fluid makes it easier and cheaper to transport, gas compression being a mature technology (Fernando *et al.*, 2008).

The compressed gas occupies less volume and then is transported by pipeline, the volume being reduced by transporting at a high pressure. Other processes like liquefaction, solidification or hydration can reduce further the gas volume. Liquefaction being an established technology for gas transport by ship, this knowledge can be transferred to the transport of CO_2 in the liquid stage. Solidification requires much more energy than the other options. The commercially viable technologies are currently used for CO_2 transport (IPCC, 2005).

2.3.1 CO_2 pipeline transportation

In CO_2 transportation by pipeline, the transport infrastructure has to be considered. For a large scale CO_2 transport a large pipelines network is required and important factors such as the rights-of-way for the pipelines and security issues if they cross densely populated zones have to be carefully taken into account in the network design (IPCC, 2005).

CO_2 pipeline transportation systems have several specifications: the minimum percentage of CO_2, the content of H_2S, N_2, NO_x and SO_x contaminants, the content of water, oxygen and the adequate temperature and pressure. These specifications have to be determined beforehand and are very relevant to the transport phase because of the corrosion rate of the pipeline material. Field experience demonstrates that there are very few problems with transportation of high-pressure dry CO_2 in carbon steel pipelines. If relative humidity is inferior to 60%, dry CO_2 does no corrode the carbon manganese steel that is generally used for pipelines. In the presence of free water, corrosion rates are much higher. In practice it is unlikely that wet CO_2 can be

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[11] **Supercritical:** at a temperature and pressure above the critical temperature and pressure of the substance concerned. The critical point represents the highest temperature and pressure at which the substance can exist as a vapour and liquid in equilibrium (IPCC, 2005).

transported in low-alloy carbon steel pipeline due to the high corrosion rate in the presence of water. However if CO_2 can not be dried, the pipeline material has to be of a corrosion-resistant alloy. Although this is an established technology it may not be economically viable (IPCC, 2005).

After the CO_2 is dried and all the transportation specifications and criteria are met, it is measured and transported to the final destination (IPCC, 2005). In pipelines CO_2 flow is driven by pumps at high pressure and ambient temperature (IPIECA and API, 2007).

The pipeline design is determined by physical, environmental and social factors. The conceptual design considers the physical characteristics of product mixture characteristics, the optimal size and pressure, the mechanical material (valves, pumps, etc.), the topography, geotechnical considerations, among others. It also has to consider how the pipeline will accommodate existing and future infrastructure and will have to obey legal and regulatory requirements. After all these considerations the study is the basis of a safety review. Pipelines operational aspects are daily operations, maintenance, and health, safety and environment (IPCC, 2005).

2.3.2 CO_2 transportation by ship

As already mentioned, pipelines are not the only option to CO_2 transport. For small CO_2 amounts the transport can occur by truck or rail. It can also be transported by ship but on a smaller scale. Ship transportation occurs in insulated containers at low temperatures and much lower pressures than pipeline transport (IPIECA and API, 2007). CO_2 transportation by ship is usually more suitable for short distances and for picking up CO_2 from smaller and/or scattered sources (Fernando *et al.*, 2008).

As a CCS system is a continuous system, CO_2 transportation by ship must include a temporary storage on land and a loading facility near the capture site. The delivery to the storage system depends on whether the delivery point is onshore or offshore. Thus the operational aspects of a marine transportation system include loading, transport to the site, unloading and return to the port (IPCC, 2005).

2.4 Carbon dioxide storage

CO_2 geological storage refers to the process of injecting CO_2 into deep reservoirs, where physical and geochemical trapping mechanisms prevent the CO_2 from migrating to the surface (Fernando *et al.*, 2008). According to Bachu, 2007a, CO_2 sequestration is its disposal in geological media permanently and CO_2 storage is its disposal in geological media for significant time periods (Bachu, 2007a). A primary trapping requisite is a layer of impermeable caprock overlying the sequestration site. CO_2 storage requires cautious characterization of storage sites to ensure that CCS project can sequester CO_2 for geologic periods of time (Fernando *et al.*, 2008).

Generally CO_2 is injected as a supercritical fluid that means it is dense as a liquid but has a gas-like viscosity that allows it to flow very easily through the pipeline and into the storage site. In reservoirs at depths grater than 800 m, CO_2 can be maintained as a supercritical fluid (Dooley *et al.*, 2006).

There are three potential CO_2 storage methods: geologic storage, ocean storage (direct release into the ocean water column or onto the deep seafloor) and industrial fixation of CO_2 into inorganic carbonates (IPCC, 2005).

2.4.1 Underground geological storage

Geological storage of CO_2 is a natural process in the Earth's upper crust, where the CO_2 derived from biological activity, igneous activity and chemical reactions between rocks and fluids accumulates in the subsurface as carbonate minerals, in solution or in a gaseous or supercritical form, either as gas mixture or pure. It is possible to store CO_2 onshore and offshore. The injection into deep geological formations is achieved by pumping fluids down into a well (IPCC, 2005).

Among the geological CO_2 storage reservoirs types are deep saline formations, depleted natural gas reservoirs, depleted oil reservoirs, deep unmineable coal seams, deep saline-filled basalt formations and others like salt caverns, organics shales and methane hydrate bearing formations (Dooley *et al.*, 2006). Figure 2.7 presents the options for storing CO_2 in deep underground and geological formations.

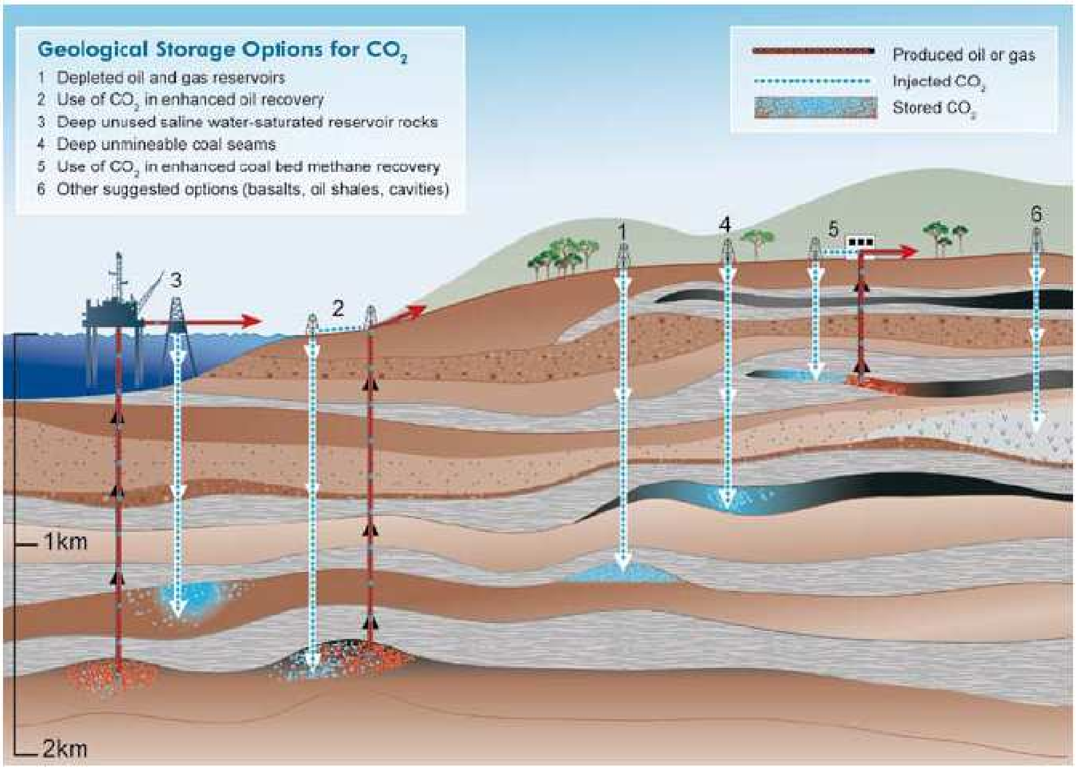

Figure 2.7 - Options for storing CO_2 in deep underground geological formations (IPCC, 2005).

Hendricks *et al.*, 2004, developed a series of methodologies to calculate the underground storage potential of different reservoir types. However, when storage capacity is mentioned, this does not mean that all storage capacity is currently available for CO_2 storage[12] (Hendricks *et al.*, 2004). In Figure 2.8 and Figure 2.9, the results achieved by Hendricks *et al.*, 2004, are presented, relating the CO_2 storage potential per type of underground reservoirs and per world region.

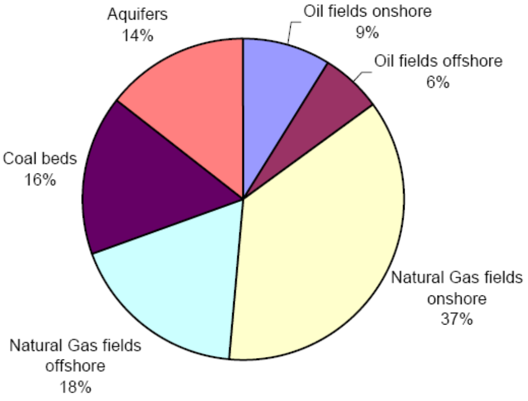

Figure 2.8 - CO_2 storage potential per type of underground reservoirs (Hendricks *et al.*, 2004).

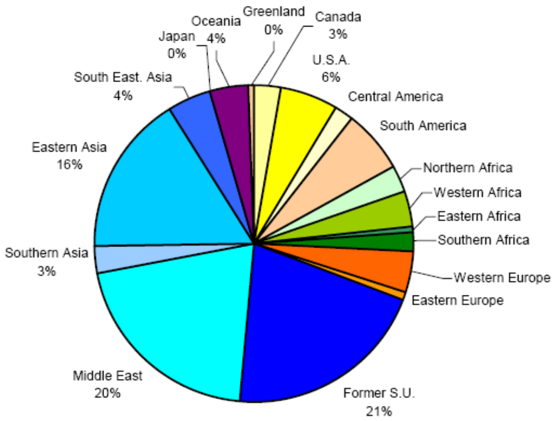

Figure 2.9 - CO_2 storage potential per world region (Hendricks *et al.*, 2004).

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[12] This is due to many factors like: hydrocarbon fields may not already be exploited or are not yet empty; there may also be a conflict of interest, e.g. the field is needed for natural gas storage; enhanced oil recovery is applied most economically before the field is abandoned and infrastructure is still in place; and re-installation of equipment might turn out very expensive (Hendricks, C., *et* al., 2004).

The assessment of the potential of storage of CO_2 in geological formations has mostly been made at regional or global level. However, the levels of detail and assessment methods vary substantially, and besides an increase in knowledge about technical issues, there has also been an increase in the uncertainties associated with the details used in the assessment scheme (Bradshaw *et al.*, 2004). Thus, and because one of the aims of capacity estimation is to guide policy directions, it is necessary that this estimations take into account several factors like injection depth and distance between source and sink (Bradshaw *et al.*, 2004), and the range of trapping mechanisms that are possible at each site, considering its different geological constraints and the different time scales (Bradshaw *et al.*, 2007).

Saline formations are deep sedimentary rocks saturated with formation waters or brines containing high concentration of dissolved salts. Due to the high salt concentration, these waters are unsuitable for agriculture and human consumption. However, the estimation of the storage capacity in deep saline formations is not simple because of the multiplicity, complexity and interactions of mechanisms that occur to store CO_2 in these formations. Among these mechanisms are physical trapping beneath low permeability caprock, dissolution and mineralization. They occur simultaneously and on different time scales. These reasons result in a main focus on physical trapping mechanisms and/or dissolution in the majority of estimates of CO_2 capacity storage in deep saline formations, making a simplifying assumption that no geochemical reactions occur simultaneous with CO_2 injection, flow and dissolution (IPCC, 2005).

As oil and gas reservoirs have accumulated these in structural and stratigraphical traps over time, they are major candidates to CO_2 storage. This also shows their integrity and safety. Furthermore, the movement and displacement behaviour and trapping of hydrocarbons is well known and as the infrastructures are already in place they can be used to CO_2 storage operations. Nevertheless these infrastructures have to be assessed to guarantee the safety of CO_2 injection and storage. Enhanced oil recovery (EOR) by CO_2 injection provides potential economic benefits because of incremental oil production, in average 13.2%. Usually, CO_2 is separated from the produced oil and reinjected into the formation, as demonstrated in Figure 2.10. For CO_2 storage in EOR operations, oil reservoirs need to meet additional criteria like depths greater than 600m. Enhanced gas recovery by CO_2 injection could enhance gas recovery by repressurizing the reservoir but some authors argue that CO_2 injection might result in lower gas recovery factors, principally for very heterogeneous fields. This technology has only been yet implemented on a pilot scale while there are several worldwide projects of CO_2-EOR (IPCC, 2005).

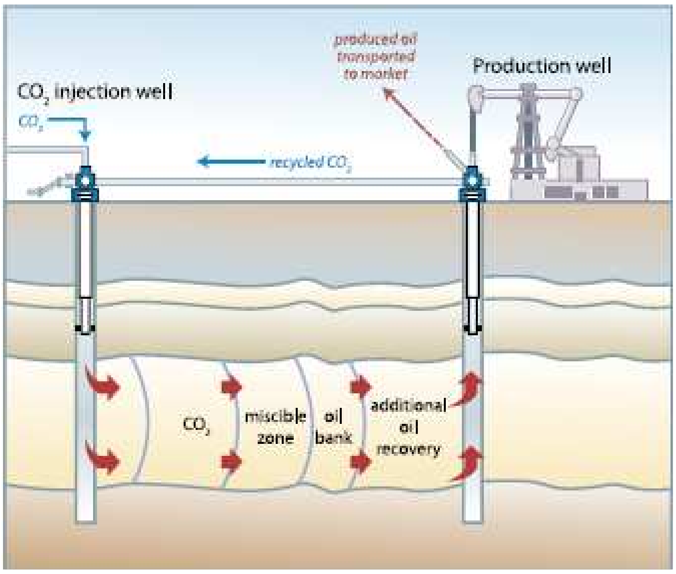

Figure 2.10 Injection of CO_2 for enhanced oil recovery with some storage of retained CO_2 (IPCC, 2005).

Coal contains cleats that impart some permeability and between these, solid coal has a very large number of micropores into which gas molecules from the cleats can diffuse and be tightly adsorbed. Coal can physically adsorb many gases and has higher affinity to adsorb gaseous CO_2 than CH_4 (see Figure 2.11). Consequently when CO_2 is injected to coal, it seems it can displace CH_4, thereby enhancing coal bed methane recovery (ECBMR) (IPCC, 2005). Considering that the injected CO_2 will replace the CH_4 in coal and will remain adsorbed in it, the freed CH_4, also a GHG, has to be captured and may be used as an energy source in ECBMR (Bachu, 2007). Compared to conventional recovery, CO_2 – ECBM has the potential to increase the amount of produced methane to nearly 90% while the first is of only 50%. If coal is not disturbed (mined or depressurized) it is likely that CO_2 will be stored for geological time (IPCC, 2005).

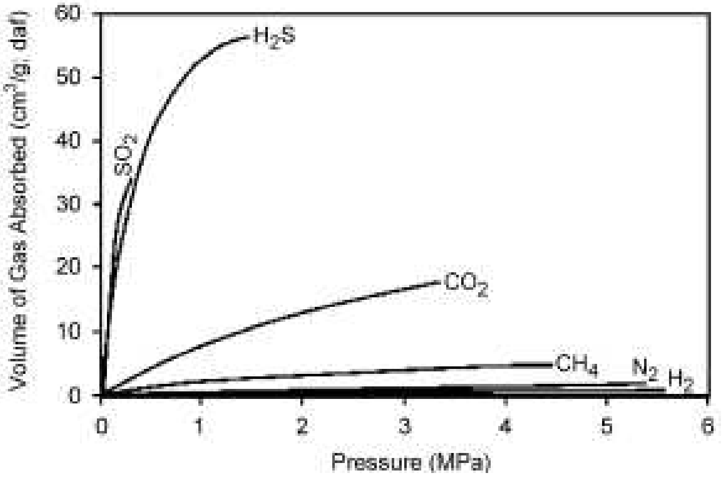

Figure 2.11 – Adsorption of different gases on coal (Bachu *et al.*, 2007a).

Before geological storage, CO_2 must be compressed, generally as a supercritical fluid. Due to the geothermal gradient[13]the density of CO_2 increases with depth, until about 800m or greater, and the injected CO_2 will be in a dense supercritical state (IPCC, 2005).

The subsurface geological formations are composed of transported and deposited rock grains organic material and minerals that form after the rocks are deposited. Pore spaces as well open cavities and fractures are occupied by fluid. Thus the injection of CO_2 into the pore spaces and fractures of a permeable formation can displace the *in situ* fluid or the CO_2 can dissolve in or mix with the fluid or react with the mineral grains, or there may be some combination of these processes (IPCC, 2005).

As injection increase the pressure near the well, CO_2 occupies the pores initially filled by the *in situ* formation fluids. The amount and spatial distribution of pressure depends on the rate of injection, the permeability and thickness of the injection formation, the presence or absence of low permeability barriers and the geometry of the hydrogeological system. After the injection, the primary flow and transport mechanisms that control the spread of CO_2 include: migration in response to pressure gradients created by the injection process; fluid flow in response to natural hydraulic gradients; buoyancy caused by the density difference between CO_2 and the formation fluids; diffusion; dispersion and fingering caused by formation heterogeneities and mobility contrast between CO_2 and formation fluid; dissolution into the formation fluid; mineralization; pore space trapping; and adsorption of CO_2 onto organic material

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[13] Rate at which temperature increases with depth.

(IPCC, 2005).

The rate of fluid flow depends on the number and properties of the fluid phases present in the formation - if CO_2 is injected into a deep saline formation in a liquid or liquid-like supercritical dense phase it is immiscible in water; if it is injected into a gas reservoir, it will locally form a miscible fluid phase of CO_2 and natural gas. As supercritical CO_2 is much less viscous than water and oil, migration is controlled by the contrast in mobility of CO_2 and the *in situ* formation fluids – because of the high mobility of CO_2 only some of the fluid will be displaced leading to an average saturation in the range of 30 -60 %. The comparatively large density differences between CO_2 and water in deep saline formations create strong buoyancy forces that drive CO_2 upwards – in gas reservoirs, as CO_2 is denser than natural gas, it will migrate downwards under buoyancy forces. The existence of a low permeability layer forms a barrier, slowing the upwards migration of CO_2, as it migrates laterally filling any stratigraphical or structural trap it encounters (IPCC, 2005).

During the migration through the formation, some of the CO_2 dissolves into the formation water. The time of dissolution depends on the flow of the formation water, taking much longer time in formations with no flow because of the absence of contact with unsaturated water. After CO_2 is dissolved in the formation fluid it will migrate with the groundwater flow. Water saturated with CO_2 is slightly denser, depending on the salinity of the original formation water. The solubility of CO_2 in brine decreases with increasing pressure, decreasing temperature and increasing salinity. During migration, CO_2 is also retained in pore spaces by capillary forces, dissolving over time in the formation water (IPCC, 2005).

CO_2 effective permanence on geological formations depends on the existent trapping mechanisms, the most effective sites being those where CO_2 is trapped under a tick, low permeability seal, or is converted to solid minerals, or is adsorbed on the surfaces of coal micropores. CO_2 trapping depends on a combination of physical and geochemical trapping mechanisms (IPCC, 2005). According to Bachu, 2007a, physical trapping of CO_2 occurs when it is immobilised as a free gas or supercritical fluid depending on the available storage volume; and chemical trapping of CO_2 can occur as adsorption trapping when it is adsorbed onto materials contained on coals and shales, or as solubility and ionic trapping, when it dissolves in subsurface fluids and may be then involved in chemical reactions with the rock matrix, designated mineral trapping

(Bachu, 2007a). Physical trapping of CO_2 can be divided into two types (Bachu, 2007a):

- "Static trapping of mobile CO_2 in stratigraphical and structural traps[14], or in man-made caverns (mobile in this context means that the flow of CO_2 is impeded by a physical low-permeability barrier, and that, if a pathway is found, CO_2 will flow driven by its own buoyancy and other forces)"; and
- "Residual-gas trapping in the pore space at irreducible gas saturation, in which case CO_2 is immobile because of the interfacial tension between CO_2 and formation water, and flow is not possible even if a pathway is available."

In relation to the chemical trapping, the adsorption occurs as already mentioned, when CO_2 is adsorbed onto materials contained on coal and shales. The solubility, ionic and mineral trapping mechanisms can be described by the following basic chemical reactions (Bachu, 2007a):

$$\text{Solubility trapping} \quad \left\{ \begin{array}{l} CO_{2\,(gaseous)} \longrightarrow CO_{2\,(aqueous)}, \\ CO_{2\,(aqueous)} + H_2O \longrightarrow H_2CO_{3\,(aqueous)} \end{array} \right.$$

$$\text{Ionic trapping} \quad \left\{ H_2CO_{3\,(aqueous)} + OH^- \longrightarrow HCO_3^-{}_{(aqueous)} + H_2O \right.$$

$$\text{Mineral trapping} \quad \left\{ \begin{array}{l} HCO_3^-{}_{(aqueous)} + OH^- \longrightarrow CO_3^{2-}{}_{(aqueous)} + H_2O \\ CO_3^{2-}{}_{(aqueous)} + Ca^{2+} \longrightarrow CaCO_{3\,(solid)} \end{array} \right.$$

Other more complex chemical reactions can take place, for example with Ca and Mg minerals. The chemical trapping mechanisms depend "on the amount of coal, formation water or rock that is available for reactions, but also on the contact area between free-phase CO_2 and coal, water or mineral, and CO_2 saturation at the interface" (Bachu, 2007a).

At first the principal means to store CO_2 in a geological formation is physical trapping below caprocks, such as very-low-permeability shale or salt beds (primary trapping

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[14] "Structural and stratigraphic traps refer to permeable geological media overlain and surrounded by low-permeability rock, whose shape precludes the upward and lateral movement of a buoyant fluid such as oil and gas (and in this case CO_2). Structural traps are the result of crust movement (faults and folds), while stratigraphic traps are the result of depositional and/or diagenetic processes" (Bachu, S., 2007).

mechanisms). Physical trapping can be stratigraphical, structural and hydrodynamic. Structural traps include those formed by folds in fractured rocks while stratigraphical traps are formed by changes in rock type caused by variation in the setting where the rocks are deposited. Hydrodynamic trapping can occur in saline formations, dissolving in the formation water and migrating with the groundwater. Geochemical trapping includes a sequence of geochemical interactions with the rock and water that will further increase storage capacity and effectiveness (secondary trapping mechanisms). When the solubility trapping occurs, CO_2 dissolves in formation water, and once dissolved it no longer exists as a separate phase. Next, as the rock dissolves, ionic species will be formed, increasing pH. Then, mineral trapping can occur if some fraction is converted to stable carbonate minerals. Mineral trapping is the most permanent form of geological storage but is slow, taking thousands of years or longer (IPCC, 2005). The secondary trapping mechanisms are much slower and occur in much larger timeframes than the primary trapping mechanisms. This time lag means that the contribution of the secondary trapping mechanisms is negligible during the injection phase and is very important to the increase of security. This doesn’t mean that the operational phase is not secure, “it only indicates that storage security may increase in time if these secondary trapping mechanisms increase their contribution to the process” (Bachu, 2007a).

Figure 2.12 presents the trapping contribution over time of the referred physical and geochemical trapping mechanisms after injection stops, and Figure 2.13 presents the operating time frame of the processes involved in CO_2 geological storage.

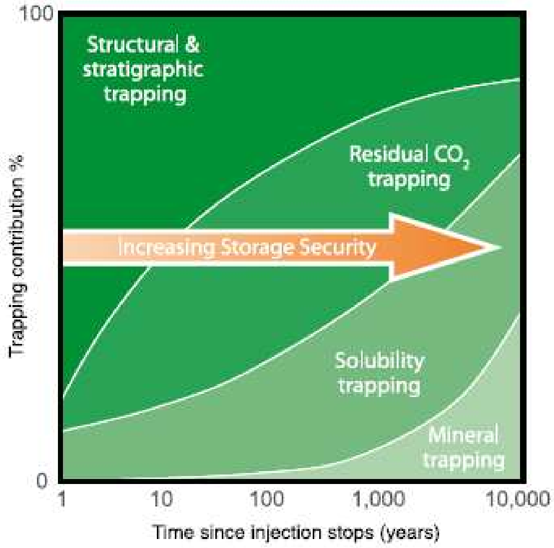

Figure 2.12 Storage security of physical and geochemical trapping mechanisms after injections stops (IPCC, 2005).

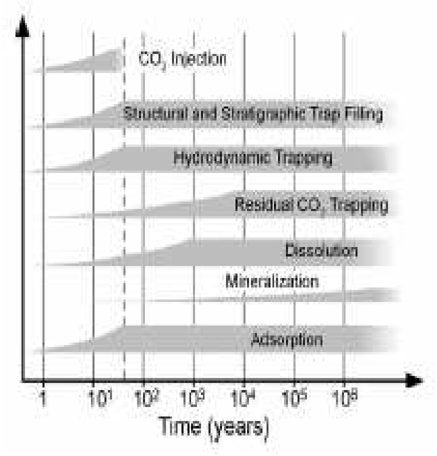

Figure 2.13 – Operating timeframe of processes involved in CO2 geological storage (Bachu *et al.*, 2007).

The presence of impurities in the CO_2 gas stream like SO_x, NO_x or H_2S also affects the injection, the trapping mechanisms and the storage capacity. These impurities affect the compressibility and reduce the storage capacity because of the space they take (IPCC, 2005).

2.4.2 Ocean storage

As part of the carbon cycle, the oceans are natural carbon sinks, being the cycle component that contains most carbon. The ocean and the atmosphere interact in a dynamic equilibrium. However the increasing concentration of GHG in the atmosphere has been driving CO_2 from the atmosphere to the ocean, leading to perturbations in the ocean surface waters chemistry, decreasing its pH.

CO_2 can be transported by ship or pipeline, and injected directly into the ocean, or deposited on the sea floor, as illustrated in Figure 2.14.

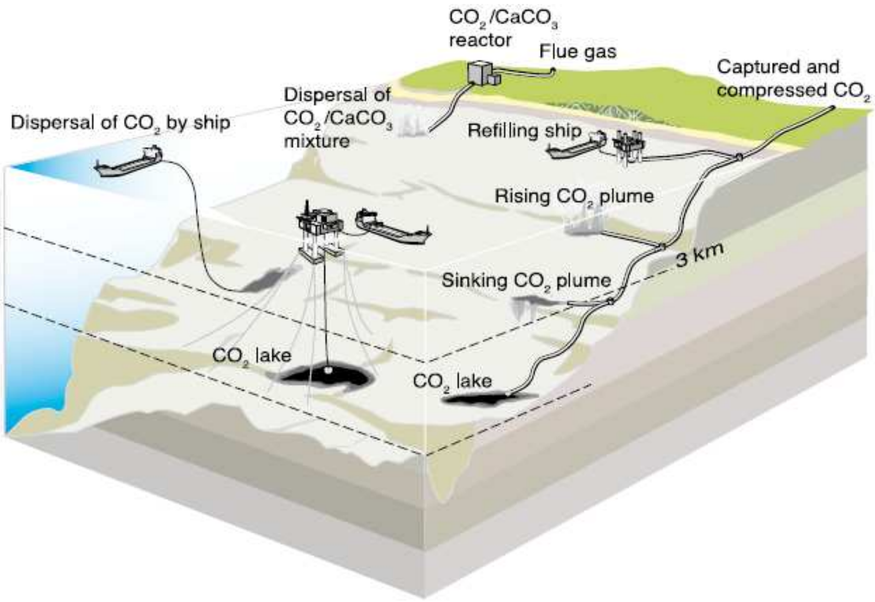

Figure 2.14 Illustration of ocean storage strategies (IPCC, 2005).

CO_2 injected in the ocean can be isolated from the atmosphere for several hundreds of years, and deeper injection implies that the fraction retained tends to be larger with deeper injection. CO_2 retention can be prolonged if solid CO_2 hydrates and liquid are formed.

CO_2 lakes form on the sea floor, and CO_2 solubility can be increased, for example dissolving mineral carbonates. The ocean mixing would result in the loss of isolation of the injected CO_2 and exchange with the atmosphere. No mechanisms for sudden or catastrophic release of injected CO_2 are known (IPCC, 2005).

Injection of large amounts of CO_2, in the order of a few $GtCO_2$, would produce a measurable change in ocean chemistry in the region of injection, and injection in the order of hundreds of $GtCO_2$ would eventually produce measurable change over the entire ocean volume. The injection of these amounts of CO_2 would cause negative effects on marine organisms and ecosystems. However, ocean storage of CO_2 has not yet been deployed or thoroughly tested (IPCC, 2005).

2.4.3 Industrial fixation of CO_2

CO_2 can be fixated in the form of inorganic carbonates (mineral carbonation or mineral sequestration) or can be utilised as a technical fluid or as a feedstock for carbon containing chemicals. In mineral carbonation the CO_2 reacts with metal-oxide bearing materials to form insoluble carbonates. The stable solids that result from mineral carbonation occur naturally and would provide storage capacity on a geological time scale. In nature, mineral carbonation is a slow process making the currently implemented processes very energy intensive because of the preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources. This technology is still in the development stage and is not yet ready for implementation. The best case studied is the wet carbonation of natural silicate olivine, which has a 30-50% energy penalty on the original power plant and accounts for a 10-40% energy penalty in the capture plant as well; a full CCS system with mineral carbonation would need 60-180% more energy than a power plant with equivalent output without CCS (IPCC, 2005).

CO_2 can also be utilised in industrial processes that require it as a product. It can be used as a gas or a liquid, or as feedstock for the production of chemicals (like urea or methanol), preventing the captured CO_2 to be emitted to the atmosphere. Industrial uses provide a carbon sink, as long as the pool size keeps growing and the lifetime of the compounds produced is long. However the lifetime of the chemicals produced in comparison with the scale of interest in CO_2 storage is too short and the contribution of industrial uses of captured CO_2 to the mitigation of climate change is expected to be small (IPCC, 2005).

2.5 Environmental impact assessment and risk evaluation

For the selection and determination of a geological formation to store CO_2, there has to be a site characterization to evaluate if it is appropriate, and an assessment of the risk of physical leakage. Site characterization is based on the evaluation of the surface area land use, the geology and local hydrogeology, its capacity to store the desired amount of CO_2, its injectivity to receive CO_2 at the rate that it is supplied from the source(s), the presence of a secure structural or stratigraphical trap or other confining unit, and possible physical leakage pathways. In risk management, a structured process taking into account stakeholder input is applied to identify and quantify the risks, to evaluate these and to identify and implement appropriate monitoring and intervention strategies to manage the remaining risks (IPIECA and API, 2007). Risks are proportional to the magnitude of the potential hazards and the probability of these hazards will occur (IPCC, 2005).

For analysis of the environmental impacts and risks of a CCS system, it can be divided into two subsystems: the operational and the *in situ* subsystems. In the operational subsystem the most common risks are associated with pipeline and well failures, and less likely risks are related to corrosion or mismanagement in the form of over-pressurization and poor engineering practices. Pipelines have safety technologies like automated shutdown valves that limit the leakage of CO_2 if a pipeline failure occurs. CO_2 is neither flammable nor explosive, and in case of leakage is expected to diffuse rapidly in the atmosphere if it is in a well-ventilated area. The operational subsystem is considered reliable and safe due to the large experience in other systems like enhanced oil recovery and acid gas injection.

The opposite situation is verified for the *in situ* subsystem because of less experience and more uncertainties related to CO_2 behaviour in a geological storage formation after injection. The main concerns of this subsystem are related to CO_2 releases to the surface and water reservoirs. Slow releases of CO_2 to the surface can occur via transmissive faults or fractures (Heinrich *et al.*, 2003). In Figure 2.15 some potential escape routes for injected CO_2 in deep saline formations and their respective remediation measures are presented.

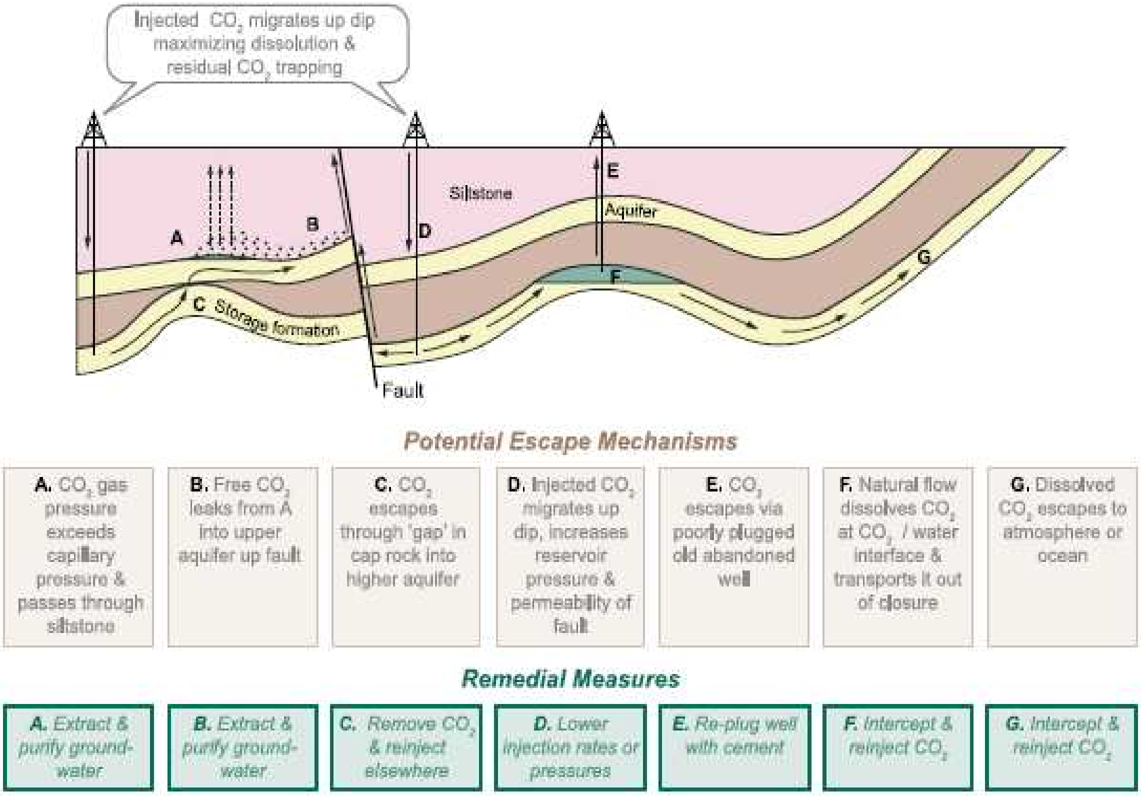

Figure 2.15 Some potential escape routes for CO_2 injected into saline formations (IPCC, 2005).

CO_2 leakages can be unnoticed as they diffuse in the atmosphere and can pose direct threats to the environment and safety if they concentrate to dangerous levels (Heinrich *et al.*, 2003). Surface topography and atmospheric conditions influence the concentration of CO_2 in the surface air. As CO_2 is 50% denser than air, it tends to migrate downwards, potentially creating higher concentrations in confined spaces than in open terrain (IPCC, 2005).

Still relating to the *in situ* subsystem, there are other risks like CO_2 migration within the geologic formation that can contaminate groundwater and originate some type of leaching of toxic metals (Heinrich *et al.*, 2003)**.** The dissolved CO_2 alters the pH of the solution because of the formation of carbonic acid and can cause indirect effects like the mobilization of toxic metals, sulphate or chloride, possibly giving the water an odd odour, colour or taste. If contamination reaches dangerous levels, the use of groundwater for drinking or irrigation has to be stopped (IPCC, 2005).

Seismic events can be induced when a large volume of fluid is injected due to the increase of the reservoir pressure and displacement of other fluids. Some studies identified the existence of biological communities deep in the subsurface at depths where CO_2 storage is likely to occur. But these communities are not well known and neither are the effects of CO_2 on these. Heinrich *et al.*, refer that even if a particular community is affected, the impact on the total biodiversity and ecosystem of the earth will be negligible (Heinrich *et al.*, 2003). On the surface, high CO_2 concentrations in ambient air can accelerate plant growth, but this is generally overlayed by the detrimental effects of elevated CO_2 concentrations in soil. CO_2 can be dangerous at concentrations above 5% and near 20% it becomes phytotoxic. The effects of high CO_2 concentrations depend on the type and density of vegetation, the exposure to other environmental stresses, the prevailing environmental, the presence of low-lying areas and the density of nearby animal populations. In marine ecosystems, CO_2 leaks can be hazardous to benthic environment as the CO_2 moves from deep geological structures through benthic sediments to the ocean (IPCC, 2005).

These local environmental effects of CO_2 storage can also be monitored. In the cases where CO_2 migrates upwards into overlaying shallow groundwater aquifers, it can be detected and assessed by changes in water quality by collecting samples and analyzing major ions like Na, K, Ca, Mg, Cl, pH, alkalinity, stable isotopes and gases. However, it is important to identify CO_2 leaks before it reaches the groundwater. This is possible utilizing the already referred indirect techniques for monitoring CO_2 migration. CO_2 in the air can be monitored by continuous sensors based on infrared detection principles, referred as infrared gas analyzers. Field applications include the measurement of CO_2 concentrations in soil air, flux from soils and ecosystem-scale carbon dynamics. In respect to terrestrial and subsurface ecosystems, the monitoring can be done directly by measuring the productivity and biodiversity of flora and fauna, and by analysing soil gas composition and soil mineralogy. In some cases the monitoring can be done indirectly by remote-sensing techniques as hyperspectral imaging (IPCC, 2005).

A cautious site selection, the definition of adequate monitoring and operation systems and the use of remediation measures to eliminate or limit the causes and impacts in case of leakage are effective ways of managing potential risks associated with CCS (IPIECA and API, 2007). The IPCC Special Report on CCS identifies remediation options for most of the leakage scenarios, as showed in Table 2.3.

Table 2.3 Remediation options for geological CO_2 storage projects (IPCC, 2005).

Scenario	**Remediation options**
Leakage up faults, fractures and spill points	• Lower injection pressure by injecting at a lower rate or through more wells; • Lower reservoir pressure by removing water or other fluids from the storage structure; • Intersect the leakage with extraction wells in the vicinity of the leak; • Create a hydraulic barrier by increasing the reservoir pressure upstream of the leak; • Lower the reservoir pressure by creating a pathway to access new compartments in the storage reservoir; • Stop injection to stabilize the project; • Stop injection, produce the CO_2 from the storage reservoir and reinject it back into a more suitable storage structure.
Leakage through active or abandoned wells	• Repair leaking injection wells with standard well recompletion techniques such as replacing the injection tubing and packers; • Repair leaking injection wells by squeezing cement behind the well casing to plug leaks behind the casing; • Plug and abandon injection wells that cannot be repaired by the methods listed above; • Stop blow-outs from injection or abandoned wells with standard techniques to ‘kill’ a well such as injecting a heavy mud into the well casing. After control of the well is re-established, the recompletion or abandonment practices described above can be used. If the wellhead is not accessible, a nearby well can be drilled to intercept the casing below the ground surface and ‘kill’ the well by pumping mud down the interception well.
Accumulation of CO_2 in the vadose zone[15] and soil gas	• Accumulations of gaseous CO_2 in groundwater can be removed or at least made immobile, by drilling wells that intersect the accumulations and extracting the CO_2. The extracted CO_2 could be vented to the atmosphere or reinjected back into a suitable storage site; • Residual CO_2 that is trapped as an immobile gas phase can be removed by dissolving it in water and extracting it as a dissolved phase through groundwater extraction well; • CO_2 that has dissolved in the shallow groundwater could be removed, if needed, by pumping to the surface and aerating it to remove the CO_2. The groundwater could

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[15] **Vadose zone:** Region from the water table to the ground surface, also called the unsaturated zone because it is partially water-saturated (IPCC, 2005).

	then either be used directly or reinjected back into the groundwater; • If metals or other trace contaminants have been mobilized by acidification of the groundwater, 'pump-and-treat' methods can be used to remove them. Alternatively, hydraulic barriers can be created to immobilize and contain the contaminants by appropriately placed injection and extraction wells. In addition to these active methods of remediation, passive methods that rely on natural biogeochemical processes may also be used.
Leakage into the vadose zone and accumulation in soil gas	• CO_2 can be extracted from the vadose zone and soil gas by standard vapour extraction techniques from horizontal or vertical wells; • Fluxes from the vadose zone to the ground surface could be decreased or stopped by caps or gas vapour barriers. Pumping below the cap or vapour barrier could be used to deplete the accumulation of CO_2 in the vadose zone; • Since CO_2 is a dense gas, it could be collected in subsurface trenches. Accumulated gas could be pumped from the trenches and released to the atmosphere or reinjected back underground; • Passive remediation techniques that rely only on diffusion and 'barometric pumping' could be used to slowly deplete one-time releases of CO_2 into the vadose zone. This method will not be effective for managing ongoing releases because it is relatively slow; • Acidification of the soils from contact with CO_2 could be remediated by irrigation and drainage. Alternatively, agricultural supplements such as lime could be used to neutralize the soil.
Large releases of CO_2 to the atmosphere	• For releases inside a building or confined space, large fans could be used to rapidly dilute CO_2 to safe levels; • For large releases spread out over a large area, dilution from natural atmospheric mixing (wind) will be the only practical method for diluting the CO_2; • For ongoing leakage in established areas, risks of exposure to high concentrations of CO_2 in confined spaces (e.g. cellar around a wellhead) or during periods of very low wind, fans could be used to keep the rate of air circulation high enough to ensure adequate dilution.
Accumulation of CO_2 in indoor environments with chronic low level leakage	• Slow releases into structures can be eliminated by using techniques that have been developed for controlling release of radon and volatile organic compounds into buildings. The two primary methods for managing indoor releases are basement/substructure venting or pressurization. Both would have the effect of diluting the CO_2 before it enters the indoor environment.
Accumulation in surface water	• Shallow surface water bodies that have significant turnover (shallow lakes) or turbulence (streams) will quickly release dissolved CO_2 back into the atmosphere; • For deep, stably stratified lakes, application of active systems for venting gas accumulations.

2.6 Monitoring, mitigation and verification systems

The objective of monitoring, mitigation and verification (MMV) systems is to provide accurate accounting of stored CO_2 and information about CO_2 movements in the storage reservoir and its effective storage, allowing the detection in advance of any possible leakage. These are continuous systems that accompany the transport, injection and storage providing crucial information to the operational system and to environment impact assessment and risk management (NETL, 2008).

The MMV systems are site-specific and are designed to detect CO_2 leaks before representing any danger. The main concern about CO_2 leakage relates to slow and undetectable leakage and its possible impacts for future generations. Further, the risk of

CO_2 leakage should decrease as a function of time after injection stops as the pressure will drop to pre-injection levels as more of the injected CO_2 dissolves into the pore fluids and begins the process of forming chemically stable carbonate precipitates (Dooley, *et al.*, 2006).

Independently of the type of plant, other gaseous emissions and liquid and/or solid wastes are produced beyond the separated CO_2 stream to storage. However, the CO_2 stream contains impurities that have impacts not only on the CO_2 stream transport and storage but also on health, safety and environment. The type and concentration of impurities like H_2S, SO_2, NO, H_2, CO or CH_4 depend on the type of capture process and plant design. The CO_2 stream from post combustion capture generally has low impuritiy concentration (IPCC, 2005). These impurities may have some impacts on monitoring activities to ensure that the captured, transported, injected and stored stream is within the set limits (IPIECA and API, 2007).

2.6.1 Monitoring of CO_2 transport

Regarding MMV systems of CO_2 transport, long-distance pipelines are instrumented with monitoring points in intervals connected to a central operations centre, allowing the flow to be monitored. Pipelines are inspected by internal pipelines inspection devices (called “pigs”), driven along the line by gas pressure. These devices can measure internal corrosion, mechanical deformation, external corrosion, the precise position of the line, and the development of spans in underwater lines. Pipeline monitoring also occurs externally from air at defined intervals. Underwater pipelines are monitored by remotely operated vehicles, small unmanned submersibles that move along the line and make video records. In some cases, pipelines have an independent leak detection system that finds leaks acoustically or by measuring chemical releases, or by picking up pressure changes or small changes in mass balance (IPCC, 2005).

2.6.2 Monitoring of CO_2 storage

Monitoring of CO_2 storage can be used to: monitor the condition of the injection well and measuring injection rates, verify the quantity of injected CO_2 that has been stored, optimize the efficiency of the storage process, demonstrate that the CO_2 remains contained in the storage formation, and detect leakage and provide an early warning for the case that mitigation actions are needed. Prior to subsurface storage monitoring, a baseline survey must be taken so it can be compared with subsequent surveys. Baseline monitoring is indispensable for seismic and other remote-sensing technologies and geochemical monitoring. A baseline of diurnal and annual cycles of CO_2 fluxes resulting from ecosystem cycling of CO_2 is useful to distinguish natural fluxes from potential storage-related releases (IPCC, 2005).

There are different technologies for monitoring injection rates and pressures and subsurface CO_2 distribution. Measurements of injection rates and of injection pressure at the surface and in the formation are common practices in the oil industry and are commercially available. Measurements of injection rates are made by gauges either at the injection wellhead or near distribution manifolds and normally use meters or others devices that relate the pressure drop across the device to the flow rate. For the measurement of injection rates, pressure gauges are installed on most injection wells through orifices in the surface piping near the wellhead and pressure sensors are available and suitable for monitoring pressures at the wellhead or in the formation. The system provides continuous data that are usually transmitted to a central control room. The system of monitoring surface pressure is utilised to ensure that the downhole pressure does not exceed the threshold of the reservoir fracture pressure. Sometimes this system is also connected to shut-off valves that will stop or reduce injection if the pressure exceeds a predetermined safe threshold or if there is a drop in pressure as result of a leak. Currently the state of the technology allows to adequately meet the requirements for monitoring injection rates, wellhead and formation pressures. The data collected from these systems combined with temperature measurements provide information about CO_2 state (supercritical, liquid or gas) and accurate measurement of the injected amount for inventories, reporting, verification and modelling. In some systems impurities are also analyzed, allowing computation of the volume of CO_2 injected (IPCC, 2005).

The monitoring of subsurface distribution of CO_2 can be made by direct and indirect techniques, according to the storage site characteristics. However, direct techniques are limited in availability at present. In CO_2 enhanced oil recovery, the injected CO_2 spreads through the reservoir in a heterogeneous manner because of permeability variations in the reservoir, and once it reaches a production well the produce volume can be readily determined. In some cases the carbon in the injected CO_2 has a different isotopic composition from the carbon in the reservoir and its distribution can be determined on a gross basis by evaluating the arrival of the introduced CO_2 at different production wells. The arrival of CO_2 in a producing area with several injection wells gives only a general indication of the distribution in the reservoir. The use of tracers (gases or gas isotopes not present in the reservoir system) injected into specific wells is a more accurate approach as the timing of arrival of tracers at production or wells indicates the movement of CO_2 through the reservoir. The movement of CO_2 beyond the storage site can be directly measured by comparison of baseline surveys of water quality, isotopic composition and geochemical techniques. It can also be measured at the surface, resorting to samples of CO_2 or tracers in soil gas and near-surface water bearing horizons, or infrared spectroscopy. Monitoring of CO_2 migration in subsurface can also be achieved by indirect techniques that can be seismic, non-seismic geophysical and geochemical. Seismic techniques are based on the measurement of the velocity and energy absorption of waves generated artificially or naturally through rocks as transmission is modified by the rock’s nature and its contained fluids. Passive seismic (microseismic) monitoring techniques can also be applied as they detect microseismic events induced by dynamic responses to the modification of pore pressures or the recreation or creation of small fractures, allowing tracking of pressure changes and possibly the movement of gas in the reservoir or saline formation. Non-seismic geophysical techniques use electrical and electromagnetic and self-potential techniques and measure the conducting of the subsurface as conductivity changes by changes in the fluid. The self-potential of the natural electrical potential of the Earth can also be measured to determine plume migration as well as gravity techniques (ground or air-based) (IPCC, 2005). In Table 2.4 a summary of direct and indirect techniques that can be used to monitor CO_2 storage is presented.

Table 2.4 Summary of direct and indirect techniques that can be used to monitor CO_2 storage projects (IPCC, 2005).

Measurement technique	**Measurement parameters**	**Example applications**
Introduced and natural tracers	Travel time Partitioning of CO_2 into brine or oil Identification sources of CO_2	Tracing movement of CO_2 in the storage formation Quantifying solubility trapping Tracing leakage
Water composition	CO_2, HCO_3^-, CO_3^{2-}. Major ions Trace elements Salinity	Quantifying solubility and mineral trapping Quantifying CO_2-water-rock interactions Detecting leakage into shallow groundwater aquifers
Subsurface pressure	Formation pressure Annulus pressure Groundwater aquifer pressure	Control of formation pressure below fracture gradient Wellbore and injection tubing condition Leakage out of the storage formation
Well logs	Brine salinity	Tracking CO_2 movement in and

	Sonic velocity CO_2 saturation	above storage formation Tracking migration of brine into shallow aquifers Calibrating seismic velocities for 3D seismic surveys
Time-lapse 3D seismic imaging	P and S wave velocity Reflection horizons Seismic amplitude attenuation	Tracking CO_2 movement in and above storage formation
Vertical seismic profiling and crosswell seismic imaging	P and S wave velocity Reflection horizons Seismic amplitude attenuation	Detecting detailed distribution of CO_2 in the storage formation Detection leakage through faults and fractures
Passive seismic monitoring	Location, magnitude and source characteristics of seismic events	Development of microfractures in formation or caprock CO_2 migration pathways
Electrical and electromagnetic techniques	Formation conductivity Electromagnetic induction	Tracking movement of CO2 in and above the storage formation Detecting migration of brine into shallow aquifers
Time-lapse gravity measurements	Density changes caused by fluid displacement	Detect CO_2 movement in or above storage formation CO_2 mass balance in the subsurface
Land surface deformation	Tilt Vertical and horizontal displacement using interferometry and GPS	Detect geomechanical effects on storage formation and caprock Locate CO2 migration pathways
Visible and infrared imaging from satellite or planes	Hyperspectral imaging of land surface	Detect vegetative stress
CO_2 land surface flux monitoring using flux chambers or eddy covariance	CO_2 fluxes between the land surface and atmosphere	Detect, locate and quantify CO_2 releases
Soil gas sampling	Soil gas composition Isotopic analysis of CO_2	Detect elevated levels of CO_2 Identify source of elevated soil gas CO_2 Evaluate ecosystem impacts

The integrity of the injection well also has to be assured. Thus there are several available technologies to monitor the activity of injection wells, like the use of cement bond logs that can help detect deterioration in the cemented portion of the well and can possibly indicate any chemical interaction of the acidized formation fluids with the cement. Injection occurs in a pipe that is lowered into the well and packed off above the perforations or open-hole portion of the well to certify that the injectant reaches the correct level. Monitoring the pressure in the space between the casing and the injection pipe (the annulus) allows the detection of changes in pressures or gas composition and helps to ensure the integrity of the packer, casing and injection pipe (IPCC, 2005).

At present, there are no standard protocols or established network designs for monitoring CO_2 leakage. These are site-specific and depend on the objectives and requirements of the monitoring programme that is determined by regulatory requirements and perceived risks posed by the site. This programme should also provide information to decrease uncertainties over time or increase monitoring demand in case things develop unexpectedly. The actual CCS projects are testing various techniques aiming to determine those that are most effective and less expensive (IPCC, 2005).

Long-term monitoring of CO_2 storage

Beyond the monitoring during the project operation, the storage location also has to be monitored in the long-term. The long-term monitoring objective is to identify CO_2 movements that may lead to releases that could impact long-term storage security and safety, as well as prompt remedial action. The techniques can be the same used during the injection phase. As geological storage can persist on a geological time scale, long-term monitoring is still an undefined issue because there are not yet defined protocols for the kind of monitoring that will be required, by whom, for how long and with what propose (IPCC, 2005).

Verification assesses the amount of CO_2 that is stored underground and the amount of CO_2 leaking back to the atmosphere, if there is any (IPCC, 2005). Thus verification involves the evaluation of the monitoring methodology and the assessment of the inclusion and correct quantification of emissions associated with capture and transport activities, the integrity of the geological reservoir for long-term storage, the amount of CO_2 that is stored underground and possible CO_2 leaks. Gas migration in the storage formation relies on models and according to the “WRI/WBCSD Protocol for Project Accounting”, modelling is an acceptable means of monitoring and verifying GHG emission reductions, as long as any uncertainties or assumptions in the modelling are transparent (IPIECA and API, 2007).

2.7 Energy and emissions balance

The application of a CCS system in a plant requires additional energy for CO_2 capture, compression and transport and storage operations. The additional energy required has associated emissions, considering that it is generated from non-renewable sources. These emissions are here designated as indirect emissions.

There are also different sources of GHG emissions across the CCS chain. Thus an emission source and assessment boundary is established for the CCS system. Figure 2.16 presents a generic scheme of potential GHG emissions sources in a CCS system.

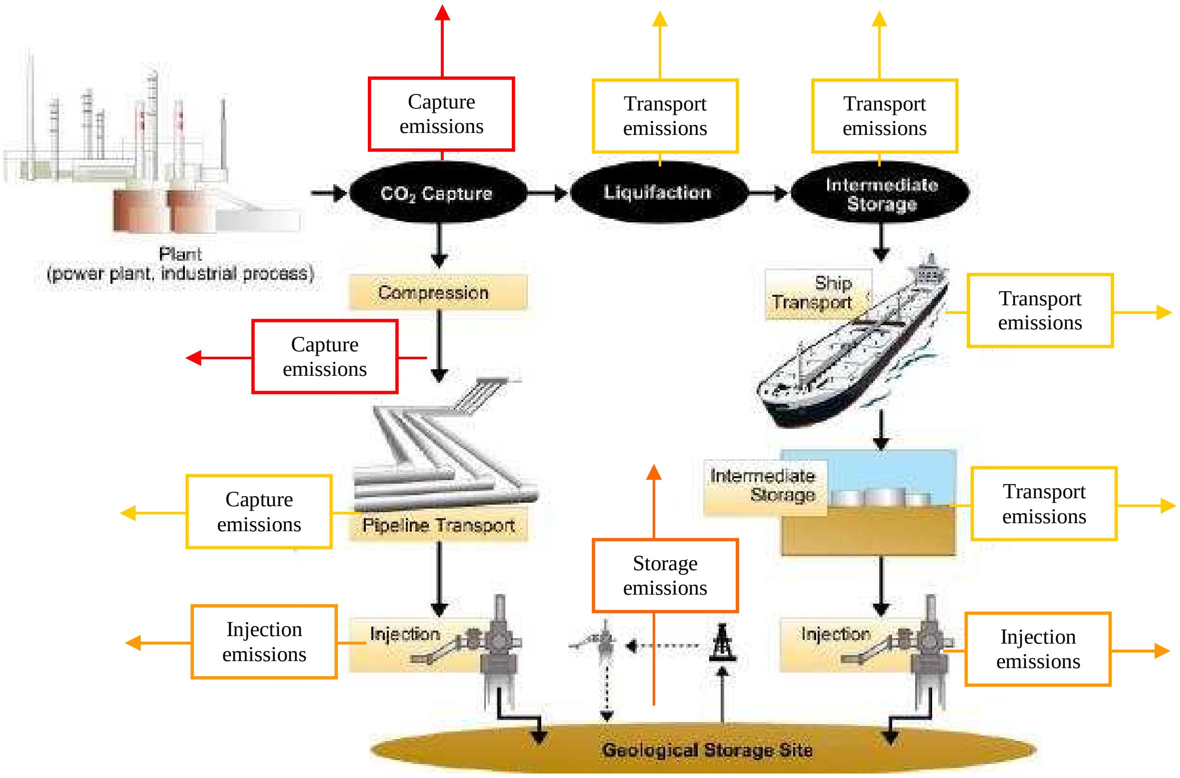

Figure 2.16 Scheme of potential GHG emissions sources in a CCS system (Adapted from (IPIECA and API, 2007)).

Beyond indirect emissions, in the CCS chain there are also vented, fugitive and combustion emissions. In the capture phase, additional energy is required, resulting in indirect emissions. As the capture process is not completely efficient, it also results in CO_2 emissions. The separation of CO_2 from other components in the captured gas, like dehydration to remove H_2O, is a potential source of combustion, vented or fugitive emissions. Compression may occur in this phase resulting in combustion or indirect emissions. During transport, fugitive emission from pressurized equipment leaks can occur. From equipment maintenance, emergency releases, intermediate storage facilities, loading/offloading, and losses in transport, vented emissions can result. There are also indirect emissions associated with the required electricity to pump stations and other equipment (IPIECA and API, 2007). Marine transportation of CO_2 induces more associated emissions than pipelines due to additional energy use for liquefaction and fuel use in ships (IPCC, 2005).

In the storage phase there are vented, fugitive, and combustion emissions from surface equipment at the injection site. For monitoring and maintenance activities, additional energy may be required, resulting in indirect emissions. CO_2 physical leakage from the storage reservoir and from wells can occur, but a cautious site selection, good operating practices and monitoring systems should make these leakages very small. EOR, EGR and ECBM projects can result in vented emissions of CO_2 as well as CH_4 (IPIECA and API, 2007).

In Table 2.5, the emission sources, emission types and the GHG species emitted during the all CCS chain are summarized.

Table 2.5 - Emissions sources, emission type and GHG species of a CCS system (IPIECA and API, 2007).

	Emission source	**Emission type**	**GHG species**
Capture	Dehydration and other gas treatment equipment to separate the CO_2 from other gas stream components	Combustion	Primarily CO_2; CH_4 and N_2O to lesser degree
		Vented	CO_2 and CH_4
		Fugitive	CO_2 and CH_4
	Fuel combustion associated with capture process (Note: compression may occur in the capture step)	Combustion	Primarily CO_2; CH_4 and N_2O to lesser degree
	Purchased electricity associated with capture process	Indirect	Primarily CO_2; CH_4 and N_2O to lesser degree
	Fraction of CO_2 or CH_4 not captured	Vented and fugitive	CO_2 and/or CH_4
	Use and disposal/incineration of CO_2 removal process/agent	Primarily energy consumption	Primarily CO_2; CH_4 and N_2O to lesser degree
Transport	Gas-fired compressor engines	Combustion	Primarily CO_2; CH_4 and N_2O to lesser degree
	Mobile source energy consumption	Combustion	Primarily CO_2; CH_4 and N_2O to lesser degree
	Purchased electricity	Indirect	Primarily CO_2; CH_4 and N_2O to lesser degree
	Pressurized equipment and pipeline leaks	Fugitive	CO_2 and potentially CH_4
	Maintenance or emergency releases	Vented	
	Intermediate storage	Vented	
	Loading/unloading	Vented	
	Losses in transport	Vented	
Injection	Gas-fired compressor engines for injection or recycle	Combustion	Primarily CO_2; CH_4 and N_2O to lesser degree
	Purchased electricity	Indirect	Primarily CO_2; CH_4 and N_2O to lesser degree
	Pressurized CO_2 injection equipment	Fugitive	CO_2 and potentially CH_4
	Maintenance or emergency releases	Vented	
	Production and injection wells	Vented	
	Dehydration and other gas treatment equipment for recycled gas	Combustion	Primarily CO_2; CH_4 and N_2O to lesser degree
		Vented	CO_2 and CH_4
		Fugitive	CO_2 and CH_4
	Purchased electricity	Indirect	Primarily CO_2; CH_4 and N_2O to lesser degree
Storage	Physical leakage from geological formations	Fugitive	CO_2 and potentially CH_4
	CO_2 leakage from wells,	Vented and/or fugitive	
	Uncaptured CO_2 co-produced with oil/gas	Vented	

The additional energy required for the operation of the CCS system and the inefficiency of the capture process itself originates a large amount of emissions associated to this process. To determine the CO_2 emissions reduction or the avoided emissions of a CCS project, it is necessary to compare the emissions of a plant with capture to a reference plant without capture. The emission reduction of a CCS project can be expressed as (IPIECA and API, 2007):

$$\text{CCS project emissions} = \text{VENT} + \text{CMB} + \text{FUG} + \text{IND}$$

where *VENT* are the vented CO_2 emissions, *CMB* are the direct combustion emissions, *FU*G are the fugitive CO_2 emissions and *IND* are the indirect emissions resultant from the additional energy required (IPIECA and API, 2007). Figure 2.17 presents the CO_2 emissions of a plant without CCS and a plant with CCS, the respective emitted and captured emissions and the net emission reduction.

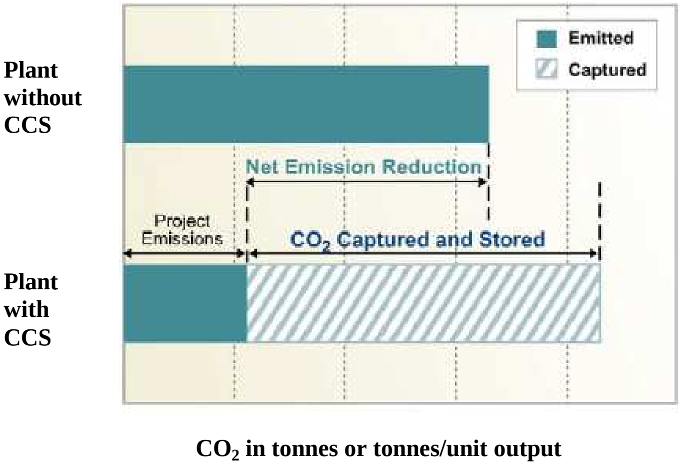

Figure 2.17 Potential emission reduction of a CCS project (Adapted from (IPIECA and API, 2007)).

2.7.1 Comparison of CO_2 capture in different power plant technologies

The application of a CCS system has consequences for power plant efficiency, CO_2 emissions, the investment and production costs and environmental impacts (IEA, 2007). Thus the comparison of the different capture technologies in the different power plant technologies is a useful exercise to understand the consequences and benefits of the application of a CCS system, comparing not only the different capture technologies in different power plant technologies, but also their performance, emissions, costs and environmental impacts with and without a CCS system.

The IEA GHG carried out several studies comparing the thermal efficiency of coal and gas-fired power plants types with and without CO_2 capture. The information from these studies is presented in Table 2.6, as well as the CO_2 emissions, the CO_2 captured and the CO_2 avoided.

Table 2.6 Power plant thermal efficiency and CO_2 emissions in gas and coal-fired power plants with and without CO_2 capture (IEA, 2007).

Fuel	**Power generation technology**	**CO_2 capture technology**	**Net efficiency %(LHV)[16]**	**CO_2 emissions (g/kWh)**	**CO_2 captured (g/kWh)**	**CO_2 avoided (g/kWh)**		
						Same technology baseline	**PF baseline**	**NGCC baseline**
Coal	Pulverised fuel (PF)	None	44.0	743	-	-	-	-
		Post-combustion	35.3	92	832	651	651	287
		Oxy-combustion	35.4	84	831	659	659	295
	IGCC, dry feed	None	43.1	763	-	-	-	-
		Pre-combustion	34.5	142	809	621	601	237
	IGCC, slurry feed	None	38.0	833	-	-	-	-
		Pre-combustion	31.5	152	851	681	591	227
Gas	NGCC	None	55.6	379	-	-	-	-
		Post-combustion	49.6	93	362	316	680	316
		Oxy-combustion	44.7	12	403	367	731	367

Natural gas-fired power plants have the highest net efficiency (55-56%). Among the different types of coal-fired power plants, PF has the highest net efficiency (44%) which is very similar to the net efficiency of dry feed IGCC (43.1%). Slurry feed IGCC plants have the lowest net efficiency, mainly due to lower efficiency of the conversion of coal to fuel gas in the slurry feed gasifier (IEA, 2007).

The application of a CO_2 capture technology requires energy resulting in the loss of efficiency at the power plants. With the application of CO_2 capture technologies at the referred power plant types, the patterns of efficiency hold steady. The NGCC power

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[16] The net efficiency is calculated on a lower heating value (LHV) basis (IEA, 2007). The lower heating value (also known as net calorific value, net CV, or LHV) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25 °C or another reference state) and returning the temperature of the combustion products to 150 °C.The LHV assumes that the latent heat of vaporization of water in the fuel and the reaction products is not recovered. It is useful in comparing fuels where condensation of the combustion products is impractical, or heat at a temperature below 150 °C cannot be put to use. By contrast, the higher heating value (HHV) (a.k.a. gross calorific value or gross CV) includes the heat of condensation of water in the combustion products (http://en.wikipedia.org/wiki/Lower_Heating_Value#cite_note-0). The HHV efficiencies of the coal-fired plants and of the gas-fired plants, are respectively, 0.956 and 0.904 times the LHV efficiencies (IEA, 2007).

plants with CO_2 capture continue to have the highest net efficiency: 49.6% when post-combustion technology is used and 44.7% when oxy-combustion technology is used, representing an efficiency reduction of 6% and 10.9%, respectively. The PF also continue to have the highest net efficiency within the coal-fired power plants: 35.3% and 35.4% with post-combustion and oxy-combustion capture technologies, respectively. The efficiency reduction of CO_2 capture in PF power plants is of 8.6-8.7%. The net efficiency of dry feed IGCC plants with pre-combustion capture is 34.5%, and of slurry feed IGCC plants is 31.5%, representing an efficiency reduction of 8.6% and 6.5%, respectively.

Concerning the power plants' efficiency reduction with CO_2 capture, despite slurry feed IGCC plants having the lowest efficiency, they have the lowest efficiency reduction compared to the other types of coal-fired plants. On the other hand, the NGCC plants that have the highest efficiency, have the highest efficiency reduction (10.9%) when the oxy-combustion capture technology is applied (and a 6.5% efficiency reduction in the case of post-combustion capture technology). Nevertheless, even in this case they have the highest net efficiency.

The loss of efficiency of CO_2 capture is associated with several factors, which vary with the fuel and technology used for combustion. These factors and their effects on plants' efficiency are presented in Figure 2.18.

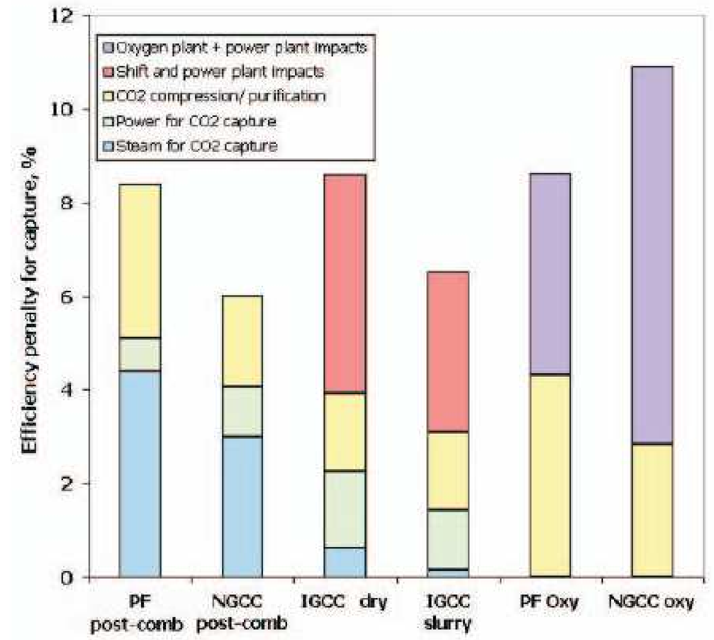

Figure 2.18 – Efficiency penalty for CO_2 capture in different power plants types (IEA, 2007).

2.8 CCS legal and political aspects

2.8.1 Legal and regulatory framework for CCS

Provided that CCS is not yet subjected to an effective framework including legal and regulatory templates and guidelines at national or international level, particularly concerning long-term issues, until today the regulatory issues have been defined on a case-by-case basis (Robertson *et al.*, 2006). The time frame of a CCS project can be simply divided into two phases according to the time scale: short term and long term. For the short-term, the time scale refers to years and decades corresponding to CO_2 capture, transport and injection. The long-term refers to centuries and millennia corresponding to CO_2 storage (IEA and OECD, 2005). The major legal and regulatory issues concerning CO_2 injection and storage are the storage itself, property rights and intellectual property rights. Regarding the long term, the major issues concern the monitoring and verification and liability (Robertson *et al.*, 2006).

Regarding the legal and regulatory issues of CO_2 storage, these include CO_2 definition and classification and the standards for well design at the storage site. CO_2 can be classified as an industrial product or as a waste, the latter being subjected to more stringent environmental regulations. CO_2 classification it also an important issue as it will determine its legality and treatment under international treaties and national laws and regulations. This is particularly true for offshore projects, which are subjected to the London Convention on the Prevention of Marine Pollution by Dumping Wastes and Other Matters (London Convention) and the Protocol to the London Convention (London Protocol), the United Nations Convention on the Law of the Sea (UNCLOS), and the Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR). However, CCS appearance is posterior to these treaties, meaning that a specific framework is needed to deal with CCS projects. In the case of onshore projects, the grey area is larger because international and national jurisdictions may overlap. The United Nations Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (Basel Convention) appears as an important international treaty to regulate trans-border aspects. However, it is not clear if this treaty is applicable to CCS due to the disagreement around CO_2 definition in CCS projects. The standards for well design purposes are to provide a high level of prevention of leakage over the long term. These standards should include operational practices, materials used, number and age of wells, potential geophysical changes, pathways in the event of leakage, and duration of storage (Robertson *et al.*, 2006).

Property rights definition is important to encourage investment and properly regulate the storage site, and has to be clearly defined as they influence liability. These can be divided into three main areas: surface (injection of the CO_2), sub-surface (reservoir), and the CO_2 itself. Nevertheless, this is a new issue not yet clearly defined, making it difficult to determine property rights in the long term. Generally, property rights are defined on a case-by-case basis. Intellectual property rights for CCS are sometimes considered a very long-term issue, not being deemed as an urgent issue and a CCS specific intellectual property rights legal regime has not yet been developed (Robertson *et al.*, 2006).

Every CCS project is a particular situation, and measurement, monitoring and verification (MMV) systems are site-specific. Thus, the best approach seems to be the establishment of guidelines instead of a single MMV framework with a uniform set of requirements. Guidelines should create consistency and uniformity when possible. For the specific kinds of monitoring that should be done for CCS in the short and long-term, including who is responsible for the monitoring process, for how long and how to determine long-term MMV responsibilities in case of existing CO_2 compliance systems such as the European Union Emissions Trading Scheme (EU-ETS), there are still few established guidelines. Liability issues can be divided into short and long term. Short term liability is related to operational issues like environmental, health and safety risks associated with capture, transport and injection of CO_2. Long term liability includes three types of issues: environmental, *in situ* and trans-national liability. The former relates to CO_2 leakage from the storage location and can also be named as climate liability. *In situ* liability refers to leakage or migration that could result in public health, environmental or ecosystem damage. Trans-border liability refers to any liability issues that may affect more than one country (Robertson *et al.*, 2006).

As already mentioned, CCS projects onshore are mainly regulated by individual national legal frameworks. Countries like the United States and Canada have legal and regulatory frameworks for CCS activities (IEA, and OECD, 2005). In the case of Australia there is no legal and regulatory framework specific to all CCS components (capture, transportation and storage) but there are existing and proposed legislative regimes in some States which permit a person to inject and store carbon dioxide underground, under the authority of a statutory licence (Minter Ellison, 2005). It is important to note, however, that there is specific legislation for the Gorgon Project in West Australia (IEA, and OECD, 2005).

In 2008, the European Commission (EC) published a proposal for a directive[17] on the geological storage of CO_2. Part of the existent European legislation can be applied to CCS and the proposal of directive establishes which terms of the existing legislation should apply to which aspects of CCS. In Table 2.7, part of the already implement European legislation is presented that can be also applied to CCS.

Table 2.7 Existent European legislation that can be also applied to CCS.

Directive	Scope	Applicability to CCS
96/61/EC	Integrated Pollution Prevention and Control	Regulation of the risks of CO_2 capture
85/337/EEC	Assessment of the environmental impacts of certain projects	Assessment of the environmental impact of CO_2 capture, pipeline transport and storage
2004/35/EC	Environmental liability	Regulation of the liability for local environmental damage from CCS
2003/87/EC	GHG emission allowance trading	Regulation of the liability for climate damage by requiring surrender of allowances for leakage

The EC proposal for a directive establishes the legal structure for the implementation of a CCS project, defining the intervenient relationship, the procedures for the determination of the storage location, the requisites for the exploration and storage permits, the rules for applications, the operation, closure and post-closure obligations, the third-party access. The EU also plans to have up to 12 CCS pilot projects running by 2015, but none have yet been built.

2.8.2 CCS and the international climate policy framework

The UNFCCC determines the first international step to tackle climate change. The UNFCCC objective established in its Article 2 is the “stabilization of greenhouse gases concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system”. The UNFCCC was signed in 1992 and ratified in 1994 by 189 countries, and established a set of principles like the principle of common but differentiated responsibilities, precaution, equity, the promotion of sustainable

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[17] COM (2008) 18 final – Proposal for a Directive of the European Parliament and of the Council on the geological storage of carbon dioxide and amending Council Directives 85/337/EEC, 96/61/EC, Directives 2000/60/EC, 2001/80/EC, 2004/35/EC, 2006/12/EC and Regulation (EC) No 1013/2006, Brussels, 23.1.2008.

development and commitments to promote scientific, technological and economic cooperation between Parties, providing special attention to developing Parties. On the basis of these principles, the UNFCCC distinguished developed and developing countries, dividing them into three groups: Annex I, Annex II and non-Annex I.The last group consists of developing countries that are not subjected to the same obligations as other Parties. Beyond these groups of countries, there is also the group of the Least Developed Countries, classified by the United Nations according to a set of criteria, which have special attention under the Convention.

The KP was adopted in 1997 and ratified in 2005. The Protocol establishes binding targets for Annex I Parties (Annex I Parties of the UNFCCC that ratified the KP) to reduce their GHG emissions 5.2% below 1990 levels in the commitment period 2008 to 2012, sharing the principles and objectives of the UNFCCC. The Non-Annex I Parties of the KP are not subjected to individual binding targets. Under the KP, three flexibility mechanisms were defined to help the Parties to achieve their targets and to promote cooperation and sustainable development among all the Parties: joint implementation (JI), clean development mechanism (CDM) and emissions trading (ET). In JI, Annex I Parties can implement projects that reduce emissions or remove carbon from the atmosphere in other Annex I Parties, receiving emission reduction units (ERUs). CDM allows Annex I Parties to implement projects that reduce emissions or remove carbon from the atmosphere in Non-Annex I Parties, contributing to the sustainable development in these countries, generating certified emission reductions (CERs). The ET allows Annex I Parties to exchange their emission credits in order to achieve the targets.

The status of CCS is neither clearly defined in the UNFCCC nor in the KP[18]. This raises a big discussion point whether CCS projects are eligible under the flexibility mechanisms of the KP in order to provide credits. This is an important issue that is being considered in the negotiations under the UNFCCC and the KP for the post-Kyoto commitment period. For the inclusion of CCS in any climate change mitigation mechanism, key greenhouse gas accounting issues must be addressed (IEA and OECD, 2005).

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[18] In Appendix I, a selection of relevant provisions under the United Nations Framework Convention on Climate Change and the Kyoto Protocol is presented.

3 Implementation of a CCS system

This chapter intends to give an overview over the selection of CO_2 storage sites, the assessment of CO_2 storage capacity, the process of identification of potential sites for CO_2 geological storage, namely deep saline aquifers and coal beds, CO_2 sources, and CCS costs.

3.1 Assessment of CO_2 storage capacity

The assessment of CO_2 storage capacity can be made trough several types of estimation depending on the nature and purpose of the assessment (Bradshaw *et al.*, 2007). It may be made at various scales – in decreasing order of size and increasing order of resolution: country, basin, regional, local and site-specific. The country-scale assessment determines the country CO_2 storage capacity, what types of storage capacity are available and what risks may exist, without necessarily quantifying the country's potential. The basin-scale assessment focuses on a particularly sedimentary basin (these are usually smaller than a country but in some cases it may straddle countries or be shared by several) to evaluate and quantify is storage potential and to identify regions and/or sites for CO_2 storage and their type, many times also considering the major stationary CO_2 sources in the basin on its vicinity. These two types of assessments should normally be performed by governmental agencies to establish future directions. The regional-scale assessment analyses a portion of the sedimentary basin that has large CO_2 stationary sources and/or because its large potential for CO_2 storage is known. The local-scale assessment is normally carried out at a pre-engineering level or prior to site-selection decisions, where the candidate sites for CO_2 storage are examined to determine site capacity, injectivity and containment. The site-scale assessment is made for the specific storage unit and normally the behaviour of the injected CO_2 is modelled. Industries are normally responsible for the local- and site scale assessments. Depending on the objectives, the regional-scale assessments can be done by governmental agencies and/or industries (Bachu *et al.*, 2007). Figure 3.1 presents the level of detail and resolution for the different assessment scales.

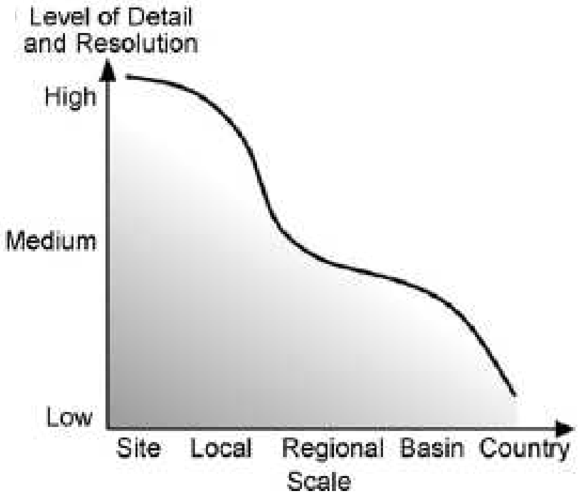

Figure 3.1- Variation in size and resolution of different storage capacities (Bachu *et al.*, 2007).

Table 3.1 describes the estimation of the CO_2 storage capacity in depleted oil and gas reservoirs, deep saline aquifers and coal beds.

Table 3.1 - Estimation of the CO_2 storage capacity in depleted oil and gas reservoirs, deep saline aquifers and coal beds (Bachu *et al.*, 2007).

Geological storage reservoirs types	**Estimation of the CO_2 storage capacity**
Depleted oil and gas reservoirs	Straightforward and is based on recoverable reserves, reservoir properties and in situ CO_2 characteristics.
Deep saline aquifers	Very complex because four trapping mechanisms that act at different rates and time scales, and they can all operate simultaneously. The level of detail and resolution required in the data make reliable and accurate estimation of CO_2 storage capacity estimation in deep saline aquifers practical only at the local and site-specific scales.
Coal beds	The theoretical CO_2 storage capacity is based on coal thickness and CO_2 adsorption isotherms, and recovery and completion factors.

Although there are defined methodologies to estimate CO_2 storage capacity, there are still major challenges due to the lack of data, particularly for coal beds and deep saline aquifers, for which "lack if knowledge about the coefficients that reduce storage capacity from theoretical to effective and to practical, and lack of knowledge about the interplay between various trapping mechanisms at work in deep saline aquifers" (Bachu *et* al., 2007).

According to Bachu et al., 2007, "CO_2 storage capacity constitutes a geological resource (or commodity) whose availability can be expressed using the concepts of resources and reserves in the same way as other energy and mineral commodities such as oil and gas, coal, uranium, iron, gold, etc., are classified". In Bradshaw et al., 2005, a similar concept of the resource pyramids[19] is presented for the capacity for CO_2 storage in geological media. Bradshaw et al., 2005, propose three resources pyramids that represent high level, trap type and effectiveness and techno-economic aspects. These pyramids are presented in Figure 3.2, Figure 3.3 and Figure 3.4, respectively.

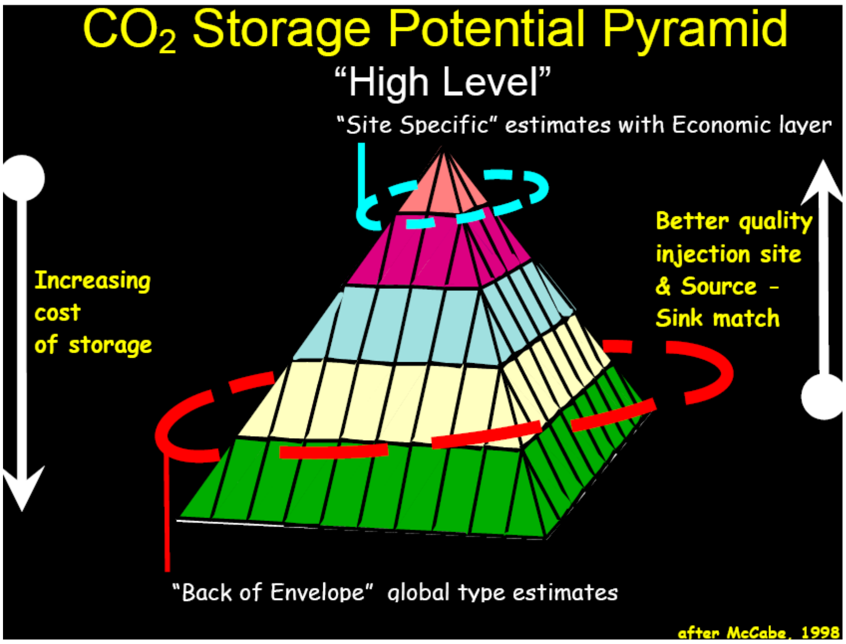

Figure 3.2 - High level resource pyramid for CO_2 geological storage (Bradshaw *et al.*, 2005).

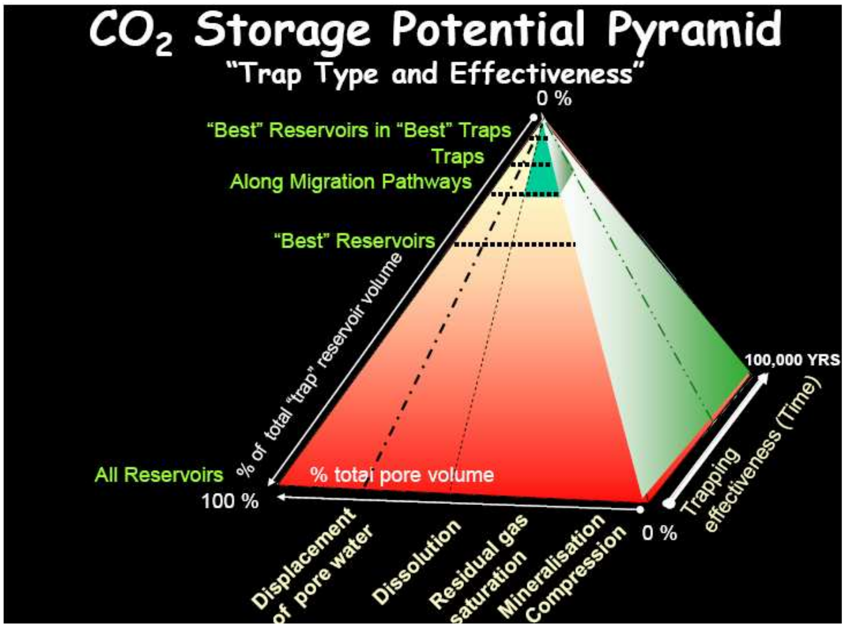

Figure 3.3 - Trap type and effectiveness resource pyramid for capacity for CO_2 geological storage (Bradshaw *et al.*, 2005).

“[19] The concept of resource pyramids was advanced by McCabe in 1988 as a method to describe the accumulation around the world of hydrocarbons in different categories” (Bradshaw, J., *et al.*, 2007).

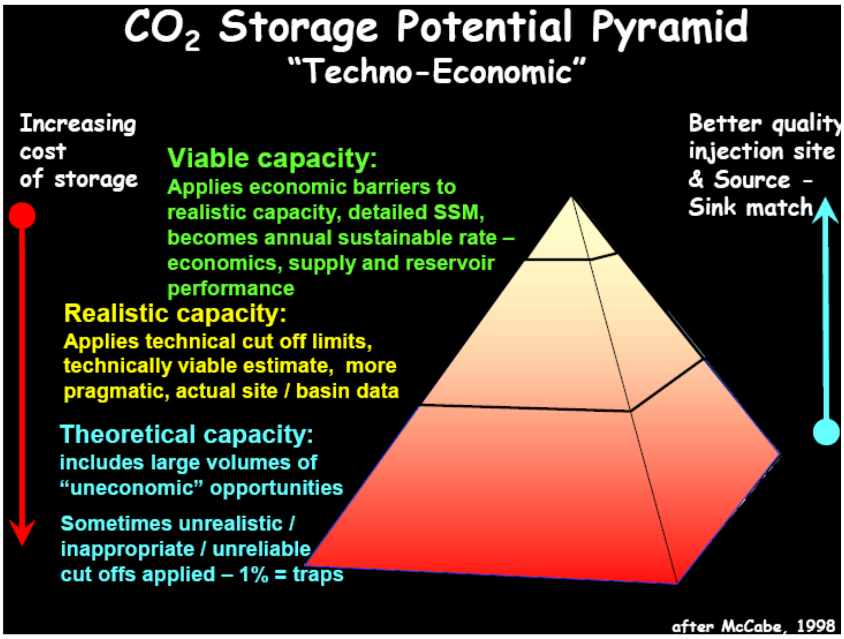

Figure 3.4 - Techno-Economic resource pyramid (Bradshaw *et al.*, 2005).

The High Level resource pyramid for CO_2 storage, Figure 3.2, has at the top "all the storage sites with good geological characteristics and that individually have large storage capacity, which are located close by to sites with low costs of capture" and at the base "the extremely difficult sites, with problematic geological conditions, small storage capacity and that are located a great distance from sources with large capture costs" (Bradshaw *et al.*, 2005). The sites at the base of this pyramid have a total potential storage capacity much greater than those at the top (Bradshaw *et al.*, 2005).

The trap type and effectiveness resource pyramid, Figure 3.3, represents the relationship between the reservoir quality and trap types (left vertical axis), trapping mechanisms (bottom axis) and the timing effectiveness of trapping (right horizontal axis). According to Bradshaw *et al.*, 2005, "at least 3 qualifiers need to be documented in this resource pyramid to explain which storage capacity estimate method has been used. At any time at a particular storage site, some of these trapping mechanisms might be mutually exclusive (e.g. dissolution into the fluids and displacement of fluids), whilst others may partially act simultaneously (e.g. residual gas saturation and compression of fluids and the rock matrix with increasing pressure), and others will compete against each other (e.g. simple compression of fluids such as occurs in a closed system versus displacement of pore fluids in an open system). Over the long term "geological" life of a storage site, many of the trapping mechanisms may actually participate in the eventual trapping mechanism history".

The techno-economic resource pyramid, Figure 3.4, considers three technical and economic categories, being theoretical, realistic and viable capacity. These are described in Table 3.2.

Table 3.2 - Technical and economic categories of the techno-economic resource pyramid (Bradshaw *et al.*, 2005) (Bradshaw, J., *et al.*, 2007).

Techno-economic resource pyramid	
Theoretical capacity	"Assumes that the whole of a reservoir formation is accessible to store CO_2 in its pore volume, or the whole of the formation water in a reservoir formation is available to have CO_2 dissolved into it, or the whole mass of coal is available to adsorb and store CO_2. This provides a maximum upper limit to a capacity estimate, however it is an unrealistic number as in practice there always will be technical and economic limitations across a region that prevent parts of the reservoir formation from being accessed and/or fully utilized. This represents the physical limit of what the geological system can accept. It occupies the whole of the resource pyramid" (Bradshaw *et al.*, 2005).
Realistic capacity	"Applies a range of technical (geological and engineering) cut-off limits to elements of an assessment such as quality of the reservoir (e.g. permeability and porosity) and seal, depth of burial, pressure and stress regimes, size of the pore volume of the reservoir and trap, and whether there may be other competing interests that could be compromised by injection of CO_2 (e.g., existing resources such as oil, gas, coal, water, national parks). This is a much more pragmatic estimate that can be done with some degree of precision, and gives important indications of technical viability of CO_2 storage. These estimates are within the main body of the resource pyramid, but exclude the basal parts of the resource pyramid" (Bradshaw *et al.*, 2005).
Viable capacity	"Is the capacity arrived at by also considering economic, legal and regulatory barriers to CO_2 geological storage, and thus builds upon the realistic capacity assessment. Detailed source/sink matching is performed at this stage to match the best and nearest storage sites to large emission sources. The source/sink matching should extend beyond just geotechnical aspects, and include social and environmental aspects of locating storage sties. At this level of assessment, it may be possible to also express the capacity estimate as an injection rate, not just as a total volume. Because the direct match of nearby suitable sites to emissions sources has been performed, the figures quoted become an annual sustainable rate of injection, where economics, supply volume and reservoir performance are integrated to define the viability of the resource. These capacity estimates are at the top of the resource pyramid" (Bradshaw *et al.*, 2005).

Bachu *et al.*, 2007, presented a new version of the techno-economic resource pyramid after Bradshaw *et al.*, 2007 and Bradshaw *et al.*, 2005 (Figure 3.5).

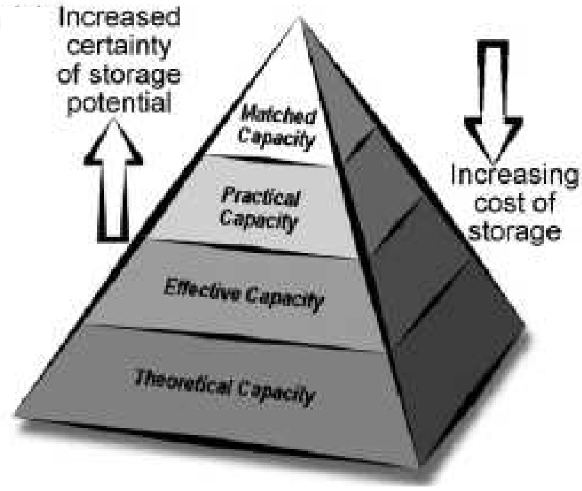

Figure 3.5 – Techno-economic pyramid after (Bradshaw *et al.*, 2007) and (Bradshaw *et al.*, 2005) (Bachu *et al.*, 2007).

In this pyramid various storage capacities are represented, and "their size and position varies in time as data, knowledge, technology, policy, regulatory framework and economics of CO_2 geological storage change" (Bachu *et al.*, 2007). Thus, when the storage capacity is estimated, it is essential that the nature of the estimate and its position in the resource pyramid are specified (Bachu *et al.*, 2007). Table 3.3 describes the categories of this version of the techno-economic resource pyramid.

Table 3.3- Technical and economic categories of the Bachu *et al.*, 2007, version of the techno-economic resource pyramid (Bachu *et al.*, 2007).

Techno-economic resource pyramid	
Effective storage capacity (called previously "Realistic capacity") (Bradshaw, J., *et al.*, 2005) (Bradshaw, J., *et al.*, 2007).	"Represents a subset of the theoretical capacity and is obtained by applying a range of technical (geological and engineering) cut-off limits to a storage capacity assessment, including consideration of that part of theoretical storage capacity that can actually be physically accessed. This estimate usually changes with the acquisition of new data and/or knowledge" (Bachu *et al.*, 2007).
Practical storage capacity (called previously "Viable capacity") (Bradshaw, J., *et al.*, 2005) (Bradshaw, J., *et al.*, 2007).	"Is that subset of the effective capacity that is obtained by considering technical, legal and regulatory, infrastructure and general economic barriers to CO_2 geological storage. As such, it is prone to rapid changes as technology, policy, regulations and/or economics change. The Practical Storage Capacity corresponds to the reserves used in the energy and mining industries" (Bachu *et al.*, 2007).
Matched storage capacity	"Is that subset of the practical capacity that is obtained by detailed matching of large stationary CO_2 sources with geological storage sites that are adequate in terms of capacity, injectivity and supply rate. This capacity is at the top of the resource pyramid and corresponds to the proved marketable reserves used by the mining industry. The difference between matched and practical storage capacities represents stranded storage capacity that cannot be realized because of lack of infrastructure and/or CO_2 sources within economic distance" (Bachu *et al.*, 2007).

The resource pyramid concept as well the concepts of different operating time frames for the various trapping mechanism and of different assessment scales, are absolutely essential to the assessment of CO_2 storage capacity (Bachu *et al.*, 2007).

3.2 Identification of potential CO_2 geological storage locations

A geological medium is considered suitable for CO_2 storage if it has the following characteristics (Bachu, 2007a) (Bachu, 2007b):

- Capacity to accept the intended volume of CO_2;
- Injectivity, to take in CO_2 at the rate at which it is supplied from the CO_2 emitters;
- Confinement to prevent the migration and leakage of buoyant and mobile CO_2 from the storage space to other places in the subsurface, to shallow potable groundwater and/or to the surface;
- Resource protection, which means that if a potential storage site meets the previous conditions, it is unacceptable if other resources are put at risk during the process.

The geological media found in sedimentary basins can present the adequate characteristics for CO_2 storage, "because generally only sandstone and carbonate rocks have the porosity needed to provide storage capacity and the permeability required for injectivity, while confining low permeability shales and evaporites (caprocks), such as salt beds and anhydrites, provide a primary physical barrier to CO_2 migration[20] and/or leakage out of the intended storage unit" (Bachu, 2007a). Coals can also be found in sedimentary basins (Bachu, 2007a).

Rocks suitable for CO_2 storage generally occur in major accumulations of sedimentary rocks known as sedimentary basins that may be up to a few kilometres thick and cover thousands of square kilometres. However, not all sedimentary basins are suitable for CO_2 storage. CO_2 geological storage has to be done under specific physical conditions and CO_2 trap can occur by different mechanisms (Holloway, 2007).

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[20] In this context, migration is defined as lateral movement within the injection stratum, while leakage is defined as upward flow across strata (Bachu, S., 2007).

The viability of geological storage depends on its available capacity to store CO_2. As water-bearing reservoir rocks have reduced economic value and are highly variable, they are not well characterized. This means that the storage capacity of water-bearing reservoirs is not known and is difficult to estimate (Holloway, 2007). Holloway, 2007, mentions that in face of this situation, it is difficult to construct representative geological models of CO_2 injection and flow in this type of reservoirs and that there are no accepted methods of estimating their storage capacity based on commonly available public domain data. In the evaluation of coal bed methane, two parameters are determinant: the total gas in place and the reservoir deliverability. After its identification, the CO_2 storage capacity has to be estimated (Bachu, 2007b).

The identification of suitable CO_2 geological storage sites involves several phases, as showed in Figure 3.6.

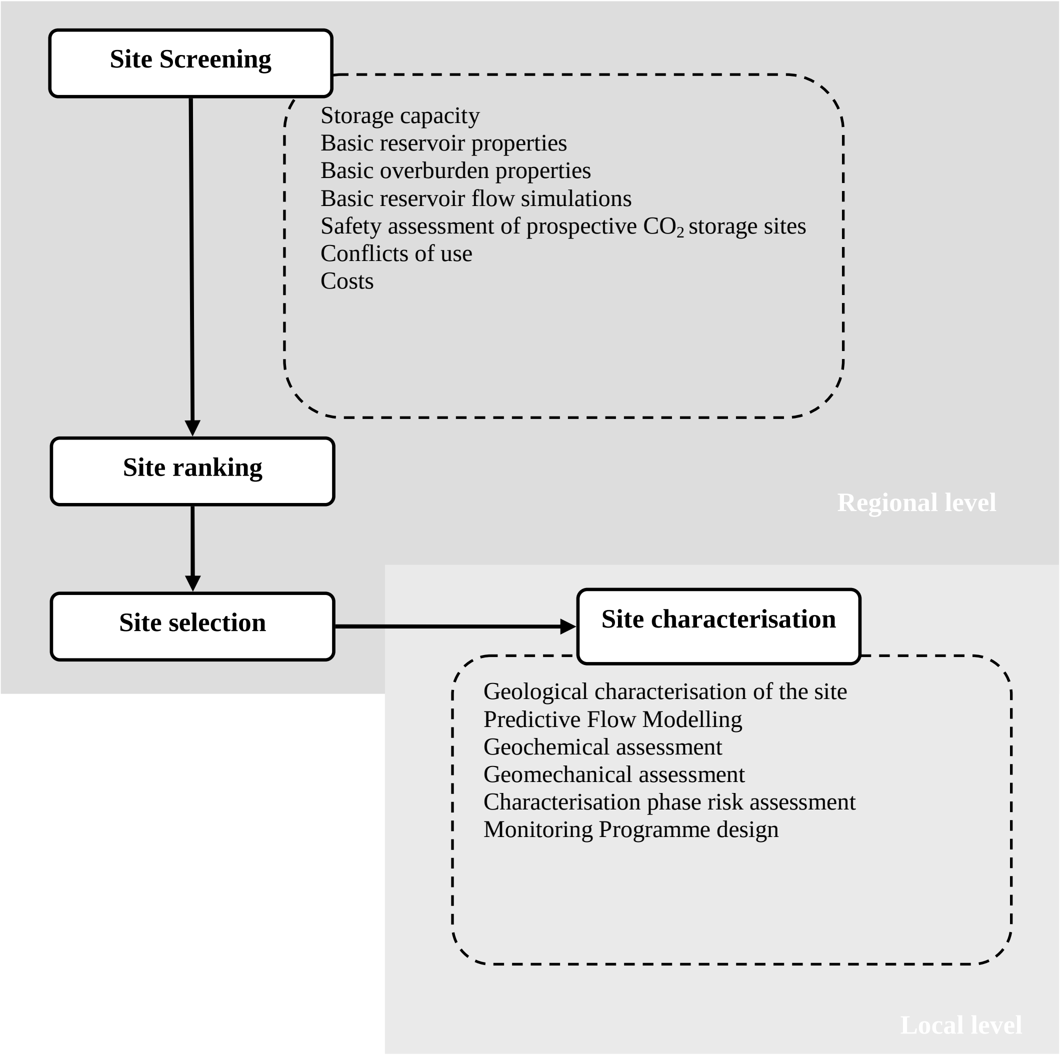

Figure 3.6 Phases of the identification of a site for CO_2 geological storage (Adapted from Chadwick *et al.*, 2006).

Site screening allows evaluating if a determined region is appropriate to store CO_2 by identifying, assessing and comparing possible candidate storage sites. Screening is based on geological, environmental, economic and logistical considerations (Chadwick *et al.*, 2006).

3.2.1 Deep saline aquifers

The main geological indicators that determine the suitability of a deep saline aquifer as a storage site are reservoir depth, thickness, porosity, permeability, seal integrity and salinity, which are presented in Table 3.4 (Chadwick *et al.*, 2006).

Table 3.4 Geological criteria to storage site suitability (Chadwick *et al.*, 2006).

	Positive indicators	**Cautionary indicators**
Storage capacity		
Total storage capacity	Total capacity of reservoir estimated to be much larger than the total amount produced from the CO_2 source	Total capacity of reservoir estimated to be similar to or less than the total amount produced from the CO_2 source
Reservoir properties		
Depth (pressure)	>1000 m <2500 m	<800 m, >2500m
Reservoir thickness (net)	>50 m	<20 m
Porosity	>20%	<10%
Permeability	> 300mD*	<10-100 mD
Salinity	> 100gl^{-1}	< 30 gl^{-1}
Caprock properties		
Lateral continuity	Unfaulted	Lateral variations, faulting
Thickness	> 100m	<20 m
Capillary entry pressure	Capillary entry pressure much greater than buoyancy force of maximum predicted CO_2 column height	Capillary entry pressure similar to buoyancy force of maximum predicted CO_2 column height

**millidarcy* (mD) (1 darcy $\approx 10^{-12}$m^2)

Suitable aquifers for CO_2 storage should contain the mentioned salinity threshold (salinity > 100 gl^{-1}) to avoid spoiling potable water resources, should exceed the referred porosity and permeability, should provide storage at depths of 800 m or more (because CO_2 is in a dense fluid phase and distant from the ground surface or sea bed), should have a minimum thickness (to limit the potential storage areal footprint) and must be overlain by low permeability caprocks. Nevertheless, they should have other boundaries permeable to the native pore fluids (mainly brine) that will allow the displacement of these pore fluids (Chadwick *et al.*, 2006).

Due to CO_2 buoyancy, efficacy of the topseal is usually a prerequisite and in dipping aquifers, the nature of lateral sealing features is very important too. The compartmentation of reservoirs, i.e. lateral sealing of reservoirs, can help retain CO_2 in the desired storage location, but can also impair injectivity and lead to elevated injection pressures (Chadwick *et al.*, 2006).

The determination of the storage capacity of a reservoir formation depends on the properties of the reservoir rock itself and on the nature of its boundaries. However, to assess aquifer storage capacity in detail, a considerable amount of additional information about the reservoir is required (Chadwick *et al.*, 2006). According to Chadwick *et al.*, 2006, volume storage in aquifers depends on many commonly poorly-determined parameters and issues, including:

- The pore volume in structural or stratigraphical traps;
- Whether any of the traps will leak;
- The achievable CO_2 saturation in traps;
- Where there are many small traps, and the percentage of these that can be accessed by a realistic number of wells;
- The amount of CO_2 that will dissolve into the saline pore fluids;
- The amount of CO_2 that will be trapped along the CO_2 migration path as a residual saturation;
- Whether local or regional pressurization of the aquifer due to CO_2 injection will limit its storage capacity.
- The density of CO_2 and any other gas components.

The determination of the storage efficiency[21] depends on several factors like the structural geometry and stratigraphical heterogeneity of the storage formation and as it

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[21] Storage efficiency is defined as that fraction (by volume) of the reservoir pore space that can be filled by CO_2 (in free or dissolved form). It is useful to distinguish between regional storage efficiency, a parameter used during screening and relating to the total pore volume of a reservoir in a (large) area covering several potential traps and local storage efficiency, a parameter normally used during site characterisation/planning and relating to the pore volume in a specific trap or linked trap system (Chadwick *et al.*, 2006).

is not an intrinsic property of reservoir, its one of the greatest uncertainty in storage estimation (Chadwick *et al.*, 2006).

After site screening, the selected sites are deeply characterised in order to refine storage capacity estimates and confirm all the requirements that will assure effective CO_2 storage in safe conditions. A reasonable geological characterization of the storage reservoir and its overburden[22] is a major step in the process, producing information on the structure of the reservoir and its stratigraphy and physical properties. This phase objective is to confirm and refine the screening studies, providing basic data for the predictive fluid flow and geochemical simulations, and including legal issues, seismic data, risk assessment, geomechanical assessments, monitoring plans and remediation strategies. The basis of the calculations of the reservoir volume is geological models (Chadwick *et al.*, 2006). According to Chadwick *et al.*, 2006, the key datasets for a robust characterisation of reservoir and overburden are:

- A regular grid of 2D seismic data over sufficient area to characterise broad reservoir structure and extents;
- A high quality 3D seismic volume over the injection site and adjacent area, tuned if possible for satisfactory resolution of both reservoir and overburden;
- Sufficient well data to permit characterisation of reservoir and overburden properties.

The geological characterization involves the characterization of the reservoir structure and its properties and the characterization of the overburden and caprock properties. The characterization of the reservoir structure is essential both at a local and regional level to the determination of CO_2 migration patterns and bulk storage potential. In this stage several studies have to be done, like structure mapping of depth to top reservoir, reservoir thickness, reservoir structural compartmentation and the estimation of the probable storage footprint. The characterization of the reservoir properties is important to assess its lateral and vertical stratigraphical and hydraulic properties, as these properties control the evolution of the CO_2 plume. A detailed geochemical and mineralogical assessment is also important to predict probable reactions between

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[22] The whole geological succession overlying the reservoir can, for convenience, be termed the overburden and, forming the lower part of this, the sealing formation directly overlying the reservoir, can be termed the caprock (Chadwick *et al.*, 2006).

dissolved and gaseous CO_2, the host rock and saline fluids within the reservoir. The characterization of the overburden and caprock properties is an important element for the assessment of safety in long-term storage. It can provide additional information about the reservoir, like the presence of other reservoirs and sealing formations in the overburden. The analysis of the long-term integrity caprock is crucial. When it cannot be robustly demonstrated, the consequences of migration scenarios should be included in risk assessment. Several laboratory and field techniques can be applied to examine the transport characteristics, like intrinsic permeability, capillary entry pressure, relative permeability, dilatancy and pathway flow (Chadwick *et al.*, 2006).

Flow modelling is a key element in the site characterization as it provides quantitative predictions of reservoir behaviour. According to Chadwick *et al.*, 2006, flow can be used to refine capacity estimates, to evaluate the likely lateral spread of CO_2 in the future (essential for designing effective monitoring programmes) and to examine putative leakage scenarios (for site risk assessment) (Chadwick *et al.*, 2006).

The geochemical assessment is an important aspect in assessing the safety of a CO_2 storage site as the reactivity between CO_2, porewater and minerals will influence the long-term storage potential of the reservoir. This phase of the site characterisation studies these chemical interactions that might change the physical characteristics of parts of the storage site and thus potentially enhance CO_2 migration towards the surface. Dry CO_2 in a dense phase is chemically inert but when it dissolves in water it will form carbonic acid, acidifying the formation water which may then alter many types of rocks. These alterations can occur in the reservoir where it is injected, in the overlying caprock(s), in fractures present in the caprock and/or the reservoir and at the wellbores (Chadwick *et al.*, 2006). The geochemical impact assessment at the storage site involves four steps, which are presented in Figure 3.7

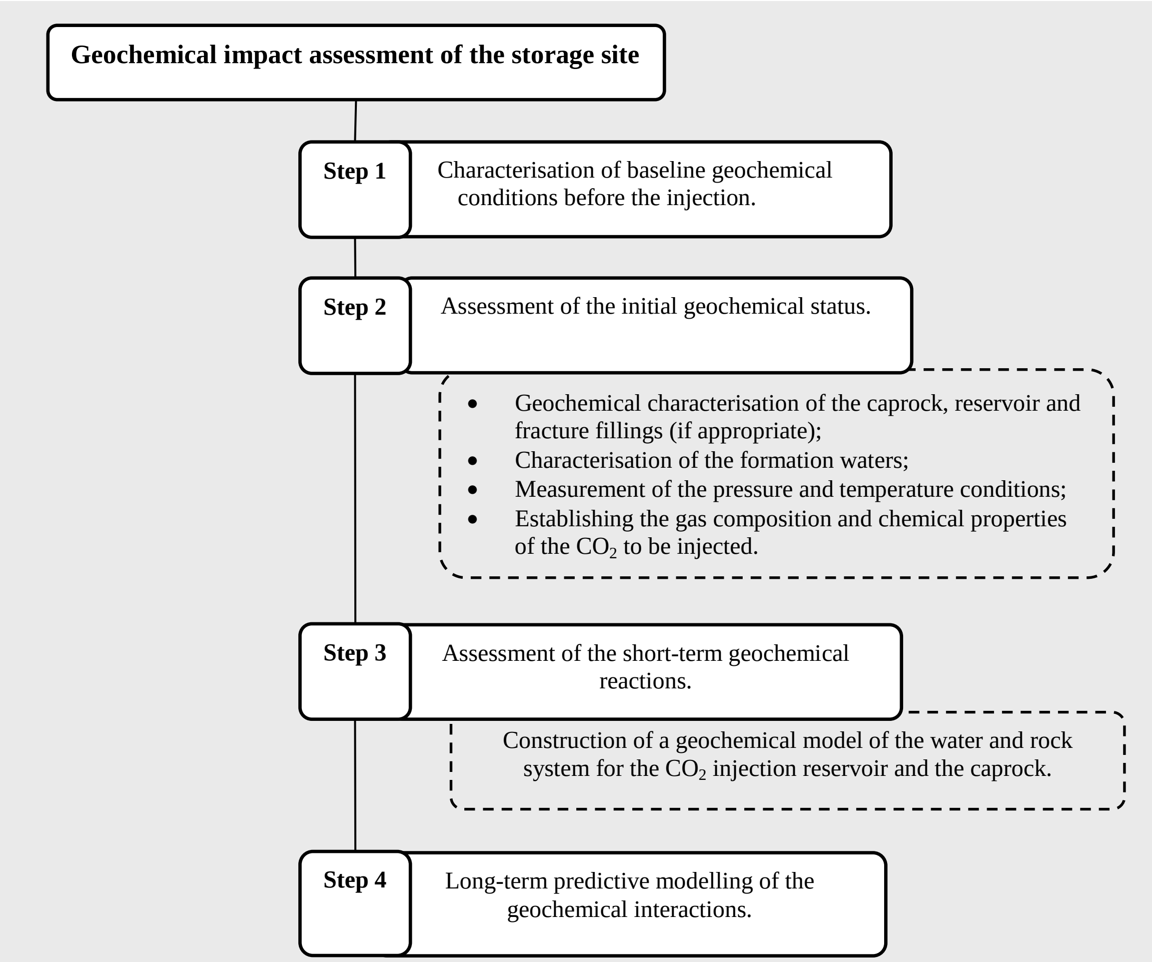

Figure 3.7 Steps for geochemical impacts assessment of the storage site (Adapted from Chadwick *et al.*, 2006).

Risk assessment can me made following the Features Events and Processes (FEP) and Scenario methodology. In the FEP method, risk assessment is based on simulations of different scenarios built up from FEPs. The monitoring programme’s aim is to provide information to enable site remediation in the case of unpredicted events and to enable a good site closure strategy because it allows demonstrating that the site is performing in accordance to predictions and will probably continue after closure (Chadwick *et al.*, 2006).

3.2.2 Coal beds

For CO_2 storage in coal beds and CBM recovery, beyond the adequate capacity, injectivity and confinement characteristics, they should (Bachu, 2007b):

- “possess adequate permeability of at least 1–5 mD (this relates to injectivity);

- have simple structure (i.e., the reservoir should be minimally faulted and/or folded);
- be homogeneous and confined (i.e., the presence of an overlying seal will prevent upward leakage of mobile CO_2 that is not adsorbed onto the coal matrix);
- have low water saturation (coals with low water saturation are preferable because the coal seam has to be dewatered before it can be used for storage);
- have high gas saturation (from a methane-production perspective);
- have concentrated coal deposits (fewer, thick seams); however, more recently this criterion has been challenged because thick coals could be mined at some time in the future, thus, rather than sterilize a potential resource, multiple thin coal seams should be used;
- be unmineable, now or in the future. Unmineable coals are coals that are too thin, too deep, or too unsafe to mine; they may be too high in sulphur or mineral matter, or be too low in heat value to be economically profitable".

This set of criteria, besides having been specifically applied in the identification of suitable CO_2 storage sites in Alberta's, Canada, coal beds, according to Bachu, 2007b, can be easily adapted and applied to other regions (Bachu, 2007b). One determinant factor in the viability of a CO_2 storage site is coal permeability, which "varies widely and generally decreases with increasing depth as a result of cleat closure with increasing effective stress" (Bachu, 2007b). The gas that is in contact with coal also affects coal permeability which can be "reduced by up to two orders of magnitude in the presence of gaseous CO_2 as a result of swelling" (Bachu, 2007b). Another important factor is that CO_2 is a plasticizer for coal, "lowering the temperature required to cause the transition from a glassy, brittle structure to a rubbery, plastic structure, destroying any pre-existing permeability that would have allowed CO_2 injection" (Bachu, 2007b). Despite these effects negatively affecting the CO_2 storage in coal beds, they depend on coal type, rank and characteristics. For temperature and pressures above the critical point, the process of CO_2 trapping in coals is still not completely understood. This lack of understanding represents some constraints to CO_2 storage in coal beds (Bachu, 2007b). Bachu, 2007b, states that this lack of understanding "indicates that, unless significant advances in science and technology are made, only coals at in situ temperature and pressure conditions where CO_2 is in gaseous phase should be considered for the time being as suitable for CO_2 storage" and that "these constraints reduce the depth window for CO_2 storage in coal beds to a range of a few hundred metres to less than 1000 m depth" (Bachu, 2007b).

3.3 Sources characterisation

In the identification of suitable sources for the application of a CCS system, several factors like the source type, the flue gas volume, the CO_2 content in the flue gas and the scale of emissions have to be considered. Source types can be divided into mobile or stationary and according to the type of industrial activity. The characterization of the composition of the flue gas is important not only to identify the concentration of CO_2 but also the CO_2 partial pressure[23]. These parameters are determinant for the selection of the capture process. Low CO_2 partial pressure requires more stringent conditions for the capture process and high partial pressure requires only dehydration and some compression, lowering capture costs. The volume of flue gas and the content of CO_2 in it depend on the type of fuel used and the excess air level used for optimal combustion conditions. Among the already identified industrial processes suitable to CCS are power generation, cement manufacture, oil refining, ammonia production, iron and steel manufacture and production of hydrogen (IPCC, 2005).

Large facilities that produce significant quantities of CO_2, designated large stationary sources, are considered as the main applicants to CCS. However there has to be a threshold for the definition of large stationary source[24]. Despite dispersed stationary sources like buildings and mobile sources like transports having high CO_2 emissions, the emission volumes from the individual sources in these sectors tend to be smaller than those from the power and industry sectors, and they are not considered suitable for the application of CCS technology due to the economies of scale associated with the capture processes as well as the difficulties and costs of transporting small amounts of CO_2 (IPCC, 2005).

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[23] Partial pressure is the pressure that would be exerted by a particular gas in a mixture of gases if the other gases were not present (IPCC, 2005).

[24] For example, in the scope of the IPCC Special Report on CCS the large stationary sources considered involve fossil fuel and biomass use in fuel combustion activities, industrial processes and natural gas processing, that emit more than 0.1 $MtCO_2\ yr^{-1}$ because sources emitting less than these value together account for less than 1% of the emissions from all the stationary sources under consideration.

3.4 Worldwide CCS projects

Worldwide, there are several CCS projects that have already occurred, others are currently in progress or planned. Some of these projects are presented in Table 3.5.

Table 3.5 – CO$_2$ storage projects (IPCC, 2005).

Project name	**Country**	**Injection start (year)**	**Approximate average daily injection rate (tCO$_2$ day^{-1})**	**Total (planned) storage (tCO$_2$)**	**Storage reservoir type**
Weyburn	Canada	2000	3000 – 5000	20000000	EOR
In Salah	Algeria	2004	3000 – 4000	17000000	Gas field
Sleipner	Norway	1996	3000	20000000	Saline formation
K12B	Netherlands	2004	100	8000000	EGR
Frio	USA	2004	177	1600	Saline formation
Fenn Big Valley	Canada	1998	50	200	ECBM
Qinshui Basin	China	2003	30	150	ECBM
Yubari	Japan	2004	10	200	ECBM
Recopol	Poland	2003	1	10	ECBM
Snohvit	Norway	2006	2000	Unknown	Saline formation
Gorgon (planned)	Australia	2009	10000	Unknown	Saline formation

The International Energy Agency Greenhouse Gases R&D Programme produced a world map of large CO$_2$ capture and storage projects, which is presented in Figure 3.8 and

Figure 3.8 – CO$_2$ capture projects
(http://www.co2captureandstorage.info/docs/IEAGHGccsworldmap.pdf).

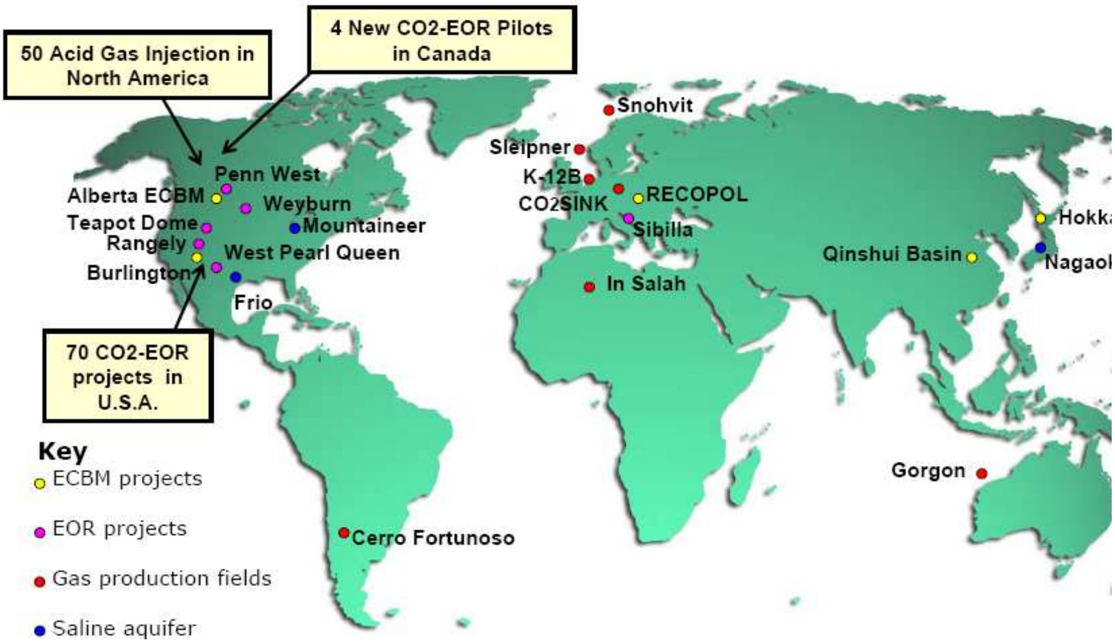

Figure 3.9 - CO_2 storage demonstration projects (http://www.co2captureandstorage.info/docs/IEAGHGccsworldmap.pdf).

3.5 CCS costs

The assessment of CCS costs considers all components of the system: capture and compression, transport, injection and storage, including monitoring costs and remediation costs if necessary. These costs are dependent on many factors like fuel prices, the cost of capital and costs for meeting potential regulatory requirements (IPCC, 2005). Other very important factors to take into account are if the CCS system will be retrofit to an existing plant or if it will be applied to a new plant, and how the application of a CCS system will reflect in the cost of the final product, like electricity in the case the system is applied on a power plant.

3.5.1 CO_2 capture costs

Considering the complete CCS system, the most expensive component refers to the CO_2 capture. This varies with the pressure and concentration of CO_2 in the flue gas or process stream, generally being cheaper in pure and high-pressure CO_2 stream. These characteristics lower the capture cost as less compressing is necessary before the CO_2 is introduced to a pipeline to be transported to the storage location. But the costs of CO_2 capture also depend considerably within technology classes (type of industrial process, plant's age, efficiency, fuel type, technology selection, emissions controls, capture process and efficiency) (Dooley *et al.*, 2006).

The total cost of CO_2 capture includes operation and maintenance costs and a substantial part of the total costs pertain to the energy requirements for capture and compression. There are different options to integrate the cost of additional energy requirements for CO_2 capture. It can be assumed that the energy needed to operate the CO_2 capture is provided within the plant boundary or it is purchased from outside the plant boundary. In some cases it is considered that new equipment is installed to generate auxiliary energy on-site (IPCC, 2005).

The IPCC Special Report on CCS defines four measures of CO_2 capture costs: capital cost, incremental product cost, cost of CO_2 avoided and cost of CO_2 captured or removed. The capital cost for CO_2 capture systems generally represents the expenses necessary to design, purchase and install the system. The best way to determine the total incremental cost of CO_2 is by calculating the difference in total cost between plants with and without CO_2 capture, producing the same amounts of product (e.g. electricity). The cost of CO_2 capture will be reflected in the cost of the final product. For example, the incremental cost of electricity is the difference in electricity cost with and without CO_2 capture. The cost of CO_2 avoided reflects the average cost of reducing atmospheric CO_2 emissions by one unit while providing the same amount of product as a plant without CCS. Sometimes, this cost is taken as a measure of the cost to society of reducing GHG emissions, in this case reflecting the average cost of moving from one situation to a different situation with lower emissions (e.g. different technologies and fuel mix). The cost of CO_2 captured reflects the economic viability of a CO_2 capture system given a market price for CO_2. The cost of CO_2 captured is numerically lower than the costs of CO_2 avoided due to the energy required to operate the capture system which raises the amount of CO_2 emitted per unit of product (IPCC, 2005).

According to Hendricks *et al.*, 2004, the financial performance of a particular capture process depends on the full load hours / yearly operating hours; the capital change rate[25]; and on the fuel costs (defined on lower heating value[26]). Hendricks *et al.*, 2004 developed a computer programme to calculate efficiency losses and capture costs

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[25] The capital change rate is used to annualise the capital investment of the plant and can be calculated from the presumed discount rate and lifetime of the capital.

[26] Lower heating value: energy released from the combustion of a fuel that excludes the latent heat of water.

depending on the size of the plant, type of fuel used, production technology, and concentration of CO_2 in the flue gas. Table 3.6 presents the costs and plant characteristics for various types of power plants (natural gas combined cycles (NGCC) integrated gasification combined cycles (IGCC) and pulverised coal-fired power plants) with capture of CO_2.

Table 3.6 Costs and plant characteristics for power with CO_2 capture (Hendricks *et al.*, 2004).

Type of capture technology	Pre-combustion	Pre-combustion	Post-combustion	Post-combustion	Post-combustion
Type of plant	Natural Gas (NGCC)	Coal (IGCC)	Natural Gas (NGCC)	Natural gas fired (steam)	Coal (pulverised)
Without capture					
Plant efficiency (%LHV)	58%	47%	58%	42%	42%
Emission factor (kgCO_2/kWh)	0.35	0.72	0.35	0.48	0.81
Power costs (€/kWh)	3.1	4.8	3.1	3.8	4.0
With capture					
Plant efficiency (%LHV)	51.5%	42.2%	52%	36.4%	33.7%
Emission factor (kgCO_2/kWh)	0.05	0.09	0.05	0.07	0.12
Loss of plant efficiency	6.5%	4.8%	6%	5.6%	8.3%
Power costs (€/kWh)	4.6	6.4	4.1	5.0	6.0
CO_2 avoided (%)	85%	88%	85%	85%	85%
Costs (€/t CO_2)	43	26	37	30	29

In Table 3.7 are showed the typical cost of CO_2 capture for industrial plants.

Table 3.7 Typical costs of CO_2 capture for industrial plants (Hendricks *et al.*, 2004).

Facility	**€/tCO_2**
Cement plants	28
Iron and steel plants	29
Ammonia plants (flue gas)	36
Ammonia plants (pure CO_2)	3
Refineries	29-42
Hydrogen (flue gas)	36
Hydrogen (pure CO_2)	3
Petrochemical plants	32-36

Applying a CCS system to existing plants might be more expensive and might cause higher efficiency losses than applying it to newly built plants (Hendricks *et al.*, 2004). The costs of retrofitting a capture system to an existing coal-fired power plant are influenced by plant age, size, low efficiency and high energy requirement for capture due to less efficient heat integration for sorbent regeneration. All these factors, in conjunction with site-specific difficulties like land availability and access to plant areas, increase the capital cost of a retrofit project relative to a new equivalent one (IPCC, 2005). The IPCC Special Report on CCS summarizes the key assumptions and results of several studies of post-combustion CO_2 capture using an amine-based absorption system at new coal-fired power plants and retrofitting to an existing coal -fired power plants (Table 3.8).

Table 3.8 CO_2 capture costs for existing and new pulverized-coal (PC) power plants using current technology (IPCC, 2005).

Study assumptions and results	Existing PC power plant		New PC power plant	
	Range		Range	
	Min	Max	Min	Max
Reference plant (without capture)				
Reference plant size/net output (MW)	248	470	462	758
Plant capacity factor [27] (%)	67	91	65	85
Net plant efficiency, LHV (%)	33	37	41	45
Coal cost, LHV (US$ GJ^{-1})	0.98	3.07	0.98	1.50
Reference plant emission rate (tCO_2 MWh^{-1})	0.90	1.00	0.74	0.81
Capture plant design				
Net plant size/output with capture (%)	140	400	329	676
Net plant efficiency, LHV (%)	19	25	30	35
CO_2 capture system efficiency (%)	90	96	85	90
CO_2 emission rate after capture (t MWh^{-1})	0.06	0.37	0.09	0.15
CO_2 captured (Mt yr^{-1})	1.48	2.66	1.83	4.17
CCS energy requirement (% more input MWh^{-1})	43	77	24	40
CO_2 reduction per kWh (%)	63	94	81	88
Cost results				
Reference plant cost of electricity (US$ MWh^{-1})	18	26	43	52
Capture plant cost of electricity (US$ MWh^{-1})	51	70	62	86
Incremental cost of electricity for capture(US$ MWh^{-1})	31	62	18	34
Percent increase in capital cost (over reference plant)			44	74
Percent increase in cost of electricity (over reference plant)	149	291	42	66
Cost of CO_2 captured (US$/tCO2)	31	56	23	35
Cost of CO_2 avoided (US$/tCO2)	45	73	29	51

The range of the cost of CO_2 captured and avoided is higher when the CCS system is applied to an existing coal-fired power plant. Although there is an increase in the cost of electricity whenever a capture system is applied, the range of incremental cost of

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[27] The net capacity factor of a power plant is the ratio of the actual output of a power plant over a period of time and its output if it had operated at full nameplate capacity the entire time.

electricity is higher for retrofitting a capture system to an existing plant. The energy requirement for a CCS system is much higher when it is retrofitted to an existing plant.

The costs presented in Table 3.8 are based on current technology and refer only to capture. The capture cost confidence level is moderate, meaning that “no commercial application for the system and/or scale of interest, but technology is commercially deployed in other applications; issues of scale-up, operability and reliability remain to be demonstrated for this application” (IPCC, 2005). Compression costs depend on the pressure that is required to the CO_2 transport. Higher pressures imply more energy and investment costs (Hendricks *et al.*, 2004).

3.5.2 CO_2 transport costs

The costs of transport and storage are much lower than the costs of capture (Friedmann *et al.*, 2006). The determination of CO_2 transport and storage costs depends on the mean of transportation, on the distance of the CO_2 source to the storage location and on the characteristics of the storage reservoir. Pipeline costs can be divided into construction costs, operation and maintenance costs (including monitoring), and other costs like design, fees and rights-of-way. The transport costs differ between onshore and offshore pipelines, the latter often being about 40% to 70% more costly than the former. Onshore pipeline transport costs depend significantly on the terrain characteristics as they could increase by 50% to 100% or more if the route is congested and heavily populated (IPCC, 2005). Assuming that the CO_2 will be transported via land-based pipelines, as this is a common via to transport this and other gases, costs like the pipeline diameter and construction issues like circuitous routing and terrain characteristics have to be considered in the overall CO_2 transport costs. From the natural gas pipeline land construction experience, the capital costs for transport pipelines are in the order of $40 000/mile per inch of pipeline diameter (Dooley *et al.*, 2006).

The tank truck and rail CO_2 transport options are more than twice as expensive as pipelines. The costs of marine transportation systems comprise investments for ships (design and operation), loading and unloading facilities, and intermediate storage and liquefaction units. Ship transport becomes cost-competitive with pipeline transport over larger distances. The cross-over point at which it happens depends on many factors like distance, loading terminals, water depth, fuel cost, construction costs and security (IPCC, 2005). In Figure 3.10, the variation of transport cost with distance for onshore and offshore pipelines and ships is presented. The costs include intermediate storage facilities, harbour fees, fuel costs, and loading/unloading activities and consider additional costs for liquefaction compared to compression.

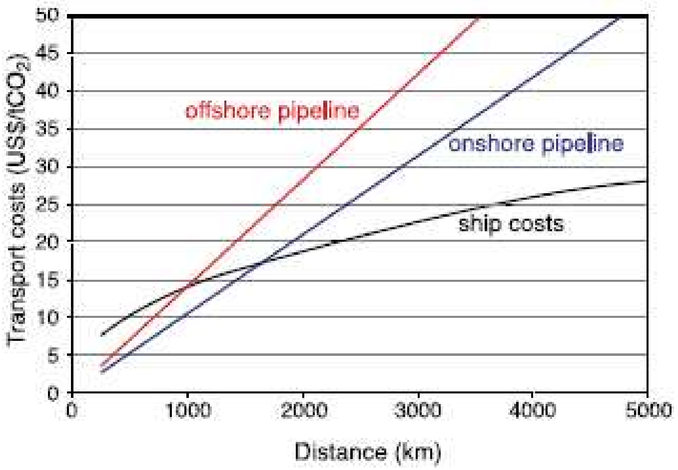

Figure 3.10 Costs of CO_2 transport against distance, for onshore and offshore pipelines, and ships (IPCC, 2005).

It also has to be considered who is responsible for the operation and maintenance of the CO_2 transport system. The costs associated with the pipeline infrastructure construction and development of the storage site can be supported by utilities, or the transport system can be constructed and operated by midstream pipeline operators, and long-term storage can be handled by another company or a government agency (Fernando *et al.*, 2008).

3.5.3 CO_2 storage costs

The costs of storage exclude those from the previous components. The main capital costs of CO_2 geological storage are drilling wells, infrastructure and project management, while operating costs include manpower, fuel and maintenance (IPCC, 2005). The injection costs depend mainly on drilling wells and operational costs. Storage costs are largely influenced by the number of required wells, which depends on the injectivity and the allowed overpressure, and the years of operation (Hendricks *et al.*, 2004). However, these costs are site-specific, depending on the type of reservoir, location, depth and other characteristics of the storage reservoir formation. The costs of offshore storage are generally higher due to higher operational costs (IPCC, 2005).

The main items of CO_2 storage in saline formations are reservoir and injection characteristics like permeability, thickness and depth that affect injection rates and well costs. In Europe, cost estimations for CO_2 geological storage in onshore saline formations for depths of 1000-3000 m are between 1.9-6.2 US$/t$CO_2$stored, the most likely value being 2.8US$/t$CO_2$ stored (IPCC, 2005).

In disused oil and gas reservoirs, the costs may benefit from reduced exploration and monitoring costs. In Europe, CO_2 storage costs on onshore in these reservoirs at depths of 1000-3000 m are in the range of 1.2-3.8 US$/t$CO_2$ stored, the most likely value being 1.7US$/t$CO_2$ stored. Offshore storage costs are 3.8-8.4 US$/t$CO_2$ stored and the most likely value is 6US$/t$CO_2$ (IPCC, 2005).

In EOR, EGR and ECBM projects that use CO_2 injection, the CO_2 is purchased, representing a significant proportion of the operating costs. The costs of CO_2 storage can be offset in these projects as CO_2 injection and storage are combined with enhanced oil or gas recovery and ECBM. Onshore EOR operation costs are in the range of 10-16 US$/t$CO_2$ (37-59 US$/tC) (IPCC, 2005). The costs of storage in EOR, EGR and ECBM projects are sensible to oil and natural gas prices (Hendricks *et al.*, 2004).

The cost elements of ocean storage include offshore transportation and injection of the CO_2, depending respectively on distance and depth. The costs of storage via mineral carbonation are uncertain because this technology is still in a research and development phase. The cost elements are mining and chemical processing (Table 3.9) (IPCC, 2005).

The monitoring costs depend on the monitoring strategy and technologies used and how these are adapted for the duration of storage projects. They also depend on regulatory requirements and how long-term monitoring strategies evolve (IPCC, 2005).

Table 3.9 presents a summary of estimates of CO_2 storage costs.

Table 3.9 Estimates of CO_2 storage costs (IPCC, 2005).

Option	**Representative Cost Range (US$/tonne CO_2 stored)**
Geological – Storage [a]	0.5-8.0
Geological – Monitoring	0.1-0.3
Ocean [b]	
Pipeline	6-31
Ship (Platform or Moving Ship Injection)	12-16
Mineral Carbonation [c]	50-100

[a] does not include monitoring costs.
[b] includes offshore transportation costs; range represents 100-500 km distance offshore and 3000 m depth.
[C] unlike geological and ocean storage, mineral carbonation requires significant energy inputs equivalent to approximately 40% of the power plant output.

4 Hypotheses for the implementation of a CCS system in mainland Portugal – source sink matching

The implementation of a CCS system involves several stages that were already described in the previous chapters. The formulation of hypotheses for the implementation of a CCS system in mainland Portugal will be based on the identification of the main large point sources of CO_2 and of the possible geological storage locations.

4.1 Methods overview

The first step was the identification of carbon dioxide stationary sources in mainland Portugal. The CO_2 stationary sources considered were the installations included in the phase II of the EU-ETS. As LPS are the main applicants to CCS, two criteria were defined for their identification. These criteria depend on the annual CO_2 emissions per installation. The last available data are from 2007. For the identification of LPS, the criteria defined were: the group of installations with the highest CO_2 emissions, until representing about 90% of the total CO_2 emissions in 2007 or the group of installations whose annual emissions in 2007 were larger than 0,1 $MtCO_2\ yr^{-1}$. This last criterion is defined in the IPCC Special Report on CCS. The results achieved with the application of these two were exactly the same – 24 LPS. The next step was the mapping of these LPS and of the potential geological CO_2 storage areas. The storage areas considered were the geological formations identified by INETI and CIAGEB studies: the zone to the west of the Anadia-Ferreira do Zêzere axis and the Pombal-Ourém region, the Setubal Peninsula zone, the Sines zone and the Douro coal basin. After the mapping of LPS and storage areas, the source-sink matching criteria were identified. Then, the analysis of the hypotheses for the implementation of CCS systems in mainland Portugal based on source-sink matching was performed, considering only the proximity of the sources and storage sites. A cost estimation for a CCS system in mainland Portugal, considering only CO_2 capture, transport and storage, was also attempted.

4.2 Sources of CO_2 in mainland Portugal

4.2.1 Overview of GHG emissions in Portugal

According to the Portuguese National Inventory Report on Greenhouse Gases[28], 1990 – 2006 (hereafter called NIR 2006) (Ferreira *et al.*, 2008), the energy sector is the main source of GHG emissions in Portugal as it is highly dependent on fossil fuels. CO_2 is the gas emitted in the largest quantities, representing 77.5 % of total GHG emissions in 2006, the energy related activities being responsible for about 90% of total CO_2 emissions in the same year. In 2006 the share of the energy sector represented 72% of national GHG emissions, transport and energy industries being responsible for 24.2% and 26.8% of total GHG emissions respectively (Figure 4.1). In the period 1990-2006 an increase of about 49% of total emissions was registered in the energy sector (Ferreira *et al.*, 2008).

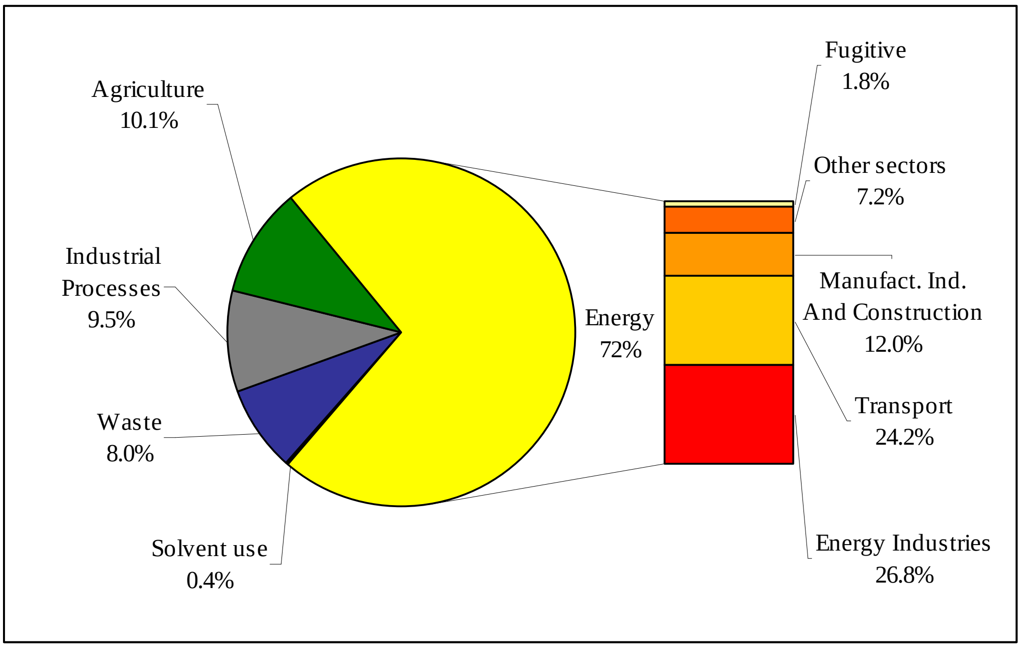

Figure 4.1 – GHG emissions in Portugal by sector in 2006 (adapted from Ferreira *et al.*, 2008).

The CO_2 emissions from energy related activities depend on the type of fuel and its carbon intensity. In the period 1990-2006, about 84% of the primary energy consumed was produced by fossil fuel combustion. In this period, the GHG with the greatest increase in emissions was CO_2, whose emissions grew by 48%. The majority of CO_2

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[28] Submitted under the United Nations Framework Convention on Climate Change and the Kyoto Protocol. In concordance with the UNFCCC Reporting Guidelines, where emissions estimates are grouped into six large IPCC categories: Energy, Industrial Processes, Solvent use, Agriculture, Land-Use Change and Forestry, and Waste.

emissions is from fossil fuel combustion in energy-related activities. The industrial processes sector, whose emissions are generated as a by-product of many non-energy-related activities (cement production, road paving, limestone and dolomite use, lime production, glass and ammonia production), also represents a considerable part of CO_2 emissions (Ferreira *et al.*, 2008). In Figure 4.2 the sources categories of CO_2 in 2006 are presented.

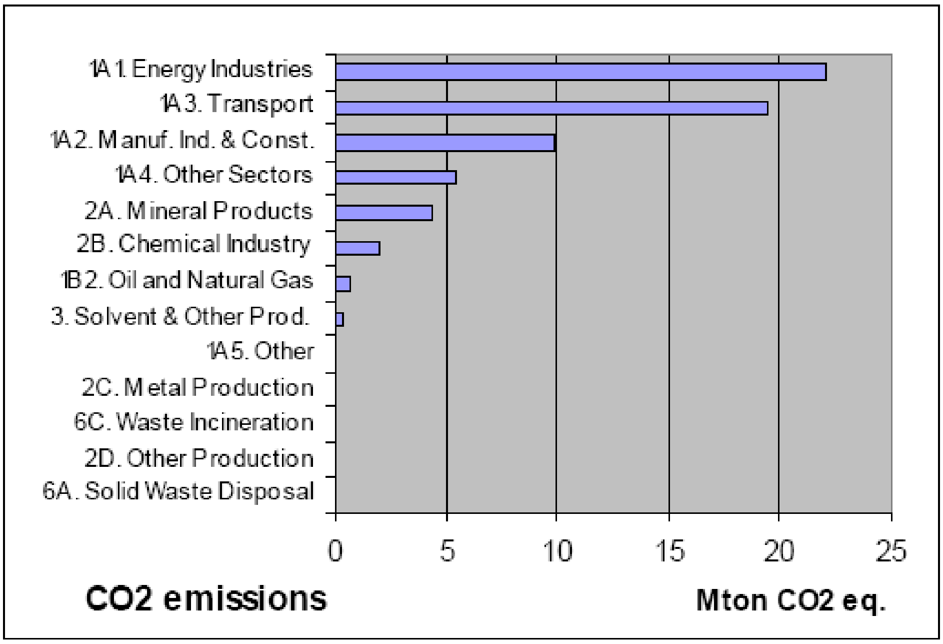

Figure 4.2 - 2006 source categories of CO_2 in mainland Portugal (from Ferreira *et al.*, 2008).

4.2.2 Identification of CO_2 stationary sources in mainland Portugal

The identification of CO_2 stationary sources in mainland Portugal was based on the installations included in the Phase II of the EU-ETS[29], corresponding to the Kyoto Protocol commitment period of 2008-2012 (see Appendix II). In this period the EU-ETS will continue to comprise mandatorily only the CO_2 emissions from the installations included in the categories of activities defined in the EU-ETS Directive (energy activities, production and processing of ferrous metals, mineral industry and pulp and paper production). The national installations included in the phase II of the EU-ETS are listed in the National Allocation Plan II (NAP II) (2008-2012) (see Appendix II). For the definition of the installations to be included in the second

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[29] Created by Directive 2003/87/EC of the European Parliament and of the Council of 13 October and amended by Directive 2004/101/EC of the European Parliament and of the Council of 27 October 2004. These Directives were transposed to the national law by Decree-Law no. 233/2004, of 14 December, Decree-Law no. 234-A/2004, of 31 December, Decree-Law no. 230/2005, of 29 December, and by Decree-Law no. 72/2006, of 24 January.

commitment period, the NAP II respected the European Union guidelines regarding the definition of combustion installation, namely[30] the EU-ETS Directive and the Directive concerning Integrated Pollution Prevention and Control (IPPC) [31] (RCM 1/2008). This reinterpretation affected the chemical and ceramic sectors, as can be seen in Figure 4.3, which compares the number of installations per sector in the EU-ETS periods of 2005-2007 and 2008-2012 (MAOTDR, 2008). The national installations included in the phase I of the EU-ETS are listed in the National Allocation Plan I (NAP I) (2005-2007).

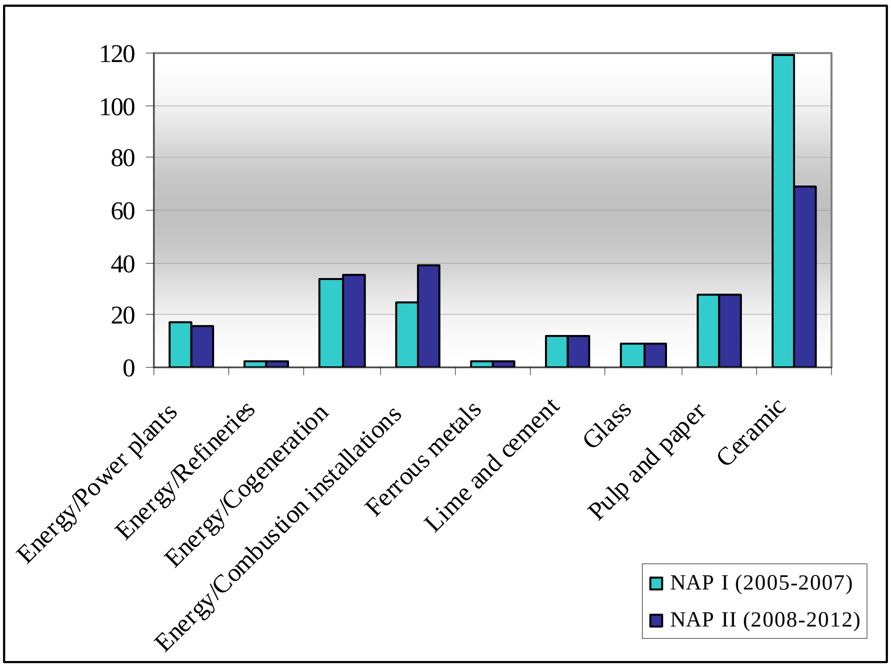

Figure 4.3 – Number of installations included in the NAP I (2005-2007) and in the NAP II (2008-2012) per sector (PNALE I, 2005) (PNALE II, 2008).

The number of installations included in the NAP I and II were 248 and 212, respectively. In the NAP II the number of installations of the ceramic sector decreased and the number of combustion installations increased. In Figure 4.4, the emissions allowances per sector for these two periods are presented.

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[30] The articulation between the EU-ETS and the IPPC Directive was clarified by the European Commission communications COM(2003)830 of 7 January 2004 and COM(2005)703 of 22 December 2005.

[31] Council Directive 96/61/EC of 24 September 1996 and amended by Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008, transferred to the national law by Decree-Law 194/2000, of 21 August. The IPPC Directive includes economic activities with which is potentially associated a pollution level that is considered significant and is defined according to the installation nature and production capacity.

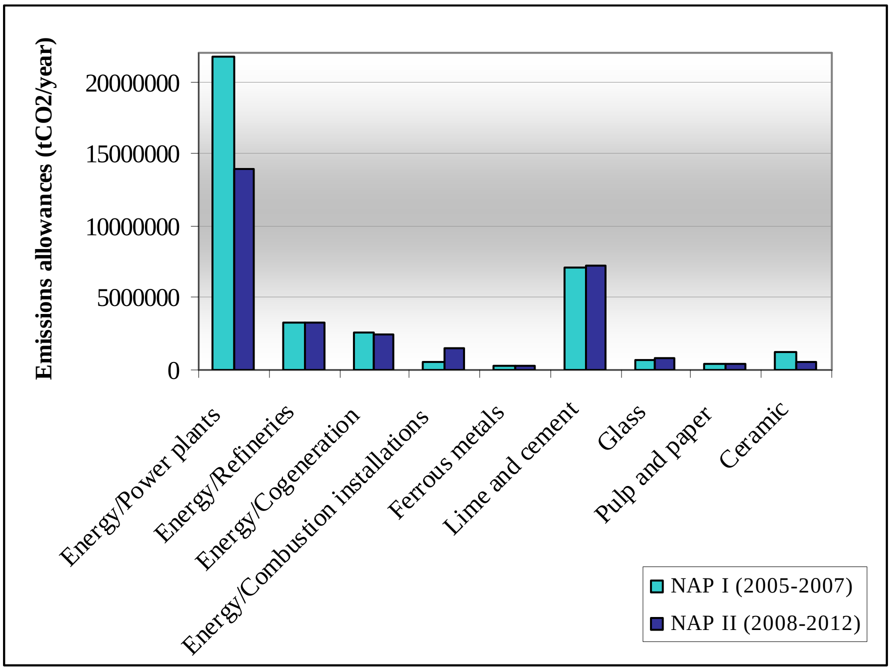

Figure 4.4 – Emissions allowances (tCO_2/year) attributed per sector in the NAP I (2005-2007) and in the NAP II (2008-2012) (PNALE I, 2005) (PNALE II, 2008).

In both periods, power plants had the greatest share of emissions allowances, followed by the lime and cement sector, refineries and cogeneration installations. In mainland Portugal, 204 installations are included in the phase II of the EU-ETS, 84 being of the energy sector (including power plants, refineries, cogeneration and combustion installations) which account for about 68% of the total annual emissions allowances attributed for the 2008-2012 period. The biggest share is assigned to power plants that, with nine installations, account for about 44% of the total annual emissions allowances. Within the power plants sector, the coal subsector has the major share of annual emissions allowances, representing about 67% of the allowances endorsed to this sector. The two refineries included in the EU-ETS account for about 11% of the total annual emissions allowances. Among the non-energy related sectors, the ceramic sector is the one with most installations included, but only represents about 2% of the total annual emissions allowances attributed for the 2008-2012 period. The cement and lime subsector account for about 25% of the total annual emissions allowances, with 13 installations included.

During the 2005-2007 period, 38,16 $MtCO_2eq$/ year were allocated to the installations included in the EU-ETS, where 36,91 $MtCO_2eq$/year correspond to the existent installations and the remaining 1,25 $MtCO_2eq$ /year were reserved to new installations. For the 2008-2012 period, the yearly amount of emissions allowances is 34,81

$MtCO_2eq$ /year, 30,5 $MtCO_2eq$ /year being attributed to the existent installations and 4,3 $MtCO_2eq$ /year constituting a reserve for new installations. The allowances attributed to this period imply the effort installations included in the EU-ETS will have to make to comply with the Kyoto targets[32] (MAOTDR, 2008).

An analysis of the phase I of the EU-ETS in Portugal (2005-2007) performed by the Portuguese Ministry for Environment, Spatial Planning and Regional Development (MAOTDR – Ministério do Ambiente, Ordenamento do Território e do Desenvolvimento Regional), concluded that the emissions of the installations included in the EU-ETS correspond to about 40% of the total national GHG emissions (MAOTDR, 2008).

The installations included in the EU-ETS have to report their annual emissions, by presenting a GHG Emissions Report to the National Authority, until the 31st of March of the following year. Figure 4.5 presents the sectoral CO_2 emissions in 2007, according to the communications of the installations to the Portuguese Environmental Agency for that year.

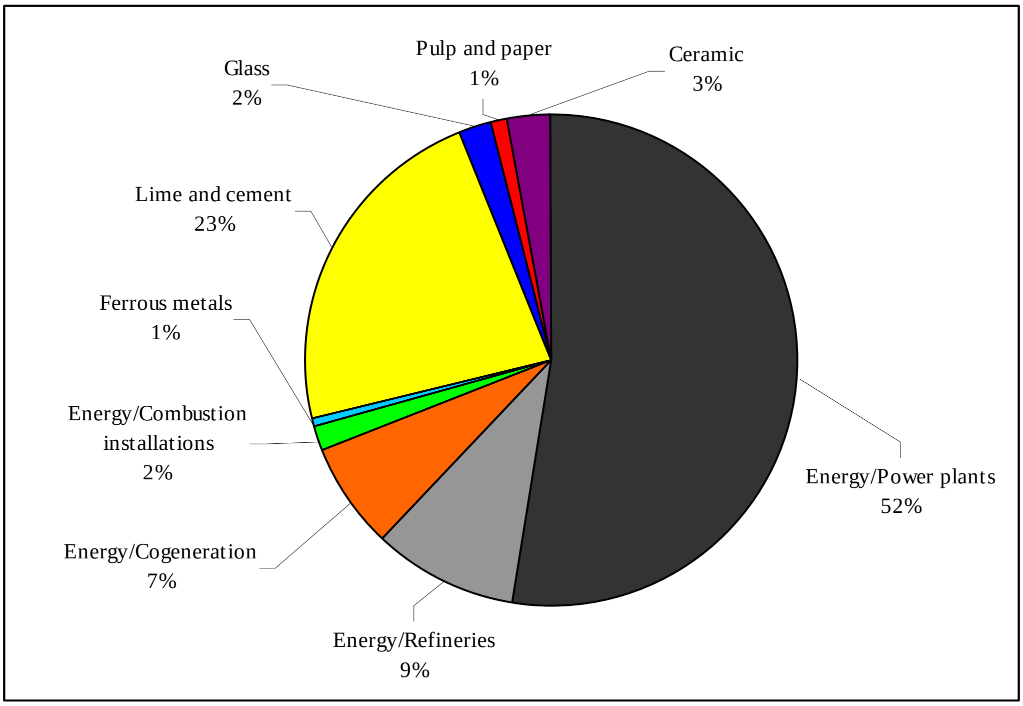

Figure 4.5 - Sectoral emissions in 2007 (APA, 2008a).

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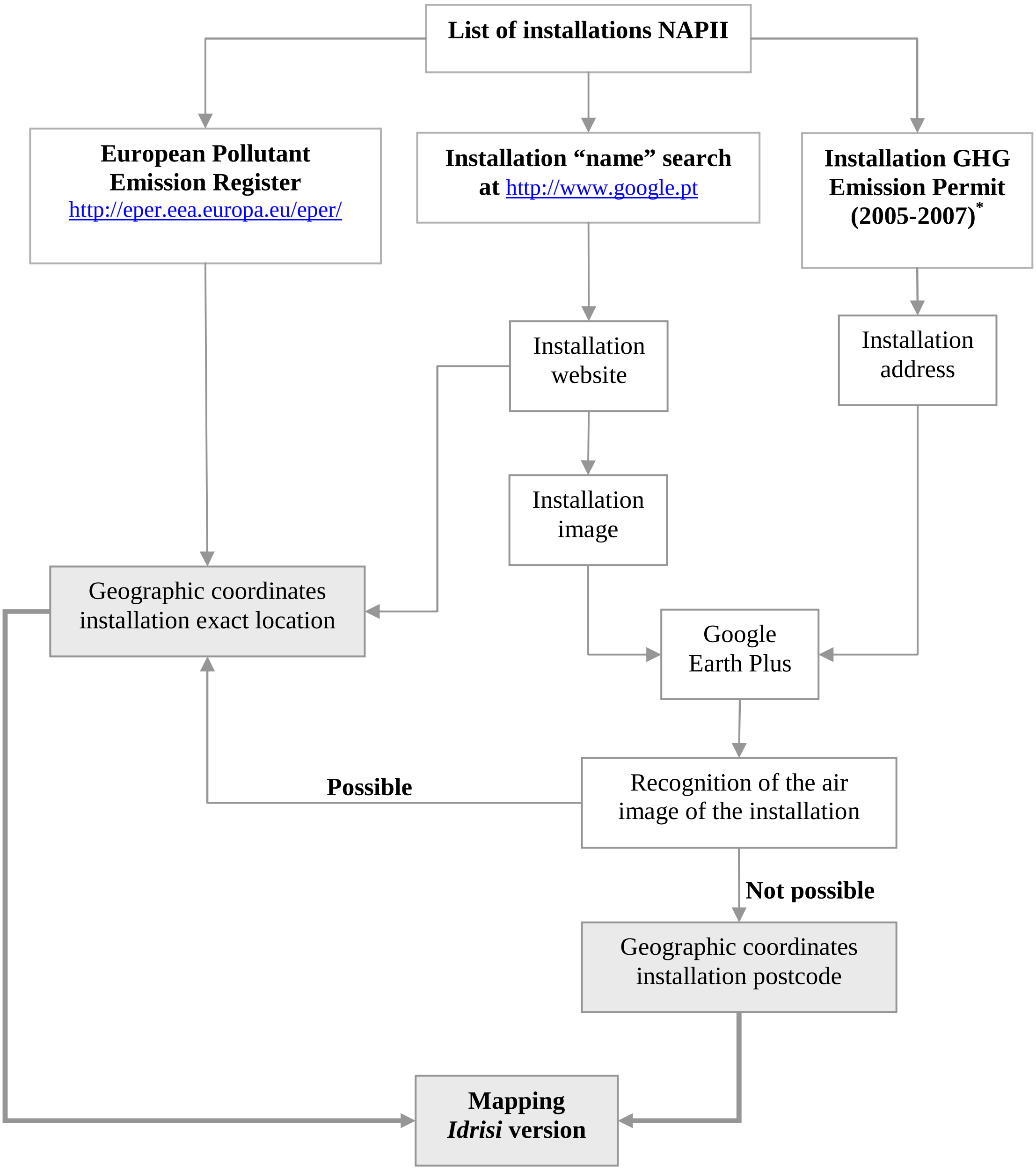
[32] The yearly amount of emissions allowances for the 2008-2012 period (30,5 $MtCO_2eq$ /year) is inferior to the emissions verified in 2005, 2006 and 2007 (36,4 $MtCO_2eq$ /year, 33,1 $MtCO_2eq$ /year and 31,2 $MtCO_2eq$ /year, respectively) (MAOTDR, 2008).

It can be concluded that the energy sector was the main responsible for CO_2 emissions in 2007, power plants being the main source. The lime and cement sector was the second responsible, accounting for about 23% of the CO_2 emissions in 2007.

Location of carbon dioxide stationary sources in mainland Portugal

The location of the mainland Portugal installations included in the NAPII was identified through the respective geographic coordinates. The methodology applied to the installations mapping is presented in Figure 4.6.



*The GHG emission permits for the 2008-2012 are not yet available at the Portuguese Environmental Agency webpage.

Figure 4.6 Installations mapping methodology.

Following the application of this methodology, the location of the mainland Portugal installations included in the NAP II is presented in Figure 4.7.

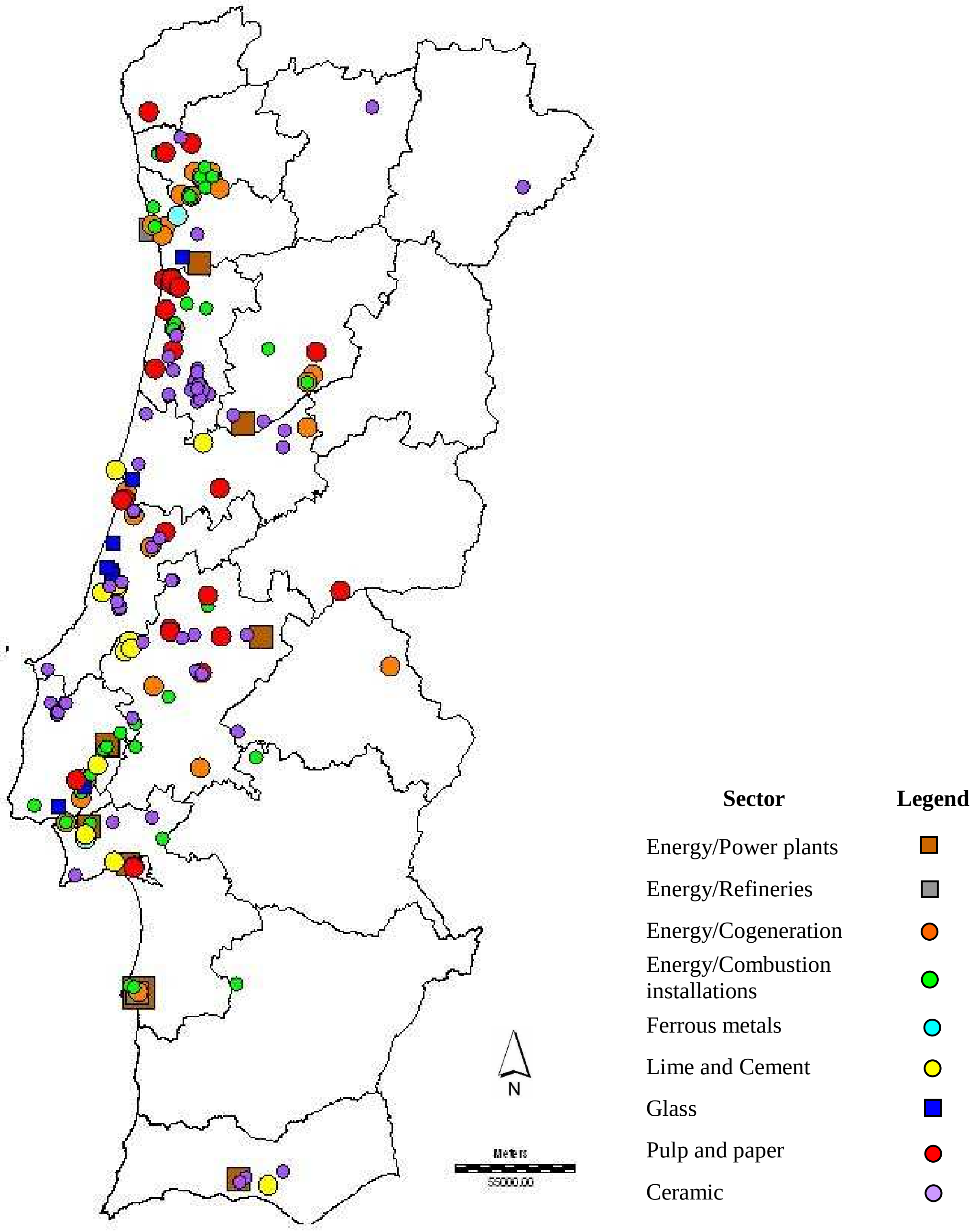


Figure 4.7- Location of the 204 installations included in PNALE II per sector.

Selection of carbon dioxide large point sources in mainland Portugal

Large point sources (LPS) of CO_2 being considered the main applicants to CCS, these will be identified in mainland Portugal. The identification of CO_2 LPS in mainland Portugal was based on the installations included in the NAP II and on the verified annual CO_2 emissions per installation. As the installations included in the NAP I (2005-2007) do not totally coincide with the ones included in the NAP II (2008-2012), it was not possible to know the annual CO_2 emissions of all the installations included in the period in analysis (2008-2012). The match between the mainland Portugal installations included in the NAP I and II resulted in 198 installations. As the NAP II includes 204 installations, six installations that were not included in the period 2005-2007 of the EU-ETS were not considered for this analysis,. From these six installations, five are included in the combustion installations sector and one in the pulp and paper sector. These six installations represent 0,62% of the annual CO_2 emissions allowances attributed for the mainland Portugal installation included in the period 2008-2012.

From the analysis of the phase I of the EU-ETS in Portugal (2005-2007) developed by MAOTDR, it was concluded that the emissions verified in 2005, 2006 and 2007 were 36,4 $MtCO_2eq$ /year, 33,1 $MtCO_2eq$ /year and 31,2 $MtCO_2eq$ /year, respectively (MAOTDR, 2008). This analysis considered all the installations and not only the ones in mainland Portugal. As the installations included in the EU-ETS have to report their annual emissions, the values of the annual CO_2 emissions per installation are available for 2005, 2006 and 2007. For this analysis, the year considered was 2007, because this is the most recent year with available data. It has to be kept in mind that this analysis is for the 198 installations that resulted from the match of the NAP I and II.

In 2007, the CO_2 emissions were verified for 179 installations and were not available for 19 installations. These 19 installations belong to the ceramic and pulp and paper sectors and represent about 0,20% of the annual CO_2 emissions allowances attributed to the mainland Portugal installations included in the period 2008-2012.

To classify the mainland Portugal LPS, the chosen criterion was the identification of the group of installations with the highest CO_2 emissions, until representing about 90% of the total CO_2 emissions verified in 2007. The application of this criterion resulted in 24 LPS in mainland Portugal. In the scope of the IPCC Special Report on CCS, the LPS considered involved fossil fuel and biomass use in fuel combustion activities, industrial processes and natural gas processing, which emit more than 0.1 $MtCO_2\ yr^{-1}$ (IPCC, 2005). This criterion was also applied to the installations considered and the results achieved were exactly the same. The 24 LPS per sector are presented in Figure 4.8 .

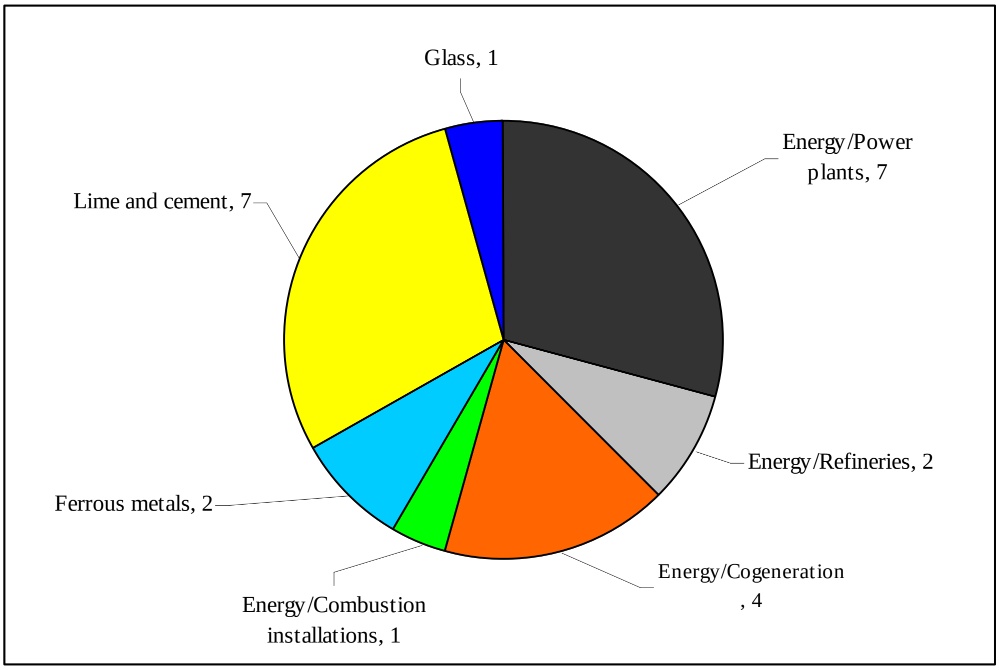


Figure 4.8 – The 24 LPS identified in mainland Portugal per sector (data from (APA; 2008b)).

None of the LPS belongs to the ceramic and pulp and paper sectors. All the installations of the ferrous metals and refineries sectors are LPS (two for both sectors). The power plants sector includes all the installations of coal, combined cycle gas turbine (CCGT) and fuel subsectors, the ones from the biomass and diesel subsectors being excluded. From the 12 installation of the lime and cement sector, seven are LPS. The cogeneration sector includes 35 installations, four of which are LPS. Only one of the 33 combustion installations is a LPS. From the nine installations of the glass sector, one is a LPS. The locations of the LPS are presented in Figure 4.9.

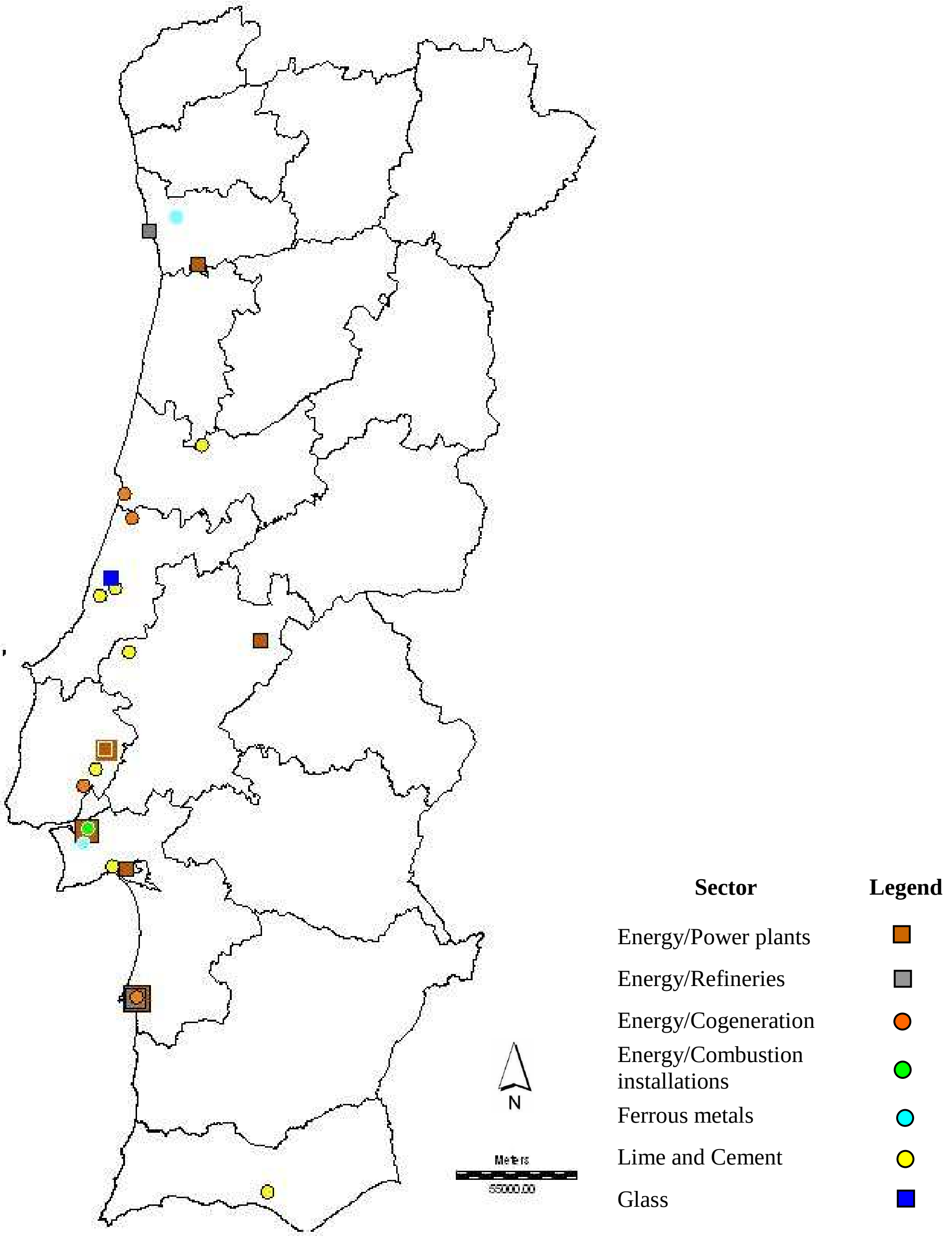


Figure 4.9 – Location of the 24 LPS.

In Figure 4.9 it is possible to observe that the majority of the LPS are concentrated on the coastline, mainly in the Setubal district, followed by the Lisbon, Leiria and Oporto districts.

4.3 Potential geological CO_2 storage sites in mainland Portugal

4.3.1 Brief description of mainland Portugal's geology

Mainland Portugal has four large morpho-structural units: the Hesperic Massif (or Iberian Massif or Ancient Massif), the Occidental Mesocenozoic Border, the Meridional

Mesocenozoic Border and the Tertiary Basins of Tejo and Sado. These are presented in Figure 4.10.

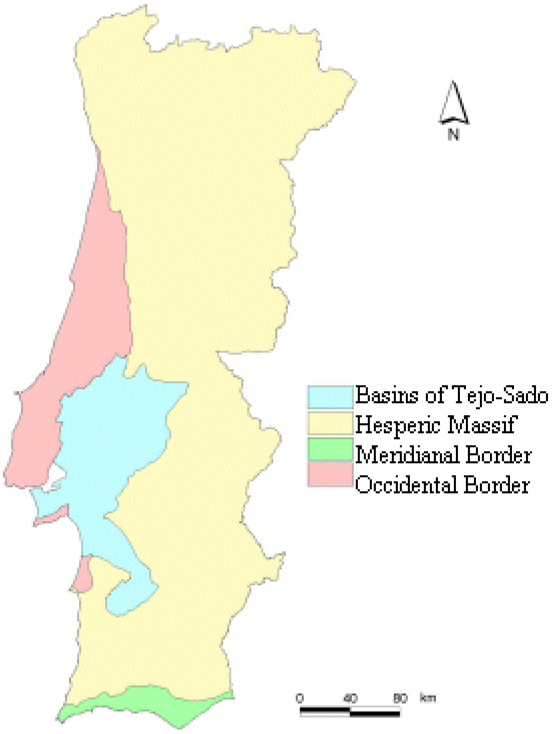


Figure 4.10 Mainland Portugal’s large morpho-structural units (Adapted from SNIRH, 2008).

In Portugal there are on and off-shore activities of prospection of petroleum in the sedimentary basins. The resultant seismic and gravity data allowed a better delineation of the Mesocenozoic sedimentary basins. These can be grouped into inner basins, which are located in the inner part of the continental margin and often extending onshore, and outer basins, which are mostly located in deeper waters to the west and south of the former. The inner basins are the Oporto Basin, the Lusitanian Basin and the Algarve Basin. The outer basins are the Galicia Interior Basin, the Peniche Basin, the Alentejo Basin, the Sagres Basin and the Gulf of Cadiz Basin (DPEP, 2008). These are presented in Figure 4.11.

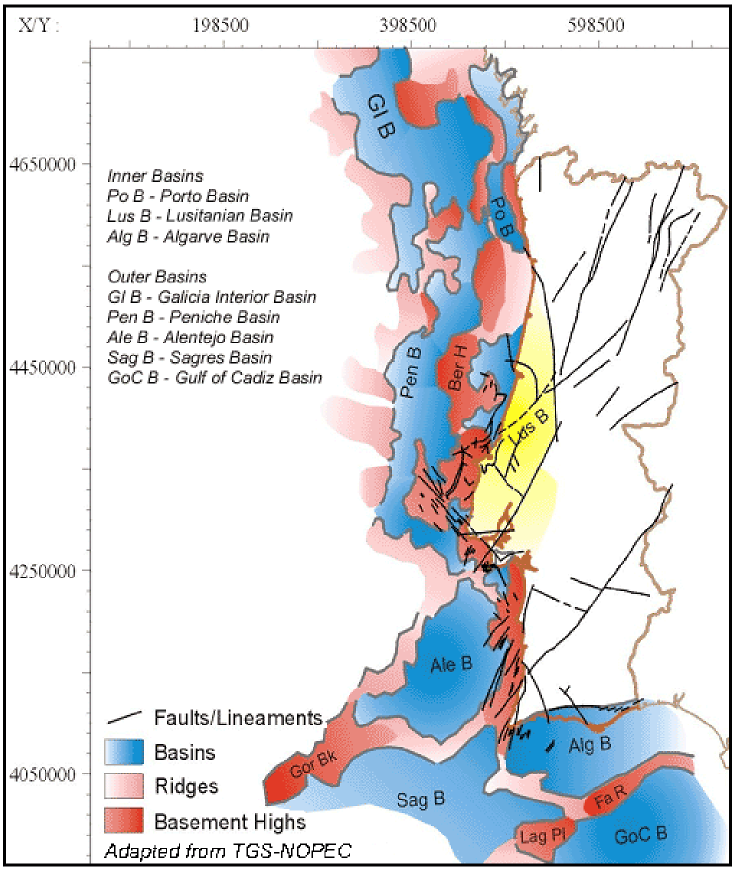


Figure 4.11 Portuguese inner and outer Mesocenozoic sedimentary basins (DPEP, 2008).

The Lusitanian basin expands from the onshore to the offshore and is the largest inner basin with a total area of about 22000 km^2 and a maximum sedimentary thickness of about 6km. Jurassic sediments are thicker than the Cretaceous sediments and the Cenozoic sediment cover is normally thin. On the other hand the Oporto basin develops entirely offshore and has an area of about 2150 km^2 (to 200m water depth) or 2800 km^2 (to 1000m water depth). This basin has up to 8 km of Late Triassic to Late Cretaceous sediments and is normally overlaid by a thin Cenozoic cover. The Algarve basin expands on and off-shore presenting an area of about 8500 km^2. According to DPEP, 2008, “Depth to the Carboniferous basement may exceed 7 km and the fill is again of Late Triassic to Recent age. The relative thickness of the Cenozoic, particularly the Neogene sediments, is larger than in the western inner basins”. Among the inner basins, the Lusitanian basin is the most explored. There is little information about the outer basins (DPEP, 2008).

4.3.2 Identification of potential geological CO_2 storage sites in mainland Portugal

The potential geological storage locations considered in this work are deep saline aquifers and the Douro coal basin. The National Institute of Engineering, Technology and Innovation (INETI – Instituto Nacional de Engenharia, Tecnologia e Inovação) presented a preliminary study for CO_2 storage in deep saline aquifers (Sampaio *et al*., 2007). It was then stated that the work developed is based on the little information available and that further studies are necessary to develop in the future to allow a deeper characterisation of the identified formations. The Global Change, Energy, Environment and Bioengineering RDID&D Unit (CIAGEB), of the Fernando Pessoa University, is currently developing a project about CO_2 sequestration in the Douro Coalfield. The objectives of this project are to define the CO_2 storage capacity in a range of coal beds of different geologic characteristics and to establish the feasibility of a CO_2-free industry based on CO_2 storage in coal seams (abandoned mines or non-mined deep seams) by a systematic study of selected sites (Sousa *et al.*, 2007).

The geological formations identified in these studies are presented in Figure 4.12.

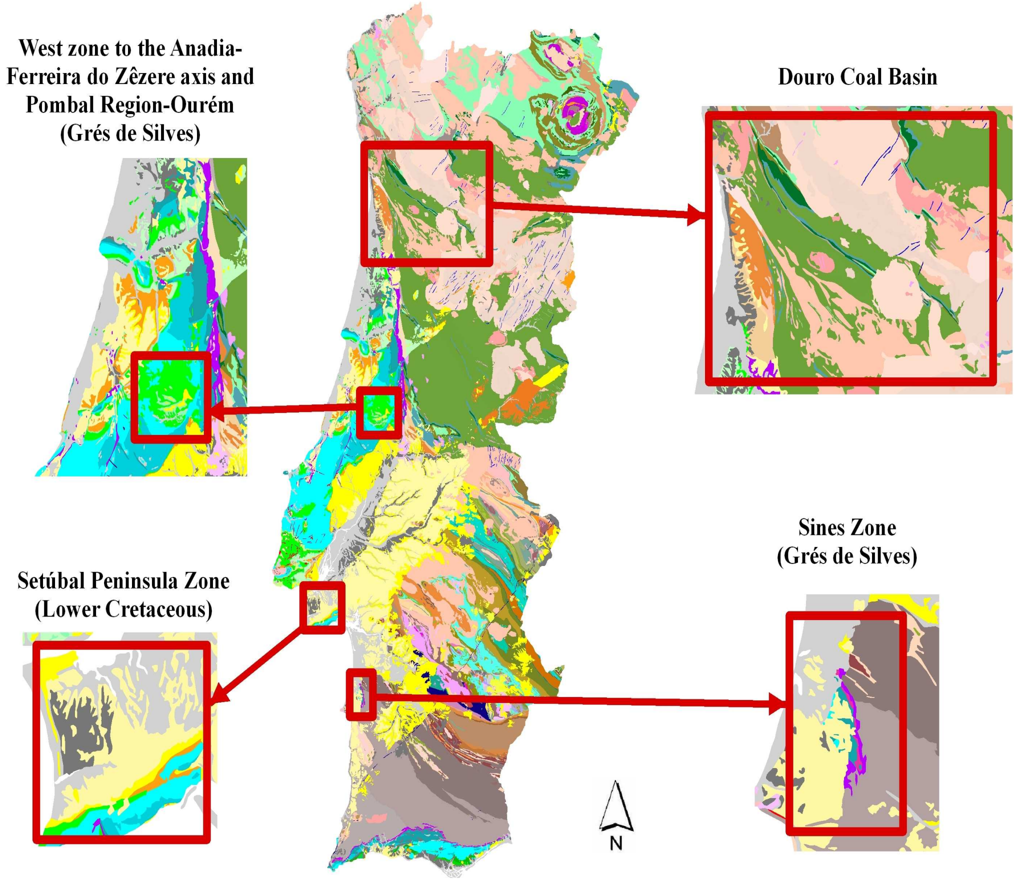


Figure 4.12 - Geological formations identified in the INETI preliminary study as potential sites for CO_2 storage (Sampaio, J., *et al.*, 2007) and Douro coalfield basin.

4.4 Source sink matching

A detailed source-sink matching is crucial to understanding the relationship between the emissions sources and the storage opportunities in order to assess the impact of CCS on emissions reduction and what the role of CCS could be among other mitigation options. A good relationship between sources and sinks leads to the possibility of significant reduction of the amount of the CO_2 emissions from these sources. However and as stated in the IPCC Special Report on CCS, if CO_2 sources and sinks "are not well matched geographically, then there will be implications for the length and size of the transmission infrastructure that is required, and this could impact significantly on the cost of CO_2 capture and storage, and on the potential to achieve deep reductions in global CO_2 emissions" (IPCC, 2005).

Source-sink matching requires a detailed assessment not only of sources and sinks but also of transport options and economic and environmental factors. If there is a high level of technical uncertainty associated with a CCS project or if the distance between sources and sinks is too large, the storage potential is compromised (IPCC, 2005).

In addition to all the technical criteria that CCS involves, the selection of CO_2 storage sites and matching with CO_2 sources should, according to Bachu, 2007b, consider the following criteria: “volume, purity and rate of the CO_2 stream; proximity of the source and storage sites; level of infrastructure for CO_2 capture and delivery; existing wells, for injection and for leak prevention; injection and production strategies; terrain and right of way; proximity to population centres; and overall costs, and economics” (Bachu, 2007b). Beyond these technical suitability criteria, further considerations will be controlled by economic, safety and environmental aspects. According to the IPCC Special Report on CCS “assigning technical risks is important for matching of CO_2 sources and storage sites, for five risk factors: storage capacity, injectivity, containment, site and natural resources” (IPCC, 2005). For all of these assessments and considerations, the project lifetime has to be taken into account and the post-closure phase must be contemplated.

For the source-sink matching in mainland Portugal, the CO_2 LPS and potential geological storage sites above identified will be considered. Figure 4.13 shows the LPS by sector and annual CO_2 emissions, which range from 0,1 $MtCO_2$/year to more than 7 $MtCO_2$/year.

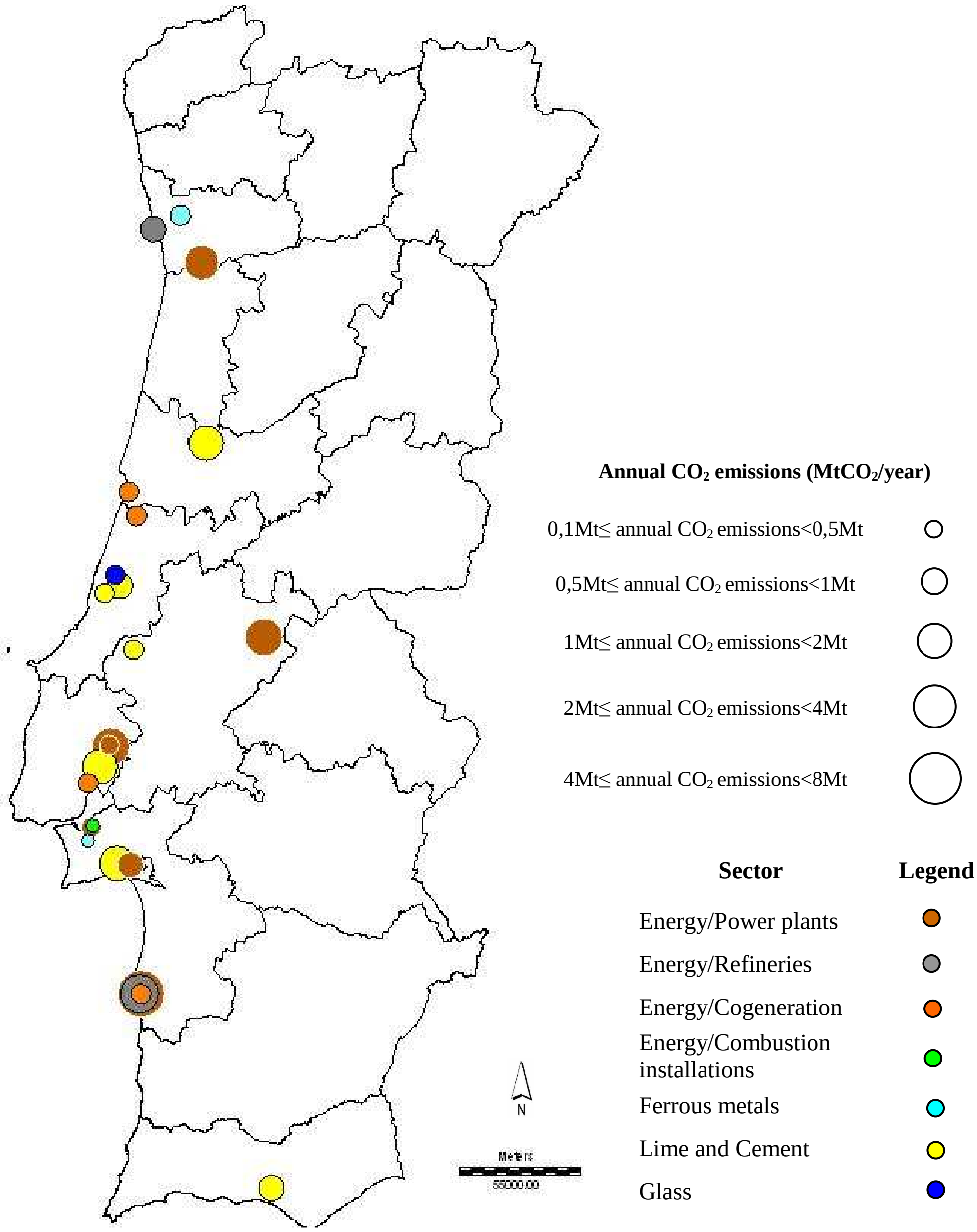


Figure 4.13 – Sectors and annual CO_2 emissions in megatons per year of the identified LPS (data from (APA; 2008b)).

From Figure 4.13, it could be concluded that the majority of the identified LPS are concentrated in the Setubal district and this is the district with the highest annual CO_2 emissions. Lisbon and Leiria districts have the same number of installations. However, the annual CO_2 emissions are higher in Lisbon, which is the second district with larger CO_2 emissions (Table 4.1). Santarem with two LPS is the district with the third largest annual CO_2 emissions, followed by Oporto with three installations. In Table 4.1, a summary of the number of LPS per district, their annual CO_2 emissions in 2007 and represented sectors is presented.

Table 4.1 – Analysis of the LPS per district.

District	**Number of LPS**	**CO_2 Emissions 2007 ($MtCO_2$/year)**	**Sectors**
Coimbra	2	2,0	Lime and cement; Energy/Cogeneration
Faro	1	0,5	Lime and cement
Leiria	4	1,5	Lime and cement; Energy/Cogeneration; Glass
Lisbon	4	4,4	Energy/power plants; Lime and cement; Energy/cogeneration
Oporto	3	2,6	Ferrous metals; Energy/refineries; Energy/power plants
Santarem	2	3,5	Energy/power plants; Lime and cement
Setubal	8	12,3	Energy/power plants; Energy/refineries; Lime and cement; Energy/cogeneration; Ferrous metals; Energy/combustion installations
total	**24**	**26,8**	
Total (for the installation whose emissions where verified in 2007)	**198**	**29,6**	

The location of the potential geological storage sites identified for mainland Portugal is presented in Figure 4.14. For the potential geological storage sites mapping, the mentioned geological formations and localities were considered. Due to the scarce information about these, however, the locations presented here are essentially illustrative.

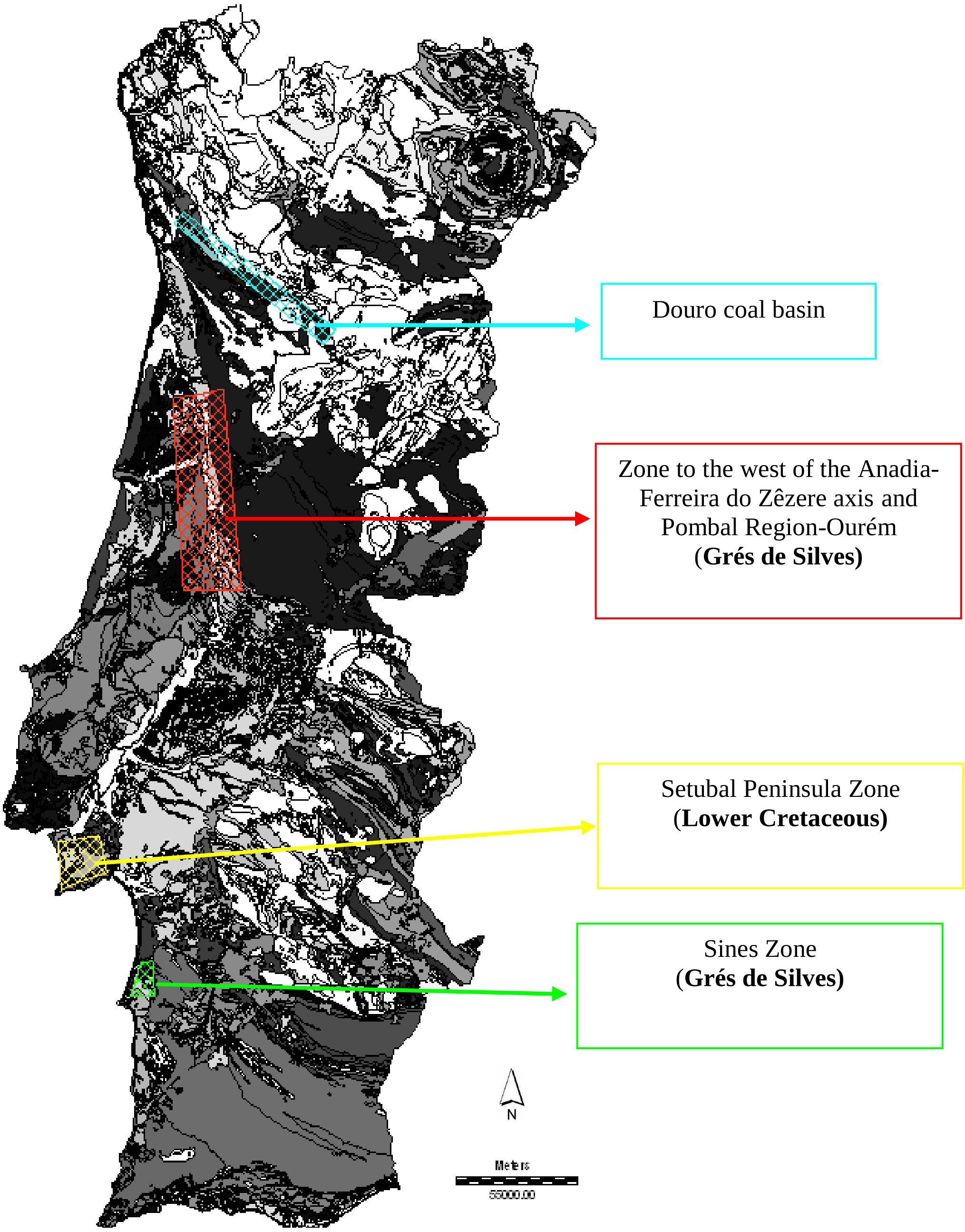


Figure 4.14 – Location of the potential geological sinks in mainland Portugal.

Figure 4.15 shows the map resulting from source- sink matching after the identification of LPS and potential geological sinks of mainland Portugal.

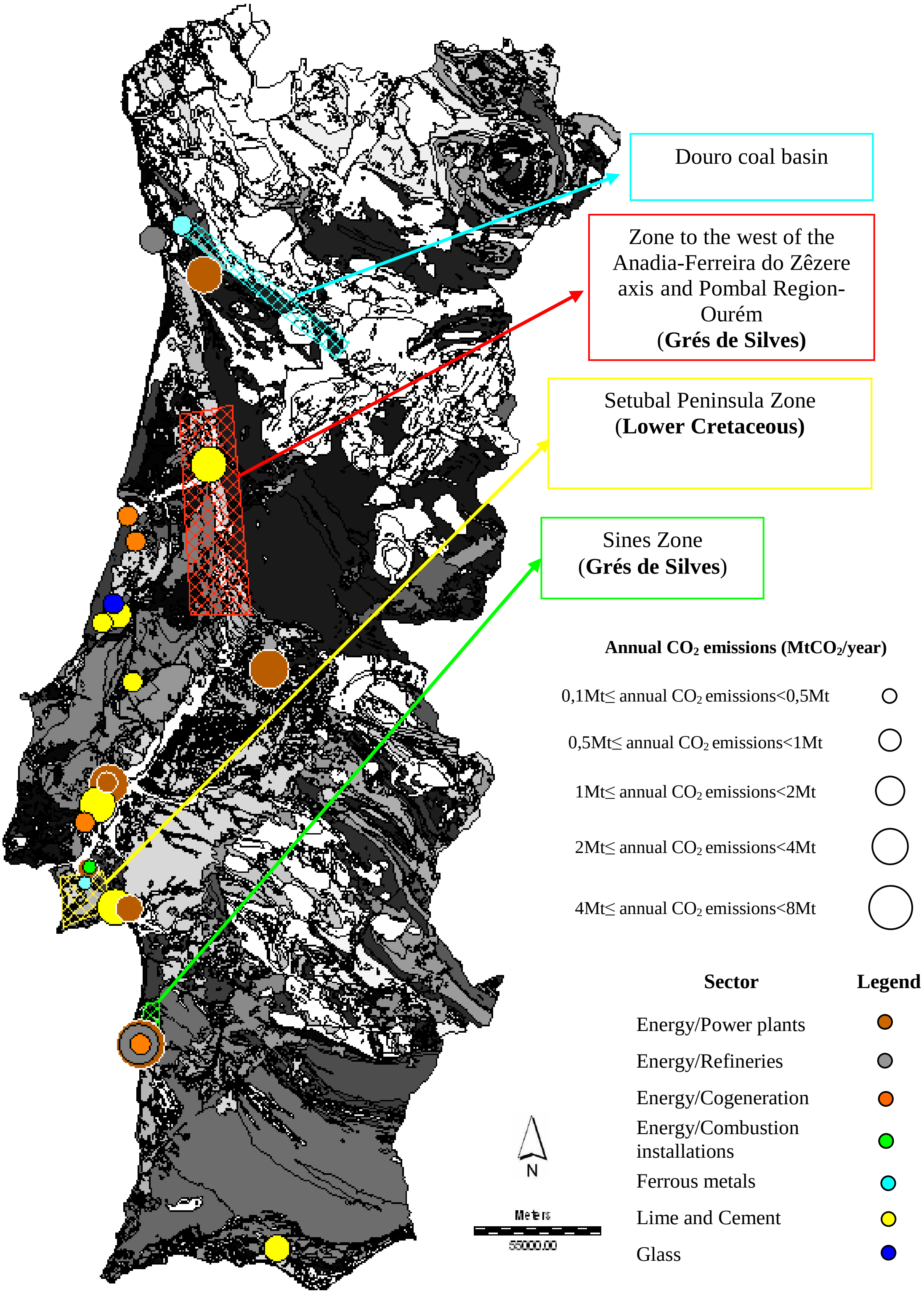


Figure 4.15 – Matching of CO_2 LPS and potential geological sinks in mainland Portugal.

By considering only the proximity of the source and storage sites, it is possible to verify that there is at least one LPS within each identified area of potential CO_2 geological storage. In Sines and on the Setubal Peninsula, there are several LPS within the potential storage area. Even for the LPS that are not within these areas, it is plausible to consider that they are relatively near.

4.5 Attempt of costs estimation

In this attempt of estimating costs of implementing a CCS system in mainland Portugal, the following factors will be considered: CO_2 capture costs by industry types, the cost of CO_2 transport by pipeline and the cost of CO_2 storage in geological formations.

The analysis will be performed by areas of potential CO_2 geological storage and considering the LPS located in the surrounding districts/localities (Table 4.2).

Table 4.2 – Distribution of the LPS by the four areas of potential geological storage.

Areas of potential CO_2 geological storage	**District/ localities**	**Number of LPS**	**CO_2 Emissions 2007 ($MtCO_2$/year)**	**Sectors**
Douro coal basin	Oporto	3	2,6	Ferrous metals; Energy/refineries; Energy/power plants
	total	**3**	**2,6**	
Zone to the west of the Anadia-Ferreira do Zêzere axis and Pombal Region-Ourém	Coimbra	2	2,0	Lime and cement; Energy/Cogeneration
	Leiria	4	1,5	Lime and cement; Energy/Cogeneration; Glass
	Santarem	2	3,5	Energy/power plants; Lime and cement
	total	**8**	**7,0**	
Setubal Peninsula Zone	Lisbon	4	4,4	Energy/power plants; Lime and cement; Energy/cogeneration
	Setubal	5	2,7	Energy/power plants; Lime and cement; Ferrous metals; Energy/combustion installations
	total	**9**	**7,1**	
Sines Zone	Sines	3	9,7	Energy/power plants; Energy/refineries; Energy/cogeneration;
	Faro	1	0,5	Lime and cement
	total	**4**	**10,2**	
	Total	**24**	**26,9**	

The CO_2 capture costs considered were based on the costs presented by Hendricks *et al.*, 2004 for the different types of industrial and power plants. In the LPS and areas of potential storage, the grouping analysis followed the methodology presented by Joanaz-Melo, 1992. The CO_2 storage cost was based on the IPCC Special Report on CCS estimates for geological storage.

The length of the pipelines was determined in *Google Earth* calculating the approximate linear distance between the groups of LPS and the LPS closest to the centre of the correspondent storage area, which was considered the CO_2 injection point.

The estimation of the investment cost of the pipeline systems considered the individual branches and shared parts of the pipeline system. This cost was calculated considering the annual CO_2 volume, the length and the diameter of the pipeline. The transport costs were shared proportionally to the sources emissions. The pipeline diameters[33] considered were 70 cm for an annual CO_2 volume larger than 2 Mt CO_2 yr^{-1}; and 40 cm for an annual CO_2 volume less than 2 Mt CO_2 yr^{-1}.

The costs were estimated for a timeframe of 15 years and assuming a 10% loss in the CO_2 capture. The following general data were also assumed:

Table 4.3 – General data considered for costs estimation.

General data	Value
70 cm pipeline cost (M€/km)[34]	0,7
40 cm pipeline cost (M€/km)[35]	0,4
Coefficient of distance aggravation	1,3
Operation cost/investment cost (%yr^{-1})	5

In Table 4.4, a summary of estimates of CCS costs in mainland Portugal is presented per storage area.

Table 4.4 - Estimates of CCS cost per area of potential CO_2 geological storage.

Areas of potential CO_2 geological storage	Estimates of CCS cost (€/tCO_2)
Douro coal basin	40-45
Zone to the west of the Anadia-Ferreira do Zêzere axis and Pombal Region-Ourém	31-46
Setubal Peninsula Zone	31-45
Sines Zone	31-46

The estimated costs range from 31 €/tCO_2 to 46 €/tCO_2. Capture costs are responsible for the major portion of the total costs. The transport costs have a direct linear relationship with distance. In the estimated costs, the transport cost is more significant for distances greater than 100 km. This is also true when the transportation investment costs are supported by a single LPS.

The cost estimation of CCS was a very rough exercise not only because of the presumed assumptions, but also because the costs of all the components of a CCS system were not considered. The capture costs depend on many factors like the capture system and

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[33] The pipeline diameters of the Portuguese system of natural gas transportation are between 15 cm and 80 cm. More than half of the pipelines have a diameter bigger than 70 cm (http://www.ren.pt/VPT/GAS/TRANSPORTE/Pages/gas-natural_transporte.aspx).

[34] Approximate value based on the reference value of $40 000/mile per inch of pipeline diameter presented by Dooley *et al.*, 2006.

[35] Approximate value based on the reference value of $40 000/mile per inch of pipeline diameter presented by Dooley *et al.*, 2006.

technology, the pressure and concentration of CO_2 in the flue gas, and the fuel type. Thus capture costs have to be specifically calculated according to the plants' technical characteristics, which did not happen in the performed estimate. For the estimate of transport costs only the annual CO_2 volume, the pipeline length and diameter and a coefficient of distance aggravation were considered. Pipeline design depends significantly on several factors like terrain characteristics (as they could increase the costs by 50% to 100% or more if the route is congested and/or heavily populated) and environmental constraints. Consequently, transport cost depends on the pipeline system configuration and on many other factors like the type of material, pumps, valves and compressors costs. The CO_2 storage cost considered was the same for all storage areas. The storage costs are site-specific depending on the type of reservoir, location, depth and other characteristics of the storage reservoir formation and also depend on injection costs. The operation and maintenance costs also have to be considered in all the components of a CCS system – capture, transport and storage.

Beyond the rough assumptions mentioned, not all the components of a CCS system could be considered. The assessment of CCS costs has to consider all components of the system: capture and compression, transport, injection and storage, including monitoring costs and remediation costs if necessary. The required environmental impact assessments also have to be a part of the overall equation. As a CCS system requires additional energy, this also has to be taken into account.

Despite the present being a very rough estimate, it still allows a perception of the order of magnitude of what the costs of implementing a CCS system in mainland Portugal can be. The estimated costs can be seen as the minimal costs of implementing a CCS system in mainland Portugal. From a strictly economic point of view, CCS can only be a viable mitigation option when the cost of a tonne of CO_2 on the carbon market is similar or higher than the cost of CCS per tonne of CO_2. Assuming the estimated costs as the minimal costs of CCS in mainland Portugal, and considering the reference price of of 12 €/tCO_2e per tonne of CO_2 on the KP flexibility mechanisms market (RCM1/2008), CCS is still far from being a viable mitigation option.

5 Conclusions

The objective of this study was to analyze the hypotheses for the implementation of carbon capture and storage (CCS) systems in mainland Portugal based on source-sink matching. It has to be noticed that due to the lack of information, this is a very preliminary analysis.

The performed analysis was based on the proximity of the sources and storage sites, which is just one of the criteria that involve the selection of CO_2 storage sites and matching with CO_2 sources. Still considering only the proximity criteria, the storage locations considered refer to areas because specific injection sites were not yet identified. From this analysis it is possible to conclude that several large point sources (LPS) are within or near the potential storage areas. By itself, this is an insufficient analysis but it can work as a base for future projects and studies.

Estimating costs of implementing a CCS system in mainland Portugal was also attempted considering the identified LPS and storage areas. This cost estimate was a very rough exercise not only because of the predefined assumptions but also because only the costs of CO_2 capture, transport and storage were considered. The cost estimate resulted in a CCS cost ranging from 31 €/tCO_2 to 46 €/tCO_2. Capture costs were responsible for the major part of the total costs. Transport costs are more significant for distances greater than 100 km and when the transportation investment costs are supported by a single LPS.

Despite the cost estimate being rough, it allows us to have an idea of the order of magnitude of the costs of implementing a CCS system in mainland Portugal. It can be seen as the minimal costs of implementing a CCS system in mainland Portugal. Assuming the estimate costs as the minimal costs of CCS in mainland Portugal, and considering the reference price of a tonne of CO_2 in the market of the Kyoto Protocol (KP) flexibility mechanisms at 12 €/tCO_2e, CCS is still far from being a viable mitigation option.

The current lack of information regarding geological storage sites is an important limitation to the assessment of implementing a CCS system in mainland Portugal. Further detailed studies are required, starting with geological site characterisation. However, the development of further studies depends on industries as these are the major stakeholders. This implicates a deep characterisation of the candidate sources to CCS from technical aspects to environmental and economical factors.

In relation to CO_2 sources, the identification of LPS was based on the annual volume of CO_2. A further characterisation of the purity and rate of the CO_2 stream is necessary. These parameters are important not only for the selection of the capture process but also to transport and storage. The level of infrastructure for CO_2 capture also has to be assessed, assessing whether a new plant should be installed or retrofitted to an existent one. The possibility to retrofit a capture system to the identified LPS will have to be assessed. Retrofitting may have some constraints relating to the availability of land for the capture equipment, the large investment of installing the equipment and the plant efficiency.

None of the criteria related to the storage sites can be verified because there is no available information about these. For the areas identified as potential CO_2 geological sinks to be considered suitable for CO_2 storage, they will mandatorily have to meet the following requirements: capacity, injectivity, confinement and site and natural resources protection. Thus, each of the potential geological sites will have to be characterised in detail. The site characterisation involves a geological characterisation, predictive flow modelling, geochemical assessment, geomechanical assessment, risk assessment and monitoring programme design. In addition to sources and sinks characterisation, the infrastructure for CO_2 transport also has to be assessed. Other major variables have to be considered in the selection of CO_2 storage sites and matching with CO_2 sources: terrain and right of way, proximity to population centres, costs, environmental impacts, risk and safety.

However, even beyond sources, transport and sinks characterisation and considering all the technical, environmental and safety aspects, many other components have to be assessed. The planning of a CCS system has to consider construction, operation, closure and post-closure phases. The implementation of a CO_2 capture, transport and storage system requires additional energy, and there are emissions during the CCS chain. This means that the energy and emissions balance of a plant with and without a CCS system is crucial to properly evaluate its deployment.

Costs are also an important factor. The assessment of CCS costs must consider all components of the system: capture and compression, transport, injection and storage, including monitoring costs and remediation costs if necessary. The required environmental impact assessments have also to be part of the overall equation. As a CCS system requires additional energy, this also has to be taken into account. The costs of each component depend on several factors. The impacts of the implementation of CCS on the cost of the final product and the cost of CO_2 captured and avoided also have to be determined. From a strictly economic point of view, CCS can only be a viable mitigation option if the cost of a tonne of CO_2 on the carbon market is similar or higher than the cost of CCS per tonne of CO_2.

There is no single solution to reduce CO_2 emissions. The solution may consist in an integrated combination of the several mitigation measures available. CCS is one of the many mitigation measures available to reduce GHG emissions. Beyond all the rigorous criteria that CCS involves to determine whether it is a viable option or not, it has to be compared with other mitigation options. Some of the factors that have to be considered in this comparison are: the potential of CO_2 emissions reduction, the available resources, the national emissions reduction commitments, the environmental impacts and the costs.

There are still many challenges and barriers in the implementation of a CCS system. These challenges and barriers are not only of scientific and technical nature but also economical, legal, political and regulatory. Public attitude and acceptance as well as the determination of the CO_2 storage capacity also constitute major challenges and barriers.

Relating to the different CO_2 storage reservoirs, many questions have not yet been answered. The behaviour of CO_2 after injection and its geochemical interactions in the subsurface are not yet clarified. It is not known if CO_2 can be injected safely, what its behaviour after injection is and what the effects and/or the risks of leakage are. CO_2 leakage constitutes a risk to health and ecosystems and can undermine mitigation efforts.

One of the main constraints is the lack of legal and regulatory issues. Many of the existent legislations can be adapted and applied to CCS, but there is no existing legislation specific to CCS. CCS requires strong legal and regulatory guidelines. However, this is not a simple task, especially relating to ownership and access rights of underground geological formations and trans-boundary aspects are required. Another major concern relates to long-term liability: the determination of who will be responsible for the stored CO_2 in the long term, for monitoring operations and remediation measures in the post-closure phase. There are already several CCS projects worldwide that have been regulated on a case-by-case basis.

The international community is developing efforts to overcome all these technical, scientific, legal and regulatory challenges and barriers. The EU is working on a CCS directive and planning several CCS pilot plants. The international climate targets can motivate the development and deployment of CCS. Within the international climate change framework, CCS is not explicitly included in or excluded from the United Nations Framework Convention on Climate Change (UNFCCC), and the same applies to the KP. One of the main discussions within the climate negotiations under the UNFCCC is the inclusion of CCS in Clean Development Mechanism (CDM).

For now, there are more questions than answers. Further work is required to overcome all the challenges and barriers that have already been identified for CCS. This is imperative for the assessment of CCS viability. The establishment of strong international regulatory, legal and liability guidelines is determinant for the implementation of any CCS project.

Portugal already exceeded its Kyoto target (a 27% increase of its GHG emissions in relation to 1990 in the 2008-2012 period). Thus it is necessary to understand which mitigation measures are available and can be more effective to reduce Portugal’s GHG emissions. At this stage, it is not possible to assess the potential for CCS in mainland Portugal. First, geological sites have to be characterised in detail. If suitable sites for CO_2 geological storage are identified, it is necessary to identify the adequate sources, the infrastructures required for the CCS systems, the environmental impacts, the risks, safety, the costs and the impact on the national reduction of CO_2 emissions. After this, CCS has to be weighted with the other mitigation options available. Although the performed analysis was based only on the proximity of the sources and storage sites, it provides a first integrated approach to the implementation of a CCS system in mainland Portugal.

6 References

Agência Portuguesa do Ambiente (APA) (2008a). *Licenças de Emissão de CO_2 Atribuídas por Sectores e respectivas Emissões Verificadas no período 2005*-2007. Agência Portuguesa do Ambiente, Amadora, Portugal.

Agência Portuguesa do Ambiente (APA) (2008b). *Licenças de emissão de CO_2 atribuídas por instalação e respectivas emissões verificadas no ano 2007.* Agência Portuguesa do Ambiente, Amadora, Portugal.

Bachu, S., (2007a). *CO_2 storage in geological media: Role, means, status and barriers to deployment*, Progress in Energy and Combustion Science 34 (2008), 254-273.

Bachu, S., (2007b). *Carbon dioxide storage capacity in uneconomic coal beds in Alberta, Canada: Methodology, potential and site identification*, International Journal of Greenhouse Gas Control I (2007), 374-385.

Bachu, S., Bonijoly D., Bradshaw, J., Burruss, R., Holloway, S., Christensen, N.P., Mathiassen, O.M., (2007). *CO_2 storage capacity estimation: Methodology and gaps*, International Journal of Greenhouse Gas Control I (2007), 430-443.

Bradshaw, J., Allinson, G., Bradshaw, B.E., Nguyen, V., Rigg, A.J., Spencer, L., Wilson, P., (2004). *Australia's CO_2 geological storage potential and matching of emissions sources to potential sinks*, Energy 29 (2004), 1623-1631.

Bradshaw, J., Bachu, S., Bonijoly, D., Burruss, R., Christensen, N.P., Mathiassen, O.M., (2005). *Discussion paper on CO_2 storage capacity estimation (Phase 1); a taskforce for review and development of standards with regards to storage capacity measurement*; CSLF-T-2005-9 15, August 2005, p16. http://www.cslforum.org/documents/Taskforce_Storage_Capacity_Estimation_Version_2.pdf.

Bradshaw, J., Bachu, S., Bonijoly D., Burruss, R., Holloway, S., Christensen, N.P., Mathiassen, O.M., (2007). *CO_2 storage capacity estimation: Issues and development of standards*, International Journal of Greenhouse Gas Control I (2007), 62-68.

Chadwick, A., Arts, R., Berstone, C., May, F., Thibeau, S. & Zweigel, P. (2006). *Best Practice for the Storage of CO_2 in Saline Aquifers (Observations and guidelines from the SACS and CO2STORE projects)*, 273 p.

Divisão para a Pesquisa e Exploração de Petróleo (DPEP) (2008). *Petroleum geology of Portugal*. Divisão para a Pesquisa e Exploração de Petróleo da Direcção Geral de Energia e Geologia, Lisboa, Portugal. Available at: http://www.dgge.pt/dpep/en/geology.htm (August 2008).

Dooley, J.J., Dahowski, R.T., Davidson, C.L., Wise, M.A., Gupta, N., Kim, S.H. Malone, E.L., (2006). *Carbon Dioxide Capture and Geological Storage: A core element of global energy technology strategy to address climate change –*

a technological report from the second phase of the global energy technology strategy program.

European Environmental Agency (EEA) (2008). *Annual European Community greenhouse gas inventory 1990–2006 and inventory report 2008 - Submission to the UNFCCC Secretariat***,** Version 27 May 2008, Technical report No 6/2008. European Environmental Agency, Copenhagen, Denmark.

Fernando, H., Venezia, J., Rigdon, C., Verma, P., (2008). *Capturing King Coal - Deploying Carbon Capture and Storage Systems in the U.S. at Scale*, World Resources Institute, Washington.

Ferreira, V.G., Pereira, T.C., Seabra, T., Torres, P. and Maciel, H., (2008). *Portuguese National Inventory Report on Greenhouse Gases, 1990-2006 Submitted under the United Nations Framework Convention on Climate Change and the Kyoto Protocol*, Portuguese Environmental Agency, Amadora.

Friedmann, S.J., Dooley, J.J., Held, H., Edenhofer, O., (2006). *The low cost of geological assessment for underground CO_2 storage: Policy and economic implications*. Energy Conversion and Management 47 (2006) 1894-1901.

Heinrich, J.J., Herzog, H.J., Reiner, D.M., (2003). *Environmental assessment of geological storage of CO_2***,** Laboratory for Energy and the Environment - Massachusetts Institute of Technology. Second National Conference on Carbon Sequestration, Washington, DC, May.

Hendricks. C., Graus, W., Van Bergen, F., (2004). *Global carbon dioxide storage potential and costs*, Ecofys and TNO-NITG, Netherlands.

Holloway, S., (2007). *Carbon dioxide capture and geological storage*, Philosophical Transactions of The Royal Society 365, 1095-1107

International Energy Agency (IEA) (2007). *Capturing CO_2*. International Energy Agency Greenhouse Gas Research&Development Programme. United Kingdom.

International Energy Agency (IEA) and Organisation for Economic Co-Operation and Development (OECD) (2003). *CO_2 Capture at Power Stations and other Major Point Sources*. International Energy Agency and Organisation for Economic Co-Operation and Development, Paris, France.

International Energy Agency (IEA) and Organisation for Economic Co-Operation and Development, (OECD) (2005). *Legal Aspects of Storing CO_2*. International Energy Agency and Organisation for Economic Co-Operation and Development, Paris, France.

Intergovernmental Panel on Climate Change (IPCC) (2005). *IPCC Special Report on Carbon Dioxide Capture and Storage*. Prepared by Working Group III of the Intergovernmental Panel on Climate Change [Metz, B., O. Davidson, H. C. de Coninck, M. Loos, and L. A. Meyer (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 442 pp.

Intergovernmental Panel on Climate Change (IPCC) (2007a). *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Core Writing Team, Pachauri, R.K. and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, 104 pp.

Intergovernmental Panel on Climate Change (IPCC) (2007b). Summary for Policymakers. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M.Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Intergovernmental Panel on Climate Change (IPCC) (2007c). Barker T., I. Bashmakov, L. Bernstein, J. E. Bogner, P. R. Bosch, R. Dave, O. R. Davidson, B. S. Fisher, S. Gupta, K. Halsnæs, G.J. Heij, S. Kahn Ribeiro, S. Kobayashi, M. D. Levine, D. L. Martino, O. Masera, B. Metz, L. A. Meyer, G.-J. Nabuurs, A. Najam, N. Nakicenovic, H. -H. Rogner, J. Roy, J. Sathaye, R. Schock, P. Shukla, R. E. H. Sims, P. Smith, D. A. Tirpak, D. Urge-Vorsatz, D. Zhou, 2007: Technical Summary. In: *Climate Change 2007: Mitigation. Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [B. Metz, O. R. Davidson, P. R. Bosch, R. Dave, L. A. Meyer (eds)], Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

International Petroleum Industry Environmental Conservation Association (IPIECA) and American Petroleum Institute (API), (2007). *Oil and Natural Gas Industry Guidelines for Greenhouse Gas Reduction Family – Part II: Carbon Capture and Geological Storage Emission Reduction Family*. International Petroleum Industry Environmental Conservation Association and American Petroleum Institute, United Kingdom and Washington DC, USA.

Joanaz Melo, J. (1992). *Optimização de Sistemas Regionalizados de Tratamento de Efluentes - O Modelo OPTTAR (versão inglesa: Optimization of Regionalized Wastewter Treatment Systems - The OPTTAR Model).* Dissertação de Doutoramento. Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa. 247 p.

Ministério do Ambiente e do Ordenamento do Território e do Desenvolvimento Regional (MAOTDR) (2008). *MEMORANDO - Estado do cumprimento do Protocolo de Quioto***.** Ministério do Ambiente e do Ordenamento do Território e do Desenvolvimento Regional, Lisboa, Portugal.

Minter Ellison, (2005). *Carbon Capture and Storage: Report to the Australian Greenhouse Office on Property Rights and Associated Liability Issues*, Australian Government – Department of the Environment and Heritage Australian Greenhouse Office.

Plano Nacional de Alocação de Licenças de Emissão I (PNALE I) (2005). *Resolução do Conselho de Ministros n.º 53/2005 – Plano Nacional de Alocação de Licenças* *de Emissão I*. Diário da República, I, série B — N.º 44 — 3 de Março de 2005.

Plano Nacional de Alocação de Licenças de Emissão II (PNALE II) (2008). *Resolução do Conselho de Ministros n.º 1/2008 - Plano Nacional de Alocação de Licenças de Emissão II***.** Diário da República, 1.ª série — N.º 3 — 4 de Janeiro de 2008.

Resolução do Conselho de Ministros (RCM) n.º 1/2008 - Diário da República, 1.ª série — N.º 3 — 4 de Janeiro de 2008.

Robertson, K., Findsen, J., Messner. S., (2006). *International Carbon Capture and Storage Projects Overcoming Legal Barriers*, National Energy and Technology Laboratory of the Department of Energy of the United States of America Government.

Sampaio, J., Machado, S., Carvalho, J., Dias, R.P., Costa, A. & Oliveira, J.T. (2007). *Armazenamento de CO2 em Aquíferos Salinos – Hipóteses para Portugal*, Departamentos de Geologia, Hidrogeologia e Geofísica, Instituto Nacional de Engenharia, tecnologia e Inovação, Lisboa, Portugal.

Sousa, M.L., Carretta, Z., (2007). *CO_2 sequestration in Douro coalfield: Presenting a Pilot Project*, Centro de Centro de Modelação e Análise de Sistemas Ambientais Modelação e Análise de Sistemas Ambientais, Universidade Fernando Pessoa – CEMAS/UFP, Porto, Portugal.

Sistema Nacional de Informação de Recursos Hídricos (SNIRH) (2008). *Unidades morfo-estruturias de Portugal Continental.* Portugal. Available at: http://snirh.pt/snirh.php?main_id=4 (July 2008).

7 Appendixes

Appendix I - Selection of relevant provisions under the United Nations Framework Convention on Climate Change and the Kyoto Protocol

Selection of relevant provisions under the United Nations Framework Convention on Climate Change and the Kyoto Protocol (IEA and OECD, 2005).

United Nations Framework Convention on Climate Change	Kyoto Protocol
Article 1 Definitions For the purposes of this Convention: […] 3. "Climate system" means the totality of the atmosphere, hydrosphere, biosphere and geosphere and their interactions. […] 7. "Reservoir" means a component or components of the climate system where a greenhouse gas or a precursor of a greenhouse gas is stored. 8. "Sink" means any process, activity or mechanism which removes a greenhouse gas, an aerosol or a precursor of a greenhouse gas from the atmosphere	**Article 2** 1. Each Party included in Annex I, in achieving its quantified emission limitation and reduction commitments under Article 3, in order to promote sustainable development, shall: (a) Implement and/or further elaborate policies and measures in accordance with its national circumstances, such as: (i) Enhancement of energy efficiency in relevant sectors of the national economy; (ii) Protection and enhancement of sinks and reservoirs of greenhouse gases not controlled by the Montreal Protocol, taking into account its commitments under relevant international environmental agreements; promotion of sustainable forest management practices, afforestation and reforestation; (iii) Promotion of sustainable forms of agriculture in light of climate change considerations; (iv) Research on, and promotion, development and increased use of, new and renewable forms of energy, of carbon dioxide sequestration technologies and of advanced and innovative environmentally sound technologies; (v) Progressive reduction or phasing out of market imperfections, fiscal incentives, tax and duty exemptions and subsidies in all greenhouse gas emitting sectors that run counter to the objective of the Convention and application of market instruments; (vi) Encouragement of appropriate reforms in relevant sectors aimed at promoting policies and measures which limit or reduce emissions of greenhouse gases not controlled by the Montreal Protocol; (vii) Measures to limit and/or reduce emissions of greenhouse gases not controlled by the Montreal Protocol in the transport sector; (viii) Limitation and/or reduction of methane emissions through recovery and use in waste management, as well as in the production, transport and distribution of energy; […]
Article 2 Objective The ultimate objective of this Convention and any related legal instruments that the Conference of the Parties may adopt is to achieve, in accordance with the relevant provisions of the Convention, stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system. Such a level should be achieved within a time-frame sufficient to allow ecosystems to adapt naturally to climate change, to ensure that food production is not threatened and to enable	**Article 3** 1. The Parties included in Annex I shall, individually or jointly, ensure that their aggregate anthropogenic carbon dioxide equivalent emissions of the greenhouse gases listed in Annex A do not exceed their assigned amounts, calculated pursuant to their quantified emission limitation and reduction commitments inscribed in Annex B and in accordance with the provisions of this Article, with a view to reducing their overall emissions of such gases by at least 5 per cent below 1990 levels in the commitment period 2008 to 2012.

economic development to proceed in a sustainable manner.	2. Each Party included in Annex I shall, by 2005, have made demonstrable progress in achieving its commitments under this Protocol. 3. The net changes in greenhouse gas emissions by sources and removals by sinks resulting from direct human-induced land-use change and forestry activities, limited to afforestation, reforestation and deforestation since 1990, measured as verifiable changes in carbon stocks in each commitment period, shall be used to meet the commitments under this Article of each Party included in Annex I. The greenhouse gas emissions by sources and removals by sinks associated with those activities shall be reported in a transparent and verifiable manner and reviewed in accordance with Articles 7 and 8. 4. Prior to the first session of the Conference of the Parties serving as the meeting of the Parties to this Protocol, each Party included in Annex I shall provide, for consideration by the Subsidiary Body for Scientific and Technological Advice, data to establish its level of carbon stocks in 1990 and to enable an estimate to be made of its changes in carbon stocks in subsequent years. The Conference of the Parties serving as the meeting of the Parties to this Protocol shall, at its first session or as soon as practicable thereafter, decide upon modalities, rules and guidelines as to how, and which, additional human-induced activities related to changes in greenhouse gas emissions by sources and removals by sinks in the agricultural soils and the land-use change and forestry categories shall be added to, or subtracted from, the assigned amounts for Parties included in Annex I, taking into account uncertainties, transparency in reporting, verifiability, the methodological work of the Intergovernmental Panel on Climate Change, the advice provided by the Subsidiary Body for Scientific and Technological Advice in accordance with Article 5 and the decisions of the Conference of the Parties. Such a decision shall apply in the second and subsequent commitment periods. A Party may choose to apply such a decision on these additional human-induced activities for its first commitment period, provided that these activities have taken place since 1990. […]
Article 3 Principles 1. Each Party included in Annex I shall have in place, no later than one year prior to the start of the first commitment period, a national system for the estimation of anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol. Guidelines for such national systems, which shall incorporate the methodologies specified in paragraph 2 below, shall be decided upon by the Conference of the Parties serving as the meeting of the Parties to this Protocol at its first session. 2. G-Methodologies for estimating anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal	**Article 5** 1. Each Party included in Annex I shall have in place, no later than one year prior to the start of the first commitment period, a national system for the estimation of anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol. Guidelines for such national systems, which shall incorporate the methodologies specified in paragraph 2 below, shall be decided upon by the Conference of the Parties serving as the meeting of the Parties to this Protocol at its first session. 2. G-Methodologies for estimating anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol shall be those accepted by the

Protocol shall be those accepted by the Intergovernmental Panel on Climate Change and agreed upon by the Conference of the Parties at its third session. Where such methodologies are not used, appropriate adjustments shall be applied according to methodologies agreed upon by the Conference of the Parties serving as the meeting of the Parties to this Protocol at its first session. Based on the work of, inter alia, the Intergovernmental Panel on Climate Change and advice provided by the Subsidiary Body for Scientific and Technological Advice, the Conference of the Parties serving as the meeting of the Parties to this Protocol shall regularly review and, as appropriate, revise such methodologies and adjustments, taking fully into account any relevant decisions by the Conference of the Parties. Any revision to methodologies or adjustments shall be used only for the purposes of ascertaining compliance with commitments under Article 3 in respect of any commitment period adopted subsequent to that revision. […]	Intergovernmental Panel on Climate Change and agreed upon by the Conference of the Parties at its third session. Where such methodologies are not used, appropriate adjustments shall be applied according to methodologies agreed upon by the Conference of the Parties serving as the meeting of the Parties to this Protocol at its first session. Based on the work of, inter alia, the Intergovernmental Panel on Climate Change and advice provided by the Subsidiary Body for Scientific and Technological Advice, the Conference of the Parties serving as the meeting of the Parties to this Protocol shall regularly review and, as appropriate, revise such methodologies and adjustments, taking fully into account any relevant decisions by the Conference of the Parties. Any revision to methodologies or adjustments shall be used only for the purposes of ascertaining compliance with commitments under Article 3 in respect of any commitment period adopted subsequent to that revision. […]
Article 4 Commitments 1. All Parties, taking into account their common but differentiated responsibilities and their specific national and regional development priorities, objectives and circumstances, shall: (a) Develop, periodically update, publish and make available to the Conference of the Parties, in accordance with Article 12, national inventories of anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol, using comparable methodologies to be agreed upon by the Conference of the Parties; (b) Formulate, implement, publish and regularly update national and, where appropriate, regional programmes containing measures to mitigate climate change by addressing anthropogenic emissions by sources and removals by sinks of all greenhouse gases not controlled by the Montreal Protocol, and measures to facilitate adequate adaptation to climate change; […] (d) Promote sustainable management, and promote and cooperate in the conservation and enhancement, as appropriate, of sinks and reservoirs of all greenhouse gases not controlled by the Montreal Protocol, including biomass, forests and oceans as well as other terrestrial, coastal and marine ecosystems; […] 2. The developed country Parties and other Parties included in Annex I commit themselves specifically as provided for in the following: (a) Each of these Parties shall adopt national1 policies and take corresponding measures on the mitigation of climate change, by limiting its anthropogenic emissions of greenhouse gases and protecting and enhancing its greenhouse gas sinks and reservoirs […].	

Appendix II – List of the mainland Portugal installations included in the National Allocation Plan II (2008-2012)

Sector	Subsector	Instalação	Operador	LE (tCO2/ano)
E/Centrais Termoeléc.	Carvão	Central Termoeléctrica do Pego	Tejo Energia, Produção e Distribuição de Energia Eléctrica, S.A.	2723011
		Central Termoeléctrica de Sines	CPPE - Companhia Portuguesa de Produção de Electricidade	5833317
	Biomassa	Central Termoeléctrica de Mortágua	O&M Serviços S..A.	1153
	CCGT	Central Termoeléctrica do Ribatejo	Companhia Portuguesa de Produção de Electricidade	1423103
		Central de Ciclo Combinado da Tapada do Outeiro	Turbogás - Produtora Energética, S.A.	1198020
	Fuel	Central Termoeléctrica do Carregado	Companhia Portuguesa de Produção de Electricidade	377234
		Central Termoeléctrica do Barreiro	Companhia Portuguesa de Produção de Electricidade	138977
		Central Termoeléctrica de Setúbal	Companhia Portuguesa de Produção de Electricidade	1118999
	Gasóleo	Central Termoeléctrica de Tunes	Companhia Portuguesa de Produção de Electricidade	4537
E/Refinação	Refinção	Refinaria de Sines	Petróleos de Portugal - Petrogal S.A.	2137550
		Refinaria do Porto	Petróleos de Portugal - Petrogal S.A.	1098025
E/Cogeração	Agroalimentar	Unicer - Central de Produção combinada de calor e electricidade	UNICER, Energia e Ambiente, S.A.	33560
		Unicer - Central de Produção combinada de calor e electricidade	UNICER, Energia e Ambiente, S.A.	10982
		CTE - Central Termoeléctrica do Estuário, Lda.	CTE - Central Termoeléctrica do Estuário, Lda.	22905
		Companhia Térmica Tagol, Lda	Companhia Térmica Tagol, Lda	41603
		RAR-Cogeração Unipessoal Lda	RAR-Cogeração Unipessoal Lda	50577
		DAI, Sociedade de Desenvolvimento AgroIndustrial, S.A.	DAI, Sociedade de Desenvolvimento AgroIndustrial, S.A.	84008
		POWERCER	GALP POWER, SGPS, S.A.	47192
	Agroflorestal	Siaf - Sociedade de Iniciativa e Aproveitamentos	Siaf - Sociedade de Iniciativa e Aproveitamentos	19480
		Enercaima - Produção de Energia, S.A.	Enercaima - Produção de Energia, S.A.	53147
		Enerbeira - Recursos Energéticos Lda.	Enerbeira - Recursos Energéticos Lda.	41028
		Sonae Indústria - Produção e Comercialização de Derivados de Madeira, S. A. - Oliveira do Hospital (Casca Sociedade de Revestimentos, S.A)	Sonae Indústria - Produção e Comercialização de Derivados de Madeira, S.A.	28953
	Pasta e papel	Central de Cogeração da Soporgen	SOPORGEN - Sociedade Portuguesa de Geração de Electridade e Calor, S.A.	239306
		ENERPULP - Cogeração Energética de Pasta, S.A. (Setúbal)	ENERPULP - Cogeração Energética de Pasta, S.A.	65832
		SPCG - Sociedade Portuguesa de Cogeração Eléctrica, S.A	SPCG - Sociedade Portuguesa de Cogeração Eléctrica, S.A	156 099
		ENERPULP Lavos	ENERPULP - Cogeração Energética de Pasta, S.A.	85807
		Central de Cogeração de CACIA	ENERPULP - Cogeração Energética de Pasta, S.A.	98590
		Caima Energia: Constância	Caima - Energia, Empresa de Gestão e Exploração de Energia, S.A.	13476
		Portucel Viana Energia	Portucel Viana Energia	206091
	Químico	Central de Cogeração da Energin	ENERGIN - Sociedade de Produção de Electricidade e Calor, S.A.	225955

		Bamiso	BAMISO - Produção e Serviços Energéticos, S.A.	53613
		Selenis Energia, S.A	Selenis Energia, S.A	51079
		Carriço Cogeração	GALP POWER, SGPS, S. A.	161539
		REPSOL - Central Termoeléctrica	Repsol - Produção de Electricidade e Calor, ACE	411058
		ENERLOUSADO - Recursos Energéticos Lda	ENERLOUSADO - Recursos Energéticos Lda	42469
	Têxtil	Saramagos	Saramagos - Soc.Prod.Energia, S.A.	56675
		Lameirinho Recursos Energéticos S.A.	Lameirinho Recursos Energéticos S.A.	38617
		SEVA - Central de produção combinada de calor e electricidade	SEVA - Sociedade Energética de Valdante, S.A.	29835
		SPE-Sociedade de Produção de Electricidade e Calor, S.A.	SPE-Sociedade de Produção de Electricidade e Calor, S.A.	46027
		Fábrica do Arco - Recursos Energéticos, S.A.	Fábrica do Arco - Recursos Energéticos, S.A.	26643
		Companhia Térmica do Serrado, ACE	Companhia Térmica do Serrado, ACE	17712
		Companhia Térmica Oliveira Ferreira, ACE	Companhia Térmica Oliveira Ferreira, ACE	11421
		Companhia Térmica Mundo Textil, ACE	Companhia Térmica Mundo Textil, ACE	20938
		MABERA - Acabamentos Têxteis, S.A.	MABERA - Acabamentos Têxteis, S.A.	13569
	Extracção de mat.min.	Unidade de Cogeração (Adelino Duarte da Mota)	Adelino Duarte da Mota, S.A	48733
	Vários	Central de Cogeração do Parque das Nações	Climaespaço - Soc. Prod.Distrib.Urb.Energia Térmica, S.A.	29259
E/Inst. de Combustão	Ind. Agroalimentar	Tagol - Companhia de Oleaginosas do Tejo S.A	Tagol - Companhia de Oleaginosas do Tejo S.A	24328
		TATE & LYLE Açúcares de Portugal (ex-Alcântara - Refinarias Açúcares, S.A.)	TATE & LYLE Açúcares de Portugal (ex-Alcântara - Refinarias Açúcares, S.A.)	38654
				18861
		Fábrica de Avanca	Nestlé Portugal, S.A.	31714
		Fábrica de Benavente	Indústrias de Alimentação IDAL, Lda	24930
		COMPAL - Central Térmica	COMPAL - Companhia Produtora de Conservas Alimentares	13374
		Rogério Leal & Filhos, S.A.	Rogério Leal & Filhos, S.A.	14765
		Instalação de Combustão (Avilafões)	Avilafões - Aviários de Lafões Lda.	4195
		SUGAL - Alimentos, S.A.	SUGAL - Alimentos, S.A.	15678
		LACTOGAL - Produtos Alimentares, S.A.	LACTOGAL - Produtos Alimentares, S.A.	11829
		SOPRAGOL - Soc. Indust.Prod.Agríc S.A:	SOPRAGOL - Soc.Ind.Prod. Agrícolas,S.A.	8732
		CAMPIL Agro Industrial do Campo do Tejo, Lda	CAMPIL Agro Industrial do Campo do Tejo, Lda	5376
		F.I.T. - Fomento da Indústria de Tomate, S.A.	F.I.T. - Fomento da Indústria de Tomate, S.A.	9667
		Tomsil - Soc. Ind. Conc.Tomate, S.A.	Tomsil - Soc.Ind. Conc. Tomate, S.A.	2112
		ITALAGRO - Ind. Transformação AlimentarS.A.	ITALAGRO - Indústria de Transformação Alimentar, S.A.	12175
		COPAM - Indústria de amidos e derivados	COPAM - Companhia Portuguesa de Amidos, S.A.	13997
		Fromageries Bel Portugal S.A.	Fromageries Bel Portugal S.A.	14717
	Ind. Agroflorestal	Luso Finsa - Indústria e Comercio de Madeiras S.A.	Luso Finsa - Indústria e Comercio de Madeiras S.A.	4426

		JOMAR - I ndústrias JOMAR - Madeiras e Derivados	JOMAR - I ndústrias JOMAR - Madeiras e Derivados	14945
		I.F.M. - Indústria de Fibras de Madeira, S.A.	I.F.M. - Indústria de Fibras de Madeira, S.A.	10097
	Ind. Met. Ferrosos	Lusosider - Aços Planos, S.A.	Lusosider - Aços Planos, S.A.	29849
	Ind. Química	Quimigal - produção de anilina e derivados e cloro alcalis	Quimigal, Quimica de Portugal, S.A.	32856
		UFAA-Unidade Fabril de Adubos de Alverca	ADP-Adubos de Portugal, S.A.	8264
		DOW - Fabrico de matérias plásticas sob formas primárias -	DOW Portugal, Produtos Químicos, SUL	48149
		UFAL - Unidade Fabril do Lavradio	AP - AMONÍACO DE PORTUGAL, S.A.	120846
		REPSOL Polímeros, Lda - Fábrica de Olefinas	REPSOL Polímeros, Lda - Fábrica de Olefinas	620936
		CIPAN - Companhia Industrial Produtora de Antibióticos, S.A.	CIPAN - Companhia Industrial Produtora de Antibióticos, S.A.	5909
		CARBOGAL - Carbonos de Porugal, S.A.	CARBOGAL - Carbonos de Porugal, S.A.	119804
		Termolan 1 - Vila de Aves	TERMOLAN	14504
		Termolan 2 - Santo Tirso	TERMOLAN	19065
	Ind. Têxtil	Riopele	Fábrica Têxtil Riopele, S.A.	4781
		Arco Têxteis, S..A.	Arco Têxteis, S..A.	7088
		TMG - Acabamentos Têxteis	TMG - Acabamentos Têxteis	17197
		Tinturaria e Acabamentos de Tecidos, Vale de Tábuas, Lda.	Tinturaria e Acabamentos de Tecidos, Vale de Tábuas, Lda.	8143
		Coelima Indústrias Têxteis, S.A.	Coelima Indústrias Têxteis, S.A.	13624
		ATB-Acabamentos Têxteis de Barcelos, Lda	ATB-Acabamentos Têxteis de Barcelos, Lda	6484
		Malhas Eica	Malhas Eica	5274
	Outros	Tabaqueira, S.A.	Tabaqueira, S.A.	5833
		Iberol - Sociedade Ibérica de Oleaginosas, S.A.	Iberol - Sociedade Ibérica de Oleaginosas, S.A.	39488
Metais ferrosos	Metais ferrosos	Fábrica do Seixal da SN Seixal Siderurgia Nacional, S.A	SN Seixal Siderurgia Nacional, S.A	197292
		Fábrica da Maia da SN Maia - Siderurgia Nacional, S.A.	Fábrica da Maia da SN Maia - Siderurgia Nacional, S.A.	138144
Cimentos e Cal	Cal	Microlime, Lda	Microlime - Produtos de Cal e Derivados, Lda	37767
		Calcidrata	Calcidrata - Indústrias de Cal, S.A.	87982
		Manuel Piedade Batista e Irmão, Lda	Manuel Piedade Batista e Irmão, Lda	17039
		LUSICAL - Indústria Mineral-Calcinação de Calcários	Lusical - Companhia Lusitana de Cal S.A	321234
	Cimentos	Secil Martingança, Lda	Secil Martingança, Lda (1)	15718
		Fábrica de Cal Hidráulica do Cabo Mondego	Fábrica de Cal Hidráulica do Cabo Mondego da CIMPOR – Indústria de Cimentos, S.A.	50886
		Fábrica Maceira-Liz	CMP - Cimentos Maceira e Pataias, S.A. (1)	762823
		Fábrica Secil-Outão	SECIL - Companhia Geral de Cal e Cimento, S.A. (1)	1489648
		Centro de Produção de Alhandra	Centro de Produção de Alhandra da CIMPOR – Indústria de Cimentos, S.A.	1748681
		Centro de Produção de Loulé	Centro de Produção de Loulé da CIMPOR – Indústria de Cimentos, S.A.	503429

		Centro de Produção de Souselas	Centro de Produção de Souselas da CIMPOR – Indústria de Cimentos, S.A.	1750901
		Fábrica Cibra-Pataias	CMP - Cimentos Maceira e Pataias, S.A. (1)	421805
Vidro	Embalagem	Saint-Gobain Mondego, S.A.	Saint-Gobain Mondego, S.A.	84342
		RICARDO GALLO - Vidro de Embalagem, S.A.	RICARDO GALLO - Vidro de Embalagem, S.A.	96530
		Santos Barosa Vidros, S.A.	Santos Barosa Vidros, S.A	154633
		Fábrica da Marinha Grande	BA- Fábrica de Vidros Barbosa & Almeida, S.A.	147401
		Fábrica de Avintes		79213
		Sotancro, embalagem de vidro, S.A.	Sotancro, embalagem de vidro, S.A.	58476
	Outros (cristalaria)	Fábrica de Vidros	Dâmaso-Vidros de Portugal, S.A.	12519
		Crisal - Cristalaria Autmoática, S.A.	Crisal - Cristalaria Autmoática, S.A	37746
	Plano	Saint-Gobain Glass Portugal, Vidro Plano, S.A.	Saint-Gobain Glass Portugal, Vidro Plano, S.A.	96177
Pasta e Papel	Integrado (papel)	Soporcel	SOPORCEL - Sociedade Portuguesa de Papel, S.A.	56467
	Pasta e papel	Portucel - Fábrica de Pasta de Setúbal (Complexo Industrial de Setúbal da Portucel)	PORTUCEL - Empresa Produtora de Pasta e Papel, S.A.	35646
	Pasta	CELBI	CELBI	62580
		Caima - Indústria de Celulose: Constância	Caima Indústria de Celulose, S.A.	0
		Fábrica de CACIA	PORTUCEL - Empresa Produtora de Pasta e Papel, S.A.	32608
		CELTEJO - Empresa de Celulose do Tejo S.A.	CELTEJO - Empresa de Celulose do Tejo S.A.	34079
	Papel	Fábrica de Papel de Ponte Redonda	Manuel José de Oliveira & Cª Lda	4881
		Companhia de Cartões do Cávado, S.A.	Companhia de Cartões do Cávado, S.A.	3160
		Sociedade Transformadora de Papéis Vouga, Lda	Sociedade Transformadora de Papéis Vouga, Lda	3470
		Fapovar - Fábrica de Papel de Ovar, S.A.	Fapovar - Fábrica de Papel de Ovar, S.A.	3371
		Fábrica de Papel e Cartão da Zarrinha, S.A.	Fábrica de Papel e Cartão da Zarrinha, S.A.	8769
		Oliveira Santos & Irmão, Lda	Oliveira Santos & Irmão, Lda	2414
		António Marques, Lda	António Marques, Lda	4407
		Fapajal - Fábrica de papel do Tojal, S.A.	Fapajal - Fábrica de papel do Tojal, S.A.	11503
		CPK - Companhia Produtora de Papel Kraftsack, S.A.	CPK - Companhia Produtora de Papel Kraftsack, S.A.	0
		Luís Santos & Monteiro, S.A.	Luís Santos & Monteiro, S.A.	5274
		Renova - Fábrica 2	Renova - Fábrica de Papel do Almonda, S.A.	27990
		Joaquim Mariz de Carvalho,& CA, Lda	Joaquim Mariz de Carvalho,& CA, Lda	2090
		Renova - Fábrica 1	Renova - Fábrica de Papel do Almonda, S.A.	11561
		Portucel Viana	Portucel Viana, Empresa Produtora de Papéis Industriais, S.A.	20673
		Fábrica de Papel da Lapa, Lda	Fábrica de Papel da Lapa, Lda	3424
		Papeleira Portuguesa, S.A.	Papeleira Portuguesa, S.A.	9624

		Cemopol Celuloses Moldadas Portuguesas, Lda	Cemopol Celuloses Moldadas Portuguesas, Lda	10529
		Gopaca - Fábrica de Papel e Cartão, S.A.	Gopaca - Fábrica de Papel e Cartão, S.A.	0
		Prado-Cartolinas da Lousã, S..A.	Prado-Cartolinas da Lousã, S..A.	0
		Prado Karton	Prado Karton - Companhia de Cartão, S.A.	16382
		ILHAVENSE - Soc. Industrial de Papel, Lda	ILHAVENSE - Soc. Industrial de Papel, Lda	4040
		FAPULME - Fábrica de Papel do Ulme, Lda	FAPULME - Fábrica de Papel do Ulme, Lda	13378
Cerâmica	Tijolos, telhas, ac.	Cerâmica Outeiro do Seixo, S.A.	Cerâmica Outeiro do Seixo, S.A.	10689
		CONSTRUCER - Cerâmica de Construção, S.A.	CONSTRUCER - Cerâmica de Construção, S.A.	408
		CEPABIL - Cerâmica de Tijolos e Pavimentos, S.A.	CEPABIL - Cerâmica de Tijolos e Pavimentos, S.A.	9489
		Cetipal - Cerâmica de Tijolos e Pavimentos, S.A.	Cetipal S.A.	7471
		Cerâmica F. Santiago, Lda.	Cerâmica F. Santiago, Lda.	10062
		Cerâmica de Santo André	Cersan 2 - Cerâmica de Coruche, Lda.	196
		A. Silva & Silva - Cerâmica, S.A.	A. Silva & Silva - Cerâmica, S.A.	6528
		Cerâmica Vala, Lda	Cerâmica Vala, Lda	3714
		Cerâmica Certrês, Lda.	Cerâmica Certrês, Lda.	218
		Cerâmica Rosário S.A.	Cerâmica Rosário S.A.	8913
		Inacer - Indústria Nacional de Cerâmica, Lda.	Cerâmica das Quintãs, Lda.	8541
		Cerâmica das Quintãs, Lda.	Cerâmica das Quintãs, Lda.	10765
		Cerâmica Domingos F. Anacleto, S.A.	Cerâmica Domingos F. Anacleto, S.A.	3402
		Cerâmica de Ferreirós, Lda.	Cerâmica de Ferreirós, Lda.	6218
		A Telheira de Chaves, Lda.	A Telheira de Chaves, Lda.	6619
		Sociedade Cerâmica Silmar, S.A.	Sociedade Cerâmica Silmar, S.A.	4616
		Cerâmica do Centro, Lda.	Cerâmica do Centro, Lda.	8605
		Faceal - Fábrica de Cerâmica do Algarve	Faceal - Fábrica de Cerâmica do Algarve	6323
		Cerâmica do Boialvo, Lda.	Cerâmica do Boialvo, Lda.	7045
		J. Coelho da Silva, Lda.	J. Coelho da Silva, Lda.	15211
		Sociedade Cerâmica do Alto, Lda	Sociedade Cerâmica do Alto, Lda	9218
		Cerâmica Castros, S.A.	Cerâmica Castros, S.A.	8079
		Cerâmica Flaviense, Lda.	Cerâmica Flaviense, Lda.	3857
		Empresa Cerâmica Cervar, S.A.	Empresa Cerâmica Cervar, S.A.	9314
		M. A. Lopes D'Avó, Lda	M. A. Lopes D'Avó, Lda	6048
		Cerâmica do Salvadorinho, S.A.	Cerâmica do Salvadorinho, S.A.	3485
		Cerâmica Torreense - F4+F5	Cerâmica Torreense	13367
		Cerâmica da Floresta, Lda	Cerâmica da Floresta, Lda	5924

		Cerâmica Estrela D'Alva	Barbosa Coimbra, S.A.	4418
		Cerâmica Moderna do Olival	Cerâmica Moderna do Olival	1424
		Tijolar - Cerâmica do Olival S.A.	Tijolar - Cerâmica do Olival S.A.	4276
		Cerâmica Avelar, S..A.	Cerâmica Avelar, S..A.	15671
		Cer. Prélis (ex.- J. Monteiro e Filhos)	Cer. Prélis (ex.- J. Monteiro e Filhos)	7793
		LUSOCERAM - Unidade Industrial de Bustos	LUSOCERAM - Empreendimentos Cerâmicos, S.A.	23703
		LUSOCERAM - Unidade Industrial do Ramalhal	LUSOCERAM - Empreendimentos Cerâmicos, S.A.	10501
		LUSOCERAM - Unidade Industrial do Outeiro	LUSOCERAM - Empreendimentos Cerâmicos, S.A.	46112
		Nergal	Nergal - Nova Cerâmica Algarvia Lda.	5116
		F. S. e Cerâmica Amaro de Macedo, S.A.	F. S. e Cerâmica Amaro de Macedo, S.A.	3306
		Cerâmica Vicente e Filhos, Lda	Cerâmica Vicente e Filhos, Lda	5446
		Campos- Fábricas Cerâmicas, S.A.	Campos- Fábricas Cerâmicas, S.A.	18019
		Cerâmica Sotelha, S.A.	Cerâmica Sotelha, S.A.	12987
		A Tijoleira Central de Estarreja, Lda	A Tijoleira Central de Estarreja, Lda	5068
		CERAVE - Cerâmica Avelense, S.A.	CERAVE - Cerâmica Avelense, S.A.	356
		Cerâmica Condestável, Lda	Cerâmica Condestável, Lda	7179
		Cerâmica das Alhadas, S.A.	Cerâmica das Alhadas, S.A.	7775
		Empresa de Cerâmica da Carriça, S.A.	Empresa de Cerâmica da Carriça, S.A.	5546
		Cosbar	Cosbar - Cerâmica do Barlavento, S.A.	7065
		Abílio Duarte da Mota & Filhos, Lda	Abílio Duarte da Mota & Filhos, Lda	12799
		Abílio Duarte da Mota, Lda	Abílio Duarte da Mota, Lda	6006
		Cerâmica do Planalto - Variz	Cerâmica do Planalto, Lda.	11656
		Unidade Industrial da Chamusca	Faceril - Fábrica de Cerâmica do Ribatejo, S.A.	4348
		Unidade Industrial de Mortágua	Cerâmica Vale da Gândara, S..A.	6210
		Martelha, Lda	Martelha - Cerâmica de Martingança, Lda	6107
		Cerâmica de Pegões	Cerâmica de Pegões - J. G. Silva, S.A.	6339
		CERPOL - Empresa Cerâmica Portugal, S.A.	CERPOL - Empresa Cerâmica Portugal, S.A.	5901
		Cerâmica da Cruz do Campo	Iberoceram	8623
		Cerâmica Central do Algoz, Lda	Cerâmica Central do Algoz, Lda	4206
		Cerâmica Torreense - F3	Cerâmica Torreense	9771
		Grésil	Grésil	1852
		Lusotelha, Telhas e Tijolos de Águeda, Lda.	Lusotelha, Telhas e Tijolos de Águeda, Lda.	6200
		Cerâmica Ulmense, Lda	Cerâmica Ulmense, Lda	7310
		ECC - Empresa Cerâmica de Candosa, Lda	ECC - Empresa Cerâmica de Candosa, Lda	703

		Preceram - Cerâmica 1	Preceram - Indústrias de Construção S.A.	20299
		Preceram - Cerâmica 2	Preceram - Indústrias de Construção S.A.	14264
		Preceram Norte (ex. Fabricel)	Preceram - Norte, Cerâmicas, S.A.	12801
		Tijolágueda - Cerâmica de Águeda - Lda	Tijolágueda - Cerâmica de Águeda - Lda	16547
		Placfort - Empresa de Pre-esforçados, S.A.	Placfort - Empresa de Pre-esforçados, S.A.	347
	Pisos e azulejos	Soladrilho, S.A.	Soladrilho, S.A.	13052
		Grestejo, Indústrias Cerâmicas, S.A.	Grestejo, Indústrias Cerâmicas, S.A.	6201