



INTERNATIONAL  
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# “Environmental assessment of electricity production with post-combustion CO<sub>2</sub> capture”

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SID: 3302130002

SCHOOL OF SCIENCE & TECHNOLOGY

A thesis submitted for the degree of

*Master of Science (MSc) in Energy Systems*

NOVEMBER 2014

THESSALONIKI – GREECE



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# Abstract

This dissertation was written as a part of the MSc in Energy Systems at the International Hellenic University. Its purpose is to evaluate via Life Cycle Analysis the environmental footprint of ‘carbonate looping’ post-combustion CO<sub>2</sub> capture technology in electricity production compared to the more mature post-combustion CO<sub>2</sub> capture technology of ‘amine scrubbing’. Carbonate looping is an ex-situ, post-combustion CO<sub>2</sub> capture technology in which carbon dioxide from the flue gases is captured by a CaO-based sorbent. CaO carbonation is a highly exothermic process and with proper heat integration of the process, this heat can be employed for the endothermic regeneration process rendering the whole technique nearly autothermal in contrast to the amine scrubbing technology where a significant amount of energy is required to regenerate the saturated amine solution.

The environmental performance of a Greek lignite-fired power plant retrofitted with the two post-combustion CO<sub>2</sub> capture technologies and the reference scenario with no capture, are examined via life cycle analysis (LCA). The investigated technology of ‘carbonate looping’ is compared with the case of electricity production at a power plant without capture technology and with the case of electricity production with amine scrubbing.

The software program of SimaPro was chosen in order to evaluate the footprint of the entire scenarios as well as the extent of the contribution of each life cycle step to the different environmental impact categories and especially the impact category of global warming and reach some conclusions in terms of possible improvements.

At this point, I would like to express my sincere gratitude to my supervisor and my professor at International Hellenic University, Dr. Eleni Heracleous, for her invaluable guidance, her constant support and most of all, for her patience throughout my dissertation writing, giving me her precious advices, as well as, I would like to express my thanks to Dr. Georgios Martinopoulos for helping me with the software program.

I would also like to thank my husband Giorgo, my son Filippo and the other members of my family, for giving me their support and being patience, throughout the dissertation time period and made possible for me to complete my studies.

Toliou Katerina

22/11/2014

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# 1. Introduction

## 1.1 The greenhouse effect

The greenhouse effect which is well-known, especially the last years, is related to the climate change problem. By greenhouse effect, we call the phenomenon of the retention of the heat that is reflected from the earth's surface inside the atmosphere. This heat is derived from the visible light coming from the sun to the earth. The so-called greenhouse gases (GHGs) act in the same way as a glass greenhouse operates, forming a layer around the earth which “traps” the reflected heat as Figure 1 shows.

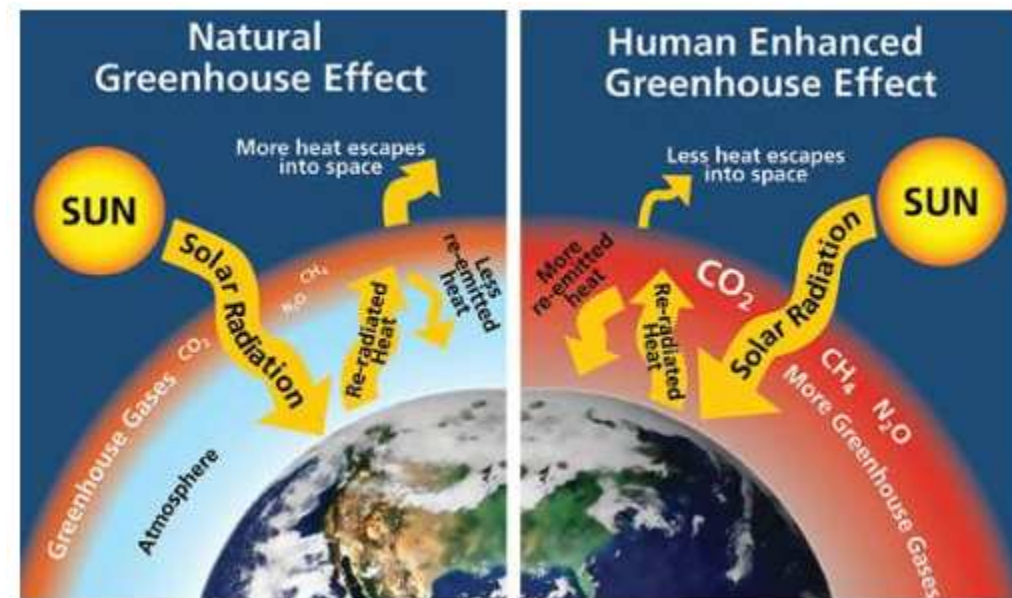


Figure 1: The Greenhouse Effect [1]

The main greenhouse gases are water vapor, carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) and ozone (O<sub>3</sub>), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF<sub>6</sub>). [2]

A certain amount of GHGs is necessary for the conservation of life on earth, because without those gases there would be very low temperatures, under the freezing temperature of water, causing the extinction of life on earth. However, the concentration of some GHGs, especially CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, has increased dramatically in the last

years due to human activities. These activities include the combustion of fossil fuels and deforestation with the simultaneous release of the organic soil carbon, as CO<sub>2</sub>, in the atmosphere. The increase of their concentration in the atmosphere above certain level causes negative effects to the environment. A negative effect is the increase of the earth's temperature which has as a result the climate change [3]. Even though CH<sub>4</sub>, N<sub>2</sub>O and (CFCs) per molecule, contribute to a higher degree to the greenhouse effect, their percentage is lower than the percentage of CO<sub>2</sub>, which makes CO<sub>2</sub> the main contributor to global warming. [3]

Besides the GHGs mentioned above, there are other gases that do not affect directly global warming but can indirectly affect terrestrial absorption of solar radiation, in a way that influences the formation of the greenhouse gasses, as well as the tropospheric and stratospheric ozone layer. These gases are carbon monoxide (CO), non-CH<sub>4</sub> volatile organic compounds (NMVOCs), nitrogen oxides (NO<sub>x</sub>) and aerosols which are produced by sulfur dioxide (SO<sub>2</sub>) and elemental carbon emissions.

There has been a lot of progress so as to understand what climate change is and with which other phenomena is associated with. Studies have shown that the Earth is warming up. There is an increase in global temperature over the last century of 1.4 °F and is anticipated to rise more up to 2.0 to 11.5 °F (1.1 to 6.4 °C). The global warming affects mainly the land areas and the areas at higher latitudes and has also some other impacts to climate change in general. Some areas especially those which already experience lack of water, will face worse droughts, while in other regions the rainfall periods will increase and will be more intense. The coastal areas will face the danger of flooding due to the decrease of snow cover and the melted ice in the sea at the poles. Moreover, there will be often heatwaves which will last for longer periods, leading to destructive fires or heavy snowfalls, appearing more frequently, with very low temperatures. Last but not least, the ocean acidification and eutrophication will influence the sea life and especially the coral reefs. Even though, it is not clear how and to what extent such changes will occur and how they will interact with the ecosystem and its biodiversity, research shows that the impacts of climate change will be more severe to the poorest countries. [4]

## 1.2 Evolution of CO<sub>2</sub> emissions and origin by sector

Until the industrial revolution in the 19<sup>th</sup> century, the level of carbon dioxide in the atmosphere was somehow stable at 280 parts per million (ppm), for a time period of some thousands of years. From the beginning of 19<sup>th</sup> century, this standard has changed. From that time on, the atmospheric CO<sub>2</sub> levels have been increasing, initially with a slow rate, due to coal burning. From the Second World War and then, there is a rapid acceleration of the use of different kind of fossil fuels leading to high concentration levels of CO<sub>2</sub> in the atmosphere. As we can in Figure 2, in 1990 the CO<sub>2</sub> concentration in the atmosphere reached 355 ppm, while in May 2013 reached a level more than 400 ppm [5], which is above the cap of 380 ppm, set by Kyoto protocol in 1996 [6], with the provision to avoid climate change.

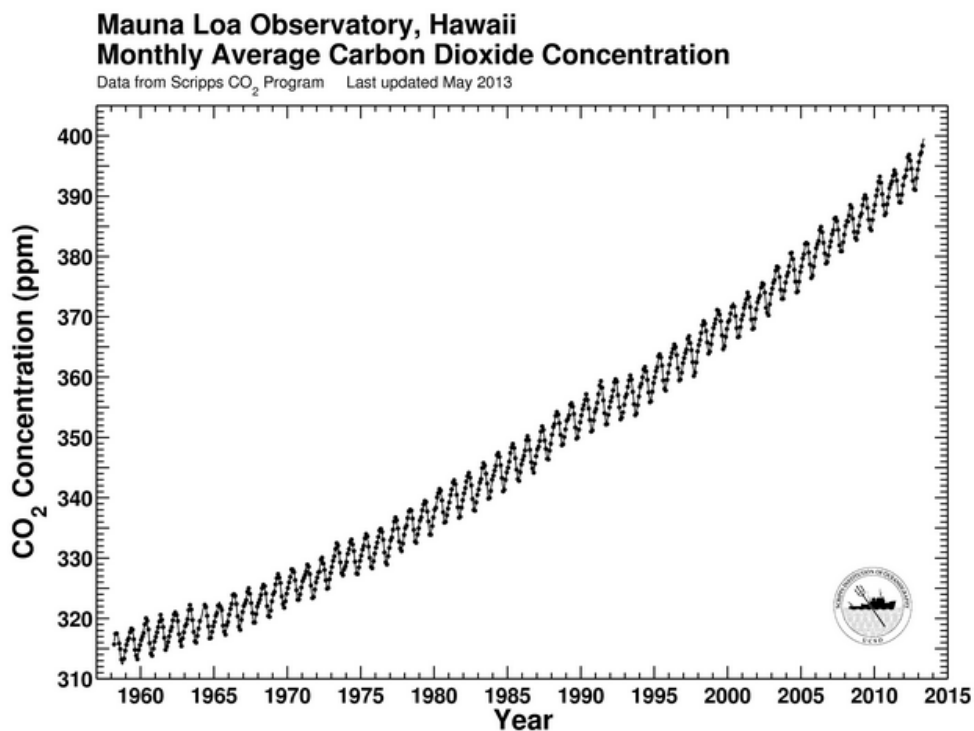


Figure 2: Monthly average carbon dioxide concentration, 2013 [7]

The global CO<sub>2</sub> emissions in 2011 were 31.3 billion tons CO<sub>2</sub> while in 2012 reached 34.5 billion tons CO<sub>2</sub>. Although, according to some indications there is a decline in the CO<sub>2</sub> emissions from the OECD countries, there is a high increase of CO<sub>2</sub> emissions in the non-OECD countries which leads to an overall increase of 1 % [4]. Moreover, the World Energy Outlook (WEO 2013) [8], in its New Policies Scenario,

projects that there will be an increase of global CO<sub>2</sub> emissions up to 37.2 GtCO<sub>2</sub> by 2035 due to fuel combustion which leads to a higher increase of temperature, 3.6<sup>0</sup>C rather than the 2<sup>0</sup>C.

A major amount of greenhouse gasses is produced by the anthropogenic activities, which contribute to the further increase of CO<sub>2</sub> emissions in the atmosphere, with the sector of the energy production having the largest share, as it is shown in Figure 3 [9].

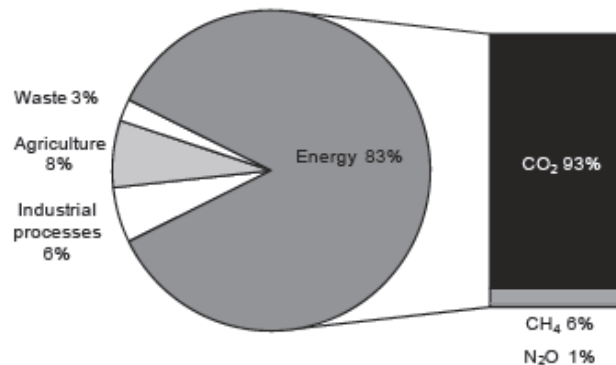


Figure 3: Share of different sectors to the anthropogenic GHG emissions in Annex I countries\*, 2011, [10]

A more detailed distribution is shown in Figure 4. It can be seen that electricity and heat generation are the two sectors which dispose a large amount of CO<sub>2</sub> emissions in the atmosphere, nearly the two-thirds, and contribute the most, followed by the transport sector.

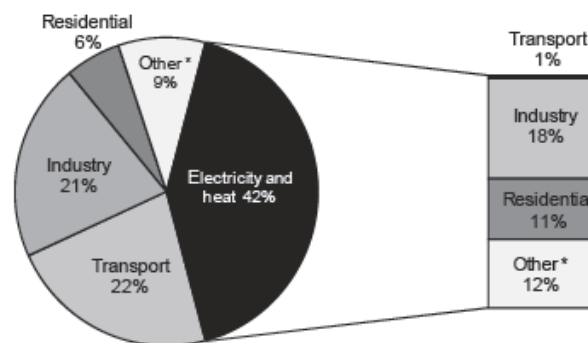


Figure 4: Contribution of different sectors to world CO<sub>2</sub> emissions in 2011 [10]

\*Annex I Parties includes Australia, Austria, Belarus, Belgium, Bulgaria, Canada, Croatia, the Czech Republic<sup>39</sup>, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Latvia, Liechtenstein (not available in this publication), Lithuania, Luxembourg, Malta, Monaco (included with France), the Netherlands, New Zealand, Norway, Poland, Portugal, Romania, Russian Federation, the Slovak Republic<sup>39</sup>, Slovenia, Spain, Sweden, Switzerland, Turkey, Ukraine, the United Kingdom and the United States

The global energy consumption in recent years is about 15 TW. From this amount, only the 20% is derived from renewable sources such as wind, biomass, solar, tidal, wave, geothermal and hydroelectric energy source. The rest of the amount for the production of energy comes from fossil fuels, which provide about 12.5 TW [11]. Even though the use of renewable energy becomes more popular, still a large percentage of the increasing energy demand, which by 2050 is expected to be doubled [10], comes from fossil fuels, which are dominant in the power sector, although their share of generation is expected to decline from 68% in 2011 to 57% in 2035 [12]. Still, fossil fuels with a capacity of 25TW of energy from already known reserves [13], will probably continue to be used, up to 2050, while they are going to cover our energy demands, up to 60%, as shown in Figure 5, where energy is in exajoules, EJ =  $10^{18}$  joules.

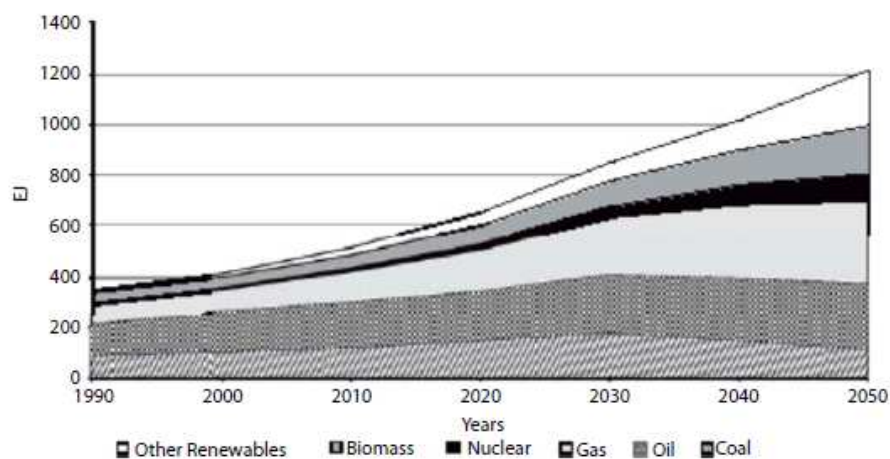


Figure 5 : Typical future energy projection by source [12]

The basic fuel for the generation of electricity and heat is coal. Coal combustion produces about 75% more CO<sub>2</sub> than natural gas. Generally, the combustion of coal is highly responsible for the increase of the CO<sub>2</sub> emissions and has a higher percentage by its use. Figure 6 shows the increase of CO<sub>2</sub> emissions the last twenty years, reaching the amount of 13 Gt of CO<sub>2</sub> emissions in 2011, only by electricity and heat production.

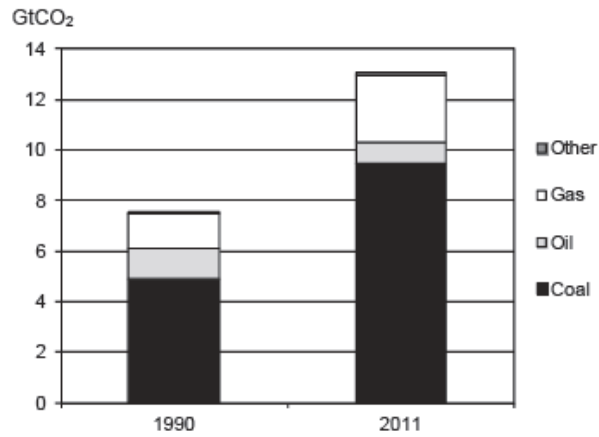


Figure 6 : CO<sub>2</sub> emissions from electricity and heat generation [10]

In global primary energy consumption, coal's share is about 30.1%. In 2013 the coal consumption grew by 3%. Figure 7 illustrates the consumption of coal provided by region showing that the percentage of coal's consumption in non-OECD countries increases constantly, with the region of Asia having the largest one [11].

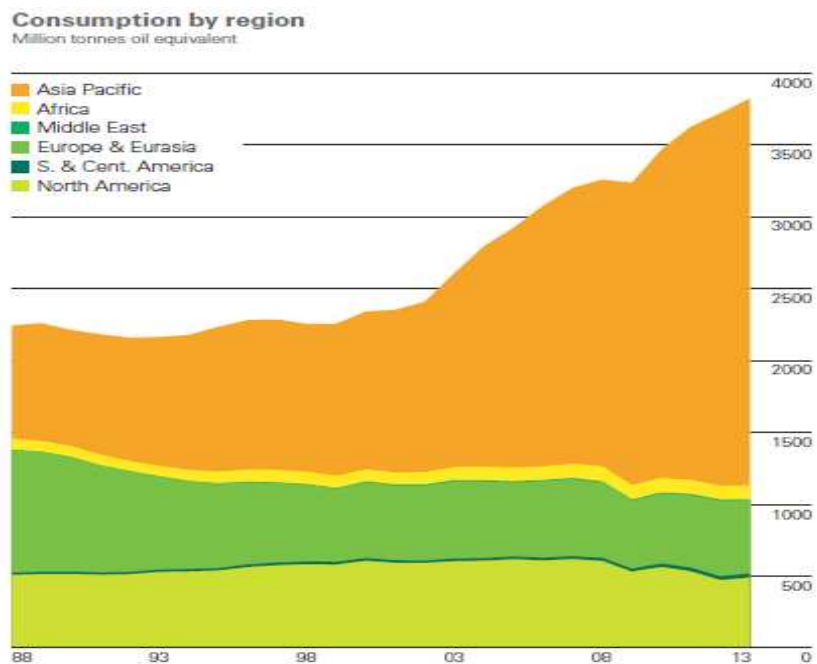


Figure 7 : Coal consumption by region [13]

### 1.3 Electricity generation and its contribution to GHG emissions in Greece

Fossil fuels, like coal are still the major source for the production of electricity all over the world. As Figure 8 presents, in 2011 the percentage for the generation of electricity from coal and peat was 41% and from natural gas was 22%. Only 16% was from renewable sources like hydropower and 12% for electricity generation by nuclear energy.

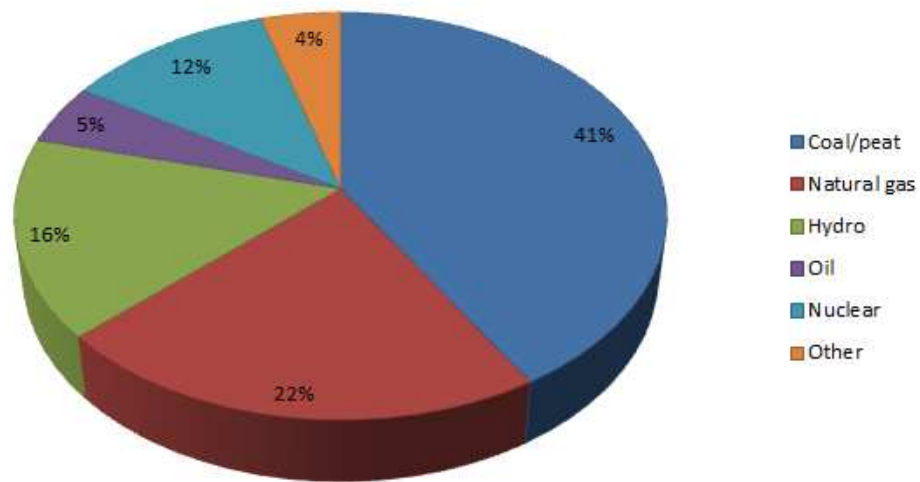


Figure 8 : World electricity generation by fuel, 2011 [14]

Likewise with the world situation, as Figure 9 shows, in European Union, coal together with nuclear energy are the major fuel sources for the generation of electricity reaching the amount of 1000 TWh each.



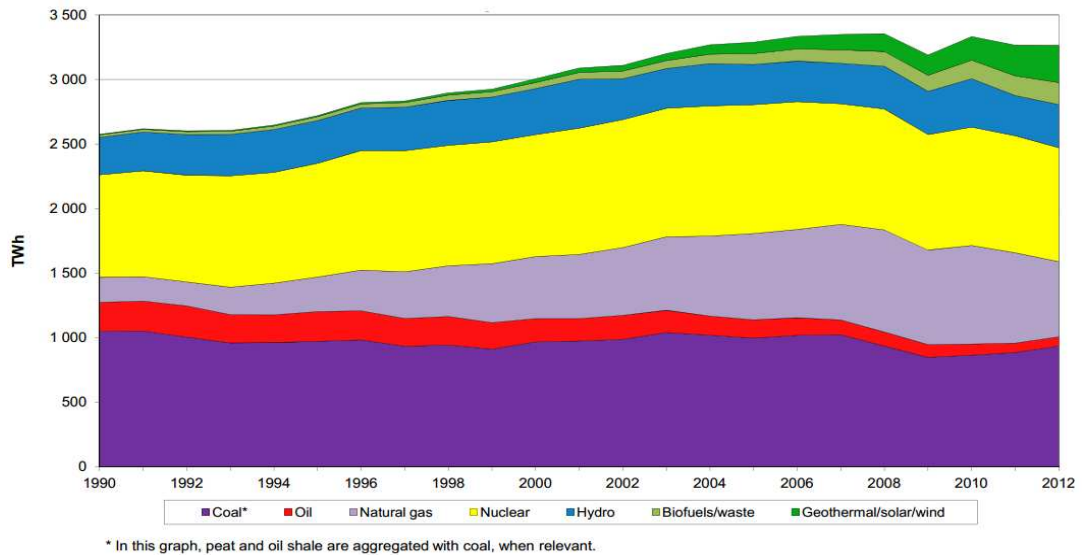


Figure 9 : Electricity generation by fuel, European Union- 28 [15]

In Greece, the main energy source for electricity generation is coal. Figure 10 shows the generation mix for producing electricity in Greece in 2010. It can be seen that more than 50% of electricity generation comes from coal.

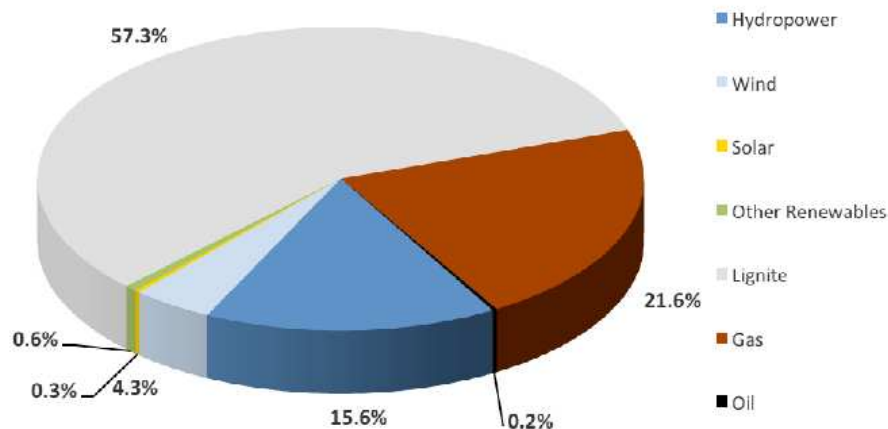


Figure 10 : Electricity generation mix in Greece, 2010 [16]

National coal resources are in the form of lignite. The remaining exploitable deposits of lignite in 2008 were 3020 million tonnes [17]. Coal is extracted by the mining division of the Public Power Corporation (PPC – DEI in Greek). Greece has no hard coal reserves and it relies only on the lignite reserves, which is the most important and dominant energy source. In the European Union, Greece is the second country in

lignite production and sixth in the world. The total proved amount of coal in place is 5800 million tons, the total coal production is 65.7 million tons per year and in 2011, only 7.32 million tons oil equivalent of coal were consumed [17].

Table 1 shows the thermal power stations in Greece and the fuel they use. There are eight main power stations with a generating capacity of 5288 MW, which produce the largest amount of electricity in Greece. The lignite power plants are located mainly in Ptolemais- Amynteo (LCPA) in Western Macedonia and in Megalopolis (LCM) in Peloponnese, close to the lignite resources.

Table 1 : Greek electricity generation system, thermal power stations (in operation end 2002)

[18]

Power Station	Start Up	Rated Power MW	Fuel Used	Location
Liptol	1959	43	Lignite	W. Macedonia
Ptolemaida	1959	850	Lignite	W. Macedonia
Kardia	1975	1200	Lignite	W. Macedonia
Agios Dimitrios	1984	1586.5	Lignite	W. Macedonia
Aminteo	1987	600	Lignite	W. Macedonia
Megalopolis-A	1970	550	Lignite	Peloponessos
Megalopolis-B	1991	300	Lignite	Peloponessos
Aliveri	1953	380	Mazut	Euboea
Lavrio	1972	450	Mazut	Attica
Lavrio (New)	1996	774	Natural Gas	Attica
Agios Georgios	1997	360	Natural Gas	Athens
Linoperamata	1965	253	Mazut-Diesel	Crete
Chania	1969	330	Diesel	Crete
Rhodes	1967	208	Diesel	Rhodes
APS	1967	547	Diesel-Mazut	Aegean Archipelago

The total lignite's generating capacity in 2010 was 9396 MW, having a large portion of the total net generating capacity, as is shown in Figure 11.

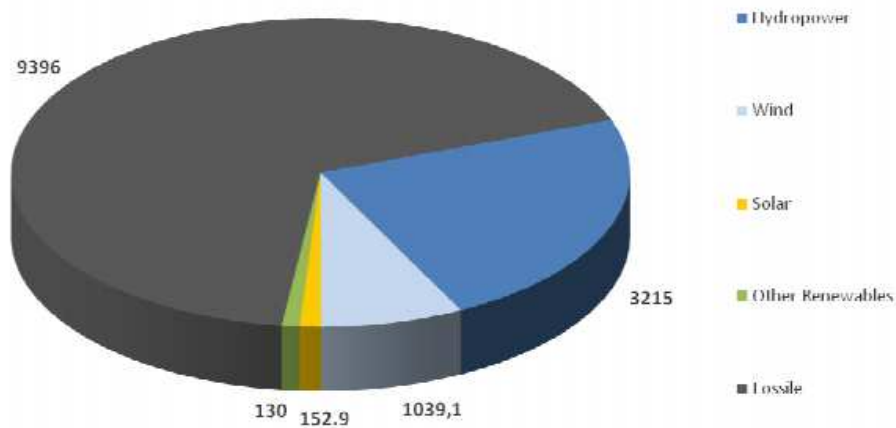


Figure 11 : Net generating capacity (MW),2010 [16]

Producing electricity at lignite fired power plants implies some negative aspects. The use of big amounts of water, the occupation of large area of resources, the disposal of hot water and the production of harmful air emissions and solid wastes are many of those negative aspects [19]. Concerning the production of air emissions, 1 ton of CO<sub>2</sub> is emitted for the production of 1 MWh from lignite combustion [20]. Figure 12 presents the contribution of lignite combustion in the national carbon dioxide emissions. In 2003, almost 34.5% of the national CO<sub>2</sub> emissions production originates from energy generation, with the CO<sub>2</sub> emissions coming from lignite's combustion having the largest share. With these values and the continuing use of lignite resources, there is a big concern whether the national Kyoto commitment is going to be fulfilled.

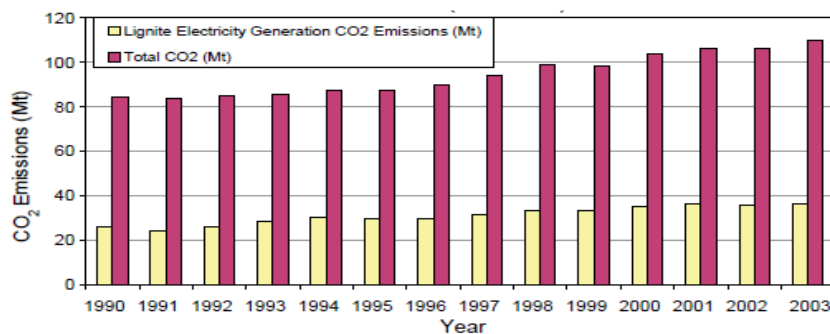


Figure 12 : Lignite Electricity Sector CO<sub>2</sub> Emissions Vs National CO<sub>2</sub> Generation (1990-2003)

[20]

In addition to CO<sub>2</sub> emissions from lignite combustion, there are also a large amount of SO<sub>2</sub> emissions due to the lignite's synthesis, originated mainly from the area near-by the power plant, with a high amount of sulphur content [21]. Figure 13 shows the annual production of SO<sub>2</sub> released in the atmosphere caused by electricity generation, with the lignite-fired stations producing the higher amount of SO<sub>2</sub> emissions.

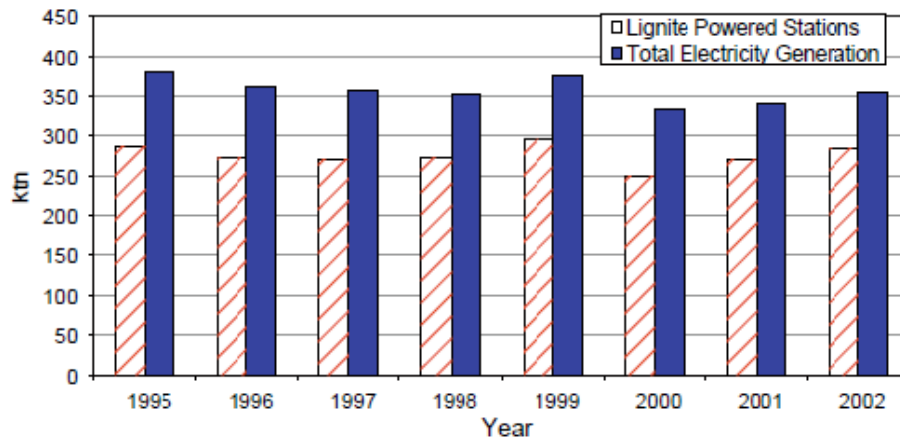


Figure 13 : Annual production of SO<sub>2</sub> due to Greek electricity generation [21]

In order to see whether it is beneficial or not, to keep using lignite as a power source for the generation of electricity in one country, from the economic side of view, along with the certain environmental impacts, a research is required. The emission trading system regulates each country's CO<sub>2</sub> emissions by allowing to have a certain cap and to trade the emission allowances within the cap. At this scheme, companies which exceed their cap could either buy an allowance for excess ton or pay a specific penalty which was for the time period 2005-2007, 40 €/tCO<sub>2</sub> and for 2008-2012, 100 €/tCO<sub>2</sub>. Similarly, companies which are in the limit or below could sell the surplus allowances [22]. The allowances prices of CO<sub>2</sub> emissions vary yearly and have now dropped from 30€/tCO<sub>2</sub> to 6.15€/tCO<sub>2</sub> [23]. Many suggest that by altering the conventional power plants with combined cycle units with natural gas could succeed to reduce the price for avoiding CO<sub>2</sub> emissions. Another solution is the upgrading of conventional power plants by the implementation of Carbon Capture and Storage (CCS) technologies (see Section 1.4 below) which capture CO<sub>2</sub> from the combustion flue gases, but with a cost of 25–40 €/t of CO<sub>2</sub> avoided. In addition to those alternations, investment to renewable energy technologies is necessary, although their cost is still high. It was estimated that until 2010, a

cost of 2–2.5 billion € was required for investments in cogeneration, renewable energy systems and in efficiency technologies for energy saving [24].

From the macroeconomic perspective, the use of local lignite resources contributes to the national economy and energy independence. For example by substituting half of electricity generation, which is about 17TWh, from lignite to imported oil of 5.5-6 Mtons per year, would cause a national debt of 2.2 billion € per year. The only cost beneficial alternative would be the exploitation of the renewable energy sources. Figure 14 and Figure 15 show the avoided oil and the avoided natural gas imports of the last 25 years due to the utilization of local lignite.

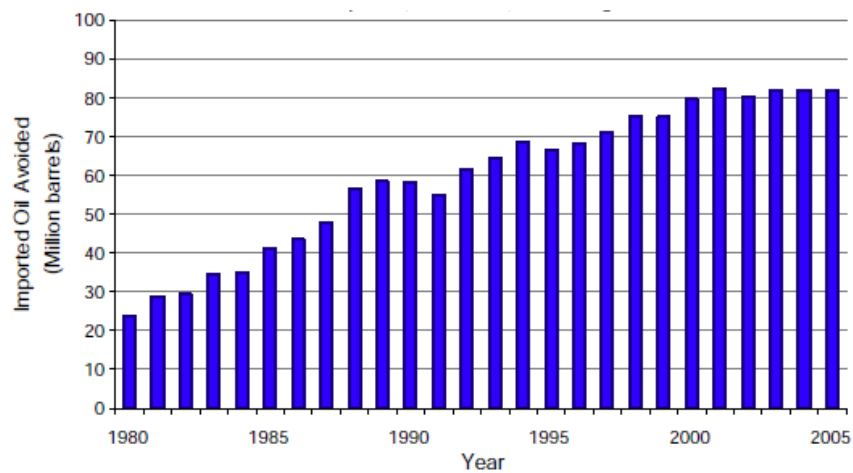


Figure 14 : Avoided oil imports (1980-2005) due to utilization of local lignite [25]

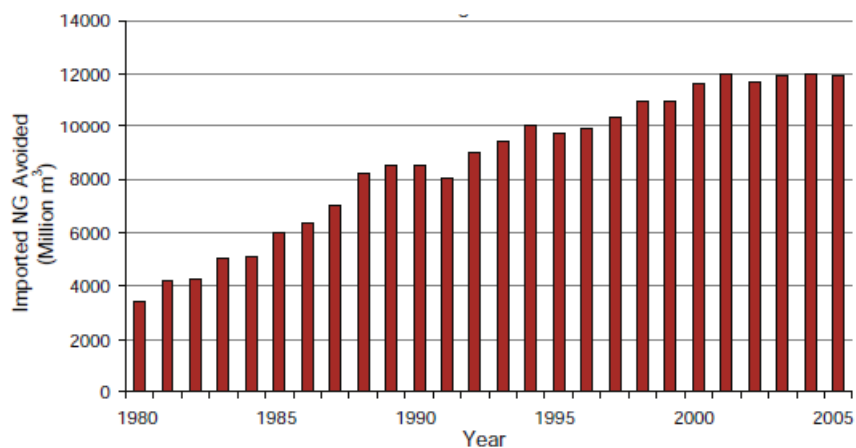


Figure 15 : Avoided nat. gas imports (1980-2005) due to utilization of local lignite [25]

Moreover, the raw material of fly ash could be utilized in other industrial sectors, like cement industry. By this extra utilization, the cost for the disposal of fly ash is eliminated by providing new profits from the sales of the waste fly ash, with a value of \$80 per ton, depending on the current price of cement [26].

Finally, there could be one more gain from the construction and operation of a new lignite power plant and its exploitation from the areas nearby the plant. The local societies could take advantage of this installation as it is going to create new job opportunities and help the employment of the overall area. For instance, the prefecture of Drama has a major problem of unemployment. As there are a lot of lignite resources in the area, with the installation of a new 300MW power plant, it is estimated that 1800 people from this area are going to be employed while the investments are going to reach the amount of 2 billion € [27].

## **1.4 Carbon Capture and Storage (CCS) for CO<sub>2</sub> mitigation**

### **1.4.1 General**

The exploitation of fossil fuels and their combustion has the negative effect of producing greenhouse gases and especially CO<sub>2</sub> emissions which are linked to climate change. Even though CO<sub>2</sub> does not have the same impact as other gases, having the lowest Global Warming Potential (GWP), still it contributes up to 80% to the total GHG gases, compared to methane and nitrous oxide. Moreover, fossil fuels play and will continue to play the dominant role at the energy sector. For this reason, measures have been taken to reduce high CO<sub>2</sub> emissions, like the Kyoto Protocol which is an international commitment of many industrialized countries and countries of the European Community, aiming to reduce the greenhouse gases emissions in the atmosphere which contribute to global warming, by 20% compared to 1990, until 2020. Other measures are the fiscal and financial incentives for using renewable resources, which are expected to reduce CO<sub>2</sub> emissions by 30%, the improvement of the efficiency of the already used systems or the use of more efficient new systems. Moreover, the shift to lower carbon intensity fuels, such as natural gas, will cause the reduction of CO<sub>2</sub> emissions by 50%. The other 20%, could be achieved with the CO<sub>2</sub> trading scheme and Carbon Capture and Storage

(CCS) technologies. Although a capture and storage capacity of 10Gt CO<sub>2</sub> per year is required, still in that way it will be possible to continue the utilization of fossil fuels to cover the growing energy demand.

Capture Carbon and Storage (CCS) technology is the process at which the CO<sub>2</sub> from the combustion of fossil fuels is:

- ❖ at first captured with different technologies
- ❖ subsequently transported by pipelines, vehicles or ships to suitable places
- ❖ finally is stored in deep depths.

Figure 16 presents the overall CCS process. CCS is not a new technology as it has already been used in industry for processing gas, so as to separate CO<sub>2</sub> from natural gas. Moreover, the transportation and the injection of the sequestered CO<sub>2</sub> in the ground are also used by the oil recovery industry. Installing a CCS system at a power plant will conduce to the use of extra fuel resources and an excess energy of 10-40% is going to be required, compared to power plants without CCS. Such installations also increase the constructional and operational cost and reduce the overall efficiency of the power plant.

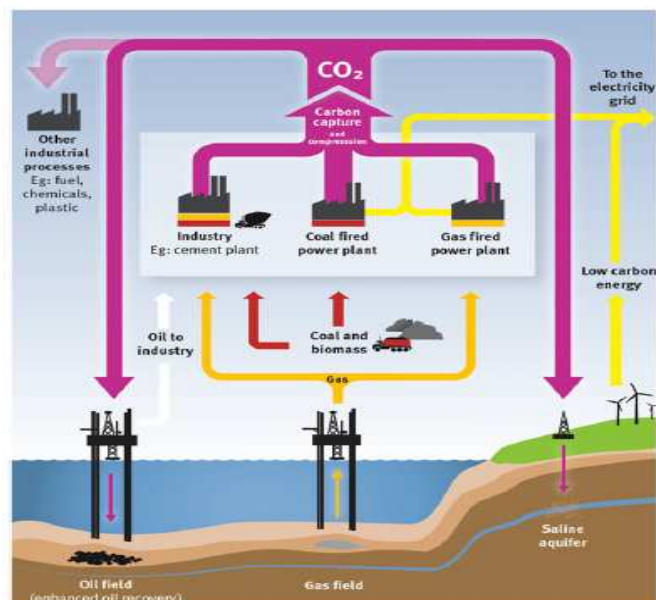


Figure 16 : The overall Carbon Capture and Storage process [28]

Nevertheless, CCS captures by 85-95% the CO<sub>2</sub> emissions of the power plant leading to a net reduction in the atmosphere by 80-90% for secure storage, compared to a power plant without CCS, as it is demonstrated in Figure 17 [29], in which the increased value of CO<sub>2</sub> is due to the efficiency loss of the power plant by the additional higher energy use from the CCS technology. According to the International Energy Agency (IEA), the growing energy demand is going to double the CO<sub>2</sub> emissions deriving from energy, to 57 GtCO<sub>2</sub> in 2050 [30]. Whereas, for the 2 degree scenario, a reduction of 43 GtCO<sub>2</sub> is needed to be implemented and CCS could decrease CO<sub>2</sub> emissions by 21%. To achieve this, a large number of coal-fired power plants should be equipped with CCS by 2050 [31].

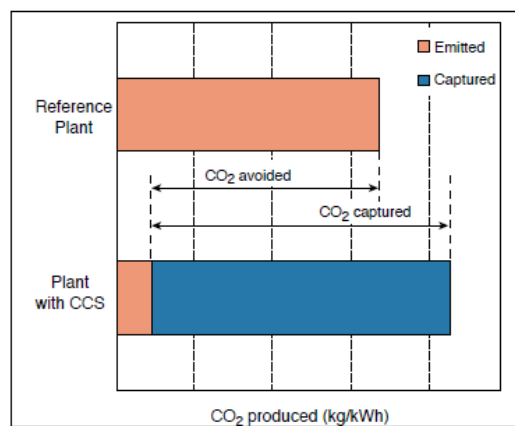


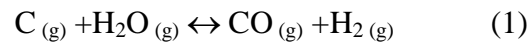
Figure 17 : CO<sub>2</sub> capture and storage from power plants [29]

In CCS, the CO<sub>2</sub> capture technologies can be divided in three major categories, depending from the composition of the gas stream and the CO<sub>2</sub> partial pressure, the basic principles of which are illustrated in Figure 18. The three CO<sub>2</sub> capture categories are:

- ❖ *Pre-combustion CO<sub>2</sub> capture*: the process in which the removal of gaseous CO<sub>2</sub> is performed before combustion. In this process, the fossil fuel, e.g. coal, is first reformed to synthesis gas via gasification (reaction 1) and then via the water gas reaction (reaction 2), is shifted to produce a fuel gas rich in hydrogen and CO<sub>2</sub>. CO<sub>2</sub> is captured by physical absorption while H<sub>2</sub> is used either as an energy source, in fertilizer manufacturing, to power fuel cells or to generate electricity in gas turbines. Even though the pre-combustion process is costly, the separation is easier due to the higher concentrations of CO<sub>2</sub> in the gas stream and the higher pressure. The produced CO<sub>2</sub> is sent to the compression unit in order to be



compressed and then stored, while hydrogen is used as input to a combine cycle so as to produce electricity.



- ❖ *Oxyfuel combustion:* In Oxyfuel combustion the fossil is combusted with high purity oxygen. The produced flue gas consists mainly of CO<sub>2</sub> and water vapor. This flue gas can be compressed and give a CO<sub>2</sub> stream with high concentration which can be transported for storage. Although the gas separation is not expensive, high energy costs arise due to oxygen separation from air.
  
- ❖ *Post-combustion CO<sub>2</sub> capture:* The process in which CO<sub>2</sub> produced from the combustion of the carbonaceous fuel with excess air is removed from the flue gases of the combustion. The capture of CO<sub>2</sub> from the post combustion flue gases can be performed by different processes, such as physical adsorption, chemical absorption, separation with membranes, cryogenic separation etc. The most commercial technique today is the capture of CO<sub>2</sub> from an aqueous amine solution using chemical absorption. In the last years, the use of a solid sorbent instead of a liquid has been investigated as a promising alternative. Since this thesis is focused on the post-combustion CO<sub>2</sub> capture, the next sections analyze in more details the classical amine-based CO<sub>2</sub> capture and the emerging calcium looping solid technology.

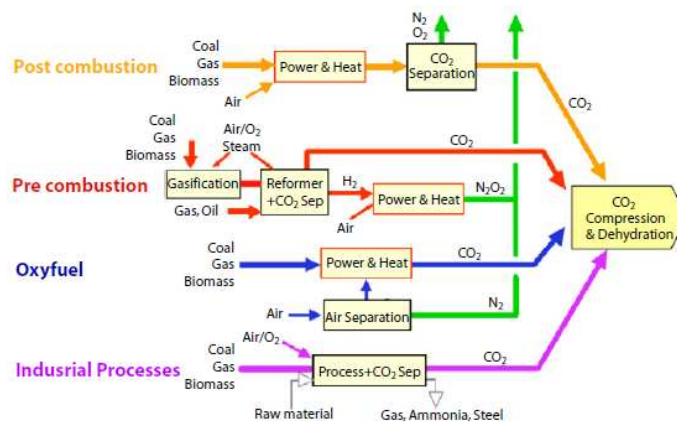


Figure 18 : The main categories of CO<sub>2</sub> capture from a power plants [13]

### 1.4.2 Post-combustion CO<sub>2</sub> capture with amines

Processes for capturing CO<sub>2</sub> from gas streams in petroleum and gas industry were developed from the beginning of 20<sup>th</sup> century [32]. From all carbon capture technologies, the most mature and advanced post-combustion capture technology is CO<sub>2</sub> absorption using solvents based on amines, like monoethanolamine (MEA), other amines and chilled ammonia. Chemical absorption is considered to be a baseline technology, widely used for gas purification and CO<sub>2</sub> removal from great volumes of low pressure gas achieving high efficiencies, in the range of 90-95%, with a conservative value of 85% [33], [34].

The CO<sub>2</sub> capture by amine scrubbing is basically a chemical reaction with an amine compound, like MEA. The CO<sub>2</sub> capture is performed in a vessel, which is called absorber, where the generated flue gas is 'scrubbed' with an amine solution. The amine solution captures by 85% to 90% the CO<sub>2</sub> from the flue gas and then enters to the regeneration vessel, which is called stripper. There, the rich-CO<sub>2</sub> sorbent is heated in order to release the CO<sub>2</sub>. The degraded amine sorbent is then sent back to the absorber, while the generated CO<sub>2</sub> stream first is being compressed and then through pipeline transportation is stored to a specific storage site [35].

While there are many types of solvents, MEA, due to its good characteristics, such as the high reactivity and stability as well as its low price, is nowadays one of the most widely used solvents from alkanolamines, suitable for the capture of CO<sub>2</sub> from low pressure gas streams with amine scrubbing process.

The last 25 years, this technology has also been applied for capturing CO<sub>2</sub> from flue gases. Nevertheless, the flue gases generated from fossil fuel power plants are not the same with the gas streams produced at petroleum and gas industry, in which chemical absorption used to be performed. Yet, the low pressure of CO<sub>2</sub>, makes amine scrubbing suitable for power industry too. However, the use of amine scrubbing may generate some problems, like the high oxygen content of flue gases which can create corrosion or oxidize amines to carboxylic acids. In addition, the degradation of amine is higher and the CO<sub>2</sub> capture efficiency is reduced. Due to the fact that flue gases, from coal power plants, contain high levels of sulphur dioxide (SO<sub>2</sub>), sulphur trioxide (SO<sub>3</sub>), fly ash and hydrogen chloride (HCl), most amines like MEA, react with irreversible way, producing stable salts causing corrosion to the parts of the power plant while there are amines losses too [32].

From economic perspective, the power plants with amine scrubbing CO<sub>2</sub> capture have higher capital and operating costs. The requirement of high amount of heat necessary for the amine reaction, the sensible heat and the heat of water and amine vaporization in the stripper, is responsible for this high use of energy, causing high operating cost.

There are many suppliers which offer commercial amine-based processes, such as the Mitsubishi Heavy Industries KM-CDR process, the Lummus Kerr-McGee process, the Aker Clean Carbon Just Catch process, the Cansolv CO<sub>2</sub> capture system, and the HTC Purenergy Process, with the most establishing process, being the Fluor Daniel Econamine FG Plus process. Table 2 shows the power plants which utilize the post-combustion capture process of amine-scrubbing, where a certain portion of the flue gas stream is sent to the capture unit, while Table 3 shows the scheduled projects with CO<sub>2</sub> capture implementation, mostly to existing power plants, at which the capture process is going to be performed to the whole flue gas stream [35].

Table 2 : Commercial post-combustion capture processes at power plants and selected industrial facilities [35]

Project Name and Location	Plant and Fuel Type	Year of Startup	Approx. Capture Plant Capacity	Capture System Type (Vendor)	CO <sub>2</sub> Captured (10 <sup>6</sup> tonnes/yr)
<b>United States</b>					
IMC Global Inc. Soda Ash Plant (Trona, CA)	Coal and petroleum coke-fired boilers	1978	43 MW	Amine (Lummus)	0.29
AES Shady Point Power Plant (Panama City, OK)	Coal-fired power plant	1991	9 MW	Amine (Lummus)	0.06
Bellingham Cogeneration Facility (Bellingham, MA)	Natural gas-fired power plant	1991	17 MW	Amine (Fluor)	0.11
Warrior Run Power Plant (Cumberland, MD)	Coal-fired power plant	2000	8 MW	Amine (Lummus)	0.05
<b>Outside the United States</b>					
Soda Ash Botswana Sua Pan Plant (Botswana)	Coal-fired power plant	1991	17 MW	Amine (Lummus)	0.11
Sumitomo Chemicals Plant (Japan)	Gas & coal boilers	1994	8 MW	Amine (Fluor)	0.05
Statoil Sleipner West Gas Field (North Sea, Norway)	Natural gas separation	1996	N/A	Amine (Aker)	1.0
Petronas Gas Processing Plant (Kuala Lumpur, Malaysia)	Natural gas-fired power plant	1999	10 MW	Amine (MHI)	0.07
BP Gas Processing Plant (In Salah, Algeria)	Natural gas separation	2004	N/A	Amine (Multiple)	1.0
Mitsubishi Chemical Kuroasaki Plant (Kuroasaki, Japan)	Natural gas-fired power plant	2005	18 MW	Amine (MHI)	0.12
Snohvit Field LNG and CO <sub>2</sub> Storage Project (North Sea, Norway)	Natural gas separation	2008	N/A	Amine (Aker)	0.7
Huaneng Co-Generation Power Plant (Beijing, China)	Coal-fired power plant	2008	0.5 MW	Amine (Huaneng)	0.003

Sources: DOE, "NETL Carbon"; IEAGHG, "CO<sub>2</sub> Capture"; MIT, "Carbon Capture"; GCCSI, "Strategic Analysis."

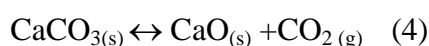
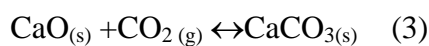
Table 3 : Planned demonstration projects at power plants with full-scale post-combustion capture [35]

Project Name and Location	Plant and Fuel Type	Year of Startup	Approx. Capture Plant Capacity	Capture System Type (Vendor)	Annual CO <sub>2</sub> Captured (10 <sup>6</sup> tonnes)	Current Status (March 2010)
<b>United States</b>						
Basin Electric Antelope Valley Station (Beulah, ND)	Coal-fired power plant	2012	120 MW	Amine (HTC)	1.0	Site Selection
Tenaska Trailblazer Energy Center (Sweetwater, TX)	Coal-fired power plant	2014	600 MW	Amine (Fluor)	4.3	Permitting
American Electric Power Mountaineer Plant (New Haven, WV)	Coal-fired power plant	2015	235 MW	Chilled Ammonia (Alstom)	1.5	Scoping
<b>Outside the United States</b>						
SaskPower Boundary Dam Polygon (Estevan, Canada)	Coal-fired power plant	2014	115 MW	Amine (Cansolv)	1.0	Plant Design
E.ON Kingsnorth Ruhrgas UK Post-Combustion Project (Kent, United Kingdom)	Coal-fired power plant	2014	300 MW <sup>a</sup>	Amine (Fluor & MHI)	1.9	Plant Design
TransAlta Project Pioneer Keephills 3 Power Plant (Wabamun, Canada)	Coal-fired power plant	2015	200 MW	Chilled Ammonia (Alstom)	1.0	Plant Design
Vattenfall Janschwalde (Janschwalde, Germany)	Coal-fired power plant	2015	125 MW	Amine (TBD)	—	Permitting
Porto Tolle (Rovigo, Italy)	Coal-fired power plant	2015	200 MW <sup>a</sup>	Amine (TBD)	1.0	Scoping

### 1.4.3 Post-combustion CO<sub>2</sub> capture based on solid CaO-based sorbents

The ‘Calcium Looping Cycle’ or ‘Ca-looping’ (CaL) is a process in which calcium-based sorbents are used in sorption/desorption cycles in order to capture CO<sub>2</sub> [36]. The CaL process is not a new technology, hence it was used in industry for syngas CO<sub>2</sub> removal since 1960s [37] while in 1994, Heesink and Temmink [38] proposed calcium looping to be also one of the zero emission coal technologies.

In ‘Calcium Looping Cycle’ the CaO-based sorbents, usually derived from limestone, undergo a reversible reaction: the exothermic gas-solid reaction which is called carbonation (reaction 3) and the endothermic decomposition reaction which is called calcination (reaction 4) in a dual fluidized bed system.



CO<sub>2</sub> in the flue gases stream reacts with CaO in a carbonator, forming CaCO<sub>3</sub>, which is then decomposed into CaO and CO<sub>2</sub> in a calciner. A simplified process scheme is presented in Figure 19. The temperature for the CO<sub>2</sub>-capture in the carbonator is around 650°C, while the temperature in the calciner is about 900°C. The calcination reaction is an endothermic one and requires heat input, which can be obtained from oxy-combustion of coal or natural gas [39]. The heat generated from the exothermic reaction of carbonation can be utilized to generate steam for extra power generation.

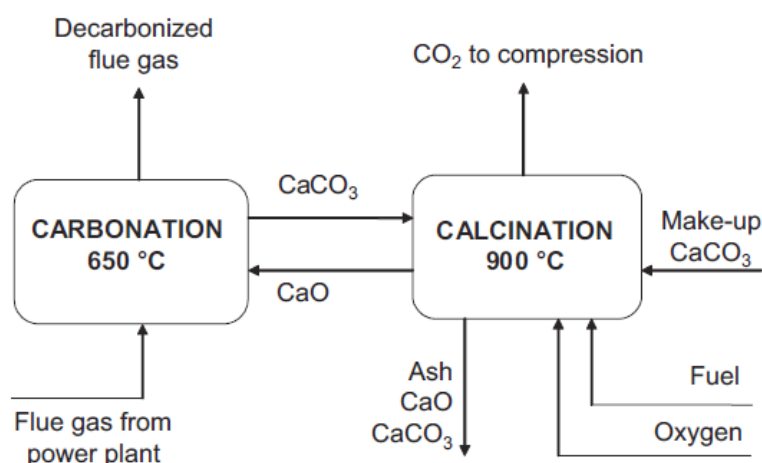


Figure 19 : Simplified process scheme for Calcium looping cycle (CaL) CO<sub>2</sub>-capture [40]

Calcium looping process, until now, is provided only in pilot scale as it is tested in pilot plant test facilities. During the last years, results of some experiment tests have been published in small fluidized bed pilot plants with different configurations [41]. Abanades et al [42] indicated the CO<sub>2</sub> capture from flue gases with the proper quality of active CaO in a fluidized bed reactor. Charitos et al [43], after having experimented in a dual 10kWth pilot plant, with a FB carbonator and a CFB calciner, displayed a report providing the proper operation variables of the carbonator in order to obtain, to some extent, the expected operation conditions in the CFB reactors. In addition, Alonso et al [39], performed tests in a 30kWth pilot plant constituted of a CFB carbonator and a CFB calciner. They reported capture CO<sub>2</sub> efficiencies about 70%-97%, while the CFB carbonator was working with realistic operation conditions. Lu et al [44], experimented in a semi-continuous 75 kW pilot plant, with a bubbling fluidized carbonator and an

oxy-fired CFB calciner, showing that the regeneration of CaO in the calciner does not influence the activity of the sorbent. After many tests in pilot plant facilities, results show that Calcium looping technology has a low energy penalty compared with other CO<sub>2</sub> capture technologies [45], [40].

Among the pilot-test facilities, at the scale of 75 kW, are one at the Instituto Nacional del Carbón (INCAR) in Spain [46], at University of Stuttgart in Germany [47], [48] and at Cranfield University in UK [49].

Lots of programs are running, aiming calcium looping process testing. Foster Wheeler, Fundación Ciudad de la Energía (CIUDEN) and ENDESA, with the support of the European Energy Program for Recovery (EEPR), are collaborating to a program with R&D tests at 0.8 MWth oxyfuel CFB pilot plant of CANMET Energy and at 30 MWth Oxy-CFB boiler of CIUDEN [44], which is under design and construction mode, in El Bierzo in Spain. The results of these tests, if are the appropriate, are going to be utilized in 300 MWe commercial plant in ENDESA's Compostilla power plant, which is planned to begin at the end of 2015.

Calcium looping in order to be used in industrial scale needs to be tested not only in pilot small scale but also in large scale, before 2020. In this prospect, ENDESA a European utility, Foster Wheeler a world manufacturer of fluidized bed combustion technology, HUNOSA the biggest coal mining company and CSIC, which is the Spanish Research Council, signed in 2009 the project 'CaOling', which is a development of post-combustion CO<sub>2</sub> capture with CaO in a large testing facility [50]. The main goal of this project is the design and the construction of a pilot plant of 1,7MWth which is going to perform tests of calcium looping technology at large scale, operating in realistic conditions for solid materials, temperature, superficial gas velocities, solid circulation rates, real flue gases and oxy-combustion conditions in the calciner in a continuous mode. The pilot plant will be built and integrated with 'La Pereda' power plant.

Likewise the 'CaOling' project a test pilot plant of 1MWth in TU Darmstadt in Germany [40], was funded by German industries and German government for the same purpose. Also, demonstration of calcium looping process at industrial scale was performed by Ohio State University but the outcome of the project is not available yet [51].

Furthermore, the tests on carbonate looping technology are also performed in cement industry as well. Cemex, one of the largest cement manufacturers in the world, owns a pilot plant in Monterrey in Mexico. Carbonate looping can be utilized in cement industry, as the exhausted sorbent of CaO can be used as feedstock in cement industry instead

using fresh limestone. In that way the direct generated CO<sub>2</sub> emissions could be reduced, until 50% [52].

## **1.5 Life Cycle Assessment (LCA)**

### **1.5.1 General**

Life Cycle Assessment (LCA) is a tool, as defined in ISO 14040 series, which evaluates the possible environmental impacts of a process or a product, including all phases during its lifetime from “cradle to grave”. The life cycle stages include the extraction of the raw material and its processing to the transportation and its use and maintenance and finally, at the end of its life, its disposal or potential recycling and reuse. Throughout these stages, the material and energy input and the generated emissions to soil, water and air are quantified in order to estimate environmental impacts and assess possible mitigations of the problem or evaluate technological systems. LCA is defined in environmental management international standards like ISO 14040 series. In ISO14040:2006 and ISO 14044:2006 the framework of the life cycle principle and all the environmental guidelines or requirements [53] are specified.

Life Cycle Assessment (LCA), which Figure 20 illustrates, can be divided in four basic stages:

- ❖ Goal and Scope Definition
- ❖ Inventory Analysis
- ❖ Impact Assessment
- ❖ Interpretation

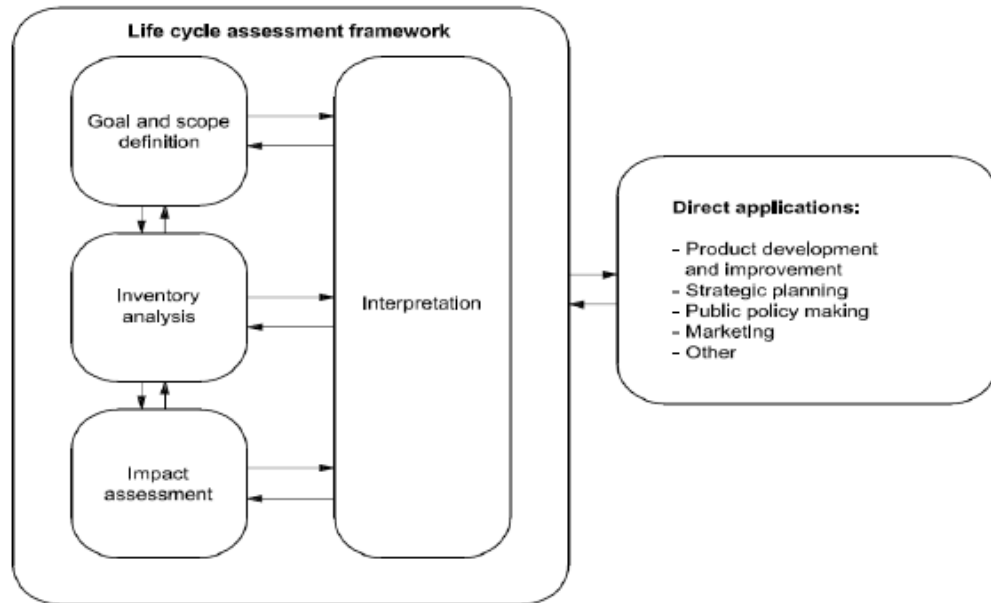


Figure 20 : LCA Framework [53]

### *Goal and Scope definition*

At this stage the aim and the method of the LCA is defined. Moreover, the boundaries of the system and the functional unit, according to which all the comparisons are performed, are determined, as well as the procedure that will be followed. The level of life cycle analysis is also determined, whether it is going to be a full or partial analysis.

### *Life Cycle Inventory*

The aim of life cycle inventory (LCI) is to collect and analyze the input data, such as the energy or the material use and the output data, like emissions of the system so as to build the model and quantify the input/output data relationship to the chosen functional unit.

### *Life Cycle Impact Assessment*

At the stage of impact assessment (LCIA), the LCI data are converted into the environmental impacts via characterization. Here, the importance of the data is being evaluated, via the use of different characterization factors for each material/emission. The ecological and human health effects are defined in impact categories such as global warming potential, acidification, human toxicity, land use etc. and are based on the specified functional unit.



### *Interpretation*

The last phase of the LCA is the interpretation of the life cycle impact assessment (LCIA) results derived from the life cycle inventory (LCI). This analysis should be in accordance with the goal and scope definition so as to give recommendations wherever is needed.

### **1.5.2 LCA studies for CO<sub>2</sub> capture**

CO<sub>2</sub> capture and storage (CCS) is considered to be an efficient technology for the reduction of global greenhouse gas emissions. Studies on LCA of CCS have shown that the CCS technologies can be applied to power plants with net power output from 115 MW to 832 MW. In addition the CO<sub>2</sub> capture efficiencies are in the range of 78% to 95%, while the most of them have capture efficiency about 90% [54]. There are different kinds of technologies for the CO<sub>2</sub> separation from flue gases which are based either on absorption and adsorption process or membranes or having other separation method. Among the different post-combustion capture technologies the baseline and the most applicable capture technology is chemical absorption process, using as a sorbent, MEA or other amines or chilled ammonia.

There is a range of studies dealing on MEA absorption process [55] [56] [57] which most of them conclude to the fact that MEA process has high thermal energy requirement, increasing the overall process cost. According to Chapel et al. [56], the major amount of energy need, this of 4.2 GJ/ton CO<sub>2</sub>, covers the 36% of the operation costs for the overall process. In addition Singh et al. [55], after having modelled the MEA process for a coal-fired power plant with a capacity of 400 MWe, found that MEA process is an energy-intensive process as it has an energy requirement of 3.8GJ/ton CO<sub>2</sub>. There are a lot of papers dealing with the life cycle assessment of coal-fired power plant with post-combustion CO<sub>2</sub> capture like Koornneef et al. [58] in which the reduction of CO<sub>2</sub> emissions at a subcritical and supercritical coal-fired electricity generation power plant using post-combustion CO<sub>2</sub> capture with monoethanolamine is shown.

As described in the previous sections, an alternative post-combustion chemical absorption capture technology is calcium looping or calcium looping (CaL), (CaO/CaCO<sub>3</sub> cycle) which can be also integrated in power plants. Shimizu et al. [59] were the first to introduce calcium looping cycle and its integration with a coal-fired power plant with a

CO<sub>2</sub> capture rate of 90.4%, showing that the two processes responsible for the increased energy consumption are firstly, the O<sub>2</sub> stream, produced by the Air Separation Unit with 100% purity, used for the coal oxy-combustion in the calciner and secondly the CO<sub>2</sub> stream compression after the calciner. However, despite these energy-intensive processes the net efficiency when using CaL process is higher compared to other capture technologies like oxy-fuel combustion. Abanades et al. [60] studied five different types of fuels such as coal, biomass and pet coke in calciners with different operation temperatures range such as 850, 950 and 1080°C and different pressures. They found that the net power efficiency, on the basis of low heating value (LHV) was ranging from 37.7% to 40.0% with capture carbon rate of 90%. Many other studies are dealing with the integration of CaL with existing coal-fired power plants showing that CaL process is marginally well-performed compared to oxy-fuel and amine scrubbing, having higher net efficiency. Nevertheless, Romeo et al. [61] at their study emphasize the importance of heat integration with the secondary steam cycle and the optimum make-up flow rate of fresh limestone in CO<sub>2</sub> capture systems [62]. Most of the studies in literature discuss about coal-fired power plants. Romeo et al. [45] studied a lignite-fired power plant but the calciner is fed with coal and not lignite. Vorrias et al. [63] investigate the implementation of CaL technology in an existing lignite-fired power plant, virtualizing the calciner also with lignite.

## **1.6 Objectives and structure of thesis**

This dissertation aims to examine via life cycle analysis (LCA) the post-combustion CO<sub>2</sub> capture from a Greek lignite power plant with the technology of CaO/CaCO<sub>3</sub> looping (CaL). The chosen technology of CaL is going to be compared, first with a baseline case of a power plant without CCS and then with a scenario of chemical absorption CO<sub>2</sub> capture using monoethanolamine (MEA). The environmental impacts of the two scenarios with CO<sub>2</sub> capture are going to be compared with the power plant reference case. This LCA is undertaken in order to evaluate the extent of the contribution of each scenario to the different environmental impact categories and reach some conclusions in terms of possible improvements that can be made.

Chapter 1, which has already been presented, gives an overview of the current situation in energy and related environmental issues, emphasizing on the global and regional CO<sub>2</sub> emissions in the atmosphere. In this chapter, the CCS technologies are also presented, with a main focus on the CaL capture technology.

In Chapter 2, the goal and scope of the LCA is provided. A brief description of the three investigated scenarios is also given, presenting first each stage of the power plant without the capture technology and then the power plant with the two post-combustion carbon capture technologies. In addition, a general presentation of the methodology that was followed for conducting the study is given.

The input and output data for the three cases is presented in Chapter 3 and a full description of the two alternative carbon capture technologies, the carbonate looping and the amine process, is provided.

Chapter 4 contains the impact of the lignite-fired power plant to the different impact categories. These results are then compared with the results from the additional processes of the capture technologies, calcium looping (CaL) and amine capture by monoethanolamine (MEA).

Chapter 5 provides an interpretation of the results derived from the Life Cycle Impact Assessment stage. The results are analyzed and an interpretation is attempted, with the general conclusions derived from the LCA results for the three different cases.

# 2. Goal and Scope Definition

## 2.1 Goal

The purpose of this thesis is to compare via the LCA method the environmental impacts of three scenarios for electricity production from a lignite-fired power plant, with and without post-combustion CO<sub>2</sub> capture. The lignite-fired power plant without CO<sub>2</sub> capture technology is used as reference case, in order to assess the additional impacts associated with the use of the CO<sub>2</sub> capture technology. Through this study, it is possible to create and estimate a greenhouse gas profile for the three scenarios and determine the environmental advantages or the possible negative implications of using CO<sub>2</sub> capture technologies. In that way, the energy use and GHG emissions over the whole life cycle can be defined and conclusions for the environmental impacts can be reached, in order for the power generation with CO<sub>2</sub> capture technology to have the most effective application.

The three cases that are going to be addressed in this thesis are:

- ❖ Case 1: The reference case which is an average sub-critical lignite-fired power plant operating in the area of Northern Greece in the year of 2014 without CO<sub>2</sub> capture technology.
- ❖ Case 2: The lignite-fired power plant of the reference case, equipped with chemical absorption with monoethanolamine (MEA).
- ❖ Case 3: The same lignite-fired power plant of the reference case, equipped with calcium looping (CaO/CaCO<sub>3</sub> cycle).

## 2.2 Geographical framework

The reference power plant is assumed to be located in Greece. Therefore, the life cycle inventory data are for the area of Greece and are derived from literature and the Eco-invent v2.0 (2007) database [64]. For the data which are not possible to find, average data for Europe or global average data are used. Also, data for supercritical lignite-fired

power plant were taken from literature [58], [63]. Moreover, it was assumed that the power plant is built at a distance of 16.5 km from a lignite mine, which is called “Notio Pedio”. The lignite is excavated from the nearby open-pit mine and then is transported via conveyors to the power plant for the electricity production.

## **2.3 Functional Unit**

The functional unit which is used as reference unit to compare the three cases is defined as the production of 1 kWh of net electricity delivered to the grid. This means that all results of the study are expressed per kWh.

## **2.4 Software**

The three LCA models were built with the LCA software program of SimaPro 7.3.3 Multiuser [65], which contains European and U.S. databases and impact assessment methodologies such as the CML 2 baseline 2000 v 2.05 [66]. SimaPro 7 is a well-known Life Cycle Assessment (LCA) software, which covers a variety of business and educational needs as is used by industry, consultancies and institutes for research in many countries around the world. SimaPro is a useful and professional tool in order to collect, analyze and model products or systems from the sustainable and life-cycle point of view. Also, complex life cycles can be analyzed in a transparent way so as to give the environmental impact of the product or system in all life cycle stages, from the time that the raw material is first extracted, then is manufactured and distributed or used to its final disposal [67].

SimaPro is used at many kinds of LCA applications and contains a variety of databases, like Eco-invent database and many impact assessment methods while users can also built complex models using the Monte Carlo analysis.

## 2.5. System boundaries

The system boundaries show the life steps that are taken into account for the analysis of each of the investigated scenario. As an example, Figure 21 shows in a conceptual drawing the boundaries for the reference scenario. For the power plant operation, the necessary energy and materials for fuel combustion and power plant infrastructure are included, thus creating an electricity generation chain from fossil fuel extraction to final electricity generation as is going to be described later on in detail. The environmental results of those operations are also included to determine the total environmental impact.

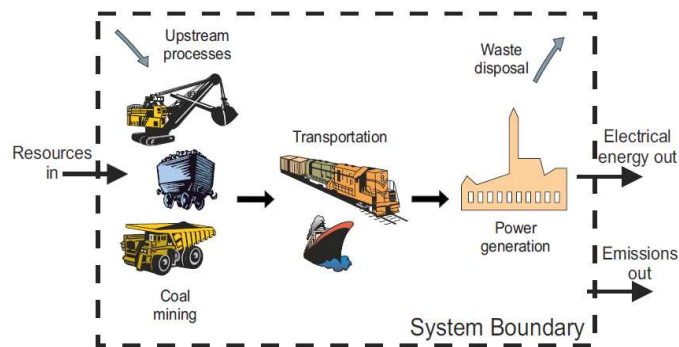


Figure 21 : Conceptual Drawing: Coal LCA System [68]

Concerning the two cases with CO<sub>2</sub> capture, not only fuel extraction and transport but also materials and energy consumption for the two different CO<sub>2</sub> capture processes are included to the life cycle and are considered in order to calculate the reduction in the net power plant output and also the power plant efficiency. The detailed system boundaries for each of the investigated scenarios are presented in detail in the following paragraphs.

### 2.5.1 Case 1: Power plant without CO<sub>2</sub> capture technology – reference scenario

The system boundaries for the reference power plant include all necessary processes for the production of electricity of 1 kWh.

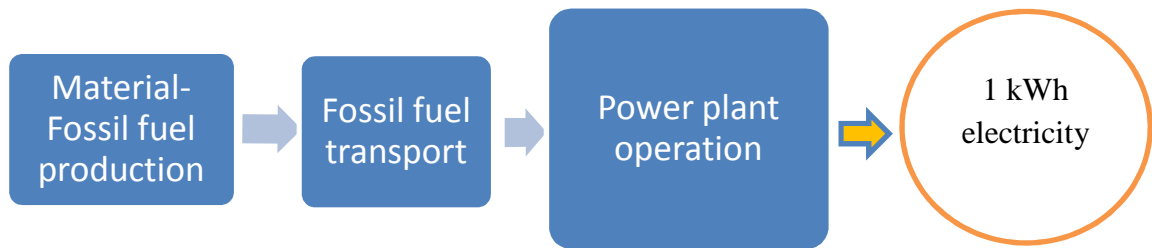


Figure 22 : System boundary of the reference power plant

As shown in Figure 22, the process of producing electricity from lignite combustion can be divided into three major subsystems which are:

- lignite mining
- lignite transportation
- electricity generation

Each subsystem includes all the used materials and the energy which are needed. Throughout the process, from lignite mining to electricity generation, the resources, the energy use and the generated emissions are quantified. The materials of the equipments manufacturing are not included to the above categories. All the data are provided from the Eco-invent database or reliable literature data.

The impacts of lignite mining include the affected area and occupation during the operation and restoration of the mine, the natural resources necessary for its construction, as well as the materials and fuels like consumed diesel and electricity as shown at Table 4. The generated emissions to air, water are also included.

Table 4 : Inputs from nature (resources) and technosphere (materials/fuels) for mining subsystem

Transformation from mineral extraction site
Occupation, mineral extraction site
Transformation to mineral extraction site
Transformation to arable
Water, well in ground
Coal, brown, in ground
Diesel, burned in building machine
Electricity, high voltage, production UCTE, at grid

The input data for the transportation are the fuel for lignite transportation and the generated emissions from the transportation of lignite by conveyors and rails, from the mining area to the power plant area. The use of trucks is only for the disposal of the waste products, so it was not taken into account. As mentioned, the distance between the mine and the power plant was assumed to be very small (16.5 km), so only the conveyor usage was taken into account.

For the generation of electricity at the power plant the necessary fuel, the required heat and raw materials used for the operation of the machinery and the overall combustion cycle of lignite are included to the input data inventory. Moreover, the generated emissions from the operation of the power plant and the burning of lignite are also included in the data inventory.

Table 5 presents the raw materials, fuels and processes which are participating at electricity generation subsystem.



Table 5 : Inputs from nature (resources) and technosphere (materials/fuels) for the electricity generation subsystem

Lignite, at mine
Water, cooling, unspecified natural origin
Chlorine, liquid, production mix, at plant
Water, completely softened, at plant
Water, decarbonized, at plant
SOx retained, in lignite flue gas desulphurization
Transport, freight, rail

The general procedure for producing electricity from the combustion of lignite includes as Figure 23 displays, the following steps:

- At first, lignite is pulverized into a lignite pulverizing system and then is ready to be fed into the furnace boiler. In the boiler the lignite is burnt at high temperature. From the combustion of lignite flue gasses of high CO<sub>2</sub> concentration and heat are produced.
- The next step is to utilize the produced heat, so as to heat the water, which is flowing in tubes lining the boiler, and produce steam at high pressure and temperature. Afterwards, the steam is fed into a turbine which consists of many sets of blades where it expands, causing the rotation of the turbine at high speed.
- Finally, the turbine is mounted with a generator. From the rotation of the turbine the generator rotor starts rotating, causing the electricity production based on Faraday's Principle.

The low pressure steam after the expansion is going to the condenser, to be condensed and return back to the boiler to restart the cycle.

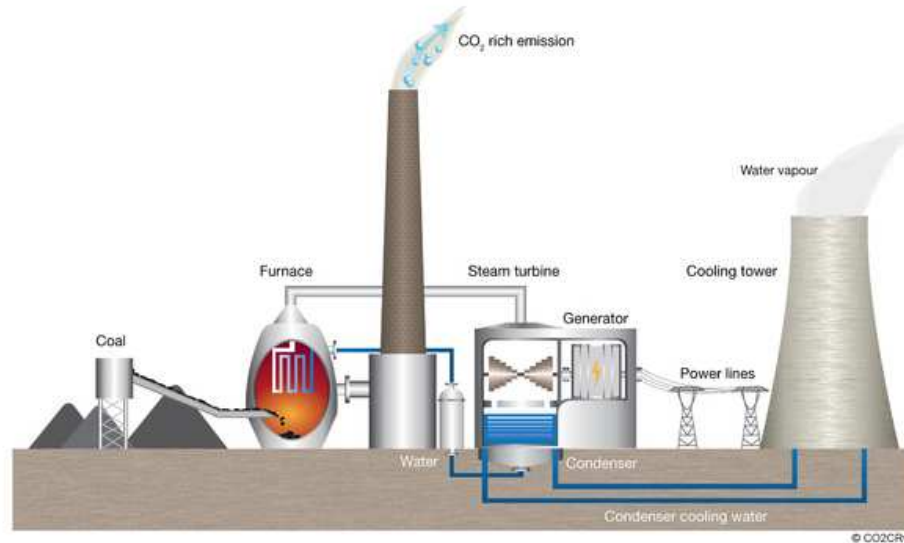


Figure 23 : Coal fired power plant [69]

### 2.5.2 Case 2: Power plant with chemical absorption CO<sub>2</sub> capture technology

Chemical absorption by monoethanolamine (MEA) or amine scrubbing is used commercially for CO<sub>2</sub> separation from flue gasses. Having already been applied in the past for CO<sub>2</sub> scrubbing at chemical process plants, this technology can also be used in the power sector. It is the most mature post-combustion capture technology [70]. The solvent of MEA is a chemical compound which belongs to amines and absorbs low concentration CO<sub>2</sub> (15-20%) from flue gas.

The system boundary for the overall process to produce 1 kWh of electricity at the base case power plant retrofitted with the amine CO<sub>2</sub> capture technology is shown in Figure 24. The major processes, which can be considered as subsystems, are still lignite mining, lignite transportation and electricity production. In addition, one more process is added, the process of post-capturing CO<sub>2</sub> with chemical absorption using amine-based solvents.

The overall process of producing electricity can be divided now into the following four subsystems:

- lignite mining
- lignite transportation
- chemical absorption
- electricity generation

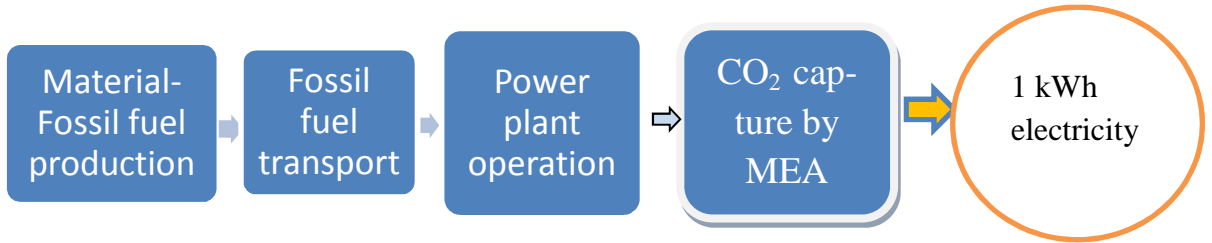


Figure 24 : System boundary of the reference power plant with CO<sub>2</sub> capture by MEA

For the scenario of the post-combustion CO<sub>2</sub> capture with amine scrubbing, the energy and materials for the subsystem of lignite mining and the generated emissions by this subsystem are the same as the base case. The same applies for the subsystem of transportation. The raw materials, the energy and heat use for the transportation section are also the same. In addition, the generated emissions to air and water and the used energy and heat for the power plant operation are also included before the final generation of electricity. Finally, for the new subsystem, this of the CO<sub>2</sub> capture, as Table 6 shows, the raw materials and chemicals used for the production of monoethanolamine and for its transportation to manufacturing plant, as well as energy use and emissions for operating the amine chemical absorption unit are taken into account.

Table 6 : Extra inputs from nature (resources) and technosphere (materials/fuels) for CO<sub>2</sub> capture by MEA capture unit

Monoethanolamine
Sodium hydroxide (concentrated)
Ammonia
Limestone
Electricity, medium voltage
Heat from lignite

### 2.5.3 Case 3: Power plant with carbonate looping CO<sub>2</sub> capture

The system boundaries of power generation with CO<sub>2</sub> capture by carbonate looping is presented in Figure 25. Similarly to the system boundary for CO<sub>2</sub> capture by MEA, the system boundary for the alternative capture technology of carbonate looping consists of the same four subsystems with the only difference, that of the capture subsystem.

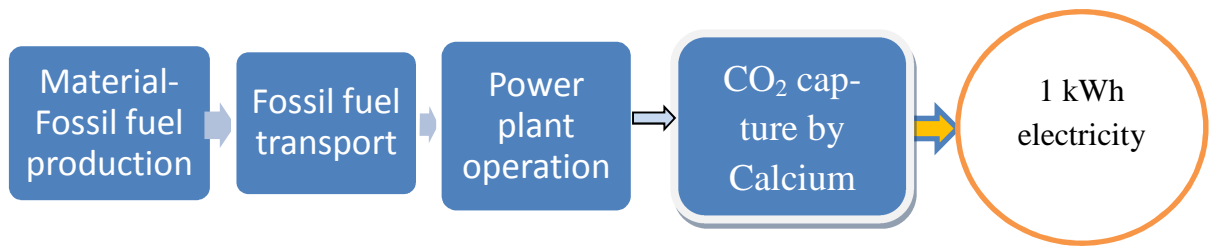


Figure 25 : System boundary of the reference power plant with CO<sub>2</sub> capture by calcium looping (CaL)

For the subsystem of CO<sub>2</sub> capture, the energy and the necessary heat, as well as the specific materials such as the limestone for the CO<sub>2</sub> capture from the flue gases are also included. At Table 7, the input data for the proper operation of calcium looping capture unit are presented.

Table 7 : Extra inputs from nature (resources) and technosphere (materials/fuels) for CO<sub>2</sub> capture by CaL capture unit

Limestone, milled ,loose, at pant
Electricity, medium voltage for auxiliaries
Heat from lignite

## 2.6 Data collection

Data for main impact categories were mainly obtained from Eco-invent database [64]. SimaPro LCA software program come with the Eco-invent database which was developed by the Swiss Centre for Life Cycle Inventories. The Eco-invent database covers

about 4000 datasets for processes, services and products which are used in LCA studies [71]. Eco-invent is the product of well-known older LCI databases and is considered to be a well updated database having for its contents information about a lot of production processes, waste treatment scenarios and environmental assessment methods. Most of Eco-invent datasets can give background data to some LCA studies. The LCI data which contains are from the area of energy with a variety of fuels like natural gas, oil, hard coal and lignite, renewable energy sources, electricity mixes and biofuels, electricity and heat production, transports, chemicals, metals, electronics, plastics, paper, woods, agricultural products, building materials and from the area of mechanical engineering and more.

## **2.7 Impact assessment methodology**

In order to evaluate the environmental impacts of the investigated systems, the LCI results have to be classified to relevant impact categories. Each impact category has its own characterization factor in order to classify and characterize the different emissions which contribute to the same impact effect.

It is possible that the same pollutant is classified to only one or many different impact categories as it can cause different environmental impacts. For example, the main contributor for global warming is CO<sub>2</sub>. NO<sub>x</sub> emissions however have a share to many impact categories such as acidification, eutrophication, human toxicity and photochemical oxidation. The impact of each pollutant can be classified by two possible ways. Either by recording the direct and indirect environmental impacts or by using specific characterization factors so as to have more clear results for each category.

After the classification of each pollutant to the specific impact category, there is the characterization part. At this step the pollutant which has been classified in one or more impact categories is now characterized with specific characterization factors using a common unit for each impact category. This way the LCI results can be compared for each impact category by their degree of contribution. For instance, the emissions related to the acidification impact category are multiplied by the specific factor, which is not the same for each pollutant. In this way, it is easy to understand the degree of contribution of each pollutant to the impact category and at the same time the different inventory inputs are converted into impact indicators able to be compared. This can be done if the

inventory data is multiplied with the characterization factor, using the following equation:

$$\text{➤ } \textit{Inventory data} \times \textit{Characterization factor} = \textit{Impact indicator}$$

For the needs of the present LCA, the CML baseline 2000 Method was used as an environmental impact assessment method. CLM is a method developed by the Centre for Environmental Studies (CML) of the University of Leiden in Netherlands in 1992 [66]. This method has a midpoint approach and is a problem orientated method before the final potential environmental damage to resources, ecosystems and human health showing the importance of the over-consumption of one resource or the generated emission to the ecosystem.

The impact categories that were considered in the current LCA were the following:

➤ **Abiotic depletion**

The abiotic depletion category refers to the extraction of raw materials and minerals such as iron and copper and extraction of fossil fuels. It is expressed in a ratio of kg equivalents of each extraction of minerals and fossil fuel used to kg of resource left in the reservoir, for example kg antimony equivalents/kg extraction and is performed at a global, regional and local scale.

➤ **Acidification**

This impact category is related to the potential impacts on groundwater, soil, surface water, biologic organisms, ecosystems and materials used for building. The accumulation of large amounts of sulfates and nitrates in the water cause phenomena like acid rain, which affect the acidity of wetlands and cause the degradation of forests. All the ecosystems do not have the same ability to absorb the same deposition that is why the affecting amount may be different for each country. Acidification potential is expressed as kg SO<sub>2</sub> equivalent and is implemented at a regional and global scale.

➤ **Eutrophication**

The impact category of eutrophication refers to the excessively large levels of macronutrients from nutrients emitted to air, water and soil in the environment. Also, the use of fertilizers in agriculture affects the quality of the groundwater. The macronutrients can result to the alteration of the number of species and their composition, while can increase biomass production in terrestrial and aquatic ecosystems such as aquatic photo-

synthetic plants which cause further oxygen consumption in the water. In addition, the presence of plants like reeds and algae in the water surface, result in limiting the solar radiation to the lower levels of the water affecting the photosynthesis and the production of oxygen. It is expressed as kg PO<sub>4</sub> equivalents and has local and regional geographical scale.

➤ **Global Warming (GWP 100)**

The impact category of global warming is associated with the harmful effects of GHG emissions to human health and the ecosystem caused by anthropogenic activities. The generated GHG emissions in the atmosphere cause the increase of temperature, which results to global warming and finally climate change. Global warming with a time horizon of 100 years (GWP 100) was considered. Global warming is expressed in kg carbon dioxide equivalents in a global geographical scale.

➤ **Ozone layer depletion**

The ozone layer depletion refers to the environmental impacts due to the thinner ozone layer. The anthropogenic emissions cause the decrease of the ozone layer which in turn results to pass a larger fraction, than it is supposed to, of UV-B radiation and reach the earth's surface. Eventually, this UV-B radiation has adverse effects on human and animal health, on aquatic and terrestrial ecosystems and on biochemical cycles and materials. The main contributor of about 80% for the depletion of ozone in the stratosphere is chlorofluorocarbons (CFC). It is expressed in kg CFC-11 equivalent for the ozone depletion potential of different gasses in a global scale.

➤ **Human toxicity**

This impact category refers to the effects of toxic substances released to air, water and soil on human health. The unit for expressing the human toxicity potential factors is kg 1,4-dichlorobenzene equivalents and has a regional, local and global scale.

➤ **Fresh water aquatic eco-toxicity**

The impact category of fresh water aquatic eco-toxicity refers to the impact of the disposal of toxic substances on aquatic, sediment and terrestrial ecosystems. Eco-toxicity potential is expressed as kg 1,4-dichlorobenzene equivalents and the geographical scope is at local scale.

➤ **Marine aquatic eco-toxicity**

The impact category of marine aquatic eco-toxicity refers to the impact of toxic substances and their emissions on marine ecosystems. It is also expressed as kg 1,4-dichlorobenzene equivalents and the geographical scope is at local scale.

➤ **Terrestrial eco-toxicity**

The impact category of terrestrial eco-toxicity refers to the impact of toxic substances and their emissions on terrestrial ecosystems. Its impact factor is expressed as kg 1,4-dichlorobenzene equivalents and the geographical scope is at local scale.

➤ **Photochemical oxidation**

Photochemical oxidation refers to the adverse effects on human health and ecosystems by the formation of reactive chemical substances, like ozone, caused by the sunlight impact on specific air pollutants. It depends on climate conditions such as average irradiation, temperature and humidity and temperature inversion in addition to the co- presence of nitrogen oxides in the troposphere. The photochemical ozone creation potential factors are expressed in kg ethylene equivalents, with time span of 5 days and in local scale.

The characterization factors for the most important pollutants and the units for each impact category, used in CML 2000 baseline, are presented analytically in Table 8.

In addition to characterization, the normalization of the impact categories can be obtained, when dividing the scores from a specific impact category with the corresponding category of a reference region like Netherlands, West Europe or World in a specific time region, such as 1990, 1995 and 1997.



Table 8 : Environmental impact categories [72]

Environmental impact category	Scale	Relevant emissions and resources	Characterization factor
<b>Abiotic depletion</b>	Global, regional, local	Quantities of minerals and fossil fuels used	Converts LCI data to a ratio of resource used to resource left. ( kg Sb eq)
<b>Acidification</b>	Regional, local	Sulfur dioxide(SO <sub>2</sub> ), Nitrogen oxides (NO <sub>x</sub> ), Hydrochloric acid (HCl), Hydrofluoric acid (HF), Ammonia (NH <sub>3</sub> )	kg SO <sub>2</sub> equivalents
<b>Eutrophication</b>	Regional, local	Phosphate (PO <sub>4</sub> ), Nitrogen Oxide (NO) Nitrogen dioxide (NO <sub>2</sub> ), Nitrates, Ammonia (NH <sub>3</sub> )	kg PO <sub>4</sub> <sup>-3</sup> equivalents
<b>Global warming</b>	Global	Carbon dioxide (CO <sub>2</sub> ), Nitrogen dioxide (NO <sub>2</sub> ), Methane (NH <sub>4</sub> ), Chlorofluorocarbons(CFCs), Hydrochlorofluorocarbons(HCFCs)	kg CO <sub>2</sub> equivalents
<b>Ozone layer depletion</b>	Global	Clorofluorocarbons(CFCs), Hydrochlorofluorocarbons(HCFCs), Halons, Methylbromide (CH <sub>3</sub> Br)	kg CFC -11 equivalents
<b>Human toxicity</b>	Global, regional, local	Arsenic, Chromium VI, Benzene, Hexachlorobenzene	kg 1,4-DB equivalents
<b>Fresh water aquatic ecotoxicity</b>	Local	Vanadium, Nickel, Beryllium	kg 1,4-DB equivalents
<b>Marine aquatic ecotoxicity</b>	Local	Nickel, Beryllium, Cobalt, Vanadium	kg 1,4-DB equivalents
<b>Terrestrial ecotoxicity</b>	Local	Arsenium, Chromium VI, Vanadium, Mercury	kg 1,4-DB equivalents
<b>Photochemical oxidation</b>	Local	Non-methane volatile organic compounds (NMVOC), Alkanes, Alkenes, Aromatic hydrocarbons	kg C <sub>2</sub> H <sub>4</sub> equivalents

# 3. Life Cycle Inventory (LCI)

## 3.1 Case 1: Reference power plant

### 3.1.1 Lignite mining

For mining 1 kg of lignite, the necessary inputs and the generated emissions to air, water and soil are shown in Table 9 and Table 10 respectively. The data was derived from the Eco-invent database in SimaPro software program, which quantifies the directly affected area and occupation during operation and restoration of the mine. Electricity requirements and some diesel for mining operation are included, as well as the groundwater pumped out of the mine. The re-cultivation to arable area is taken into account. In addition, electricity and diesel use are included. Electricity supply is modeled with the Union for the Co-ordination of Transmission of Electricity (UCTE) mix.

Heat requirements are not accounted for because: heat use is only mentioned in a few cases; heat is also used for briquette production and its allocation to different uses is not given; heat is usually produced as co-product by mine-mouth cogenerating plants for which no module has been developed.

Particle emissions are calculated on the basis of direct measurements of total particles made in Germany between mining areas and nearest populated areas. Radon emissions are extrapolated from data for hard coal mining. Methane emissions are directly taken from literature. Emissions to water are only roughly estimated on the basis of limited information from Germany and Spain and may not reflect specific conditions. They are assumed to be released to rivers. Possible emissions to groundwater have not been accounted for. Solid wastes are deposited in the same open pit and therefore not taken into account in the module. The data are for average European conditions around the beginning of the 1990s.

Table 9 : Inputs from nature (resources) and technosphere (materials/fuels) need, for mining 1kg of lignite

Transformation from mineral extraction site	0.000074 m <sup>2</sup>
Occupation, mineral extraction site	0.001111 m <sup>2</sup> a
Transformation to mineral extraction site	0.000037 m <sup>2</sup>
Transformation to arable	0.000037 m <sup>2</sup>
Water, well in ground	0.0035 m <sup>3</sup>
Coal, brown, in ground	1 kg
Diesel, burned in building machine	0.015 MJ
Electricity, high voltage	0.02 kWh

Table 10 : Emissions to air, water and soil from the mining of 1kg of lignite

Emissions to air		Emissions to water	
Carbon dioxide, fossil	11.73 g	Calcium, ion	36.0 g
Heat, waste	228.56 kJ	Chloride	4.99 g
Hydrogen-3, Tritium	1.58 Bq	Heat, waste	14.4 kJ
Noble gases, radioactive, unspecified	2.65 kBq	Hydrogen-3, Tritium	118.25 Bq
Radon-222	4.94 kBq	Magnesium	19.8 g
		Phosphate	7.01 g
		Potassium, ion	11.31 g
		Silicon	15.8 g
		Sodium, ion	19.76 g
		Sulfate	164.62 g
		Emissions to soil	
		Heat, waste	56.97 J
		Oils	3.43 mg

However, for the generation 1 kWh by the lignite combustion at the power plant, the necessary amount of fossil fuel is 1.99 kg of lignite, as calculated by SimaPro program. Figure 26 shows a schematic representation of 1.99 kg lignite mining also by SimaPro program.

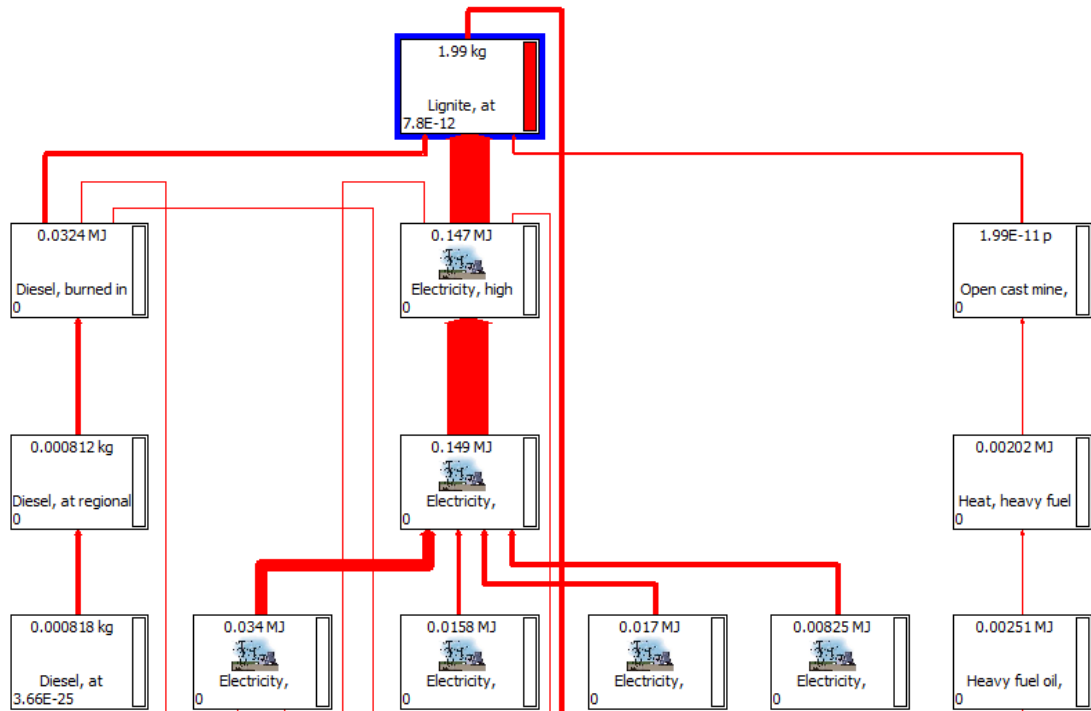


Figure 26 : Schematic representation of mining for 1.99 kg lignite, by SimaPro program

### 3.1.2 Lignite transportation

For the purposes of this study, it was assumed that lignite is transported to the mine by rail with a capacity of  $2.315E-5$  ton, which is necessary for the generation of 1kWh of electricity. The distance between the mine and the power plant was assumed equal to 16.5 km. Based on these assumptions, the transportation demands for lignite from the mine to the power plant were calculated equal to 0.000382 tkm. The input data used for transportation of 1 tkm and the final emissions in the environment are shown at the Table 11 and Table 12. The data were obtained from the Eco-invent database by SimaPro software program. The module from the program calls the modules ‘operation of vehicle’; ‘production, maintenance and disposal of vehicles’; ‘construction and maintenance and disposal of railway tracks’.

Inventory refers to the entire transport life cycle. For rail infrastructure, expenditures and environmental interventions due to construction, renewal and disposal of roads have been allocated based on the Gross tone kilometer performance. Expenditures due to operation of the rail infrastructure, as well as land use have been allocated based on the yearly train kilometer performance.

Data refers to average transport conditions in Europe (EU 15: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Luxembourg, Netherlands, Portugal, Spain, Sweden and the UK). The data for rail infrastructure reflect Swiss conditions. Data for vehicle manufacturing and maintenance represents generic European data. Data for the vehicle disposal reflect Swiss situation.

For vehicle operation all technologies are included in the average data. Rail construction addresses conventional gravel track beddings. For the manufacturing of vehicles, the data reflects a current modern locomotive.

Figure 27 shows a schematic representation of lignite transportation, necessary for the generation of 1 kWh of electricity, provided by SimaPro program.

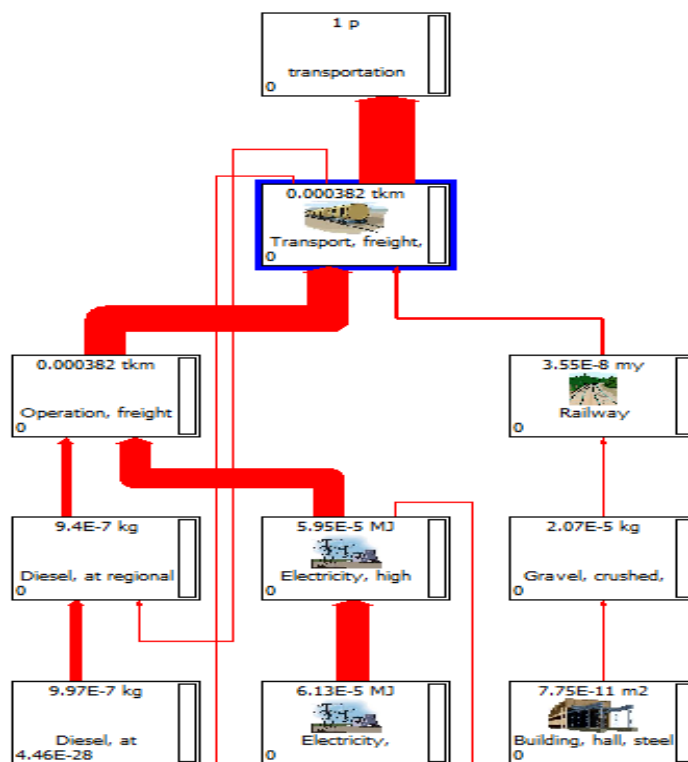


Figure 27 : Schematic representation of the construction and operation of transportation, by SimaPro program

For the transportation of 1tkm of lignite, the input data of the raw material used and the generated output emissions to air, water and soil, are shown at Table11 and Table 12 as calculated by SimaPro program.

Table 11 : Inputs from nature (resources) and technosphere (materials/fuels) need, for 1tkm of lignite transportation

Input raw material/fuels	
Coal, brown, in ground	8,32 g
Coal, hard, in ground	6,38 g
Energy	39 kJ
Natural gas, in ground	2,60 l
Gravel, in ground	66,05 g
Oil, crude, in ground	4,28 g
Water, turbine use	222 l

Table 12 : Emissions to air, water and soil for 1tkm of lignite transportation

Emissions to air	
Carbon dioxide, fossil	37,54 g
Carbon monoxide, fossil	110,27 mg
Dinitrogen monoxide	1,01 mg
Heat, waste	680,61 kJ
Methane, fossil	56,85 mg
Nitrogen oxides	188,57 mg
Noble gases, radioactive	6,26 kBq
Particulates, < 2.5 um	12,67 mg
Particulates, > 10 um	42,05 mg
Particulates, >2.5um,and < 10um	16,08 mg
Radon-222	12,09 kBq
Sulfur dioxide	97,69 mg
Hydrogen chloride	1,66 mg
Hydrogen-3, Tritium	3,69 Bq

Emissions to water	
Heat, waste	33,05 kJ
Hydrogen-3, Tritium	279,47 Bq
Radium-226	1,07 Bq
Sulfate	1,85 g
Chloride	258,17 mg
Aluminium	42,72 mg

Emissions to soil	
Chloride	2,19 mg
Heat, waste	263,29 J
Iron	60,79 mg
Oils	18,67 mg

### 3.1.3 Electricity generation from lignite fired power plant

The module in SimaPro software program uses the average net efficiency of Greek lignite power plants (35.2%). The module describes the electricity production of an average plant for the country. The plant is used for middle load with 6,000 hours of operation at full capacity per year. The plant is assumed to operate 200,000 hours during its lifetime.

The reference power plant is a typical lignite-fired power plant in Greece with a typical capacity of 300 MWe, located in Northern Greece [63]. As already mentioned, the fossil fuel which is mostly used for power generation in Greece is lignite. Lignite is a fuel with low heating value, about 5-6.3 MJ/kg. The raw lignite analysis is shown in Table 13 and is in accordance with European Benchmark Task Force (EBTF) definitions [73].

Table 13 : Raw lignite analysis

C	H	S	O	N	H <sub>2</sub> O	Ash	LHV
(w/w %)	(w/w %)	(w/w %)	(w/w %)	(w/w %)	(w/w%)	(w/w%)	(kJ/kg)
22.58	2.07	0.94	9.88	0.37	36.8	27.36	7831

Due to the fact that lignite is a high moisture fuel, a drying system is considered. The pre-drying system comprises a bubbling fluidized bed dryer at which the fluidized agent is part of the moisture removed from the lignite which is then mixed with the recirculating steam [74]. The necessary heat for the drying process is provided by the other part of the moisture which is condensed in an internal heat exchanger. For the compression of the fluidized steam and the compression of the stream which is fed to the heat exchanger, two blowers are needed. The installation of the drying system contributes to increase of the power plant's efficiency.

A subcritical Sulzer-type boiler is installed in the plant. The combustion technology used for the generation of electricity is the "Pulverized Coal Combustion" (PPC) technology. PPC is a mature technology and can be applied to many kinds of coal, like lignite. The efficiencies of the steam cycle and the boiler are those which mostly determine the efficiency of a PPC power plant. The reference power plant has an average efficien-

cy of 35.2%. The sub-critical power plants usually operate at conditions with steam pressures below 220 bar and temperatures below 540°C [75]. The thermal power plants usually are constructed near the mining area of the fossil fuel. The thermal plants with high power generation consist of many power production units. Each unit has its own boiler, circulation piping system, electric pumps, generator, turbine and chimney, which may be shared with another unit.

The steam cycle consists of, firstly the boiler, which produces high pressure steam at 171.4 bar and 540°C. The boiler has an efficiency of 87%.

The produced steam from the boiler is being superheated and then is expanded at the high pressure (HP) steam turbine. After being reheated, it enters the intermediate pressure steam turbine (IP) then the low pressure (LP) steam turbine and finally goes to the condenser.

At the end of the turbine, which turns with 3000 rounds per second, a generator is mounted which transforms kinetic energy to electric energy. The generator through a transformer raises the voltage from 21 kV to 400 kV and then the high voltage goes to the national high voltage grid.

The extracted steam from the steam turbines goes to electrically driven feedwater pumps. The water coolant flow is cooled by a wet natural draught cooling tower so as the heat at the condenser to be dissipated. The pressure of the condenser is 0.05 bar and the inlet temperature of the cooling water is around 35°C. From the condenser the condensed steam goes through the circulator to the preheaters so as to raise the water temperature from 35°C to 250°C. There are also preheaters at the end of the boiler.

Based on the above, for the generation of 1 kWh of electricity, with an average efficiency of the power plant at 35.2%, around 1.99 kg of lignite with 5.44 MJ/kg heating value and 2.5 lit of cooling water are needed. The technical characteristics of the plant are presented in Table 14.

Table 14 : Main characteristics of the reference power plant

Power output	MW <sub>el</sub>	300
Electrical efficiency	%	35.2
Coal consumption	kg/kWh	1.99
Specific CO <sub>2</sub> emissions	kgCO <sub>2</sub> /kWh <sub>el</sub>	1.28



For the generation of 1kWh of electricity from lignite combustion, the necessary inputs of the raw material used and the generated emissions to air, water and soil are shown in Table 15 while Table 16 shows the generated emissions to air, water and soil. The data was derived from the Eco-invent database by SimaPro program.

Table 15 : Inputs from nature (resources) and technosphere (materials/fuels) for the generation of 1kWh of electricity, by lignite combustion

Lignite, at mine	1.99 kg
Water, cooling, unspecified natural origin/m <sup>3</sup>	0.035 m <sup>3</sup>
Chlorine, liquid, production mix, at plant	0.0001 kg
Water, completely softened, at plant	0.062 kg
Water, decarbonized, at plant	1.54 kg
SOx retained, in lignite flue gas de-sulphurization	0.002 kg
Transport, freight, rail	0.00038 tkm



Figure 28 shows a schematic representation of electricity production of 1 kWh with 35.2% efficiency by SimaPro program.

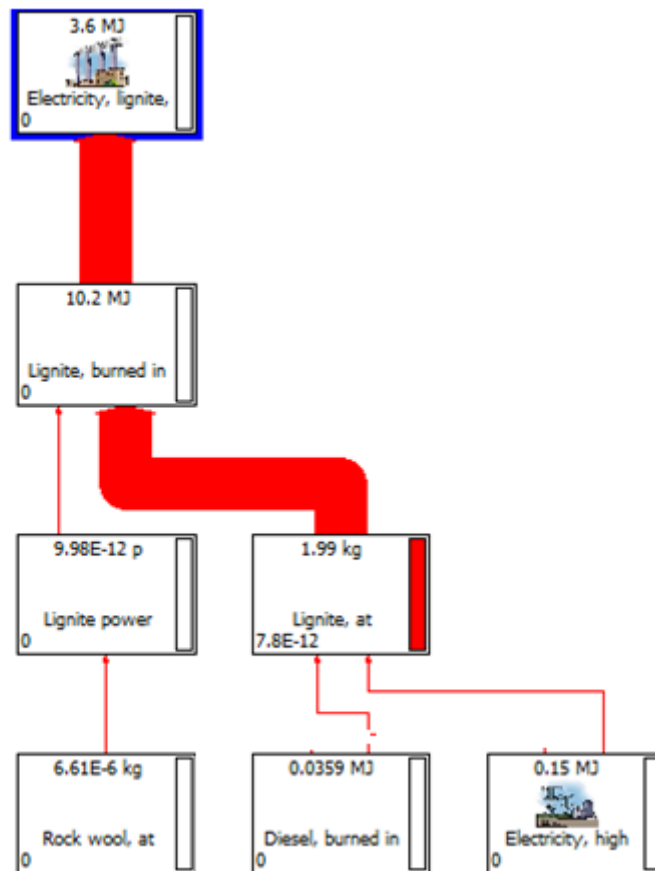


Figure 28 : Schematic representation of electricity generation of 1 kWh, with 35.2% efficiency

Since the life stages up to the CO<sub>2</sub> capture step are common for all three scenarios, only the CO<sub>2</sub> capture technology will be discussed for each CO<sub>2</sub> capture case in the following paragraphs.

### 3.2 Case 2: Power plant with CO<sub>2</sub> capture by monoethanolamine (MEA)

The technology which is commercially available for the post-combustion capture of CO<sub>2</sub> is amine scrubbing, using an amine based liquid solvent, usually monoethanola-

mine (MEA) [29]. At the absorption process the aqueous alkaline solvent of amine reacts reversibly with an acid or sour gas. The amine scrubbing process flow diagram is presented in Figure 29.

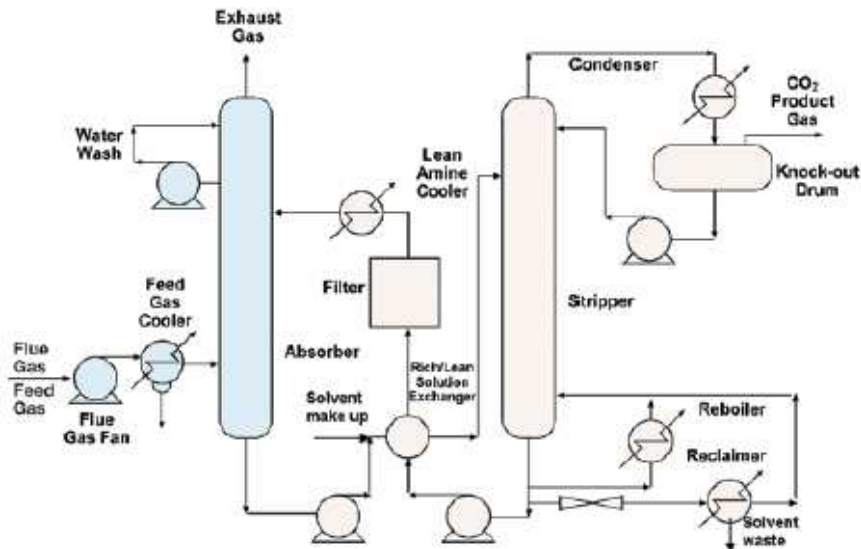


Figure 29 : Flow diagram of amine scrubbing process [76]

The flue gas from the lignite power plant enters the absorption column, called absorber, where it is cooled to a temperature of 40-60°C. From the top of the absorber a mixture comprised of water and MEA solution, usually 15-30% or 40%, enters the absorber. The mixture is brought into contact with the flue gas and from the reaction of MEA with CO<sub>2</sub> a carbonate salt is formed. A blower increases the pressure drop to 1.124 bar. The flue gas, clean of CO<sub>2</sub>, exits the absorber from the top while the carbonate salt leaves the absorber from the bottom and is then pumped to the top of a stripper (regeneration vessel). In the stripper, the rich-CO<sub>2</sub> sorbent is heated at temperatures of 100-140°C in order to strip off the CO<sub>2</sub>. The generated amine is then transferred to the reboiler where is heated so as to be transferred back to the stripper. This extra heat requirement for the maintenance of the regeneration conditions leads to a thermal energy penalty of 4 MJ/kg CO<sub>2</sub>. The CO<sub>2</sub> stream before being compressed and transported to a storage site, it is cooled for any solvent droplets or solvent vapor. In addition to thermal energy, electrical energy is also required for the operation of the liquid pumps, used for pumping the amine solution and for the operation of the flue gas blowers used for the pressure drop [74].

Finally, extra energy is used by the cooling pumps and a multistage compression unit for the CO<sub>2</sub> compression at the necessary pressure of 110 bar as well as for its cooling at

the temperature of 20°C for the final transportation and storage. For a better understanding of such installations, Figure 30 shows the embodiment of the post-combustion capture system by MEA in a power plant.

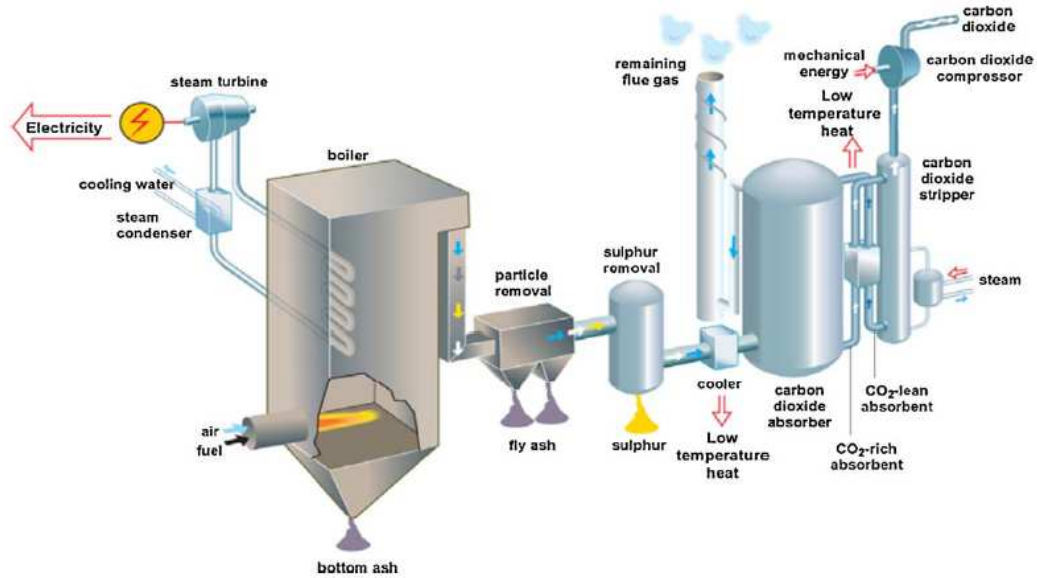


Figure 30 : Schematic of a post-combustion CO<sub>2</sub> capture system in a power plant [77]

The input data and the generated emissions from amine scrubbing post-combustion CO<sub>2</sub> capture process are shown in the Table 17. The data were obtained from Koornneef J. et al, 2008 [58]. The data were adjusted for the capture of 1 kg CO<sub>2</sub> emission by lignite combustion, at a Greek lignite-fired subcritical power plant.

Table 17 : Inputs from nature (resources) and technosphere (materials/fuels) for capturing 1 kg CO<sub>2</sub> by the amine scrubbing process

Monoethanolamine	3.28 gr
Sodium hydroxide (concentrated)	0.6 gr
Ammonia	3.4 gr
Limestone	12.1 gr
Electricity, medium voltage	0.136 MJ
Heat	6.4 MJ
CO <sub>2</sub> emission from electricity production flue gases	1 kg

The output emissions in air, water and soil for the capture of 1 kg CO<sub>2</sub>, are shown at Table 18. The data were calculated for all the resources, the raw materials and fuels which were used by MEA capture unit by SimaPro software program.

Table 18 : Emissions to air, water and soil for capturing 1 kg CO<sub>2</sub> by the amine scrubbing process

Emissions to air		Emissions to water	
Carbon-14	1.31 Bq	Aluminium	5.61 g
Carbon dioxide	8.22 g	Calcium, ion	77.28 g
Carbon dioxide, fossil	355.97 g	Chloride	12.71 g
Carbon monoxide, fossil	1.09 g	Heat, waste	1.5 MJ
Heat, waste	15.24 MJ	Hydrogen-3	568.5 Bq
Hydrogen-3, Tritium	7.58 Bq	Iron, ion	10.07 g
Methane, fossil	2.68 g	Magnesium	36.54 g
Nitrogen oxides	3.14 g	Manganese	2.74 g
Noble gases, radioactive,	12.765 k Bq	Nitrate	3.64 g
Particulates, < 2.5 um	0.91 g	Phosphate	12.13 g
Particulates, > 10 um	1.55 g	Potassium, ion	20.40 g
Polonium-210	1.12 Bq	Radioactive species, Nuclides	1.28 Bq
Radon-220	1.98 Bq	Radium-226	2.11 Bq
Radon-222	23.86 kBq	Silicon	56.14 g
Sulfur dioxide	9.21 g	Sodium, ion	35.28 g
Xenon-133	1.46 Bq	Solids, inorganic	5.64 g
		Strontium	1.25 g
		Strontium-90	1.84 Bq
		Sulfate	304.07 g
		Emissions to soil	
		Calcium	1.72 mg
		Carbon	1.02 mg
		Chloride	2.36 mg
		Heat, waste	2.04 kJ
		Iron	8.72 mg
		Oils	41.64 mg

Figure 31 shows a schematic representation of the input data in MEA capture unit by SimaPro program for the CO<sub>2</sub> capture from 1 kWh of electricity.

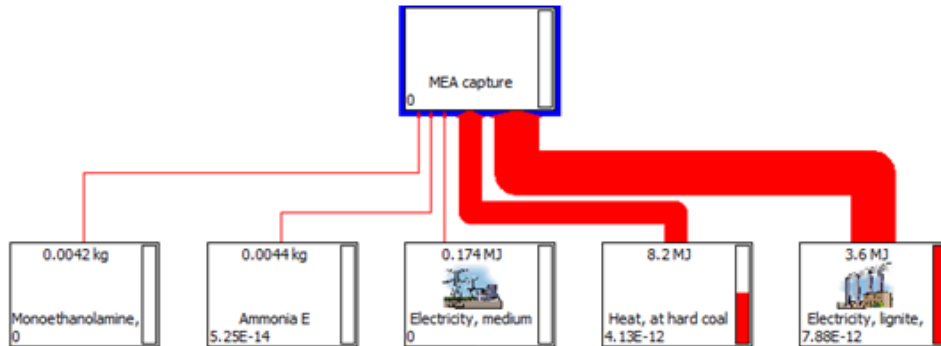


Figure 31 : Schematic representation of MEA capture unit by SimaPro program

### 3.3 Case 3: Power plant with CO<sub>2</sub> capture by Carbonate looping (CaL)

An alternative technology for post-combustion CO<sub>2</sub> capture is the process called “Calcium Looping”. Calcium looping is a promising technology for CO<sub>2</sub> capture from power plants and it was firstly proposed by Heesink and Temmink, in 1994 [38]. Its difference to conventional amine scrubbing is that it utilizes a solid sorbent material like CaO in a system comprised of two fluidized bed reactors. The separation of CO<sub>2</sub> from the flue gas stream is performed through a reversible reaction, the exothermic reaction of CaO and CO<sub>2</sub> in the carbonator to form calcium carbonate and the endothermic reaction of CaCO<sub>3</sub> in the calciner, so as to regenerate the sorbent as Figure 32 presents and it was initially proposed by Shimizu et al. [59].

The flue gas stream that exits the boiler of the power plant is transferred to the carbonator. There, at temperature around 650°C the CO<sub>2</sub> from the flue gas is absorbed by CaO and from the exothermic reaction, CaCO<sub>3</sub> is formed. The solids exiting the carbonator are sent to the calciner, where through the endothermic reaction at around 900°C, CaCO<sub>3</sub> produced by the carbonation reaction, is decomposed back to CaO while at the same time, a CO<sub>2</sub> stream is released.

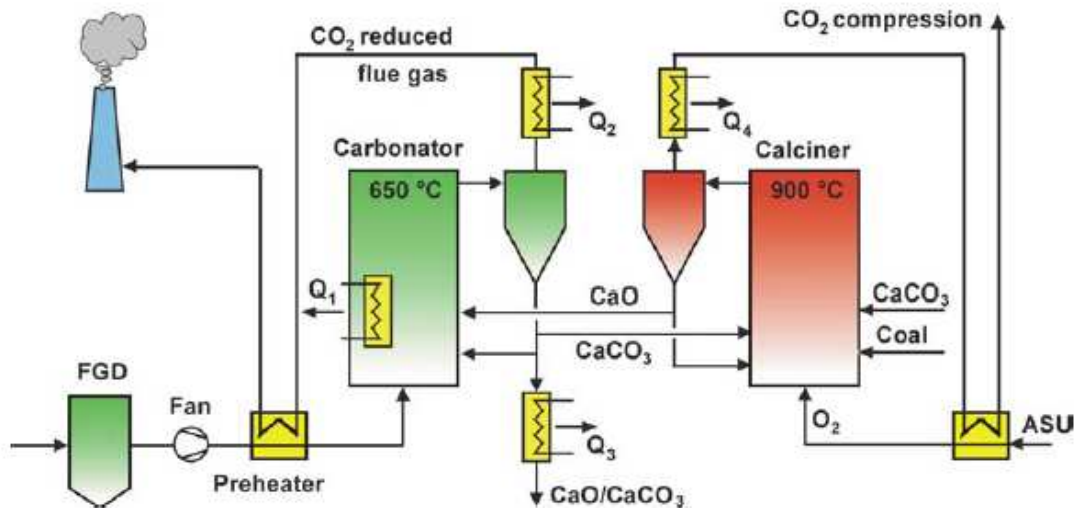


Figure 32 : Capture cycle general layout [40]

The  $\text{CO}_2$  stream is then led for possible compression and for final storage, while  $\text{CaO}$  is recycled back to the carbonator for a continuous operation of the cycle. The extra heat requirement for the calcination is obtained by the combustion of the extra fuel fired with oxygen-rich stream in order to produce a  $\text{CO}_2$  stream with high purity. Nevertheless, the gas streams exiting the two reactors generate additional heat which can be utilized by the power plant for power generation. After a number of carbonation and calcination cycles the concentration of  $\text{CaO}$  in the calciner is getting lower and this affects the  $\text{CO}_2$  absorptivity. To make up this  $\text{CaO}$  loss, fresh  $\text{CaCO}_3$  is supplied in the calciner. In addition, even though the coal burned has low sulfur content, as there is a desulfurization unit at the power plant, still a small amount of  $\text{SO}_2$  reacts with the  $\text{CaO}$  and forms  $\text{CaSO}_4$  (gypsum) contributing to this extra demand of  $\text{CaCO}_3$ .

However, despite the fact that there is an energy loss due to the oxygen supply in the calciner, the overall energy penalty using the ‘Calcium Looping’ process is less than using the alternative post-combustion technology of  $\text{CO}_2$  capture by ‘amine scrubbing’. According to I. Vorrias et al. [63] for a supercritical power plant with net power output of 304.15 MWel and net efficiency of 39.05%, the energy penalty for the ‘Calcium Looping’ process is 4.95% while for the process using ‘amine scrubbing’ is 7.8%.



### 3.3.1 Air Separation Unit (ASU)

The Air Separation Unit (ASU), as Figure 33 shows, is where a large amount of pure oxygen is produced with the cryogenic method. In this unit the stream of air is separated into two streams, the one which is pure in oxygen and the one which is pure in nitrogen. This separation occurred due to the different dew point of oxygen and nitrogen in conditions with high pressure. The general process starts with the entrance of the air stream into the inter-cooled compressor so as to be compressed after passing its four stages. Then, in order for the moisture to be removed, the air is cooled to 12°C and this can be obtained at the two-staged Direct Contact Air Cooler (DCAC). For further cooling at 9°C, the air enters in the evaporative coolers. There, the air is cooled down due to the presence of a nitrogen stream.

Moreover, the air stream passes through the molecular siever absorbers so as to be cleaned from water or impurities, before entering the main heat exchanger. Afterwards, the separation of air is performed, firstly by being cooled to dew point and then by entering in two distillation columns, which have different operating pressures. The 34% of the separation is occurred in the column with the high pressure conditions. The final separation of O<sub>2</sub> concludes, when the streams after exiting the high pressure column (HP) and passing through the throttle valves, enter in the low pressure column (LP).

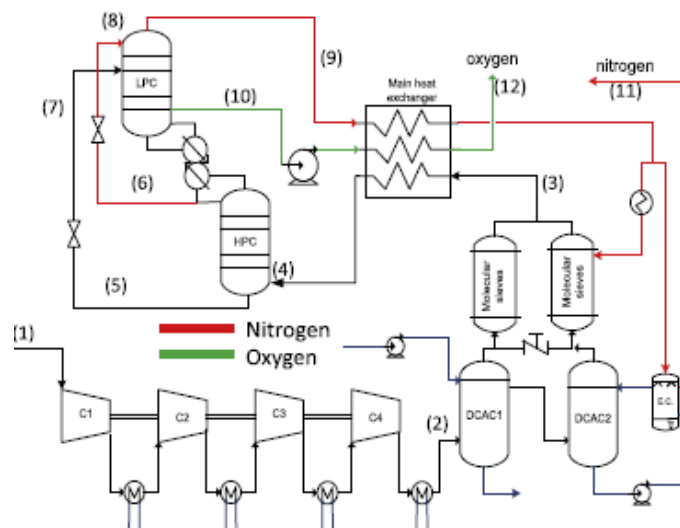


Figure 33 : Typical flow diagram of the Air Separation Unit (ASU) [63]

There is no use of any external heat or cooling because for the condensation in the high pressure column the necessary cooling load is obtained from the generated heat from the evaporation in the re-boiler in the low pressure column. For the overall process to be concluded, the streams after exiting the low pressure column are then heated in the main heat exchanger to a temperature of 15°C as the air comes from the molecular sieves. Table 19 presents the process parameters according to EBTF in order to be produced 95% pure oxygen stream [73]. Finally, the temperatures of the streams from the reboiler and the condenser are the one which specify the pressures in the two columns, the LP and HP column.

Table 19 : Process parameters of the ASU modeling

HPC and LPC pressure	5.50/1.92 bar
Oxygen pressure outlet	1.35 bar
Air compressor isentropic efficiency	86.5 %
O <sub>2</sub> recovery efficiency	99.1 %
N <sub>2</sub> recovery efficiency	99.7 %
Oxygen purity	95.0 % v/v
Nitrogen purity	99.6 % v/v
Specific O <sub>2</sub> production	222.36 kWh/ tnO <sub>2</sub>

### 3.3.2 Heat Exchanger

Chemical absorption systems are characterized by the fact that the absorption reactor has lower temperature than the higher temperature of the generation reactor. For the elimination of the energy penalty between the main two streams, a heat exchanger is added. In carbonate looping, there is a major temperature difference between the carbonator and the calciner and by exchanging the heat between the solid streams, with the use of a heat exchanger, has an advantageous impact on the total efficiency [62]. A unit of a heat exchanger as Figure 34 shows could be the one of two concentric L-valves.

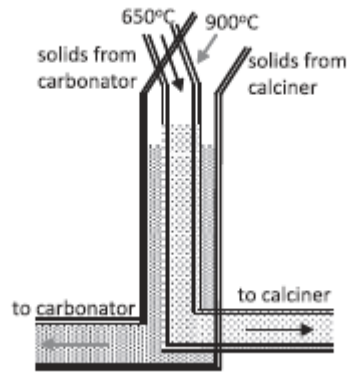


Figure 34 : Concentric L-valves for heat exchange [63]

The L-valves of the two fluidized bed reactors are placed concentrically and act as heat exchanger while the two solid streams pass through them, having as a result the same output temperature. The heat exchange increases when the vertical parts of the L-valves are fixed beds, while the dimension of the unit is reduced. Even though there are many uncertainties about the coupled operation, still the concentric L-valves operation conduces to a heat exchange between the solid streams to a great extent.

### 3.3.3 Secondary steam cycle - Heat utilization

Calcium looping capture process, is a process which operates in high temperatures and generates a great amount of heat energy. This heat energy, with a superheated steam at 650°C, can be recovered in order to generate additional power in a secondary steam cycle, increasing in that way the electrical power production of the power plant. The produced electrical power can be utilized in driving the CO<sub>2</sub> compression unit and especially the air separation unit, which consumes a high amount of energy. In that case, the energy penalty, caused by the capture process can be reduced while the overall efficiency of the power plant is increased [62], [63], [78].

The secondary steam cycle as Figure 35 shows, includes high , medium and low pressure turbines, heat recovery, steam generator, economizer, superheater, reheater, high and low pressure feedwater reheaters and deaerator.

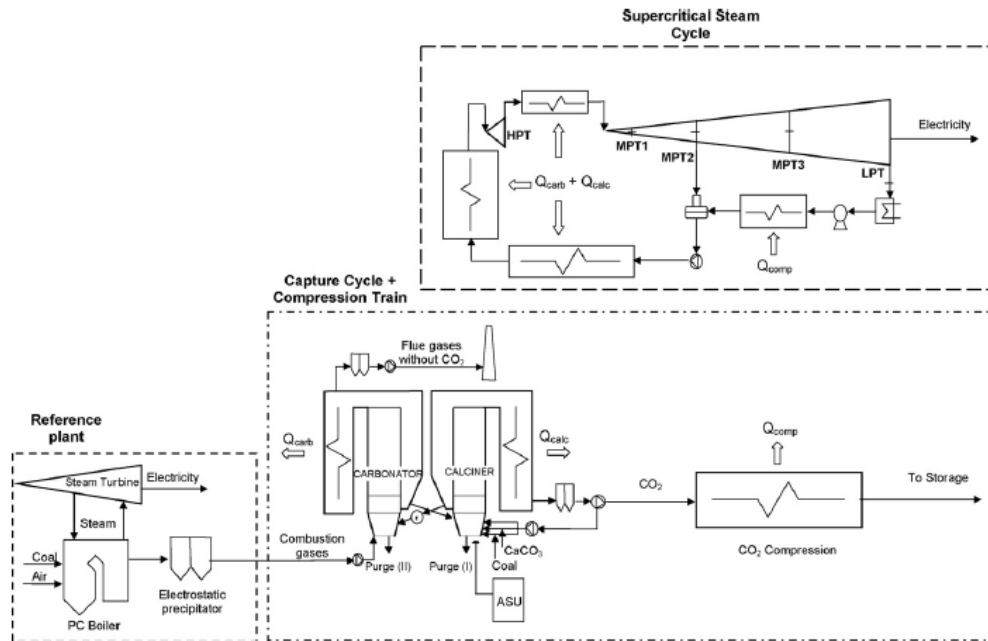


Figure 35 : Integration of heat from calcium looping to a steam cycle [62]

The energy sources for possible integration are:

- The recovered heat from calciner, as the concentrated  $\text{CO}_2$  stream exits the calciner with a temperature of  $900^\circ\text{C}$ , which first it can be cooled down to  $150^\circ\text{C}$  and then can be splitted.
- The recovery heat from carbonator's flue gases, produced by the reaction of  $\text{CO}_2$  with  $\text{CaO}$  at  $650^\circ\text{C}$ .
- The flue gas stream with low  $\text{CO}_2$  emissions that exits the carbonator at  $650^\circ\text{C}$ , which can be cooled down to  $100\text{-}120^\circ\text{C}$  before being stacked.
- The  $\text{CO}_2$  stream which is going to be purified and then compressed, before its condensation can be cooled down to  $80^\circ\text{C}$ .
- The heated solid purge at  $900^\circ\text{C}$ , leaving the calciner, before being disposed or sent to a cement plant, can be cooled down while the recovered heat can be utilized.

In addition, the cooling water leaving the heat exchangers can be used for district heating, as it has high mass flow rate and a temperature of  $88^\circ\text{C}$ . This utilization can increase further the efficiency of the power plant.

Finally, an efficiency increase can be obtained, when the recovered heat from the purge stream cooling is used for preheating the oxygen and the  $\text{CO}_2$  stream in the fluidized calciner.

### 3.3.4. Advantages

In general, calcium looping technology offers potential benefits which make it an alternative capture process with good operating characteristics, such as [79], [50], [80], [81] [82] [83]:

- i. Lower energy penalties for CO<sub>2</sub> capture. The energy penalties for calcium looping are 6-8% points while the energy penalties of amine scrubbing post-combustion process are 10-12% points [28].
- ii. With the intergration of calcium looping with chemical looping, which is still in research condition, the high energy requirement for the CO<sub>2</sub> capture it is possible to be reduced. At this process composite CaO/CuO-based materials are used, with the CuO having the role of oxygen carrier providing the necessary amount of oxygen for the regeneration of the sorbent in CaL. In that way the ASU consumes less power and the overall energy penalty of post-combustion CO<sub>2</sub> capture is reduced further more.
- iii. Providing an additional steam cycle. The energy penalty caused by the air separation can be reduced by the utilization of heat from the hot sorbent material and the hot CO<sub>2</sub> stream to generate additional steam.
- iv. In calcium looping, the technical scale-up risks are reduced due to the use of mature large-scale equipment, like the circulating fluidized bed (CFB) boiler.
- v. The use of natural limestone as a sorbent in calcium looping, is a low cost raw material. Despite the fact that after multiple cycles of CO<sub>2</sub> capture the sorbent is losing its capacity and high amount of fresh limestone needs to be supplement, so as the CO<sub>2</sub> capture efficiency to be kept to a proper level, due to its low price is not a drawback for the integration of calcium looping to power industry.
- vi. Provides the possibility of collaboration for power and cement industry, as both are heavy-emitting industries, when the exhausted sorbent of CaO (lime), after having used by power industry is used by cement industry as feedstock.
- vii. The high energy consumption of Air Separation Unit (ASU) in oxy-combustion, is reduced in calcium looping combustion, as the consumed power is reduced to 1/3.

### 3.3.5 Inventory data for “Carbonate looping”

For the Calcium Looping (CaL) process, the inventory input and output data were obtained by Vorrias I. et al, 2013 [63]. Table 20 presents the main characteristics for the calcium looping process.

Table 20 : The input data of the main characteristics for the CaL process

IN	
CO <sub>2</sub> from the main boiler	49.83 kg/s
Electricity for air separation	0.78 MJ/kgCO <sub>2</sub> capt.
Heat for combustion	3.65 MJ/kgCO <sub>2</sub> capt.
Fresh limestone	17.7 kg/s

Table 21 shows the input CO<sub>2</sub> emissions in kgCO<sub>2</sub>/s from the different sources which entering the carbon capture system and the CO<sub>2</sub> emissions in kgCO<sub>2</sub>/s which are captured, as well as the emitted CO<sub>2</sub> emissions in kgCO<sub>2</sub>/s.

Table 21 : CO<sub>2</sub> balance at the carbon capture system

IN (kg CO <sub>2</sub> /s)		OUT (kg CO <sub>2</sub> /s)	
From the main boiler flue gases	49.83	Captured	80.48
From lignite combustion at the calciner	30.87	Emitted	5.20
From make-up limestone degradation	4.98		
Total	85.68		

The input data with the amount of the make-up limestone ( $\text{CaCO}_3$ ), the electricity and the heat used, for capturing 1 kg  $\text{CO}_2$  by calcium looping  $\text{CO}_2$  capture process are shown in Table 22.

Table 22 : Inputs from nature (resources) and technosphere (materials/fuels) for capturing 1 kg  $\text{CO}_2$  via carbonate looping

Limestone, milled ,loose, at pant	0.25 kg
Electricity, medium voltage for auxiliaries	0.89 MJ
Heat	4.2 MJ
$\text{CO}_2$ emission from electricity production flue gases	1 kg

Figure 36, displays a schematic representation of the input data in CaL capture unit, by SimaPro program, for capturing the  $\text{CO}_2$  emissions by generating 1 kWh of electricity.

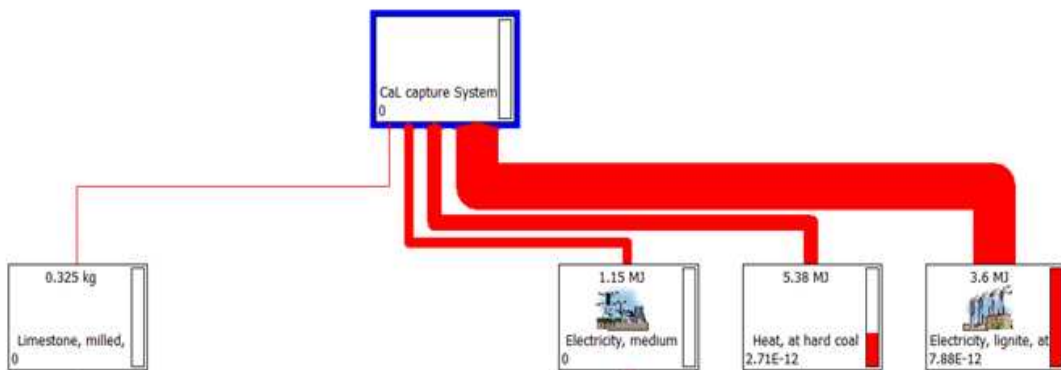


Figure 36 : Schematic representation of CaL capture unit, by SimaPro

The output emissions in air, water and soil, for capturing 1 kg  $\text{CO}_2$ , are calculated for all the resources, the raw materials and fuels entering the capture unit, by SimaPro software program as Table 23 shows.

Table 23 : Emissions to air, water and soil for capturing 1 kg CO<sub>2</sub> by carbonate looping process

Emissions to air		Emissions to water	
Carbon-14	1.17 Bq	Aluminium	6.12 g
Carbon dioxide, fossil	328.05 g	Calcium, ion	87.45 g
Carbon monoxide, fossil	0.85 g	Chloride	12.65 g
Heat, waste	13.36 MJ	Heat, waste	1.78 MJ
Hydrogen-3	6.57 Bq	Hydrogen-3, Tritium	496 Bq
Methane, fossil	1.95 g	Iron, ion	11.41 g
Nitrogen oxides	2.7 g	Magnesium	41.1 g
Noble gases, radioactive	11.13 kBq	Manganese	3.08 g
Particulates, < 2.5 um	0.97 g	Nitrate	4.07 g
Particulates, > 10 um	1.43 g	Phosphate	13.65 g
Polonium-210	0.96 Bq	Potassium, ion	22.78 g
Radon-220	2.28 Bq	Radioactive species, Nuclides.	1.12 Bq
Radon-222	21.25 kBq	Radium-226	1.92 Bq
Sulfur dioxide	8.71 g	Silicon	62.78 g
Xenon-133	1.89 Bq	Sodium, ion	39.64 g
		Solids, inorganic	6.53 g
		Strontium	1.39 g
		Strontium-90	1.53 Bq
		Sulfate	343.04 g
		Emissions to soil	
		Calcium	2.47 mg
		Carbon	1.64 mg
		Chloride	2.67 mg
		Heat, waste	6.83 kJ
		Iron	8.04 mg
		Oils	6.28 mg
		Sodium	1.02 mg



# 4. Life Cycle Impact Assessment (LCIA)

At this chapter, the performance of the three following scenarios is analyzed: Case 1 'Electricity production' without having any capture technology, Case 2, 'Electricity production with MEA' which is 'Electricity production' case, with CO<sub>2</sub> capture technology with MEA and Case 3, 'Electricity production with Calcium looping' which is 'Electricity production' case, with CO<sub>2</sub> capture technology with Calcium looping.

At first, the efficiency and the CO<sub>2</sub> capture rate for the three cases are going to be presented. Afterwards, the environmental impact categories of this LCA, are going to be analyzed with tables and figures, showing the processes and the raw materials which participate in the operation of the three cases, for electricity production of 1 kWh, with or without capture technology, as well as with tables and figures, which present the pollutant substances which are responsible for the increase of each environmental impact category. For each of the ten different environmental impact categories, one table with one figure are presented, in order to illustrate the processes or the raw materials which contribute the most and calculate the value of characterization factor of each impact category. One table with one figure, are also presented, with the pollutants which are emitted from the processes for each case and are responsible for the increase of the value of characterization factor, of the corresponding environmental impact category.

## 4.1 Efficiency

Case 1, 'Electricity production', is a subcritical lignite-fired power plant with an average efficiency of 35.2%. Case 2, 'Electricity production with MEA', has an efficiency of 19.38% (energy penalty of 15.8%) and Case 3, 'Electricity production with Calcium looping', has an efficiency of 21.5% with an energy penalty of 13.7% as Table 24 presents. The requirement of high amount of heat for the two CO<sub>2</sub> capture systems makes them to be energy-intensive processes and is responsible for the high energy penalty. In addition, the fact that the power plant of Case 1, is a subcritical and not a supercritical power plant, also contribute to the high energy penalty score as the two capture process-

es have better performance at supercritical power plants. Moreover, the energy penalty for a lignite-fired power plant with capture technology is higher compared to a coal-fired power plant, also with capture technology, due to the fact that lignite has lower calorific value and higher moisture than coal [84]. As we can see Case 2, ‘Electricity production with MEA’, has higher energy penalty than Case 3, ‘Electricity production with Calcium looping’. The fact that the efficiency of Case 3 is higher than Case 2, apart from its better CO<sub>2</sub> capture performance, is also because ‘Electricity production with Calcium looping utilizes the 40% of the heat generated by the capture process to a secondary steam cycle and produces extra electricity.

Table 24 : Efficiencies for the three investigated scenarios

	<b>Electricity production (Case 1)</b>	<b>Electricity production with MEA (Case 2)</b>	<b>Electricity production with Calcium looping (Case 3)</b>
<b>Efficiency</b>	35.2%	19.38%	21.5%

## 4.2 CO<sub>2</sub> capture rate

The CO<sub>2</sub> emissions for Case1, ‘Electricity production’ are 1.28 kg CO<sub>2</sub> per kWh while the CO<sub>2</sub> emissions for Case 2, ‘Electricity production with MEA’, are 0.39kg CO<sub>2</sub> per kWh electricity generation with MEA process and is thus capable of capturing 90.73% of the generated CO<sub>2</sub> emissions from lignite combustion. The total CO<sub>2</sub> emissions for ‘Electricity production with MEA’, containing the CO<sub>2</sub> emissions from all processes, from lignite mining to electricity generation, as well as the CO<sub>2</sub> equiv. emissions from the other substances which are also emitted during the operational phase of the power plant, like methane, nitrous monoxide and carbon monoxide are 0.55 kg CO<sub>2</sub> equiv. emissions. The overall amount of CO<sub>2</sub> avoided in ‘Electricity production with MEA’, is calculated to be 87.1%. For Case 3, ‘Electricity production with Calcium looping’ together with 40% utilization of heat from this process, the generated CO<sub>2</sub> equiv. emis-

sions from lignite combustion are 0.095 kg CO<sub>2</sub> per kWh electricity generation, with carbonate looping technology being capable of capturing 97.3% of the generated CO<sub>2</sub> equiv. emissions. However, the total CO<sub>2</sub> equiv. emissions for ‘Electricity production with Calcium looping’, containing the CO<sub>2</sub> equiv. emissions from all processes, from lignite mining to electricity generation, and the other substances which are also emitted during the operational phase of the power plant, like methane, nitrous monoxide and carbon monoxide are 0.49 kg CO<sub>2</sub> emissions. So, the overall amount of CO<sub>2</sub> avoided in ‘Electricity production with Calcium looping’ is calculated to be 86.5%.

Table 25 presents the CO<sub>2</sub> capture rates for the two capture processes, with ‘Electricity production with Calcium looping’ process having the higher score for capturing the generated CO<sub>2</sub> equiv. emissions from lignite combustion, while the score of the avoided CO<sub>2</sub> equiv. emissions from overall power plant being almost the same for the two capture processes. The LCA for electricity production with the two capture processes suggest almost equivalent lifecycle performance. However, for ‘Electricity production with Calcium looping’ by improving the operating conditions, such as, the maximum power output, the maximum efficiency and the minimum fresh sorbent input, will contribute to a revenue increase, whereas for ‘Electricity production with MEA’, the only possibility for the increase the power output and the efficiency of the system, would be to use more power from the power plant performing the capture process, which have as a result the reduction of capture efficiency and simultaneous increase of the life cycle emissions.

Table 25 : CO<sub>2</sub> capture rates for the 2 Cases with CO<sub>2</sub> capture technology

	<b>Electricity production with MEA (Case 2)</b>	<b>Electricity production with Calcium looping (Case 3)</b>
<b>% CO<sub>2</sub> captured from lignite combustion</b>	90.73%	97.3%
<b>% CO<sub>2</sub> captured from overall power plant</b>	87.1%	86.5%

### 4.3 Global warming potential (GWP 100)

As we can see from the results for the impact category of global warming, there is a great reduction of CO<sub>2</sub> equiv. in the two cases with the post-combustion CO<sub>2</sub> capture technology compared to 'Electricity production' with no CO<sub>2</sub> capture technology. The emissions produced by the lignite combustion at the power plant for electricity generation, cover the major percent of the direct CO<sub>2</sub> emissions. Table 26, presents the overall processes and raw materials, which participate in the operation of the three Cases, from 'cradle to grave' and produce the higher amounts of CO<sub>2</sub> equiv. emissions, when comparing 'Electricity production' and 'Electricity production with Calcium looping', with Electricity production with MEA. For all cases the main source of CO<sub>2</sub> equiv. emissions is the lignite supply chain and especially the lignite combustion. The generated emissions by the mining and transport chain as well as by the MEA and limestone production chain are lower in relation to lignite chain and lignite combustion.

As we can see at Table 26, for 'Electricity production' case, the generated emissions only by lignite combustion process, for electricity generation, are 1.26 kg CO<sub>2</sub> equiv. For the two cases with the capture technology, the amount of kg CO<sub>2</sub> equiv. generated by lignite combustion, are referred to the extra electricity used, by lignite combustion, for the operation of the capture processes. The emitted kg CO<sub>2</sub> equiv., after the flue gases have passed through the capture units, are also shown for each of the two capture technologies, which are 0.39 kg CO<sub>2</sub> equiv. for 'Electricity production with MEA' and 0.095 kg CO<sub>2</sub> equiv. for 'Electricity production with Calcium looping'. For that reason by increasing the CO<sub>2</sub> separation rates at the power plant, we can achieve a further reduction of CO<sub>2</sub> emissions in the atmosphere.

If we want to calculate the amount of kg CO<sub>2</sub> avoided from lignite combustion, we have to subtract the direct emissions from the power plant with the capture unit from the power plant without the capture unit and calculate the avoidance efficiency. As we have already calculated above, the avoidance efficiency of Case 2, 'Electricity production with MEA' process is 90.73% and for Case 3, 'Electricity production with Calcium looping', is 97.3%.

However for both cases with capture technology, we assumed that there is no leakage of CO<sub>2</sub> from the reservoir. Whether there is a CO<sub>2</sub> leakage, the avoidance efficiency would be reduced. Still, in that case the CO<sub>2</sub> emissions in the atmosphere would occur with a low rate and in a long-term time horizon. As a result, the CO<sub>2</sub> concentration in the at-

mosphere would be performed in slower rates, giving to the animals and plants the opportunity to be adjusted, so the overall damage would be less. Moreover, even though in absolute levels may create the same environmental damage by delaying the CO<sub>2</sub> emissions in the atmosphere, they are also offering some economic benefits. First of all, by postponing the climate change, for a positive discount rate when CO<sub>2</sub> is sequestered, the net present value of damage costs is reduced. Additionally, the net present value of damage costs is also reduced in case that the discount rate increases faster than the abatement cost. Also, by postponing the climate change, it offers the necessary time for the development of new mitigation process for the CO<sub>2</sub> emissions.

Table 26 : Global warming potential pollutant processes per kWh electricity, for the whole power plant

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Sodium hydroxide	kg CO <sub>2</sub> eq	0.00E+00	1.11E-03	0.00E+00
Natural gas, burned in power plant	kg CO <sub>2</sub> eq	1.99E-04	4.06E-03	2.66E-02
CO <sub>2</sub> emissions after MEA capture unit	kg CO <sub>2</sub> eq	0.00E+00	3.94E-01	0.00E+00
Lignite combustion	kg CO <sub>2</sub> eq	1.26E+00	5.12E-02	2.60E-01
CO <sub>2</sub> emissions after CaL capture unit	kg CO <sub>2</sub> eq	0.00E+00	0.00E+00	9.50E-02
Heat, lignite, extra for capture process	kg CO <sub>2</sub> eq	0.00E+00	7.14E-02	4.69E-02
Ethylene	kg CO <sub>2</sub> eq	7.65E-07	3.49E-03	2.21E-06
Ammonia	kg CO <sub>2</sub> eq	3.05E-05	1.65E-02	6.42E-05
Heavy fuel oil, burned in power plant	kg CO <sub>2</sub> eq	1.00E-04	5.47E-03	3.60E-02
Remaining processes	kg CO <sub>2</sub> eq	3.75E-02	7.99E-03	2.40E-02

For the three cases, the values of the total kg CO<sub>2</sub> equiv. produced by the emitting processes are shown at Figure 37. As we can see, ‘Electricity production’ without capture unit generates the higher amount of kg CO<sub>2</sub> equiv. in the atmosphere, followed by ‘Electricity production with MEA’ and finally ‘Electricity production with Calcium looping’, generates the lower amount of kg CO<sub>2</sub> equiv.

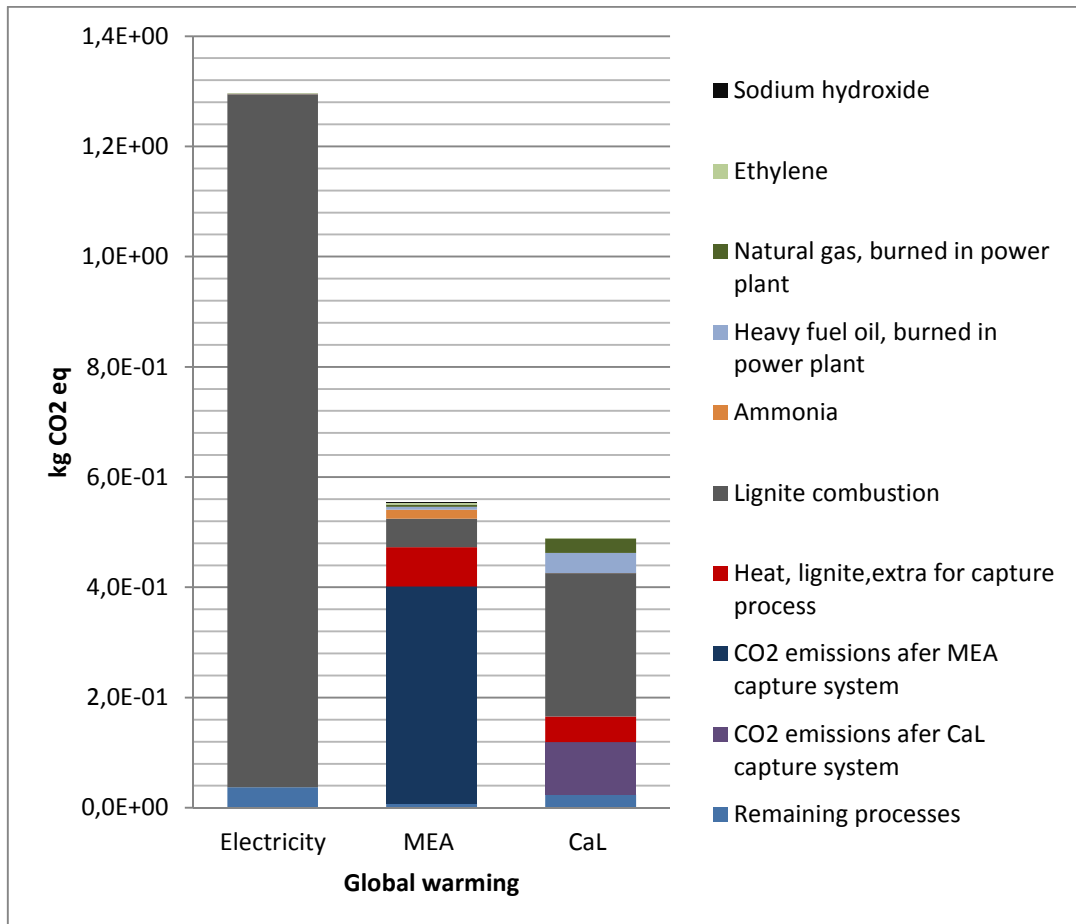


Figure 37 : Global warming potential pollutant processes per kWh electricity, for the whole power plant

In Table 27 and Figure 38, we can see that besides carbon dioxide, there are also other substances like methane, carbon monoxide and dinitrogen monoxide, with global warming potential, which also produce some kg CO<sub>2</sub> equiv. emissions during the operation of the power plant. For the two capture processes, the score for the substance of methane is higher due to the fact that for the operation of these capture processes extra electricity is required and this means extra lignite mining, which is responsible for methane emis-

sions. Other contributors to the increase of methane are also the MEA production chain and the disposal chain of reclaimer bottoms.

Table 27 : Global Warming Potential impact category inventory characterization per kWh electricity, for the whole power plant

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Carbon dioxide, fossil	kg CO <sub>2</sub> eq	1.28E+00	4.56E-01	4.20E-01
Methane, fossil	kg CO <sub>2</sub> eq	1.17E-02	8.01E-02	5.94E-02
Dinitrogen monoxide	kg CO <sub>2</sub> eq	1.74E-03	5.97E-03	6.63E-03
Carbon monoxide, fossil	kg CO <sub>2</sub> eq	3.81E-04	2.21E-03	1.72E-03
Total	kg CO <sub>2</sub> eq	1.30E+00	5.44E-01	4.88E-01

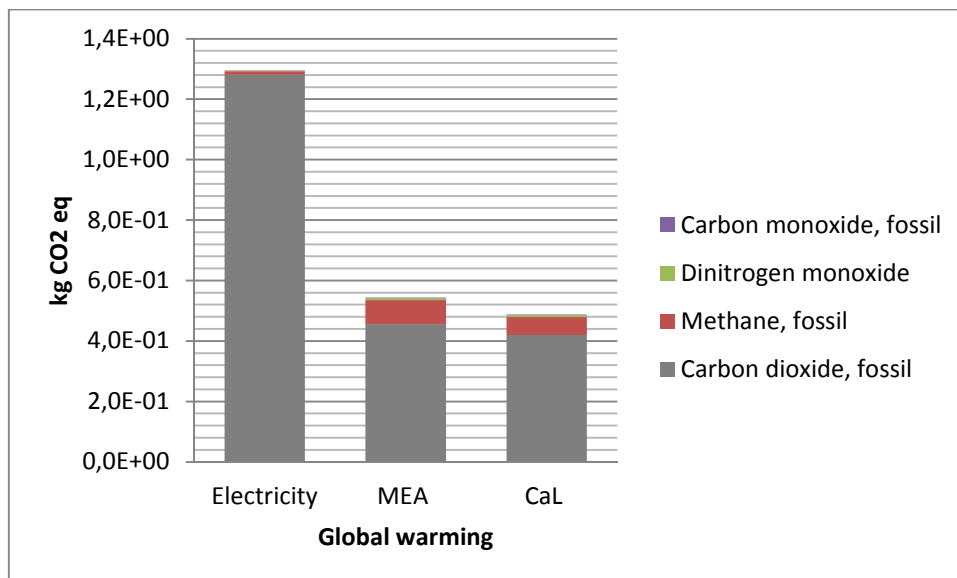


Figure 38 : Global warming potential impact category inventory characterization per kWh electricity, for the whole power plant

For the following environmental impact categories, at the tables and figures corresponding to the participating processes or raw materials for the three Cases, the process ‘heat, lignite, extra for capture system’ is referring to the extra heat used by Case 2 and Case 3, which utilize the capture technology, while the process ‘electricity production’ is Case 1 with its whole life cycle for electricity production of 1 kWh, by lignite combustion, which is also utilized in Case 2 and Case 3.

## 4.4 Abiotic depletion

The extraction of fossil resources is expressed via the abiotic depletion category. At Table 28, derived from SimaPro software program, we can see all the processes and the raw materials which contribute to the increase of abiotic depletion impact category. Especially, there is an increase of this category for the two capture processes due to the fact that, for the operation of the capture units more materials are required. The use of extra amount of raw materials like, lignite, natural gas and limestone for the generation of the specific amount of electricity or heat used for the operation of the capture units, have as a result the production of more fly ash, bottom ash and solid wastes which also result to the overall increase of this impact category.

As we can see at Table 28, the high amount of electricity and heat used by ‘Electricity production with MEA’ capture system and the use of high amount of electricity, heat and lignite by ‘Electricity production with Calcium looping’, are responsible for the high value of abiotic depletion for both capture technologies.

Table 28 : Abiotic depletion pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Crude oil	kg Sb eq	3.38E-05	5.97E-05	2.53E-04
Natural Gas	kg Sb eq	3.10E-05	7.48E-05	2.35E-04
Lignite, at mine	kg Sb eq	1.33E-02	4.02E-04	2.62E-03
Heat, lignite, extra for capture process	kg Sb eq	0.00E+00	7.06E-03	4.63E-03
Electricity production	kg Sb eq	0.00E+00	1.35E-02	1.35E-02
Remaining processes	kg Sb eq	7.66E-05	2.04E-04	9.05E-05



Figure 39, shows the overall value of the abiotic depletion impact category for the three cases. For ‘Electricity production’ case, the value of abiotic depletion is lower than the value of ‘Electricity production with MEA’ and ‘Electricity production with Calcium looping’.

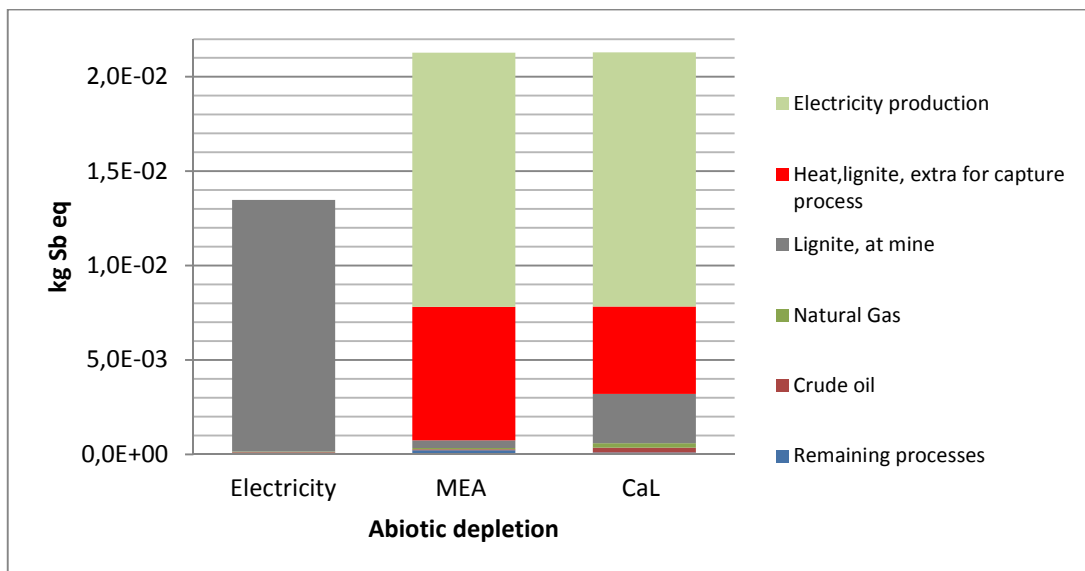


Figure 39 : Abiotic depletion impact category process contribution per kWh electricity

Table 29 and Figure 40 present the substances which contribute to the increase of abiotic depletion impact category. The increase of natural resources use, like natural gas, crude oil and especially lignite, for the two capture processes, which are necessary for the proper operation and construction of those capture units are responsible for the increase of abiotic depletion category.

Table 29 : Abiotic depletion impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Lignite	kg Sb eq	1.34E-02	2.06E-02	2.04E-02
Natural gas	kg Sb eq	4.04E-05	4.11E-04	4.42E-04
Oil, crude	kg Sb eq	3.53E-05	2.87E-04	3.92E-04
Remaining substances	kg Sb eq	5.10E-08	1.04E-05	1.70E-07
Total	kg Sb eq	1.35E-02	2.13E-02	2.12E-02

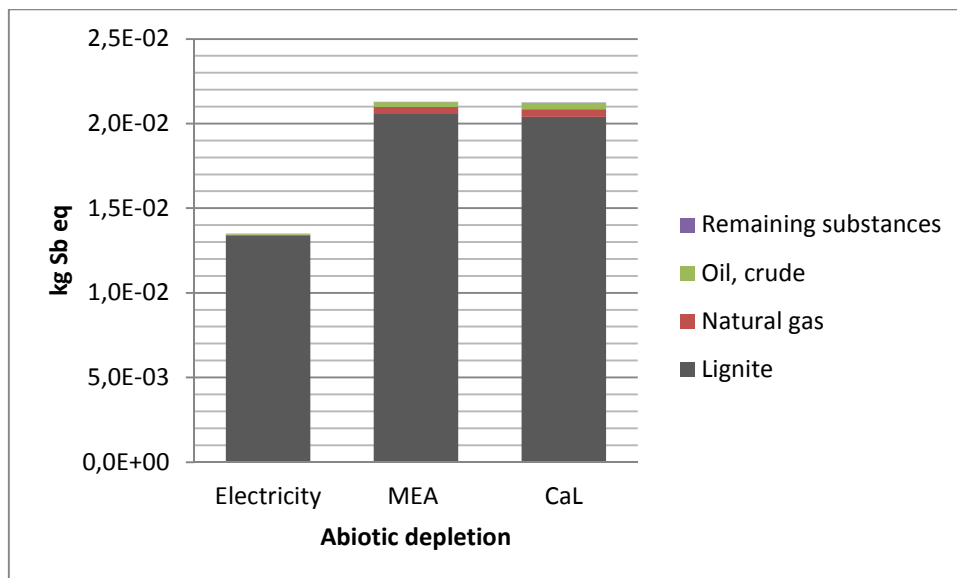


Figure 40 : Abiotic depletion impact category inventory characterization per kWh electricity

## 4.5 Acidification

The values of acid gases like SO<sub>x</sub>, NO<sub>x</sub>, HCl and HF are increasing mainly due to the extra need of lignite, for the two capture units. Moreover, the power plant emits more NO<sub>x</sub> per kWh due to the efficiency penalty, as Figure 41 and Table 30 show.

For 'Electricity production with MEA', the values of the impact category of acidification are higher not only by the high use of heat and electricity but also by the fact that the amount of NH<sub>3</sub> emissions get higher, from the degradation of MEA, the fuel supply

chain and from the production process of MEA. However, it is possible to get a further reduction of the NH<sub>3</sub> emissions, by installing a water wash section at the top of the absorber of the ‘Electricity production with MEA’ unit.

At ‘Electricity production with Calcium looping’ the high value of consumption of electricity for the air separation unit, as well as the extra use of heat, for the operation of the process, are responsible for the high value of acidification impact category.

Table 30 presents with more details the processes or the raw materials which contribute to the increase of the value of acidification impact category for the three cases, showing the higher value for ‘Electricity production with MEA’, due to the higher consumption of heat and electricity.

Table 30 : Acidification impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Electricity production	kg SO <sub>2</sub> eq	0.00E+00	7.97E-03	7.97E-03
Heat, lignite, extra for capture process	kg SO <sub>2</sub> eq	0.00E+00	7.87E-03	5.16E-03
Heavy fuel oil, burned in power plant	kg SO <sub>2</sub> eq	9.37E-07	5.10E-05	3.36E-04
Lignite, burned in power plant	kg SO <sub>2</sub> eq	7.84E-03	2.33E-04	1.54E-03
Natural gas	kg SO <sub>2</sub> eq	4.38E-06	7.86E-06	3.29E-05
Remaining processes	kg SO <sub>2</sub> eq	1.25E-04	8.70E-05	1.13E-04

Figure 41 shows the acidification values for the three cases, showing that ‘Electricity production with MEA’ has the higher value.

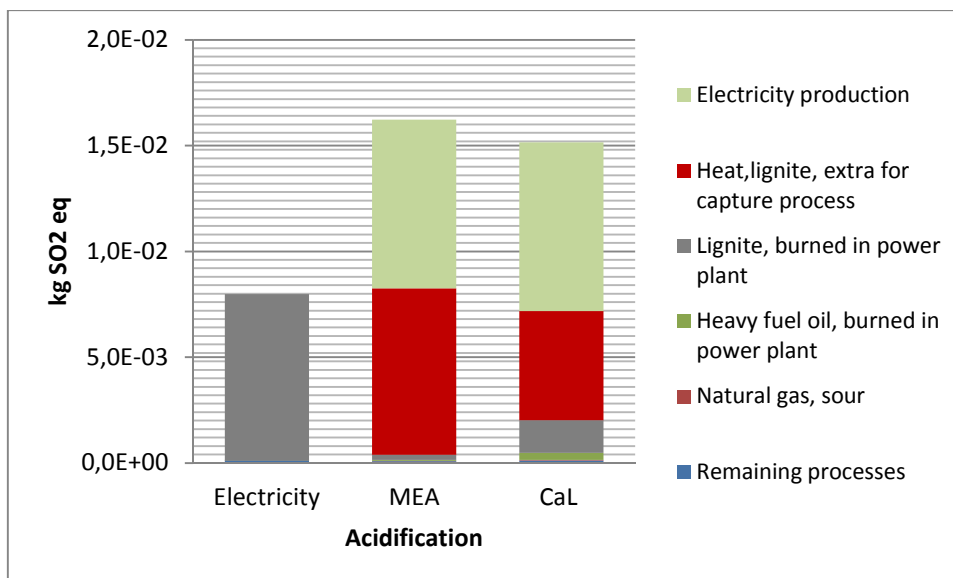


Figure 41 : Acidification impact category pollutant processes per kWh electricity

As Table 31 and Figure 42 presents the production of sulfur dioxide and nitrogen oxides emissions from the extra use of electricity and heat at the two capture systems, influence the values of acidification. In addition due to the energy penalty, more fuel will be needed, increasing in that way the amount of nitrogen oxides produced.

Table 31 : Acidification impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Sulfur dioxide	kg SO <sub>2</sub> eq	7.26E-03	1.42E-02	1.34E-02
Nitrogen oxides	kg SO <sub>2</sub> eq	7.17E-04	2.01E-03	1.73E-03
Ammonia	kg SO <sub>2</sub> eq	8.44E-07	4.50E-05	2.56E-05
Total	kg SO <sub>2</sub> eq	7.97E-03	1.62E-02	1.52E-02

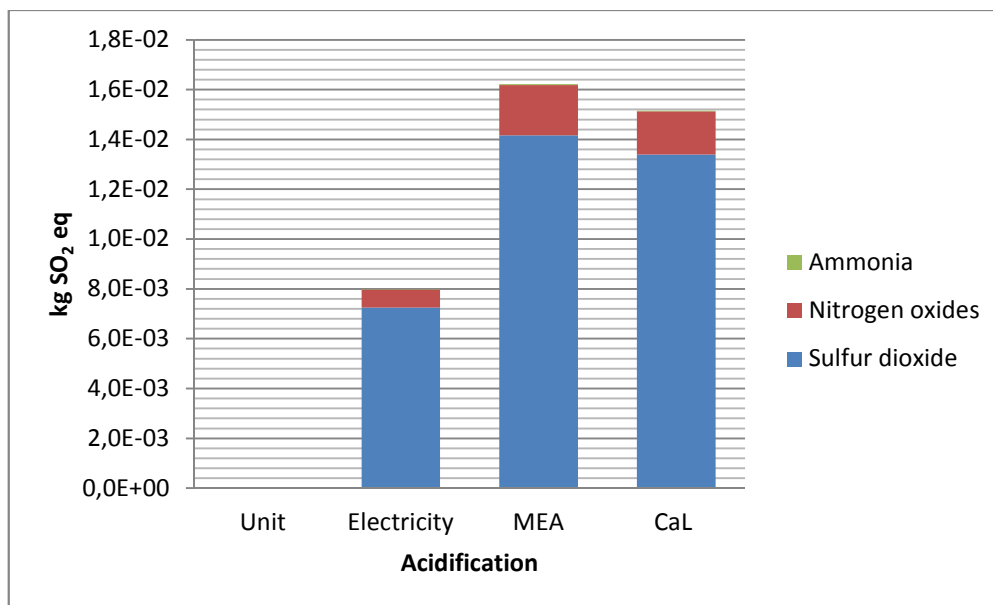


Figure 42 : Acidification impact category inventory characterization per kWh electricity

## 4.6 Eutrophication

Likewise to the acidification impact category, the NH<sub>3</sub> emissions are responsible for the higher values of eutrophication impact category for the cases with capture units, compared to those of Case1, 'Electricity production'. Again, for 'Electricity production with MEA', the extra NH<sub>3</sub> emissions are caused by MEA production and its degradation as well as by the reduction of the net efficiency of the power plant, having as a result the extra usage of fossil fuel. This increase of eutrophication is caused firstly by the higher NH<sub>3</sub> emissions from MEA production and its degradation and secondly by the NO<sub>x</sub> emissions generated from the operation of the power plant. For 'Electricity production with Calcium looping', as Figure 43 shows, the higher values of eutrophication is mainly due to the higher electricity consumption used at capture process and the disposal of lignite from mining subsystem.

Table 32 presents the three cases, showing the origin of eutrophication values for each process, while Figure 43 shows the total values for eutrophication impact category, with the value of 'Electricity production with Calcium looping' being the higher one of the three cases.

Table 32 : Eutrophication impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Disposal, spoil from lignite mining	kg PO <sub>4</sub> <sup>---</sup> eq	1.4E-02	4.3E-04	2.8E-03
Electricity production	kg PO <sub>4</sub> <sup>---</sup> eq	0.0E+00	1.5E-02	1.5E-02
Heat, lignite, extra for capture process	kg PO <sub>4</sub> <sup>---</sup> eq	0.0E+00	1.5E-03	9.6E-04
Lignite, burned in power plant	kg PO <sub>4</sub> <sup>---</sup> eq	1.8E-04	5.2E-06	3.5E-05
Remaining processes	kg PO <sub>4</sub> <sup>---</sup> eq	9.1E-05	2.7E-05	4.5E-05

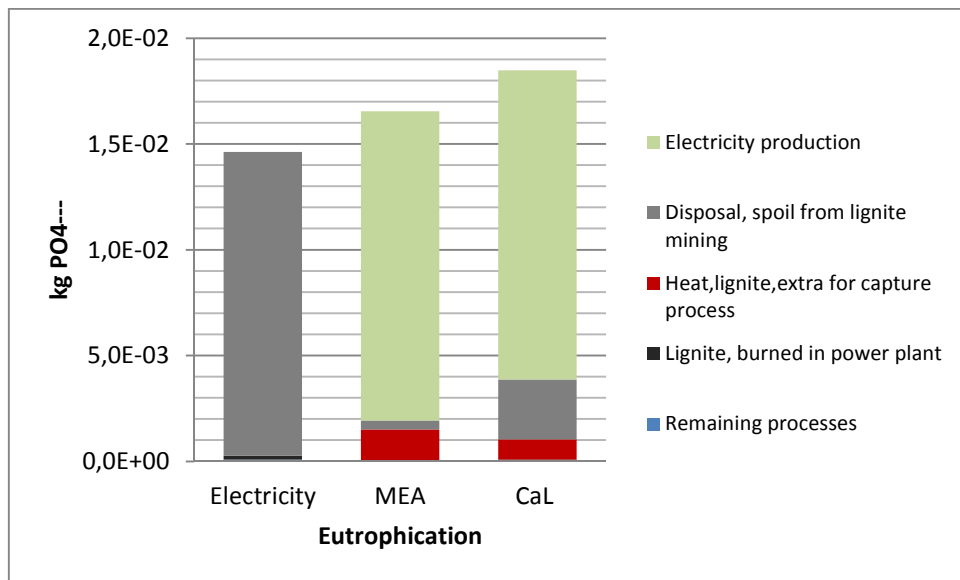


Figure 43 : Eutrophication impact category pollutant processes per kWh electricity

The production of high amount of phosphate emissions from the above processes and the used raw materials is the major contributor for eutrophication impact category. As we can see at Table 33 and Figure 44 nitrogen oxides and nitrate are also responsible for the increase of this impact category.

Table 33 : Eutrophication impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Phosphate	kg PO <sub>4</sub> --- eq	1.40E-02	1.55E-02	1.75E-02
Nitrogen oxides	kg PO <sub>4</sub> --- eq	1.86E-04	5.23E-04	4.51E-04
Nitrate	kg PO <sub>4</sub> --- eq	4.18E-04	4.66E-04	5.21E-04
Total	kg PO <sub>4</sub> --- eq	1.46E-02	1.65E-02	1.85E-02

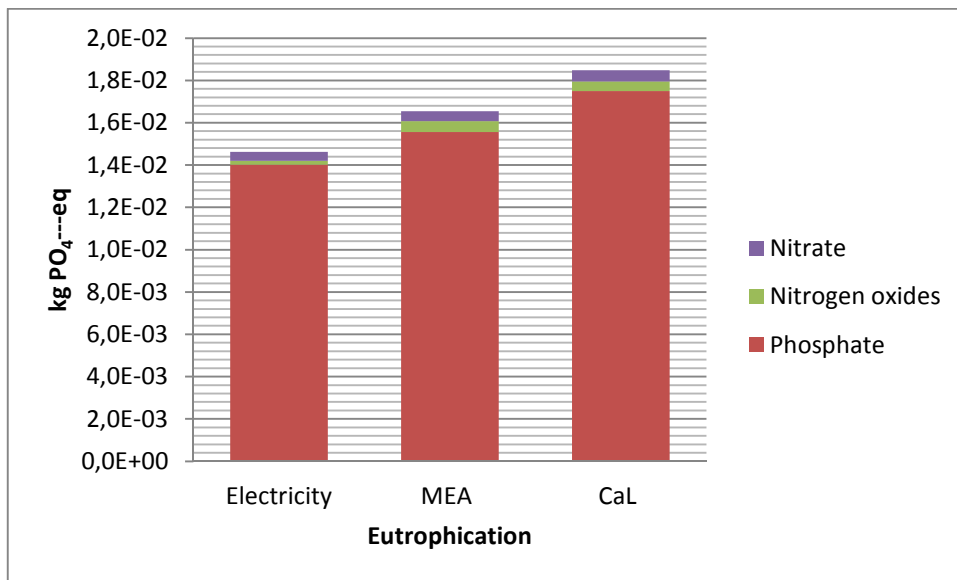


Figure 44 : Eutrophication impact category inventory characterization per kWh electricity

## 4.7 Ozone layer depletion

The impact category of ozone depletion shows the potential destruction of ozone in stratosphere zone by chemicals which contain chlorine or bromine, trifluorobromomethane and halocarbon. The main processes which cause ozone depletion are those associated with the production of crude oil, the lignite supply chain and the fuel trans-

portation. The additional processes for the construction and operation of the two capture systems increase the amount of lignite and fuels, having as a result a further production of harmful emissions. For 'Electricity production with Calcium looping' as Figure 45 shows, the major process contributor for the high values of ozone layer depletion category is the use of crude oil.

Table 34 and Figure 45 show analytically the sources of the emissions for this impact category, which the major percent is from fossil fuels used for the generation of heat and electricity, while other processes which generate emissions are the transportation and the use of the raw materials of chlorine and crude oil, with crude oil having the highest share.

Table 34 : Ozone layer depletion impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Chlorine	kg CFC-11 eq	2.86E-10	1.36E-11	6.75E-11
Crude oil	kg CFC-11 eq	7.30E-10	1.27E-09	5.46E-09
Electricity production	kg CFC-11 eq	0.00E+00	1.75E-09	1.75E-09
Heat, lignite, extra for capture process	kg CFC-11 eq	0.00E+00	4.34E-09	2.85E-09
Transport, natural gas	kg CFC-11 eq	5.28E-10	1.28E-09	4.02E-09
Remaining processes	kg CFC-11 eq	1.43E-11	4.82E-11	6.10E-11



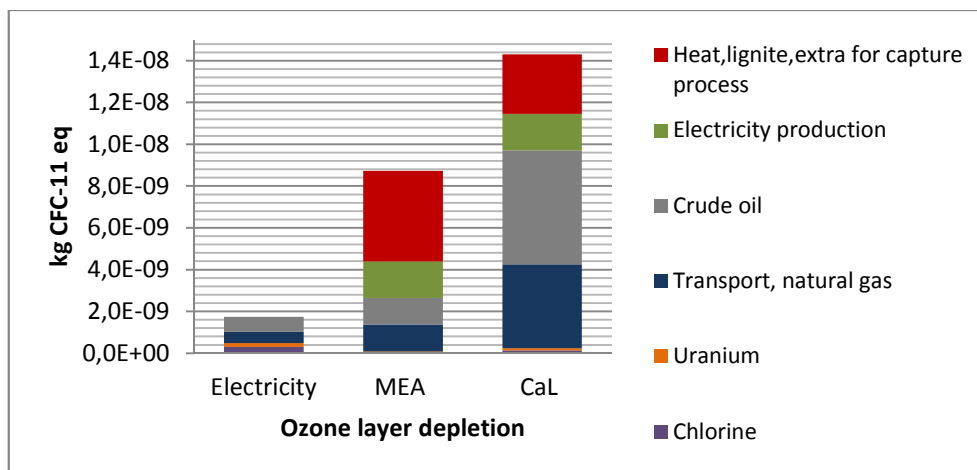


Figure 45 : Ozone layer depletion impact category pollutant processes per kWh electricity

For ‘Electricity production with Calcium looping’ as Figure 46 and Table 35 show, the major contributors for the high values of ozone layer depletion category are methane, ethane and halon emissions which result for ‘Electricity production with Calcium looping’ Case, to have the highest value of the three.

Table 35 : Ozone layer depletion impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Methane, bromotrifluoro-, Halon 1301	kg CFC-11 eq	7.32E-10	5.00E-09	8.16E-09
Methane, bromochlorodifluoro-, Halon 1211	kg CFC-11 eq	5.22E-10	2.74E-09	5.12E-09
Ethane, 1,2-dichloro-1,1,2,2-tetrafluoro-, CFC-114	kg CFC-11 eq	1.90E-10	5.80E-10	5.29E-10
Methane, tetrachloro-, CFC-10	kg CFC-11 eq	2.87E-10	3.19E-10	3.67E-10
Methane, chlorodifluoro-, HCFC-22	kg CFC-11 eq	1.70E-11	7.81E-11	1.29E-10
Total	kg CFC-11 eq	1.75E-09	8.73E-09	1.43E-08

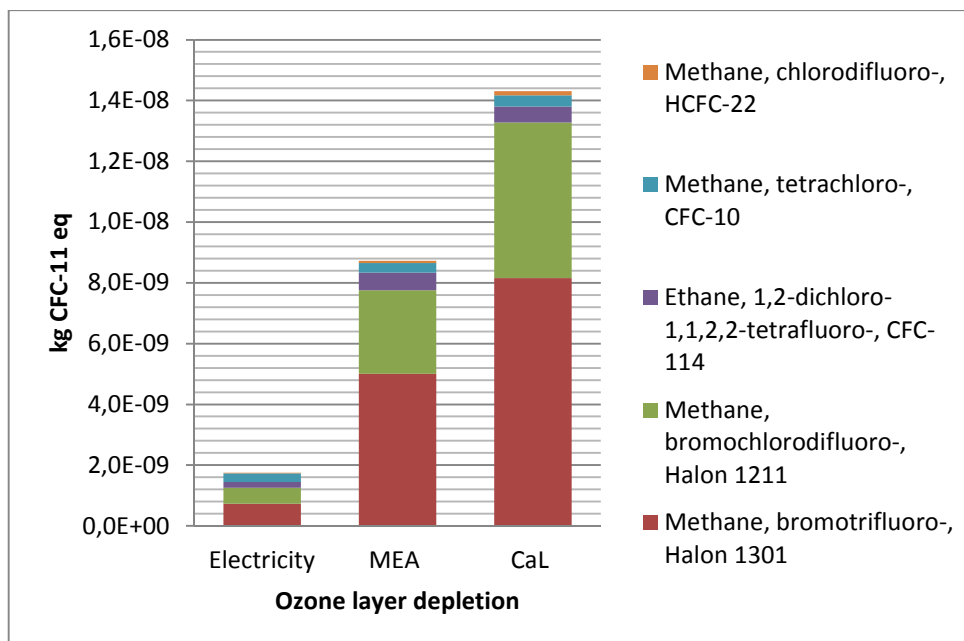


Figure 46 : Ozone layer depl. impact category inventory characterization per kWh electricity

## 4.8 Human toxicity

The high level of HF in the atmosphere causes the increase of the human toxicity potential category. The material production for the further infrastructure which emits heavy metals in the atmosphere is the main contributor for the increase of human toxicity. In the case of ‘Electricity production with MEA’ the emission of ethylene oxide in the air during MEA consumption and in the water during MEA production are also the main causes for human toxicity. In ‘Electricity production with Calcium looping’, the main source of human toxicity is the extra energy and the higher electricity usage for the capture system along with the lignite disposal from lignite combustion chain. Figure 47 shows the major emissions for ‘Electricity production with Calcium looping’, such as Selenium, Molybdenum, Nickel, Barium and Cadmium.

However, the capture process can reduce the fly ash contained in the flue gases by passing through the flue gas desulphurization (FGD) unit and this result to lower the emissions at the power plant level. Nevertheless, in this LCI data it is not taken into account the removal efficiency of SO<sub>x</sub> and NO<sub>x</sub> from the capture systems. Also, some studies like IEA GHG (2006) [76] and Chapel et al. (1999) [85] use lower values for the MEA consumption and this may alter the total score of the human toxicity impact category.

The processes which contribute the most to the generation of human toxically emissions as Table 36 shows, are the disposal of spoil from lignite mining and lignite ash, as well as the electricity and heat generation. The two capture processes have higher values due to the extra lignite consumption.

Table 36 : Human toxicity impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Copper	kg 1,4-DB eq	1.53E-03	8.56E-04	2.07E-03
Natural gas	kg 1,4-DB eq	1.64E-05	3.34E-04	2.19E-03
Well for exploration	kg 1,4-DB eq	3.06E-04	6.77E-04	2.49E-03
Lignite, burned in power plant	kg 1,4-DB eq	9.31E-02	2.76E-03	1.82E-02
Heavy fuel oil, burned in power plant	kg 1,4-DB eq	6.49E-05	3.53E-03	2.33E-02
Disposal, lignite ash	kg 1,4-DB eq	2.86E-01	8.50E-03	5.60E-02
Heat, lignite, extra for capture process	kg 1,4-DB eq	0.00E+00	4.00E-01	2.63E-01
Electricity production	kg 1,4-DB eq	0.00E+00	1.47E+00	1.47E+00
Remaining processes	kg 1,4-DB eq	1.13E-02	1.75E-01	1.08E-02

As Figure 47 presents the higher value of human toxicity has ‘Electricity production with MEA’, followed by ‘Electricity production with Calcium looping’ and finally Electricity production.

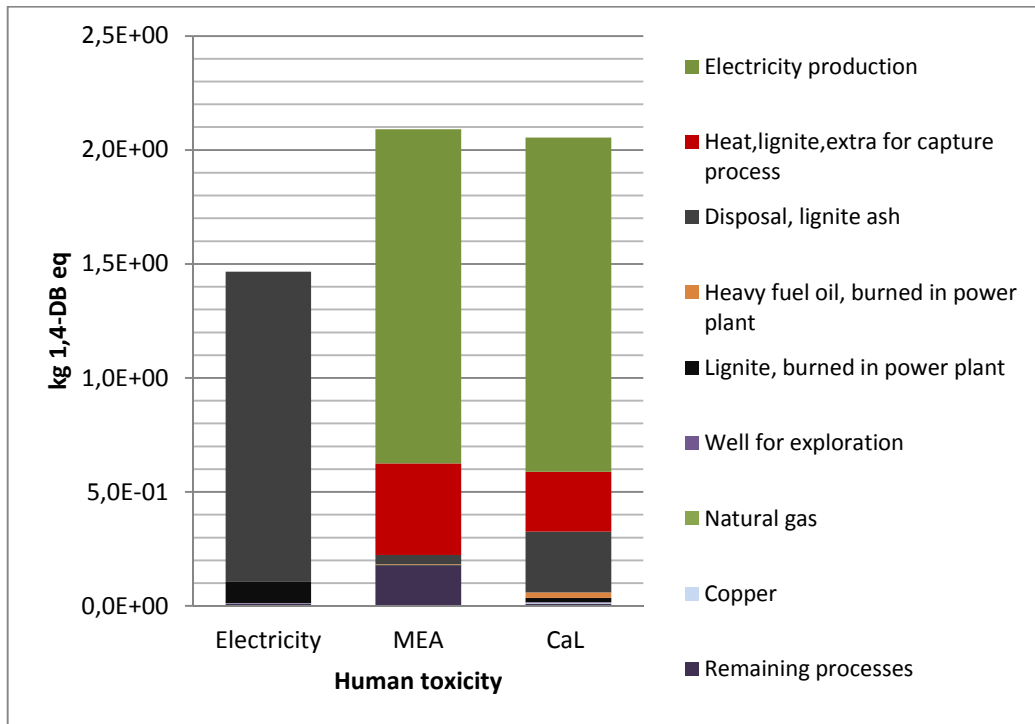


Figure 47 : Human toxicity impact category pollutant processes per kWh electricity

For all Cases, as Figure 48 and Table 37 show, the major contributors for the high values of human toxicity category are Selenium, Molybdenum, Nickel, Arsenic, Chromium, Vanadium and Barium with ‘Electricity production with MEA’ and ‘Electricity production with Calcium looping’ having almost the same value.

Table 37 : Human toxicity impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Selenium	kg 1,4-DB eq	7.19E-01	8.12E-01	9.07E-01
Molybdenum	kg 1,4-DB eq	1.22E-01	1.37E-01	1.54E-01
Nickel, ion	kg 1,4-DB eq	1.22E-01	1.36E-01	1.53E-01
Arsenic	kg 1,4-DB eq	3.61E-02	1.32E-01	1.09E-01
Chromium VI	kg 1,4-DB eq	1.68E-02	1.20E-01	8.86E-02
Vanadium, ion	kg 1,4-DB eq	9.76E-02	1.16E-01	1.27E-01
Barium	kg 1,4-DB eq	1.02E-01	1.13E-01	1.27E-01
Ethylene oxide	kg 1,4-DB eq	9.02E-08	9.74E-02	4.81E-07
Beryllium	kg 1,4-DB eq	8.10E-02	9.19E-02	1.02E-01
Thallium	kg 1,4-DB eq	6.76E-02	8.58E-02	9.21E-02
Antimony	kg 1,4-DB eq	2.53E-02	2.78E-02	3.14E-02
PAH, polycyclic aromatic hydrocarbons	kg 1,4-DB eq	8.52E-03	1.85E-02	1.97E-02
Benzene	kg 1,4-DB eq	4.40E-03	1.53E-02	1.24E-02
Cobalt	kg 1,4-DB eq	8.81E-03	9.72E-03	1.10E-02
Hydrogen fluoride	kg 1,4-DB eq	5.79E-03	7.73E-03	8.09E-03
Cadmium	kg 1,4-DB eq	1.93E-03	4.98E-03	4.81E-03
Nitrogen oxides	kg 1,4-DB eq	1.72E-03	4.83E-03	4.16E-03
Total	kg 1,4-DB eq	1.42E+00	1.93E+00	1.95E+00

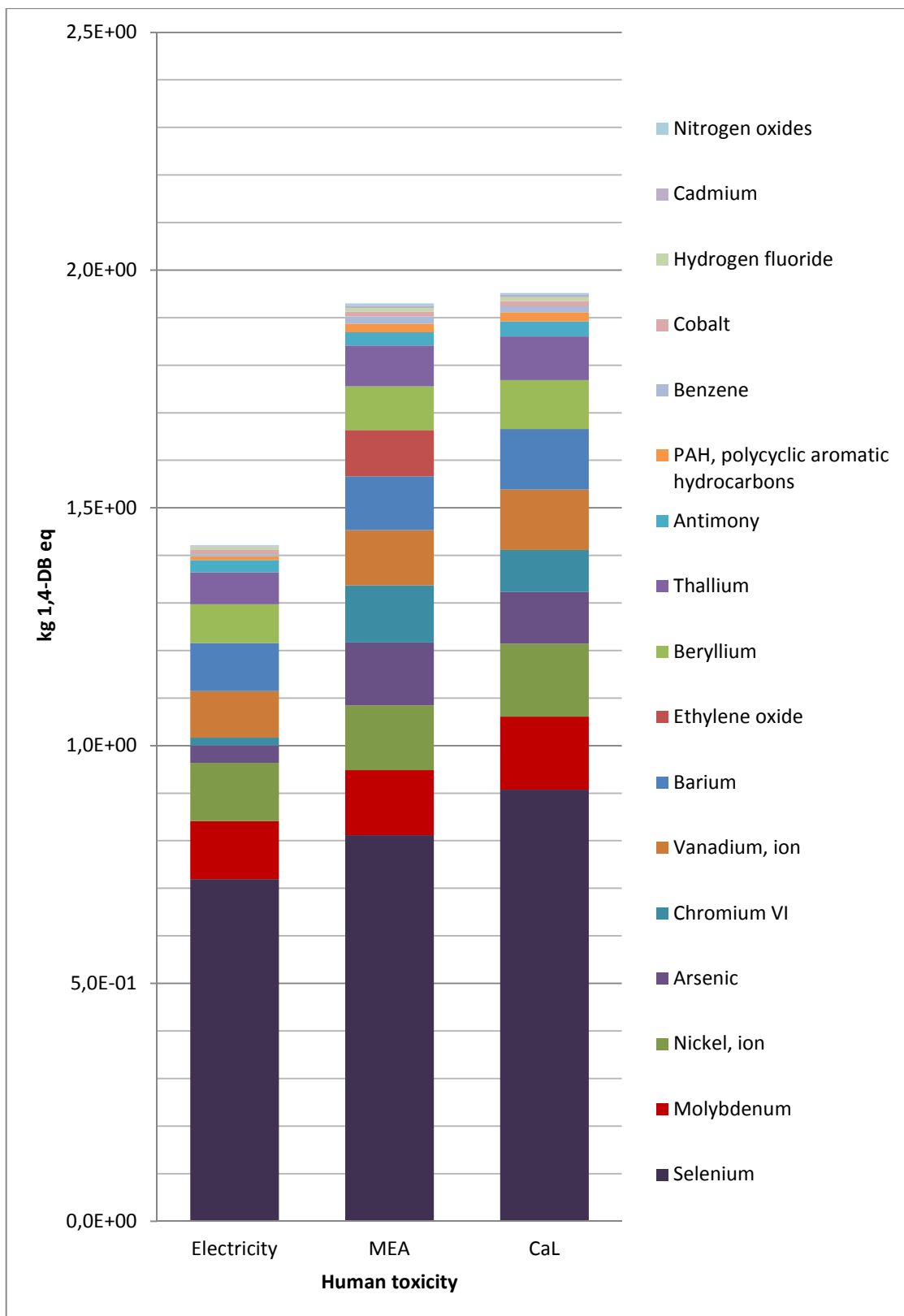


Figure 48 : Human toxicity impact category inventory characterization per kWh electricity

## 4.9 Fresh water aquatic eco-toxicity

The emissions of metals in the water and in the air, contribute to the high score of the impact category of fresh water aquatic eco-toxicity. The disposal wastes are not only from the power plant but are also from the capture unit. The land filled wastes occurred from the coal combustion, the flue gas desulphurization and from the production of steel which at first are disposed in the environment and later on are drained, producing the harmful emissions. In addition, from the production of steel, which is used for the transport infrastructure and during the transport of the fossil fuel, indirect and direct emissions are released in the atmosphere.

The processes which contribute the most to the generation of human toxically emissions and affect the fresh water aquatic eco-toxicity impact category as Table 38 shows, are the disposal of spoil from lignite mining and lignite ash as well as the additional generated heat for the two capture systems.

Table 38 : Fresh water aquatic eco-toxicity impact category pollutant processes

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Disposal, lignite ash	kg 1,4-DB eq	3.79E-01	1.13E-02	7.43E-02
Heat, lignite, extra for capture process	kg 1,4-DB eq	0.00E+00	2.40E-01	1.57E-01
Disposal, spoil from lignite mining	kg 1,4-DB eq	2.12E+00	6.38E-02	4.15E-01
Electricity production	kg 1,4-DB eq	0.00E+00	2.50E+00	2.50E+00
Remaining processes	kg 1,4-DB eq	6.04E-03	2.45E-03	6.23E-03

As Figure 49 illustrates that the higher value of fresh water aquatic eco-toxicity impact category has ‘Electricity production with Calcium looping’ as the spoil from lignite mining and its disposal to landfill increase the score of this impact category, followed by ‘Electricity production with MEA’ and finally with the lower value is ‘Electricity production’.

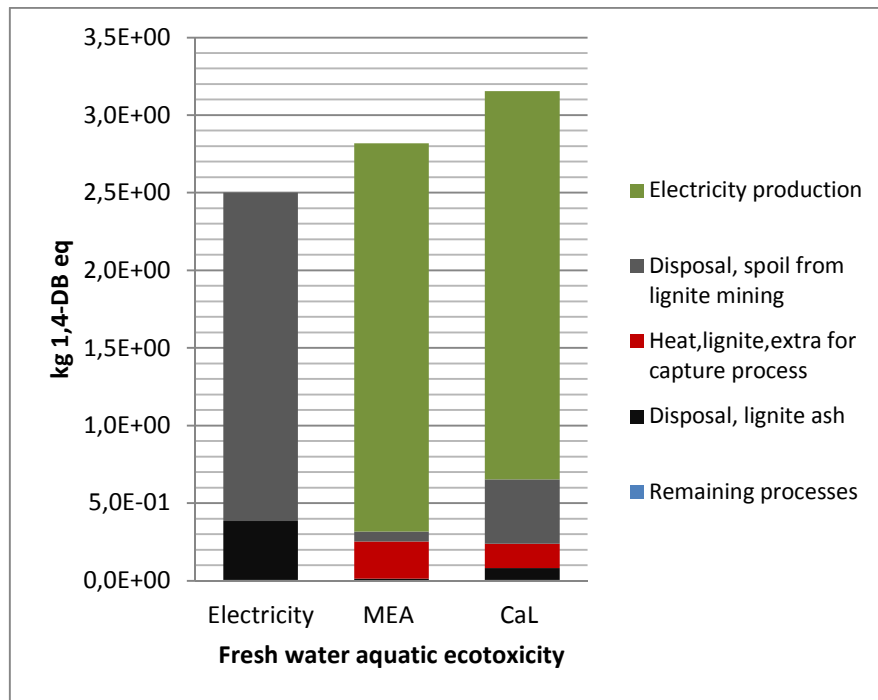


Figure 49 : Fresh water aquatic eco-toxicity impact category pollutant processes

For ‘Electricity production with MEA’, the direct emissions of MEA and formaldehyde contribute to the overall score of this impact category, as well as the emissions from ammonia and ethylene oxide production during the production of MEA.

As Table 39 and Figure 50 show, for ‘Electricity production with Calcium looping’ the major pollutants for this impact category are Nickel, Beryllium, Cobalt and Vanadium.



Table 39 : Fresh water aquatic eco-toxicity impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Nickel, ion	kg 1,4-DB eq	1.20E+00	1.34E+00	1.50E+00
Beryllium	kg 1,4-DB eq	5.28E-01	5.99E-01	6.68E-01
Cobalt	kg 1,4-DB eq	3.11E-01	3.43E-01	3.87E-01
Vanadium, ion	kg 1,4-DB eq	2.77E-01	3.28E-01	3.60E-01
Copper, ion	kg 1,4-DB eq	5.30E-02	6.03E-02	6.73E-02
Selenium	kg 1,4-DB eq	3.75E-02	4.23E-02	4.73E-02
Barium	kg 1,4-DB eq	3.67E-02	4.09E-02	4.60E-02
Zinc, ion	kg 1,4-DB eq	3.46E-02	3.93E-02	4.39E-02
Molybdenum	kg 1,4-DB eq	1.06E-02	1.18E-02	1.33E-02
Cadmium, ion	kg 1,4-DB eq	3.88E-03	4.43E-03	4.94E-03
Arsenic, ion	kg 1,4-DB eq	3.37E-03	4.06E-03	4.42E-03
Thallium	kg 1,4-DB eq	2.41E-03	3.05E-03	3.28E-03
Total	kg 1,4-DB eq	2.50E+00	2.82E+00	3.15E+00

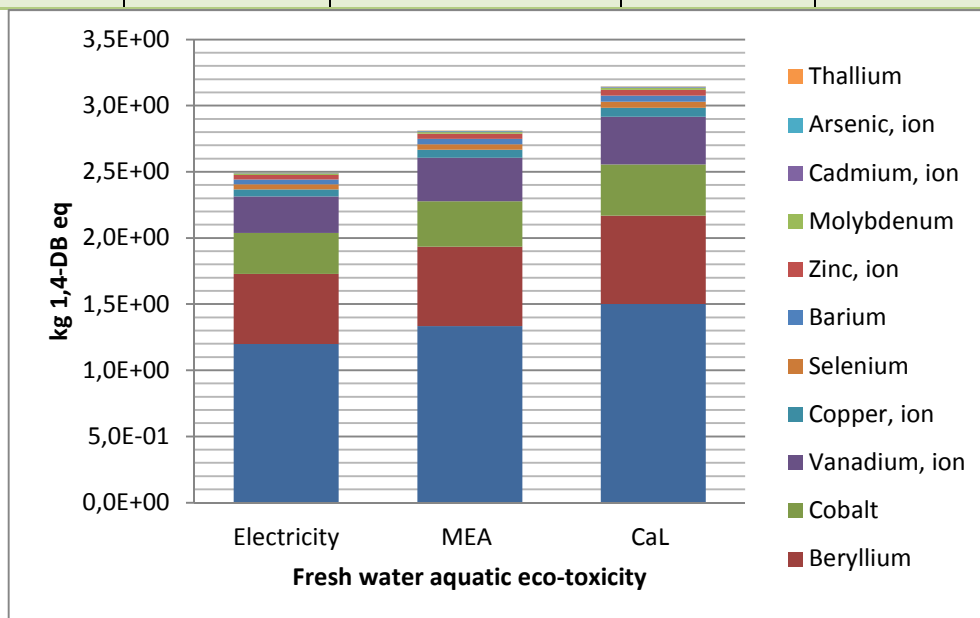


Figure 50 : Fresh water aquatic eco-toxicity impact category inventory characterization per kWh electricity

## 4.10 Marine aquatic eco-toxicity potential

The impact category of marine aquatic eco-toxicity is dominated by the disposal of wastes from the power plant and from the capture units. For the power plant with the capture units, the main emissions are from the infrastructure. Furthermore, the ammonia and MEA production process results for the increase of the emissions for ‘Electricity production with MEA’.

However, there is a discussion upon marine aquatic eco-toxicity impact category made in literature. There is a doubt for the characterization factors used for HF emissions in the CML impact assessment method, whether are far too high or not. Many authors suggest this fact and highlight that this leads for the environmental impact of HF emissions to be estimated high enough, resulting in turn to a high score of marine aquatic eco-toxicity potential impact category.

As Table 40 and Figure 51 present, the higher value of marine aquatic eco-toxicity impact category has ‘Electricity production with Calcium looping’ as the spoil from lignite mining and the use of high amount of heat, increase the score of this impact category, followed by ‘Electricity production with MEA’ and finally with the lower value is ‘Electricity production’.

Table 40 : Marine aquatic eco-toxicity impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Heavy fuel oil	kg 1,4-DB eq	4.24E-02	2.31E+00	1.52E+01
Disposal, lignite ash	kg 1,4-DB eq	8.87E+02	2.63E+01	1.74E+02
Heat, lignite, extra for capture process	kg 1,4-DB eq	0.00E+00	5.37E+02	3.53E+02
Disposal, spoil from lignite mining	kg 1,4-DB eq	4.25E+03	1.28E+02	8.34E+02
Electricity, lignite, from flue gases	kg 1,4-DB eq	0.00E+00	5.18E+03	5.18E+03
Remaining processes	kg 1,4-DB eq	4.51E+01	7.18E+00	1.80E+01

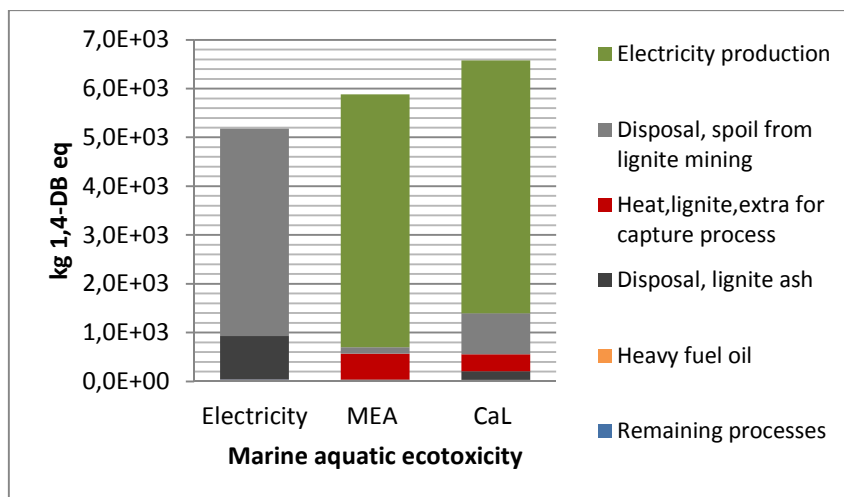


Figure 51 : Marine aquatic eco-toxicity impact category pollutant processes per kWh electricity

Likewise the fresh water aquatic eco-toxicity, also at marine aquatic eco-toxicity impact category, for all Cases the major pollutants are Nickel, Beryllium, Cobalt Selenium and Vanadium, as Table 41 and Figure 52 present, with 'Electricity production with Calcium looping' having the higher score.

Table 41 : Marine aq. eco-tox. impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Beryllium	kg 1,4-DB eq	3.12E+03	3.54E+03	3.95E+03
Nickel, ion	kg 1,4-DB eq	8.33E+02	9.27E+02	1.04E+03
Cobalt	kg 1,4-DB eq	3.99E+02	4.40E+02	4.97E+02
Selenium	kg 1,4-DB eq	3.25E+02	3.67E+02	4.10E+02
Vanadium, ion	kg 1,4-DB eq	2.65E+02	3.14E+02	3.44E+02
Barium	kg 1,4-DB eq	1.34E+02	1.50E+02	1.69E+02
Molybdenum	kg 1,4-DB eq	4.64E+01	5.19E+01	5.82E+01
Hydrogen fluoride	kg 1,4-DB eq	2.32E+01	3.09E+01	3.24E+01
Copper, ion	kg 1,4-DB eq	1.07E+01	1.21E+01	1.35E+01
Thallium	kg 1,4-DB eq	8.00E+00	1.01E+01	1.09E+01
Zinc, ion	kg 1,4-DB eq	5.21E+00	5.95E+00	6.65E+00
Total	kg 1,4-DB eq	5.18E+03	5.88E+03	6.58E+03

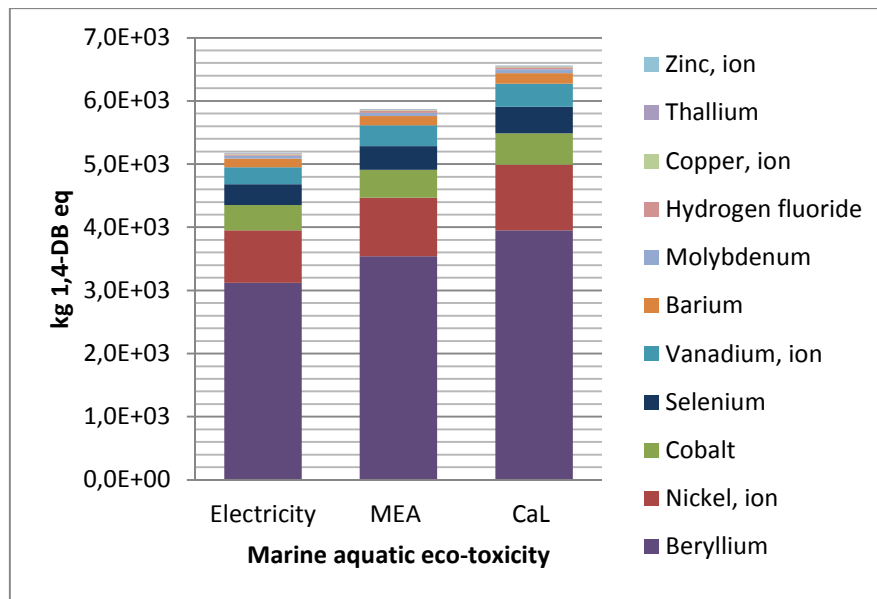


Figure 52 : Marine aquatic eco-toxicity impact category inventory characterization per kWh electricity

## 4.11 Terrestrial eco-toxicity potential (TEP)

The main contributor for the terrestrial eco-toxicity potential category is the presence of mercury (Hg) and other heavy metals. The efficiency penalty from the CO<sub>2</sub> capture process results to a higher score. Also, to the increase of the score contributes the infrastructure development and the direct emissions generated from the facility of the plant in addition to the emissions from the MEA production chain. In this LCA is not taken into account the possibility of capturing the mercury and the other heavy metals from the flue gases during the CO<sub>2</sub> capture process. In the case that this removal can be applied, the score of terrestrial eco-toxicity potential is getting lower.

The processes which have a high contribution to the increase of the value of terrestrial eco-toxicity impact category, as Table 42 and Figure 53 present, the heavy fuel oil which is burned in the power plant, as well as the additional generated heat for the two capture systems.

Table 42 : Terrest. eco-tox. potential impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Copper	kg 1,4-DB eq	6.32E-06	3.53E-06	8.51E-06
Steel	kg 1,4-DB eq	2.37E-05	3.59E-06	1.27E-05
Disposal, spoil from lignite mining	kg 1,4-DB eq	9.99E-04	3.01E-05	1.96E-04
Transmission network, electr. med., volt.	kg 1,4-DB eq	2.05E-06	6.21E-05	3.82E-04
Lignite, burned in power plant	kg 1,4-DB eq	2.75E-03	8.17E-05	5.39E-04
Heavy fuel oil, burned in power plant	kg 1,4-DB eq	2.20E-06	1.20E-04	7.90E-04
Heat, lignite, extra for capture process	kg 1,4-DB eq	0.00E+00	1.98E-03	1.30E-03
Electricity production	kg 1,4-DB eq	0.00E+00	3.85E-03	3.85E-03
Remaining process	kg 1,4-DB eq	6.41E-05	9.62E-05	4.56E-05

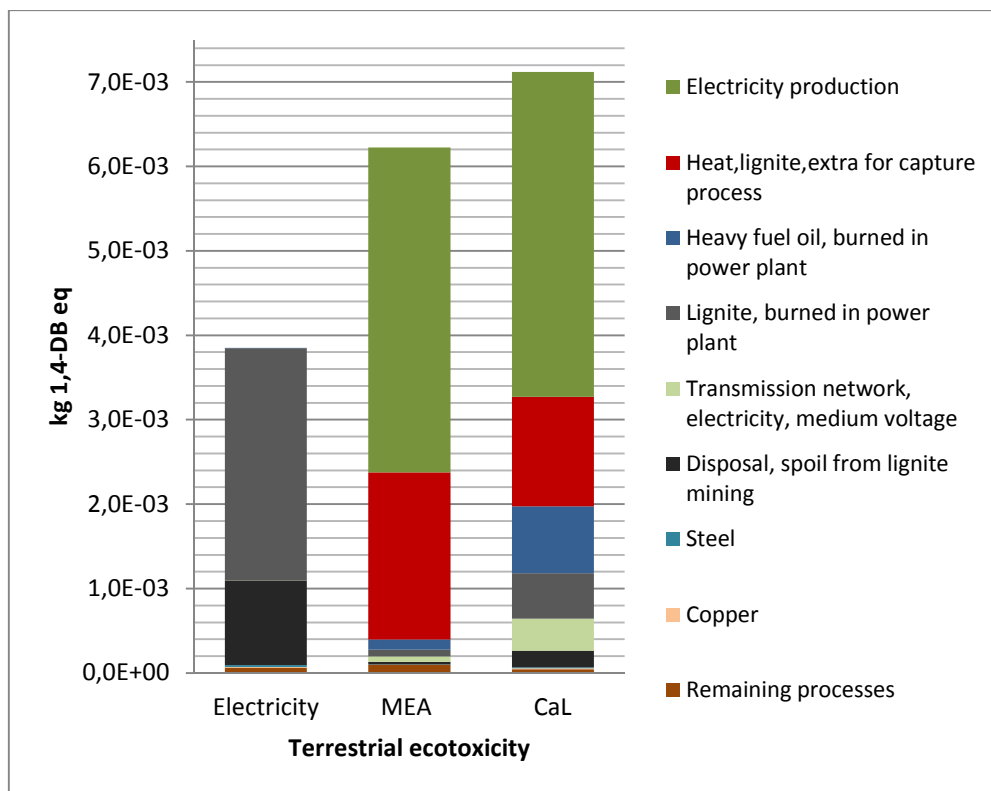


Figure 53 : Terr. eco-tox. potential impact category pollutant processes per kWh electricity

The pollutants which are dominant to terrestrial impact category are Mercury, Vanadium, Arsenic, Chromium etc., as Table 43 and Figure 54 present. The Case which has the higher score is ‘Electricity production with Calcium looping’, having a small difference with the Case of ‘Electricity production with MEA’.

Table 43 : Terrestrial eco-toxicity potential impact category inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Mercury	kg 1,4-DB eq	2.46E-03	3.44E-03	3.55E-03
Vanadium	kg 1,4-DB eq	1.43E-04	6.36E-04	1.11E-03
Arsenic	kg 1,4-DB eq	1.67E-04	6.11E-04	5.04E-04
Chromium VI	kg 1,4-DB eq	2.94E-06	1.38E-04	4.35E-04
Nickel	kg 1,4-DB eq	1.82E-05	6.41E-05	8.27E-05
Selenium	kg 1,4-DB eq	1.77E-05	2.39E-05	2.52E-05
Beryllium	kg 1,4-DB eq	6.72E-08	2.32E-05	1.53E-05
Lead	kg 1,4-DB eq	1.60E-06	1.45E-05	1.10E-05
Cobalt	kg 1,4-DB eq	4.66E-06	9.64E-06	1.24E-05
Zinc	kg 1,4-DB eq	6.53E-06	7.86E-06	9.16E-06
Barium	kg 1,4-DB eq	1.35E-06	7.73E-06	5.78E-06
Total	kg 1,4-DB eq	3.85E-03	6.22E-03	7.12E-03

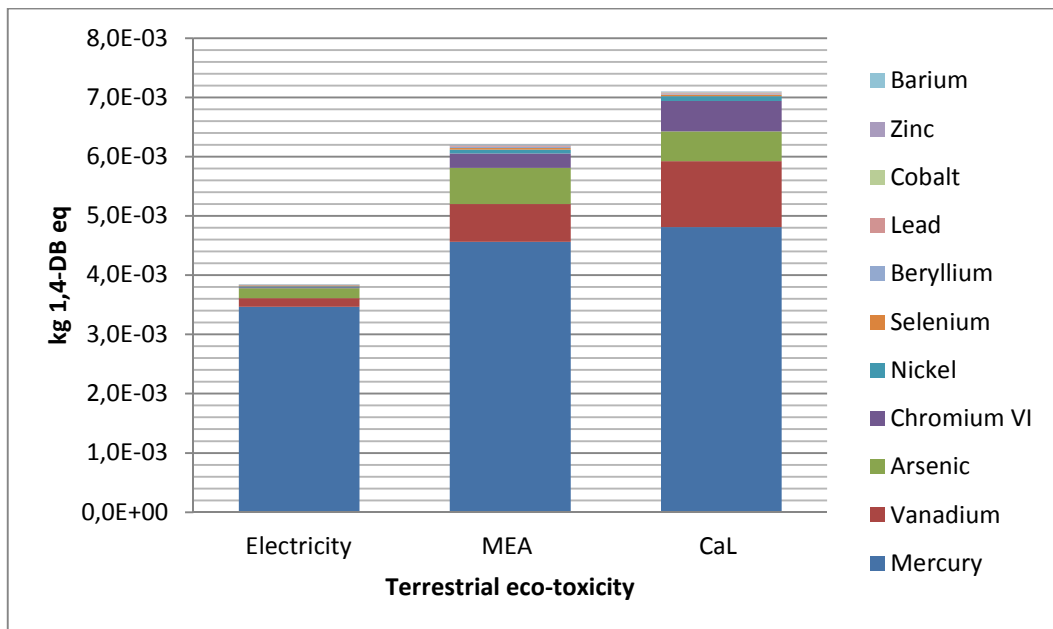


Figure 54 : Terrestrial eco-toxicity potential impact category inventory characterization per kWh electricity

## 4.12 Photochemical oxidation

The score of photochemical oxidation potential impact category depends on the amount of SO<sub>2</sub>, NO<sub>x</sub> and methane emissions in the atmosphere. The sources of those emissions are the plant facility and the fuel combustion which produce a high amount of NO<sub>x</sub> emissions. Furthermore, the infrastructure, the lignite transportation and the nature gas mining chain also produce methane and SO<sub>2</sub> emissions which are added to the overall emissions.

However, the score of photochemical oxidation potential alters between the different assessment methods. Specifically, Nie (2009) [86], using the CML baseline method reports a negative characterization factor based on the LOTOS-Euros model [87]. In addition, the software program used for the LCA plays also an important role.

As we can see at Table 44 and Figure 55 the higher value for the environmental impact category of photochemical oxidation is for ‘Electricity production with MEA’, due to the use of higher amount of heat.

Table 44 : Photochemical oxidation impact category pollutant processes per kWh electricity

Process/Raw material	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Natural gas, burned in power plant	kg C <sub>2</sub> H <sub>4</sub>	6.33E-09	1.29E-07	8.46E-07
Heavy fuel oil, at refinery	kg C <sub>2</sub> H <sub>4</sub>	5.60E-08	2.52E-07	1.02E-06
Lignite, burned in power plant	kg C <sub>2</sub> H <sub>4</sub>	2.95E-04	8.75E-06	5.77E-05
Heat, lignite, extra for capture process	kg C <sub>2</sub> H <sub>4</sub>	0.00E+00	3.56E-04	2.33E-04
Electricity production	kg C <sub>2</sub> H <sub>4</sub>	0.00E+00	3.03E-04	3.03E-04
Remaining proc.	kg C <sub>2</sub> H <sub>4</sub>	7.86E-06	4.53E-06	5.57E-06



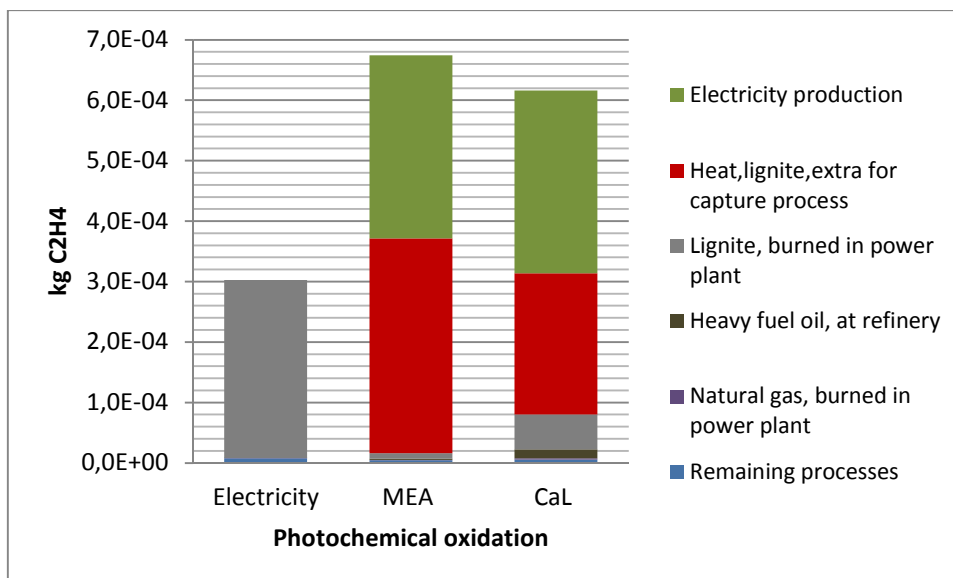


Figure 55 : Photochemical oxidation impact category pollutant processes per kWh electricity

For the higher values of photochemical oxidation for Case 2 and Case 3, the high amount of sulfur dioxide (SO<sub>2</sub>) emissions, which are generated by the lignite combustion, are mostly responsible, as Table 45 and Figure 56 present. The other pollutants with lower values, for the photochemical oxidation impact category, are carbon monoxide, ethane, methane etc.

Table 45 : Photochemical oxidation impact cat. inventory characterization per kWh electricity

Pollutant substance	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Sulfur dioxide	kg C <sub>2</sub> H <sub>4</sub>	2.90E-04	5.67E-04	5.36E-04
Carbon monoxide, fossil	kg C <sub>2</sub> H <sub>4</sub>	6.56E-06	3.80E-05	2.96E-05
Ethene	kg C <sub>2</sub> H <sub>4</sub>	2.16E-08	3.17E-05	2.03E-05
Methane, fossil	kg C <sub>2</sub> H <sub>4</sub>	3.04E-06	2.06E-05	1.55E-05
Propene	kg C <sub>2</sub> H <sub>4</sub>	1.93E-07	6.02E-06	4.08E-06
Benzene	kg C <sub>2</sub> H <sub>4</sub>	5.05E-07	1.75E-06	1.43E-06
Toluene	kg C <sub>2</sub> H <sub>4</sub>	7.30E-07	1.56E-06	1.45E-06
Pentane	kg C <sub>2</sub> H <sub>4</sub>	6.83E-07	1.14E-06	1.58E-06
Formaldehyde	kg C <sub>2</sub> H <sub>4</sub>	3.33E-07	8.46E-07	8.73E-07
Total	kg C <sub>2</sub> H <sub>4</sub>	3.03E-04	6.74E-04	6.16E-04

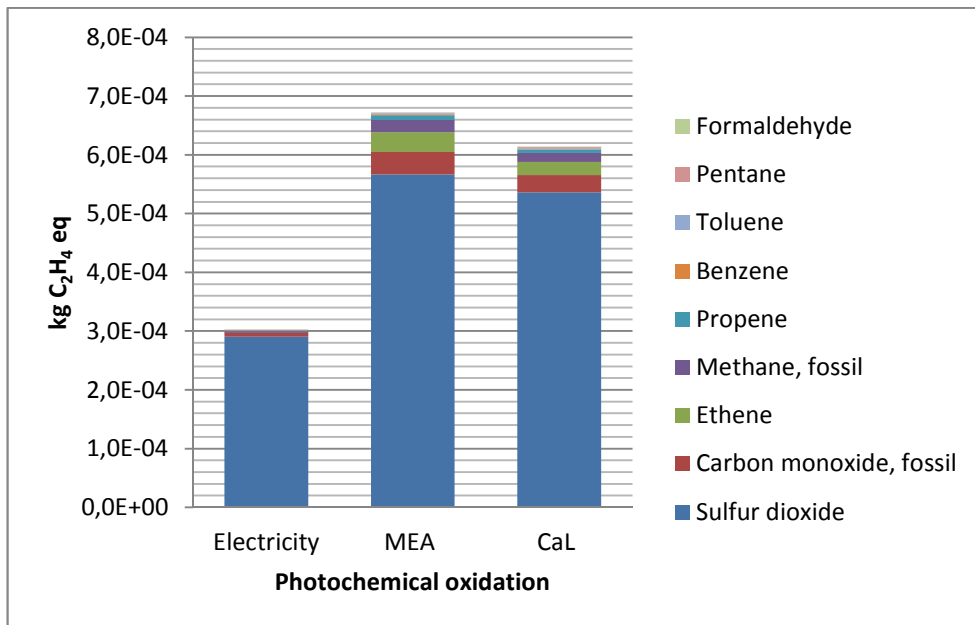


Figure 56 : Photochemical oxidation impact cat. inventory characterization per kWh electricity

## 4.13 Overall results

### 4.13.1 Case 1: Electricity production

Table 46 summarizes the ten environmental impact categories for Case 1, which is 'Electricity production' of 1 kWh, by lignite combustion with 35.2% average net efficiency. At the table the total value of the corresponding characterization factor of each impact category is shown, including the emissions generated by the subsystems participating in 'Electricity production' case.

Table 46 : Impact categories for Electricity production per kWh electricity

Impact category	Unit	Electricity production
Abiotic depletion	kg Sb eq	1.35E-02
Acidification	kg SO <sub>2</sub> eq	7.97E-03
Eutrophication	kg PO <sub>4</sub> <sup>---</sup> eq	1.46E-02
Global warming (GWP100)	kg CO <sub>2</sub> eq	1.30E+00
Ozone layer depletion (ODP)	kg CFC-11 eq	1.75E-09
Human toxicity	kg 1,4-DB eq	1.47E+00
Fresh water aquatic ecotox.	kg 1,4-DB eq	2.50E+00
Marine aquatic ecotoxicity	kg 1,4-DB eq	5.18E+03
Terrestrial ecotoxicity	kg 1,4-DB eq	3.85E-03
Photochemical oxidation	kg C <sub>2</sub> H <sub>4</sub>	3.03E-04

### 4.13.2 Case 2: Electricity production with MEA

Table 47 summarizes the ten environmental impact categories for Case 2, 'Electricity production with MEA', which comprises 'Electricity production' with CO<sub>2</sub> capture unit with MEA. For each impact category the participating processes or raw materials for the operation of Case 2 and the total value of the corresponding characterization factor of each impact category are shown. As we can see, the extra processes at MEA capture unit, which result to the high value of 'global warming' and 'abiotic depletion' impact categories, are the additional heat and the high amount of electricity used during the CO<sub>2</sub> capture process.

Table 47 : Impact categories for 'Electricity production with MEA' per kWh electricity

Impact category	Unit	Total	CO <sub>2</sub> emissions after MEA capture unit	MEA	Sodium hydroxide	Ammonia	Limestone	Electricity, for auxiliaries	Heat for capture unit	Electricity production by lignite combustion
Abiotic depl.	kg Sb eq	2.13E-02	0.00E+00	1.64E-04	6.15E-06	8.97E-05	1.35E-06	4.79E-04	7.06E-03	1.35E-02
Acidification	kg SO2 eq	1.62E-02	0.00E+00	5.54E-05	5.83E-06	1.44E-05	1.02E-06	3.02E-04	7.87E-03	7.97E-03
Eutrophication	kg PO4---eq	1.65E-02	0.00E+00	2.48E-05	3.21E-07	2.03E-06	2.91E-07	4.37E-04	1.47E-03	1.46E-02
Global warming	kg CO2 eq	5.55E-01	3.94E-01	1.44E-02	1.11E-03	1.05E-02	2.04E-04	4.97E-02	7.14E-02	1.38E-02
Ozone layer depletion	kg CFC-11 eq	8.73E-09	0.00E+00	1.23E-09	0.00E+00	0.00E+00	2.74E-11	1.38E-09	4.34E-09	1.75E-09
Human ecotoxicity	kg 1,4-DB eq	2.09E+00	0.00E+00	1.75E-01	7.47E-06	1.75E-05	1.07E-04	4.90E-02	4.00E-01	1.47E+00
Fresh water ecotoxicity	kg 1,4-DB eq	2.82E+00	0.00E+00	2.55E-03	4.49E-06	3.03E-06	3.51E-05	7.49E-02	2.40E-01	2.50E+00
Marine ecotoxicity	kg 1,4-DB eq	5.88E+03	0.00E+00	6.57E+00	3.67E-03	4.15E-03	7.33E-02	1.57E+02	5.37E+02	5.18E+03
Terrestrial ecotoxicity	kg 1,4-DB eq	6.22E-03	0.00E+00	9.60E-05	4.00E-06	1.37E-07	7.74E-07	2.96E-04	1.98E-03	3.85E-03
Photochemical oxidation	kg C2H4	6.74E-04	0.00E+00	3.03E-06	2.61E-07	7.03E-07	3.40E-08	1.20E-05	3.56E-04	3.03E-04

Figure 57 presents the contribution of each process and input raw material of electricity production with amine CO<sub>2</sub> capture to each environmental impact category at a scale of 100%. 'MEA capture system' at 'global warming' impact category represents the percentage of greenhouse gases released in the atmosphere by the CO<sub>2</sub> capture unit. 'Ammonia', Monoethanolamine', 'Sodium hydroxide' and 'Limestone' are the raw materials used in the CO<sub>2</sub> capture unit. 'Heat' and 'Electricity, medium voltage' are the extra heat and electricity use due to the capture process. Finally, 'Electricity, lignite, at power plant' is the flue gases from lignite combustion.

As we can see apart from the lignite combustion, for generating the flue gases of 1 kWh electricity, the other pollutant processes, for the most of the impact categories, are the extra 'heat and 'electricity, medium voltage', used by the capture unit, while monoethanolamine and ammonia influence mostly the ozone depletion and human toxicity impact category.

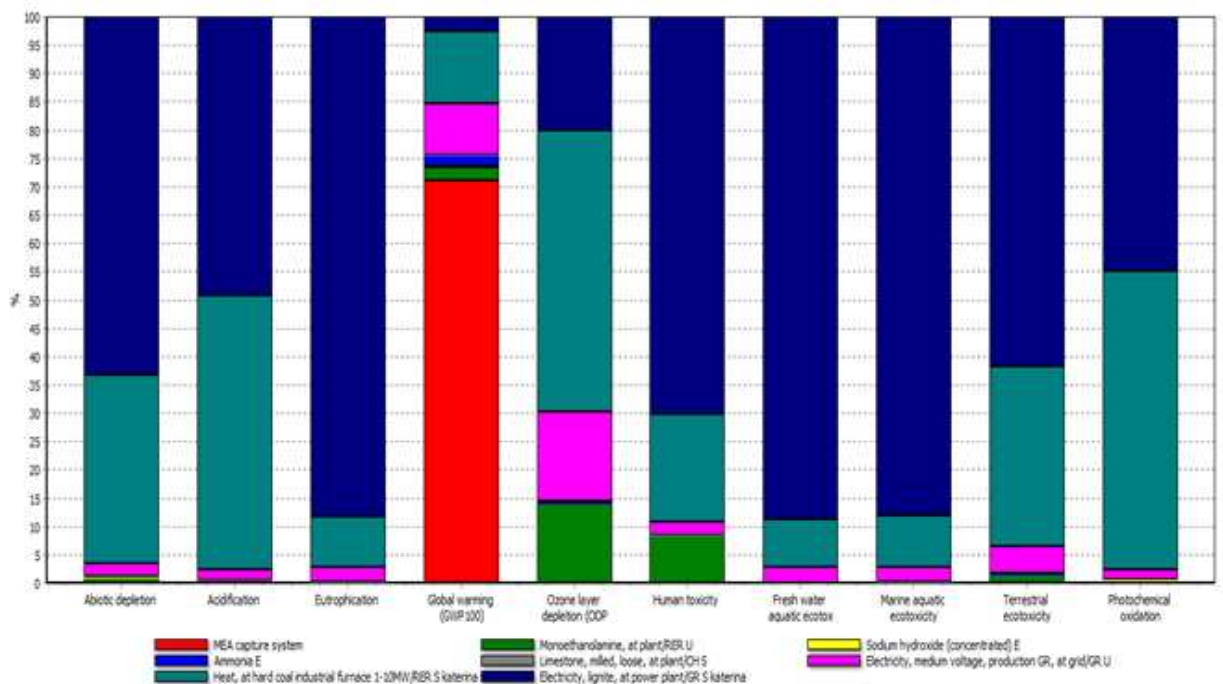


Figure 57 : Impact categories for 'Electricity production with MEA' per kWh electricity, by SimaPro

### 4.13.3 Case 3: Electricity production with Calcium looping

Table 48 summarizes the ten environmental impact categories for Case 3, which is ‘Electricity production with Calcium looping’. The contribution of the participating processes and raw materials utilized in Case 3 is also presented. The processes which are responsible for the high value of ‘abiotic depletion’ impact category are ‘heat, for capture unit’ and ‘electricity for auxiliaries’, while ‘electricity for auxiliaries’ process is also the major contributor for the high value of ‘global warming’ impact category with the process of ‘heat for capture unit’ following.

Table 48 : Impact categories for ‘Electricity production with Calcium looping’ per kWh electricity

Impact category	Unit	Total	CO <sub>2</sub> emissions after CaL capture unit	Limestone	Electricity, for auxiliaries(elect. medium volt)	Heat for capture unit (at industrial furnace)	Electricity production by lignite combustion
Abiotic depletion	kg Sb eq	2.13E-02	0.00E+00	2.81E-05	3.17E-03	4.63E-03	1.35E-02
Acidification	kg SO <sub>2</sub> eq	1.52E-02	0.00E+00	2.12E-05	2.00E-03	5.16E-03	7.97E-03
Eutrophication	kg PO <sub>4</sub> <sup>---</sup> eq	1.85E-02	0.00E+00	6.07E-06	2.89E-03	9.62E-04	1.46E-02
Global warming (GWP100)	kg CO <sub>2</sub> eq	4.89E-01	9.50E-02	4.26E-03	3.29E-01	4.69E-02	1.38E-02
Ozone layer depletion (ODP)	kg CFC-11 eq	1.43E-08	0.00E+00	5.73E-10	9.14E-09	2.85E-09	1.75E-09
Human toxicity	kg 1,4-DB eq	2.05E+00	0.00E+00	2.24E-03	3.24E-01	2.63E-01	1.47E+00
Fresh water eco-toxicity	kg 1,4-DB eq	3.15E+00	0.00E+00	7.32E-04	4.95E-01	1.57E-01	2.50E+00
Marine eco-toxicity	kg 1,4-DB eq	6.58E+03	0.00E+00	1.53E+00	1.04E+03	3.53E+02	5.18E+03
Terrestrial eco-toxicity	kg 1,4-DB eq	7.12E-03	0.00E+00	1.62E-05	1.96E-03	1.30E-03	3.85E-03
Photochemical oxidation	kg C <sub>2</sub> H <sub>4</sub>	6.16E-04	0.00E+00	7.11E-07	7.96E-05	2.33E-04	3.03E-04

Figure 58 presents the contribution of each process and input raw material, of electricity production with carbonate looping, in each environmental impact category at a scale of 100%.'CaL capture system' at 'global warming' impact category represents the greenhouse gases released in the atmosphere by the CO<sub>2</sub> capture unit. 'Limestone', is the raw material used in the CO<sub>2</sub> capture unit. 'Heat' and 'Electricity, medium voltage' are the extra heat and electricity use, due to the capture process. Likewise to 'Electricity production with MEA', the most pollutant process for all the impact categories is mainly 'electricity, medium voltage' and then 'heat' which both of them are used by the capture unit. The raw material of 'limestone' contributes to the ozone depletion impact category.

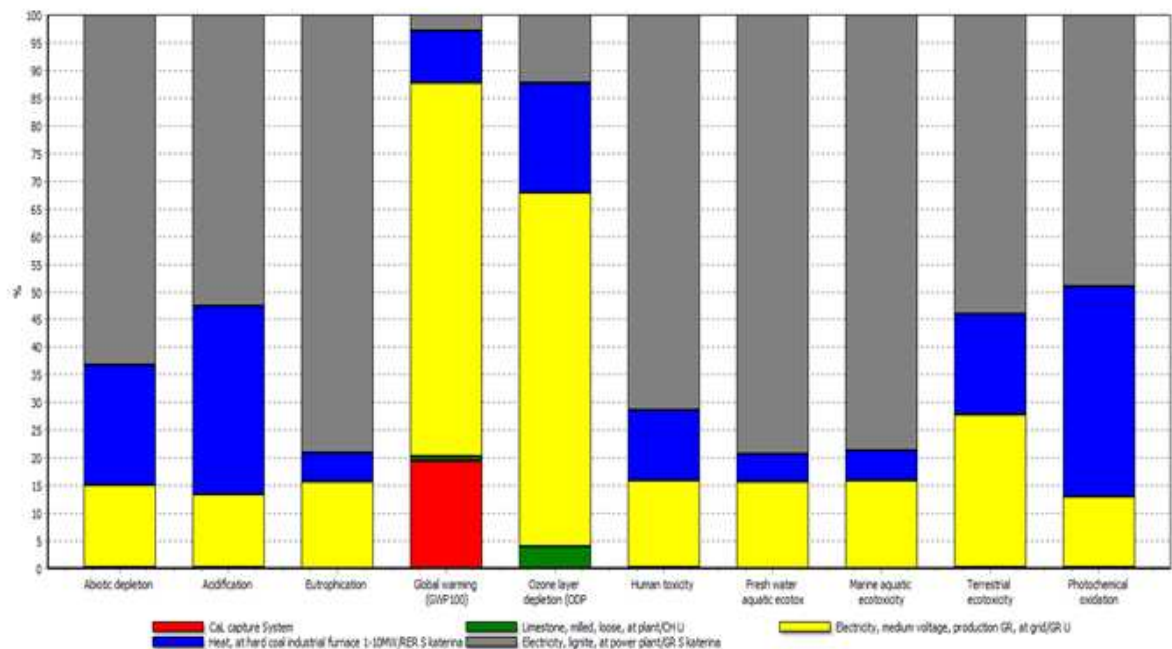


Figure 58 : Impact categories for 'Electricity production with Calcium looping' per kWh electricity, by SimaPro

#### 4.13.4 Overall comparison of the three investigated scenarios

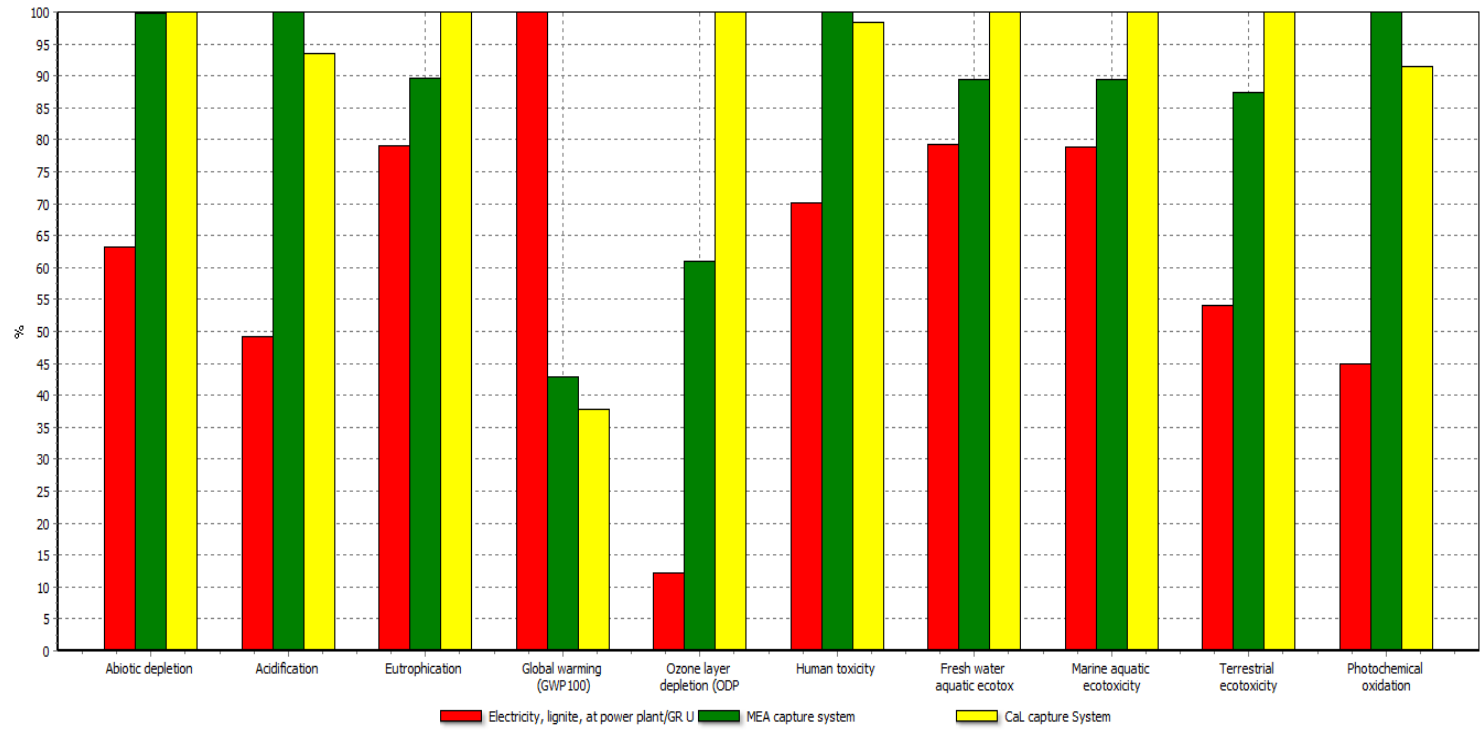
The total values of each Case, for the ten environmental impact categories, are presented in Table 49. Figure 59 presents the % contribution of each process and input raw material, of each scenario in the different environmental impact categories. We can see that for the impact category of 'global warming' the Case with the lower value of kg CO<sub>2</sub> equiv. is 'Electricity production with Calcium looping' while for the impact category

‘abiotic depletion’, ‘Electricity production with Calcium looping’ and ‘Electricity production with MEA’ have the same value.

Table 49 : Environmental impact categories for the three Cases per kWh electricity

Impact category	Unit	Electricity production	Electricity production with MEA	Electricity production with Calcium looping
Abiotic depletion	kg Sb eq	1.35E-02	2.13E-02	2.13E-02
Acidification	kg SO <sub>2</sub> eq	7.97E-03	1.62E-02	1.52E-02
Eutrophication	kg PO <sub>4</sub> <sup>---</sup> eq	1.46E-02	1.65E-02	1.85E-02
Global warming (GWP100)	kg CO <sub>2</sub> eq	1.30E+00	5.55E-01	4.89E-01
Ozone layer depletion (ODP)	kg CFC-11 eq	1.75E-09	8.73E-09	1.43E-08
Human toxicity	kg 1,4-DB eq	1.47E+00	2.09E+00	2.05E+00
Fresh water aquatic ecotox.	kg 1,4-DB eq	2.50E+00	2.82E+00	3.15E+00
Marine aquatic ecotoxicity	kg 1,4-DB eq	5.18E+03	5.88E+03	6.58E+03
Terrestrial ecotoxicity	kg 1,4-DB eq	3.85E-03	6.22E-03	7.12E-03
Photochemical oxidation	kg C <sub>2</sub> H <sub>4</sub>	3.03E-04	6.74E-04	6.16E-04





Comparing 1 kWh 'Electricity, lignite, at power plant/GR U', 1 kg 'MEA capture system' and 1 kg 'CaL capture System';  
 Method: CML 2 baseline 2000 V2.05 / the Netherlands, 1997 / Characterization

Figure 59 : Environmental impact categories for the three Cases per kWh electricity, by SimaPro

# 5. Interpretation- Conclusion

The implementation of CO<sub>2</sub> capturing processes evokes a lot of arguments and raises questions about the possibility of causing other collateral impacts to the environment even though it helps reducing the climate change by reducing the CO<sub>2</sub> emissions in the atmosphere. The LCA method gives us a wider view about the CO<sub>2</sub> capture processes with its reverberations to the environment and it was used to compare Case 1, 'Electricity production' of 1 kWh by lignite combustion, Case 2 'Electricity production with MEA', which is 'Electricity production' of 1 kWh integrated with the post-combustion CO<sub>2</sub> capture process of amine- scrubbing with monoethanolamine (MEA) and Case 3, 'Electricity production with Calcium looping', which is 'Electricity production' of 1 kWh integrated with the post-combustion CO<sub>2</sub> capture process of Calcium looping (CaL).

The inventory data for Case1, 'Electricity production' at lignite –fired power plant was obtained from the Ecoinvent v2.0 (2007) database. For the two post-combustion CO<sub>2</sub> capture technologies, Case 2, 'Electricity production with MEA' and Case 3 'Electricity production with Calcium looping', the inventory data were derived from literature. All three scenarios were analyzed by SimaPro software program. The environmental impact assessment was performed with the CML baseline 2000 method. The ten environmental midpoint categories which were analyzed were the following: abiotic depletion, acidification, eutrophication, global warming, ozone layer depletion, human toxicity, fresh water aquatic eco-toxicity, marine aquatic eco-toxicity, terrestrial eco-toxicity and photo-chemical oxidation.

Electricity production consists of three subsystems, those of lignite mining, lignite transportation and lignite combustion. The two CO<sub>2</sub> capture technologies comprise of those three subsystems in addition to the capture unit which imposes additional fuel consumption and energy use for its operation.

The different subsystems, lignite mining, transportation and lignite combustion firstly, and secondly the two different post-combustion CO<sub>2</sub> capture technologies at the power plant do not have the same impact to each environmental category and contribute differently to the total score. The results of the present LCA show that the implementation of the CO<sub>2</sub> capture technology on the one hand, has a major positive impact in reducing

the CO<sub>2</sub> emissions in the atmosphere. However, on the other hand, other impact categories are burdened a lot in a different way for the two CO<sub>2</sub> capture technologies. Both CO<sub>2</sub> capture technologies decrease as expected the efficiency of the electricity generation.

The efficiency drop for 'Electricity production with Calcium looping' is lower than the efficiency drop of 'Electricity production with MEA', with a difference of 2.12 % as 'Electricity production with Calcium looping' provides higher electric production and higher efficiency for the retrofitted power plant. This is due to the fact that carbonate looping operates at higher temperatures than amine scrubbing and the fact that the carbonation reaction is exothermic. This heat can be exploited to produce additional electricity.

Moreover, carbonate looping demonstrates a higher CO<sub>2</sub> capture rate of 97.3%, compared to 86.5% capture achieved with amine scrubbing. However, the CO<sub>2</sub> capture rates for the overall power plant are almost the same for the two capture processes because carbonate looping technology acquires higher amount of electricity, for the air separation unit and higher amount of lignite, in order to have the proper conditions in the calciner, than amine scrubbing technology needs.

Furthermore, as far as the environmental impact concerns, the two capture technologies have almost the same or different values for the different environmental impact categories, but definitely higher than the values of electricity production without having a capture technology. For the abiotic depletion impact category, amine scrubbing process has the same value as carbonate looping process. The value of abiotic depletion impact category increases by the additional consumption of natural resources like natural gas, crude oil and especially lignite for the two capture processes, which are necessary for the proper operation and construction of those capture units. Amine scrubbing has also higher value for the acidification impact category, than carbonate looping process, as both capture processes produce high amounts of sulfur dioxide and nitrogen oxides emissions caused by the energy penalty of using extra amount of electricity, higher for carbonate looping, and heat, higher for amine scrubbing, at the capture systems. For the eutrophication and ozone depletion impact categories, from the two capture processes, carbonate looping has the higher value, due to the high amount of phosphate, nitrogen oxides and nitrate emissions produced by the high lignite consumption and the high amount of methane, ethane and halon emissions produced by the high electricity consumption, for the proper capture operation conditions, respectively.

In addition, for the human toxicity impact category, the two capture technologies have also almost the same value, higher for carbonate looping process, as both processes produce high amounts of Selenium, Molybdenum, Nickel, Arsenic, Chromium, Vanadium and Barium emissions due to the extra use of heat and electricity at the capture processes. Carbonate looping, for the impact categories of fresh water aquatic eco-toxicity and marine aquatic eco-toxicity as having higher values for Nickel, Beryllium, Cobalt and Vanadium emissions and the terrestrial eco-toxicity, with higher values for Mercury, Vanadium, Arsenic, Chromium and etc., has higher environmental impact caused by the high amount of lignite consumption and its disposal spoil. Finally, for the photochemical oxidation impact category, amine scrubbing process has higher environmental impact due to the increased amount of sulfur dioxide (SO<sub>2</sub>) emissions produced by the higher heat consumption.

In general, even though calcium looping is still in research level and has mostly been studied in pilot-scale, it demonstrates many advantages compared to the mature amine scrubbing post-combustion CO<sub>2</sub> capture technology. Calcium looping demonstrates lower energy penalties in comparison with amine scrubbing process. Moreover, it is possible for the generated heat produced by the capture process to be utilized in a secondary steam cycle, reducing in that way the energy penalty. In addition, CaO (lime) which is the by-product of calcium looping process can be used as a raw material in the cement industry as feedstock, reducing further CO<sub>2</sub> emissions. Finally, a further reduction of the energy penalty is achieved when calcium looping is integrated with chemical looping process, making in this way, calcium looping process, one of the most competitive post-combustion CO<sub>2</sub> capture technology.

# Bibliography

- [1] "SLC Geog Blog," St Lawrence College, 2014. [Online]. Available: <http://geographyslc.wordpress.com/2014/02/21/gr-8-the-enhanced-greenhouse-effect/>. [Accessed 21 February 2014].
- [2] "Advancing the Science of Climate Change, Report in brief, America's Climate Choices," The National Academy of Sciences, 2010.
- [3] EPA. [Online]. Available: <http://www.epa.gov/climatechange/Downloads/ghgemissions/07ES.pdf>.
- [4] (PBL), Jos G.J. Olivier; (IES-JRC), Greet Janssens-Maenhout; (IES-JRC), Marilena Muntean; (PBL), Jeroen A.H.W. Peters, "Trends in global CO2 emissions: 2013 Report," PBL Netherlands Environmental Assessment Agency, The Hague, 2013.
- [5] Vanek Francis M., Albright Louis D., "Energy Systems Engineering, Evaluation & Implementation," McGraw-Hill Companies, 2008, pp. 77-78.
- [6] "United Nations Framework Convention on Climate Change," [Online]. Available: [http://unfccc.int/kyoto\\_protocol/items/3145.php](http://unfccc.int/kyoto_protocol/items/3145.php).
- [7] Mauna Loa Observatory, Hawaii, Scripps Institution of Oceanography, [Online]. Available: <http://www.washingtonpost.com/blogs/capital-weather-gang/wp/2013/05/10/atmospheric-carbon-dioxide-concentration-400-parts-per-million/>.
- [8] IEA, "World energy outlook 2013, executive summary," OECD/IEA, Paris, 2013. [Online]. Available: [http://www.iea.org/publications/freepublications/publication/WEO2013\\_Executive\\_Summary\\_English.pdf](http://www.iea.org/publications/freepublications/publication/WEO2013_Executive_Summary_English.pdf).
- [9] "Shell Energy Scenarios to 2050," 2008. [Online]. Available: <http://s00.static-shell.com/content/dam/shell/static/future-energy/downloads/shell-scenarios/shell-energy-scenarios2050.pdf>.
- [10] IEA, "World energy outlook 2013 Factsheet," OECD/IEA, Paris, 2013. [Online]. Available: [http://www.iea.org/media/files/WEO2013\\_factsheets.pdf](http://www.iea.org/media/files/WEO2013_factsheets.pdf).
- [11] "CO2 emissions from fuel combustion, Highlights (2013 Edition)," OECD/IEA, Paris, 2013. [Online]. Available:

<http://www.iea.org/publications/freepublications/publication/co2emissionsfromfuelcombustionhighlights2013.pdf>.

- [12] IEA, "Key world energy statistics," OECD/IEA, Paris, 2011. [Online]. Available: [http://www.iea.org/publications/freepublications/publication/key\\_world\\_energy\\_stats-1.pdf](http://www.iea.org/publications/freepublications/publication/key_world_energy_stats-1.pdf).
- [13] BP, "BP Statistical Review of World Energy," 2014. [Online]. Available: <http://www.bp.com/content/dam/bp/pdf/Energy-economics/statistical-review-2014/BP-statistical-review-of-world-energy-2014-full-report.pdf>.
- [14] IEA, "Key World Energy STATISTICS," OECD/IEA, Paris, 2013. [Online]. Available: <http://www.iea.org/publications/freepublications/publication/KeyWorld2013.pdf>.
- [15] IEA, "International Energy Agency," OECD/IEA, 2014. [Online]. Available: <http://www.iea.org/stats/WebGraphs/EU282.pdf>.
- [16] Georgios Maroulis, Raffaele Piria, Edoardo Binda Zane (eclareon), Rebekka Frank, Dierk Bauknecht (Öko-Institut), "Integration of electricity from renewables to the electricity grid and to the electricity market – RES-INTEGRATION, National report: Greece," Berlin, 2011.
- [17] Council, World Energy, "World Energy Resources: Coal," 2013. [Online]. Available: [http://www.worldenergy.org/wp-content/uploads/2013/10/WER\\_2013\\_1\\_Coal.pdf](http://www.worldenergy.org/wp-content/uploads/2013/10/WER_2013_1_Coal.pdf).
- [18] Chalvatzis K.J., Spyropoulos G.C., Kaldellis J.K., "The contribution of the Greek electricity," in *Protection and restoration of the environment VII*, Mykonos, 2004.
- [19] Kaldellis J.K., Zafirakis D., Kondili E., "Contribution of lignite in the Greek electricity generation: Review and future prospects," *Fuel*, vol. 88, pp. 475-489, 2009.
- [20] Kaldellis J.K., Spyropoulos G., Chalvatzis K.J., "The impact of Greek electricity generation sector on the national air pollution problem," *Fresen Environ Bull*, vol. 13, pp. 647-56, 2004.
- [21] Kaldellis J.K., Voutsinas M., Paliatsos A.G., Koronakis P.S., "Temporal evolution of the sulfur oxides emissions from Greek electricity generation sector.," *J Environ Technol*, vol. 25, pp. 1371-84, 2004.
- [22] VGB Working Panel, "CO2 Capture and Storage. VGB Report on the State of the Art," VGB PowerTech e.V., Essen, 2004.

- [23] "Bloomberg," [Online]. Available: <http://www.bloomberg.com/energy/>. [Accessed 07 2014].
- [24] Tigas K.,Yannakidis G.,Damasiotis M.,Siakkis,F.,Vassos S., Kiliyas V., "Analysis of the greek electricity generation system in view of the Kyoto target," in *Technical chamber of Greece*, Athens,Greece, 9-10 June 2005.
- [25] Kaldellis J.K.,Zafirakis D.,Kondili E., "Contribution of lignite in the Greek electricity generation:Review and future prospects," *Fuel*, vol. 88, pp. 475-489, 2009.
- [26] Foner H.A.,Robl T.A., Hower J.C., Graham U.M., "Characterization of fly ash from Israel with reference to its possible utilization," *Fuel*, vol. 78, pp. 215-23, 1999.
- [27] Lalasidis G., "Lignites of drama and socioeconomic development," in *National conference for the lignite and natural gas in the national electricity generation.Technical chamber of Greece*, Athens,Greece, 9–10 June 2005.
- [28] Florin N.H., Fennell P.S., "Briefing paper No. 3," Imperial College London, Grantham Institute for Climate Change, November 2010.
- [29] Intergovernmental Panel on Climate Change, "IPCC Special Report on Carbon Dioxide Capture and Storage," Cambridge University Press, New York, 2005.
- [30] IEA, "Energy technology perspectives 2008.Scenarios and strategies to 2050," OECD/IEA, Paris, 2008.
- [31] IEA, "World Energy Outlook 2012," OECD/IEA, Paris, 2012.
- [32] DTI International Technology Service Mission to the USA and Canada, "Carbon Dioxide Capture and Storage," Advanced Power Generation Technology Forum, 2003.
- [33] IEA GHG, "CO2 Capture in the Cement Industry,," IEA Greenhouse Gas R&D Programme, 2008.
- [34] UNIDO, "Global Technology Roadmap for CCS in Industry,In:Sectoral Assessment:Cement," Mott MacDonald,United Nations Industrial Development Organization, 2010.
- [35] Folger Peter,Specialist in Energy and Natural Resources Policy, "Carbon Capture: A Technology Assessment," Congressional Research Service, 2013.
- [36] Anthony E.J., "Solid looping cycles: a new technology for coal conversion," *Ind.*

*Eng. Chem. Res.*, vol. 47, pp. 1747-1754, 2008.

- [37] Curran G., Fink C., Gorin E., "CO<sub>2</sub> acceptor gasification process studies of acceptor properties.," *Fuel Gasification. Advances in Chemistry. American Chemical Society*, vol. 69, pp. 141-65[chapter10], 1967.
- [38] H. A. and T. H., "Process for removing carbon dioxide regeneratively from gas streams". Patent PCTWO94/01203, 1994.
- [39] Alanso, M; Rodriguez, N; Gonzalez, B; Grasa, G; Murillo, R; Abanades, JC, "CO<sub>2</sub> capture from combustion flue gases with a calcium oxide chemical loop," *Intl. Journal of Greenhouse Gas Control*, vol. 4, no. Special Issue 2, pp. 167-173, 2010.
- [40] Ströle J., Galloy A., Epple B., "Feasibility study on carbonate looping process for post-combustion CO<sub>2</sub> capture from coal-fired power plants.," *Energy Procedia*, vol. 1, no. 1, pp. 1313-1320, 2009.
- [41] Sánchez-Biezma A., Ballesteros J.C., Diaz L., de Zárraga E., Álvarez F.J., López J., Arias B., Grasa G., Abanades J.C., "Postcombustion CO<sub>2</sub> capture with CaO. Status of the technology and next steps towards large scale demonstration".
- [42] Abanades J. C., Rubin E. S., Anthony E. J., "Sorbent cost and performance in CO<sub>2</sub> capture systems.," *Ind. Eng. Chem. Res.*, no. 43, pp. 3462-3466, 2004.
- [43] Charitos A., Hawthorne C., Bidwe A.R., Sivalingam S., Schuster A., Spliethoff H., Scheffknecht G., "Parametric investigation of the calcium looping process for CO<sub>2</sub> capture in a 10kWth dual fluidized bed.," *International Journal of Greenhouse Gas Control*, no. doi: 10.1016/j.ijggc.2010.04.009., 2010.
- [44] Lu D.Y., Hughes R.W., Anthony E.J., "Ca-based sorbent looping combustion for CO<sub>2</sub> capture in pilot-scale dual fluidized beds.," *Fuel Processing Technology*., no. 89, pp. 1386-1395, 2008.
- [45] Romeo L.M., Abanades J.C., Escosa J.M., Paño J., Giménez A., Sánchez-Biezma A., Ballesteros J.C., "Oxyfuel carbonation/calcination cycle for low cost CO<sub>2</sub> capture in existing power plants," *Energy Conversion and Management*, no. 49(10), pp. 2809-2814, 2008.
- [46] Abanades J.C., Alonso M., Rodriguez N., Gonzalez B., Fuentes F., Grasa G. and Murillo R., "Capture of CO<sub>2</sub> from flue gases with CaO: results from a 30 kW interconnected fluidized bed facility. In-Situ Carbon Removal.," Imperial College, London, 2008.



- [47] Hawthorne C., Charitos A., Perez-Pulido C.A., Bing Z., Scheffknecht G., "Design of a dual fluidised bed system for the post-combustion removal of CO<sub>2</sub> using CaO. Part I: CFB carbonator reactor model.," in *9th International Conference on Circulating Fluidized Beds.*, Hamburg, Germany, 2008.
- [48] Charitos A., Hawthorne C., Bidwe A., He L., Scheffknecht G., "Design of a dual fluidised bed system for the post-combustion removal of CO<sub>2</sub> using CaO. Part II: scaled cold model investigation.," in *9th International Conference on Circulating Fluidized Beds.*, Hamburg, Germany., 2008.
- [49] Masek O., Bosoaga A., Oakey J., "Progress in Ca-based CO<sub>2</sub> Capture Research at Cranfield University. In-Situ Carbon Removal 4.," Imperial College, London, 2008.
- [50] European Commission, "Periodic Report Summary - CAOLING (Development of postcombustion CO<sub>2</sub> capture with CaO in a large testing facility: "CaOling")," ENDESA GENERACION SA, R&D Unit, Madrid, Spain, 2014.
- [51] F. L.S., G.-d. A. and M. S., "Calcium carbonate sorbent and methods of making and using same." USA Patent US Patent Application 08/584089, 1998.
- [52] Röder A., "CEMEX– Climate Change Strategy and CCS.in Innovation and Investment Opportunities in Carbon Capture and Storage," Imperial College, London, UK., 2008.
- [53] ISO, "ISO 14040:2006 Environmental Management-Life Cycle Assessment - Principles and Framework," International Organization for Standardization, Geneva, 2006.
- [54] Hurst T., Cockerill T., Florin N., "Life cycle greenhouse gas assessment of a coal-fired power station with calcium looping CO<sub>2</sub> capture and offshore geological storage," *Energy & Environmental Science*, no. 5, pp. 7132-7150, 2012.
- [55] Singh D., Croiset E., Douglas P., Douglas M., "Technoeconomic study of CO<sub>2</sub> capture from an existing coal-fired power plant: MEA scrubbing vs. O<sub>2</sub>/CO<sub>2</sub> recycle combustion.," *Energy Convers. Manage.*, no. 44, pp. 3073-3091, 2003.
- [56] Chapel D., Ernst J., Mariz C., "Recovery of CO<sub>2</sub> from flue gases: commercial trends.," *Can. Soc. Chem. Eng.*, 1999.
- [57] Rao A.B., Rubin E.S., "A technical, economic and environmental assessment of amine-based CO<sub>2</sub> capture technology for power plant greenhouse gas control.," *Environ. Sci. Technol.* , no. 36, pp. 4467-4475, 2002.

- [58] Koornneef J., Van Keulen T., Faaij A., Turkenburg W., "Life cycle assessment of a pulverized coal power plant with post-combustion capture, transport and storage of CO<sub>2</sub>," *International Journal of Greenhouse Gas Control*, pp. IJGGC-117, 2008.
- [59] Shimizu T., Hiramata T., Hosoda H., Kitano, K., Inagaki M., Tejima K., "A twin fluid-bed reactor for removal of CO<sub>2</sub> from combustion processes.," *Transactions of the Institute of Chemical Engineers.*, vol. 77, pp. 62-68, 1999.
- [60] Abanades J.C., Anthony E.J., Wang J., Oakey J.E., "Fluidized bed combustion systems integrating CO<sub>2</sub> capture with CaO.," *Environmental Science and Technology*, no. 39(8), pp. 2861-2866, 2005.
- [61] Romeo L.M., Uson S., Valero A., Escosa J.M. , "Exergy analysis as a tool for the integration of very complex energy systems: the case of carbonation/calcination CO<sub>2</sub> systems in existing coal power plants.," *Int J Greenhouse Gas Control*, no. 4, pp. 647-654, 2010.
- [62] Romeo L.M., Lara Y., Lisbona P., Escosa J.M., "Optimizing make-up flow in a CO<sub>2</sub> capture system using CaO," *Chem Eng J*, no. 147, pp. 252-258, 2009.
- [63] Vorrias I., Atsonios K., Nikolopoulos A., Nikolopoulos N., Grammelis P., Kakaras E., "Calcium looping for CO<sub>2</sub> capture from a lignite fired power plant," *Fuel*, pp. 826-236, 2013.
- [64] "Ecoinvent v2.0," Swiss Centre for Life Cycle Inventories , Dubendorf, 2007.
- [65] PRé Consultants, "SimaPro 7.3.3 Multi user".
- [66] Universiteit Leiden, Institute of Environmental Science (CML) , "CML-IA Characterisation Factors".
- [67] [Online]. Available: <http://www.simapro.co.uk/simapro8flyer.pdf>.
- [68] Spath L. Pamela, Mann K. Margaret, Kerr R. Dawn, "Life Cycle Assessment of Coal-fired Power Production," NREL, National Renewable Energy Laboratory, Colorado, 1999.
- [69] [Online]. Available: <http://www.CO2CRC.com>.
- [70] IEA, "Environmental evaluation of CCS using life cycle assessment (LCA)," IEA Greenhouse Gas R&D Programme, 2010/TR2, May 2010. [Online].
- [71] Frischknecht R., Jungbluth N., "Ecoinvent Overview and Methodology Data v2.0,"

Swiss Centre for Life Cycle Inventories, Dubendorf, 2007.

- [72] Guinée J.B.,Corrée M.,Heijungs R.,Huppes G.,Kleijn R.,Koning A.,de Oers L.,van Wegener Sleeswijk A.,Suh S.,Udo de Haes H.A.,Bruijn H.,de Duin R.,van Huijbregts M.A.J., Handbook on Life Cycle Assessment: Operational Guide to the ISO Standards., Dordrecht: Kluwer academic Publishers, 2002.
- [73] "European best practice guidelines for assessment of CO2 capture technologies.," CAESAR D 4.9 Report.
- [74] Kakaras E., Koumanakos A., Doukelis A., "Greek Lignite-Fired Power Plants with CO2 Capture for the Electricity Generation Sector," *CHEMICAL ENGINEERING TRANSACTIONS*, 2013.
- [75] MIT, Future of Coal – Options for a carbon-constrained world., Massachusetts (USA): Massachusetts Institute of Technology, 2007.
- [76] IEA GHG, "Environmental impact of solvent scrubbing of CO2," TNO Science and Industry,IEA Greenhouse Gas R&D Programme,2006/14, 2006.
- [77] Strömberg L., "ENCAP Integrated Project," in *Seminar in Billund, Denmark*, 2006.
- [78] Martínez I., Murillo R., Grasa G., Abanades J. C., "Integration of a Ca looping system for CO2 capture in existing power plants," *AIChE Journal* , no. 57(9), pp. 2599-2607, 2011.
- [79] Blamey J.,Anthony E.J.,Wang J.,Fennell P.S., "The calcium looping cycle for large-scale Co2 capture," *Prog. Energy Combust. Sci.*, no. 36, pp. 260-279, 2010.
- [80] Dean C.,Blamey J.,Florin N.,Al-Jeboori M.,Fennel P., *Chem. Eng. Res. Des.*, no. 89, pp. 836-855, 2011.
- [81] Grasa G.,Abanades J., "CO2 capture capacity of CaO in long series of carbonation/calcination cycles," *Ind. Eng. Chem. Res.*, no. 45(26), pp. 8846-8851, 2006.
- [82] Rodriguez N.,Alonso M.,Graca G.,Abanades J.C., "Process for capturing CO2 arising from the calcination of the CaCO3 used in cement manufacture.," *Environ. Sci. Technol.*, no. 42, pp. 6980-6984, 2008.
- [83] Zhen-shan Li.,Ning-sheng Cai.,Croiset E., "Process analysis of CO2 capture from flue gas using carbonation/calcination cycles," *AIChE J.*, no. 54, pp. 1912-1925, 2008.

- [84] Pehnt M., Henkel J., "Life cycle assessment of carbon dioxide capture and storage from lignite power plants," *Int. Greenhouse Gas Contr.*, no. 3, pp. 49-66, 2009.
- [85] Chapel D.G., Mariz C.L., Ernest J., "Recovery of CO<sub>2</sub> from flue gases: commercial trends," Proceedings of the Canadian Society of Chemical Engineers Annual Meeting, Saskatoon, Saskatchewan, 1999.
- [86] Nie Z., "Life cycle modeling of carbon dioxide capture and geological storage in energy production," PhD thesis Imperial College London, 2009.
- [87] Van Zelm R., Huijbregts M., den Hollander ., van Jaarsveld H., Sauter F., Struijs J., van Wijnen H., van de Meent D., "European characterization factors for human health damage of PM<sub>10</sub> and ozone in life cycle impact assessment.," *Atmos. Environ.*, vol. 42, pp. 441-453, 2008.