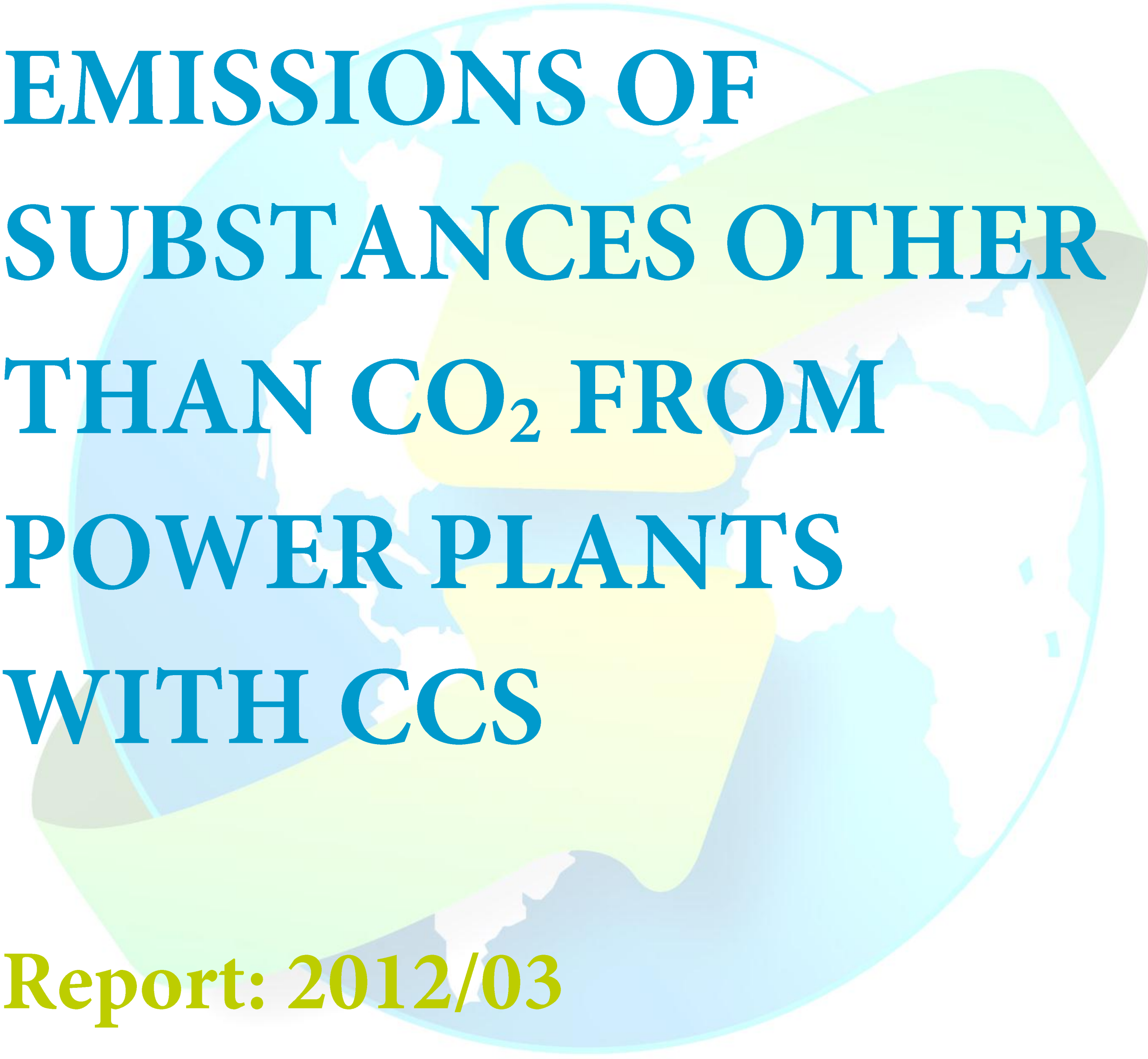
ieaghg

Evaluating technology options to mitigate greenhouse gas emissions



EMISSIONS OF SUBSTANCES OTHER THAN CO_2 FROM POWER PLANTS WITH CCS

Report: 2012/03

March 2012

INTERNATIONAL ENERGY AGENCY

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 28 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. IEAGHG is one of these Implementing Agreements.

DISCLAIMER

This report was prepared as an account of the work sponsored by IEAGHG. The views and opinions of the authors expressed herein do not necessarily reflect those of the IEAGHG, its members, the International Energy Agency, the organisations listed below, nor any employee or persons acting on behalf of any of them. In addition, none of these make any warranty, express or implied, assumes any liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product of process disclosed or represents that its use would not infringe privately owned rights, including any parties intellectual property rights. Reference herein to any commercial product, process, service or trade name, trade mark or manufacturer does not necessarily constitute or imply any endorsement, recommendation or any favouring of such products.

COPYRIGHT

ACKNOWLEDGEMENTS AND CITATIONS

This report describes research sponsored by IEAGHG. This report was prepared by:

TNO, The Netherlands

The principal researchers were:

- Eva Sanchez Fernadez (TNO)
- Earl L V Goetheer (TNO)
- Magdalena Juzwicka (TNO)
- Toon van Harmelen (TNO)
- Arjan van Horssen (TNO)

To ensure the quality and technical integrity of the research undertaken by IEAGHG each study is managed by an appointed IEAGHG manager. The report is also reviewed by a panel of independent technical experts before its release.

The IEAGHG manager for this report was:

M R Haines and Mohammad Abu Zahra

The expert reviewers for this report were:

• Dr Paitoon Tontiwachwuthikul	University of Regina
• Andrea Ramirez	University of Utrecht
• Anna Korre	ICL
• Joris Korneef	Ecofys
• Paul Feron	CSIRO

The report should be cited in literature as follows:

'IEAGHG, "Emissions of substances other than CO_2 from power plants with CCS", 2012/03, March, 2012.'

Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre,
Stoke Orchard, Cheltenham,
GLOS., GL52 7RZ, UK
Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758
E-mail: mail@ieaghg.org
Internet: www.ieaghg.org

EMISSIONS OF SUBSTANCES OTHER THAN CO_2 FROM POWER PLANTS WITH CCS

Introduction

The emissions of CO_2 from power plants equipped with carbon dioxide capture systems are reduced by upwards of 85% compared to equivalent plants without capture. However the full environmental impact of a plant fitted with CO_2 capture will depend also on what changes are induced in emissions of other substances in gaseous, liquid and solid form. Furthermore due to the increase in fuel and chemicals consumption typical for a CCS plant emissions due to the “upstream” and “downstream” processes and particularly those associated with increased fuel use, will also increase. Both these effects need to be taken into account if the technology is to be assessed on a life cycle basis. This study focuses only on the changes which are to be expected in the direct emissions, discharges and solid wastes of substances other than CO_2 from within the boundary of power plants fitted with CO_2 capture.

Approach

The study was awarded to TNO, The Netherlands on the basis of competitive tender. The assessment covers the main technologies for CO_2 capture for coal and natural gas fired systems and includes the three main technology routes of post, pre and oxy combustion. Estimation of emissions and wastes is complex and accurate prediction of the amounts and composition of some categories of waste at the design stage is not possible. Hence TNO adopted two approaches in making their estimations. The first was to base estimates on the literature references which include both theoretical predictions and actual measurements from pilot, demonstration and commercial units. The second approach was to use modeling to come up with an estimate of emissions and wastes. The results would thus show the degree of variation and hence indicate areas of uncertainty and would also by comparison of the two approaches indicate where undue optimism or pessimism might prevail in the modeling methods being used for design of CCS plants. The modeling approach also relies on data extracted from literature, typically for estimating the removal efficiency of the unit operations employed in CCS. A clear distinction is made between these two approachs. The literature based approach is taking plant emission values as reported in literature. The modeling synthesizes the values for each of the selected processes based on estimates of the performance of the various unit operations which make up the complete power plant.

A part of the literature based estimation was to make appropriate allowances for variations in baseline assumptions for the various plants in the references. This “harmonization” methodology was applied to take account of variations in sulphur content of coals and the percentage capture of CO_2 where solvent based absorption processes were applied. This process thus attempts to ensure that “like for like” situations are being compared. All the raw and harmonized data from the literature was assembled in a database which was used to make statistical estimations of the most likely changes in emissions and wastes and also the ranges which could be expected.

Results and discussion

General

Baseline data was collected for three types of power plant without capture:-

- an Ultra Supercritical (USC) Pulverized Coal (PC) fired steam plant,
- a coal fired integrated gasification and combined cycle power plant (IGCC)
- a natural gas fired combined cycle power plant (NGCC).

Data for 4 CCS plants for comparison with these baselines was collected for:-

- a USC PC plant with post combustion capture using an MEA solvent,
- an oxyfueled USC PC plant using the CO_2 separation and clean up process of Air Products,
- an IGCC plant adapted for CO_2 capture using Selexol to recover the CO_2
- an NGCC plant fitted with post combustion capture again using an MEA solvent.

A total of 37 references were found in the literature and these were used to populate a database of 176 different cases. However complete datasets could not be generated for all of these cases as the amount of information varied quite widely. This data formed the basis for estimation of emissions using the harmonization approach. It is thus expected to yield “average” values based on current experience. The range of values will also give some indication of the best and worst which might be expected and hence also represents the full range of technologies.

In contrast the modelling method of estimation used a design approach to estimating emissions and for this the researchers chose generally to model “Best Available Technology” (BAT). In practice they have chosen, what is considered to be state of the art versions of processes, which are considered to be economically applicable and thus may have not have explored the extremes of possible performance. Hence it may be more accurate to describe the choice as Best Available Technology Not Entailing Excessive Cost (BATNEEC)

The results of the analysis finally allow comparison of emissions and wastes against baseline for 4 technologies.

Coal fired USC Post and oxy-combustion against coal fired USC
Pre-combustion IGCC against conventional IGCC
Post combustion NGCC against conventional NGCC

For the coal fired plants with and without post combustion the baseline the plants included SOx control using wet limestone flue gas desulphurization and NOx emissions control using overfire air, lowNOx burners and Selective Catalystic Reduction (SCR). For the NGCC cases low NOx burners and SCR were included.

The emissions and wastes which are compared include (where data is available)

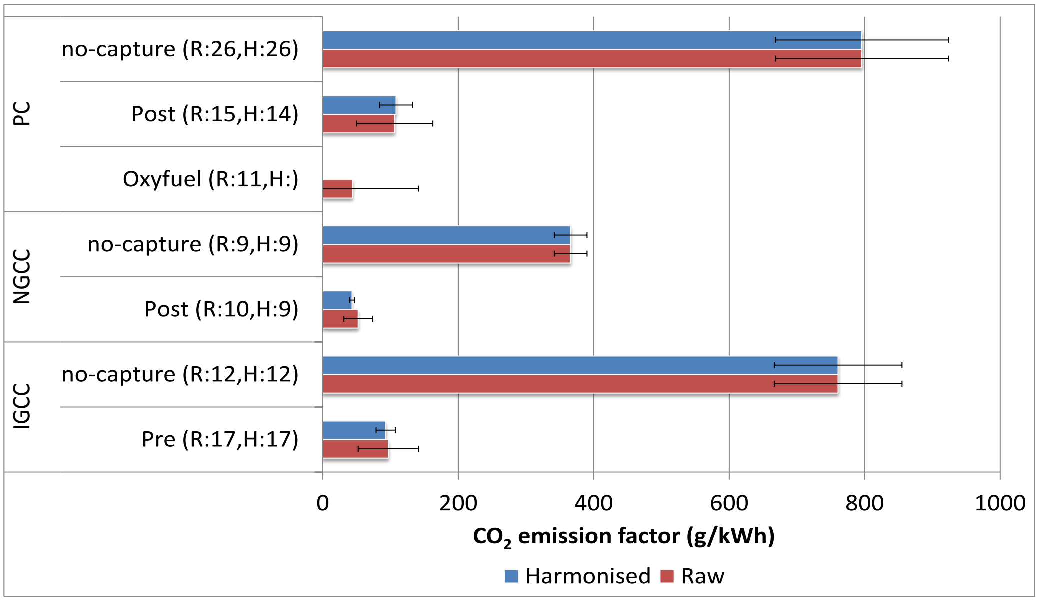
Gaseous emissions
- Acid gases
    - CO_2
    - SOx (Broken down to SO_2 and SO_3)
    - NOx (Broken down in to NO and NO_2)
    - HCL
    - HF
    - CO
- Trace elements
    - Mercury (Hg^0,Hg^{2+},Hg(p))
    - Trace metals (As,Cd,Cr,Co,Pb,MN,Ni,Se,Zn,Cu and by class 1,2 3)
- Other compounds
    - Ammonia
    - Chemical degradation products (NB subject of separate report)
    - VOC's
- Particulates
    - PM
    - PM_{10}

Solid and liquid waste categories.
- Gypsum
- Particulates from ESP
- Furnace bottom ash/
- Coarse slag
- Fly ash /
- Fine slag
- Mill rejects
- Sludges from WWT
- Reclaimer waste
- Activated carbon
- Waste water

Assessment results for each type of emission

CO_2 emissions

The chart below summarises the emissions levels of CO_2 found from the literature and shows the raw as well as harmonized data. The red bar shows the average of the raw data and the blue bar the average after harmonisation

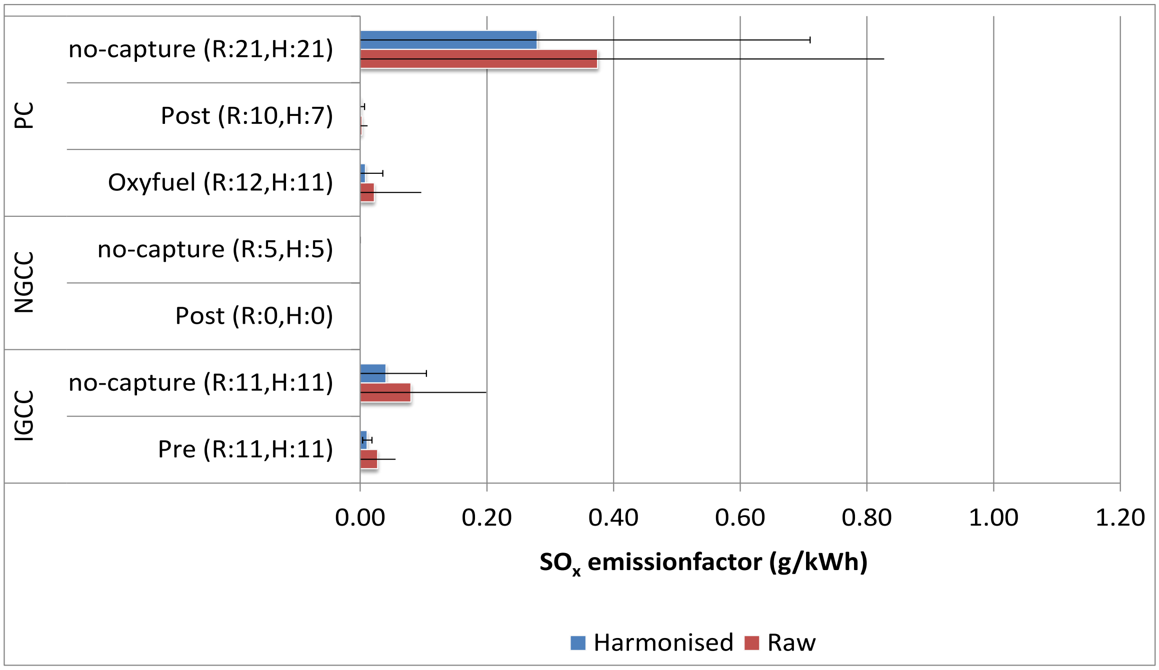


Harmonised v Raw CO2 emission factors in g/kWh net electricity produced

The black lines indicate the range of data upon which the average is based. It is noticeable that the harmonization process reduces the spread of data for the capture cases considerably. This indicates that the variations in capture rate and fuel sulphur content for which compensation was applied did indeed widen the range of reported emissions.

Acid gas emissions other than CO_2

Both the reference data base and the modeling method suggest almost complete elimination of gaseous sulphur compound emissions as a result of adding either post or oxy combustion CCS to pulverised coal steam power plant. IGCC has only modeling results which suggest a reduction of only about 85% although in principle the sulphur recovery plant responsible for the emissions can be designed to reduce them further. Also for the case of NGCC only modeling results are available. Sulphur emissions of the base case are already very low because of the low sulphur content of natural gas. The model shows virtually all sulphur emissions eliminated. The chart below illustrates the results from the harmonization assessment. Note the rather wide range of sulphur emissions reported in the literature from plants without capture.

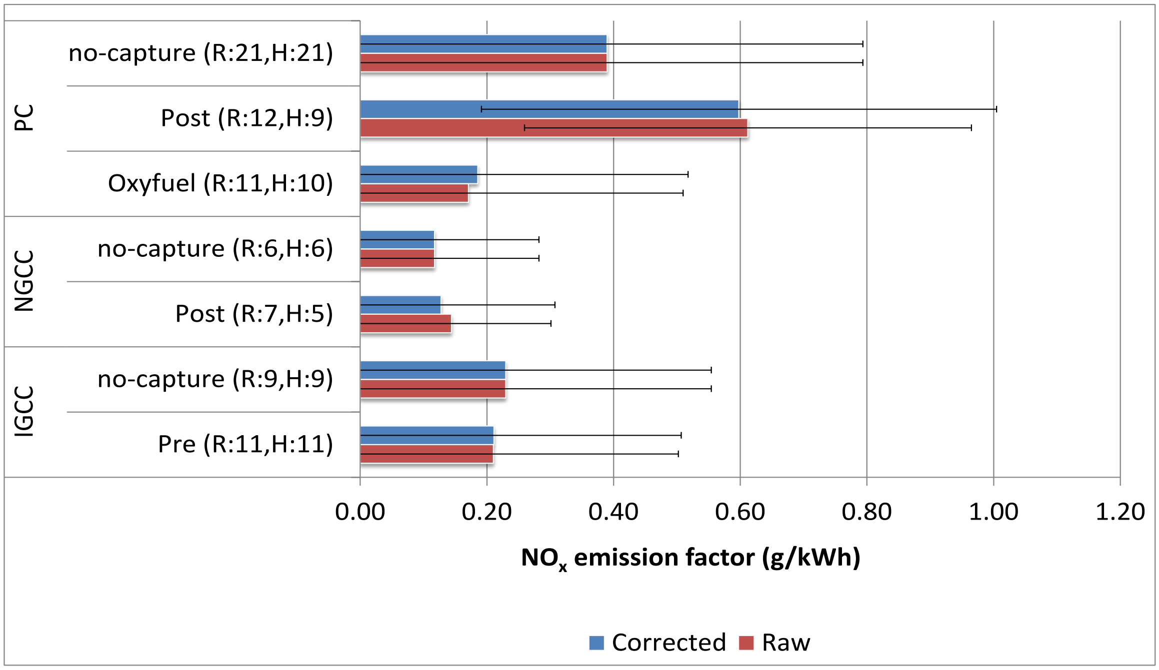


Harmonised v Raw SOx emissions as g/kWh net electricity produced

Nitrogen oxides consist mainly of NO with some N_2O. Both reference data and models suggest that NO will not be removed by addition of post combustion CCS and thus NOx emissions are expected to increase slightly roughly in proportion to the increased fuel use. Average values from the literature show an increase somewhat in excess of this. No explanation was found for this result. Modelling suggests that some N_2O will be removed by the absorption unit but as most of the NOx is in the form of NO there will be an overall increase.

No references were found for IGCC NOx emissions but modeling suggests no significant change. The emissions are solely due to NOx formed in the gas turbine. Fuel efficiency is reduced which would lead to increased emissions. The modelling is thus assuming some advances in NOx control for hydrogen burning as distinct to syngas burning gas turbines which may or may not materialize. Likewise NOx emissions were not evaluated for Oxy-combustion. Expert reviewers are expecting up to 99% destruction of Nitrogen oxides in the reactors of the clean up process. However any NO which passes into the cryogenic separation section will partition into the inerts vent stream and thus be emitted.

For oxy combustion modeling currently suggests that NOx emissions will be eliminated. However the literature shows wide variation and suggests only a partial reduction. The oxy combustion CO_2 clean up process has undergone rapid development in the last few years. The harmonized reference data is using averages and the data shows variations from complete to limited reduction. In this case the modeling result is probably more reliable. The chart below shows the harmonization results based on literature references. Notice the NOx figures for oxycombustion do not reflect the current expectations of very low levels.



Harmonised v Raw NOx emissions as g/kWh net electricity produced

HCl, HF and CO emissions reductions were considered only through modeling and only for coal fired USC PC steam systems. The strongly acidic components HCl and HF are predicted to be reduced by 95% in the case of post combustion and to be completely eliminated in oxy combustion CCS systems. CO is not expected to be absorbed in post combustion. The report gives no evaluation of the CO emissions from oxycombustion. However expert reviewers suggest that two light gases CO and NO will partition into the vent stream in the cold CO_2 clean up process and thus CO emissions will remain roughly the same perhaps increasing due to the additional fuel usage. However experts also suggest that by including a catalyst in the vent stream after it has been heated prior to expansion down to atmospheric pressure any remaining CO might be oxidized.

The study shows CO emissions from IGCC with and without CCS as virtually the same based on literature reference. However given that in CCS nearly all CO is removed expert reviewers questioned this.

Trace elements

Trace elements usually encountered are the metals Hg,As,Cd,Cr,Co,Pb,Mn,Ni,Se, Sb,Zn,Cu.These are divided into three classes according to the way they tend to partition between gaseous emission and solid waste. Hg and Se are considered volatile and fall into Class 3. As, Cd, Sb and Pb are semi-volatile falling into Class 2 and the rest are considered non volatile and fall into Class 1.

Information on the removal of these components by the CCS processes is limited. For those CCS systems which pass flue gas through a solvent system a conservative assumption that only 20% of classes 1 and 2 would be removed has been made. This is roughly equivalent to the increased fuel usage so that trace metal emissions in these classes would be unchanged. However given that these materials tend to partition to the solid phase it might be expected that the additional contacting in absorber columns and direct contact coolers might make bigger reductions. In order to verify this it will be necessary to make measurements of these components in flue gases from CCS plants.

The effect of MEA scrubbing on mercury depends on the oxidation state. There is evidence that Hg^{2+} is absorbed in MEA and in modeling a removal of 76% has been assumed. Elemental mercury is not chemically absorbed in MEA solutions and a low reduction factor of only 8% has been assumed in the modeling for this study. Since about ¾ of the mercury is typically present as elemental mercury there is only a small reduction in emission concentration in the absorber which will be offset by the increased flow. Again more accurate measurements of emissions and build up in the solvent are needed to determine the partition effect.

Particulate Matter

Particulate matter is reduced by several processes within power plants. The final reductions are mainly achieved in the Electrostatic Precipitator (ESP) if fitted and the Flue Gas Desulphurisation unit (FGD) if fitted. Without these units reliance is placed on drop out in the boiler at various points and removal by filtration. The literature gives a confusing view of how particulate emissions will be affected suggesting an increase whereas modeling assumes that where an absorption unit or direct contact cooler provides additional liquid gas contacting a reduction of 50% of particulates would occur. Thus even allowing for the increased fuel use there should be a net reduction in particulate emissions. The increased particulate emission levels for CCS processes reported in the literature thus need to be treated with caution as no explanation for the increase is forthcoming. There is thus a need to better understand why the literature results are an average higher and also for a better measurement of the effect of additional gas liquid contacting equipment on particulate emissions. Oxy-combustion should exhibit zero particulate emissions since the only remaining gaseous stream is a small flow of inerts from the CO_2 clean up unit which is unlikely to contain particulates as it will have passed through several gas liquid contacts in the clean up reactors and the cold box. Literature also shows almost but not quite complete elimination of particulate emissions from oxy-combustion plants.

Other substances

Ammonia is emitted from plants without capture if SCR is installed and there is any ammonia slippage. The harmonized data shows a small average ammonia emission for pulverised coal plants without capture. The data for NGCC plants without capture suggests very low average levels probably because it is less common to add SCR to such plants. Ammonia is a volatile degradation product of plants using MEA (and also for plants using other amines). The literature thus suggests a substantial increase in

Ammonia emissions from Coal fired USC CCS plants. No data is available for NGCC plants with post combustion capture but similar effects could be expected. Ammonia emissions were not estimated by modeling and this and other MEA degradation products is being addressed in a separate IEAGHG study on chemical emissions from post combustion capture plants. Ammonia emission from IGCC plant were not evaluated but expert reviewers suggest that these are absent since they are already removed upstream of the acid gas removal system in the wet scrubbing system of such plants.

Assessment results for each type of solid and liquid waste

For the coal fired cases the amount of solid waste increases more or less in line with the increased fuel usage. Sludge from waste water treatment increases similarly. Gypsum production in the post combustion capture case may increases slightly more than this due to deeper sulphur removal. This depends on whether the FGD is configured to produce lower SOx levels or whether all of the reduction needed to meet Amine scrubbing inlet specifications is achieved by caustic scrubbing or similar. On the other hand there is no gypsum byproduct in oxy-combustion since the SO_2 is removed as Sulphuric acid in solution. NGCC does not produce any ash wastes.

Reclaimer waste and a small amount of spent activated carbon from solvent clean up are two new wastes emanating from post combustion plants fueled either with gas or coal. Oxycombustion plants have to remove mercury using mercury guard beds which may use activated carbon or pre-sulphided adsorbent in order to protect the aluminium cold box in the CO_2 clean up unit.. Thess materials may also have to be used in base line coal and IGCC plants to reduce mercury emissions to meet tightening regulations . However no data on the quantities of this waste bed material is reported in this study.

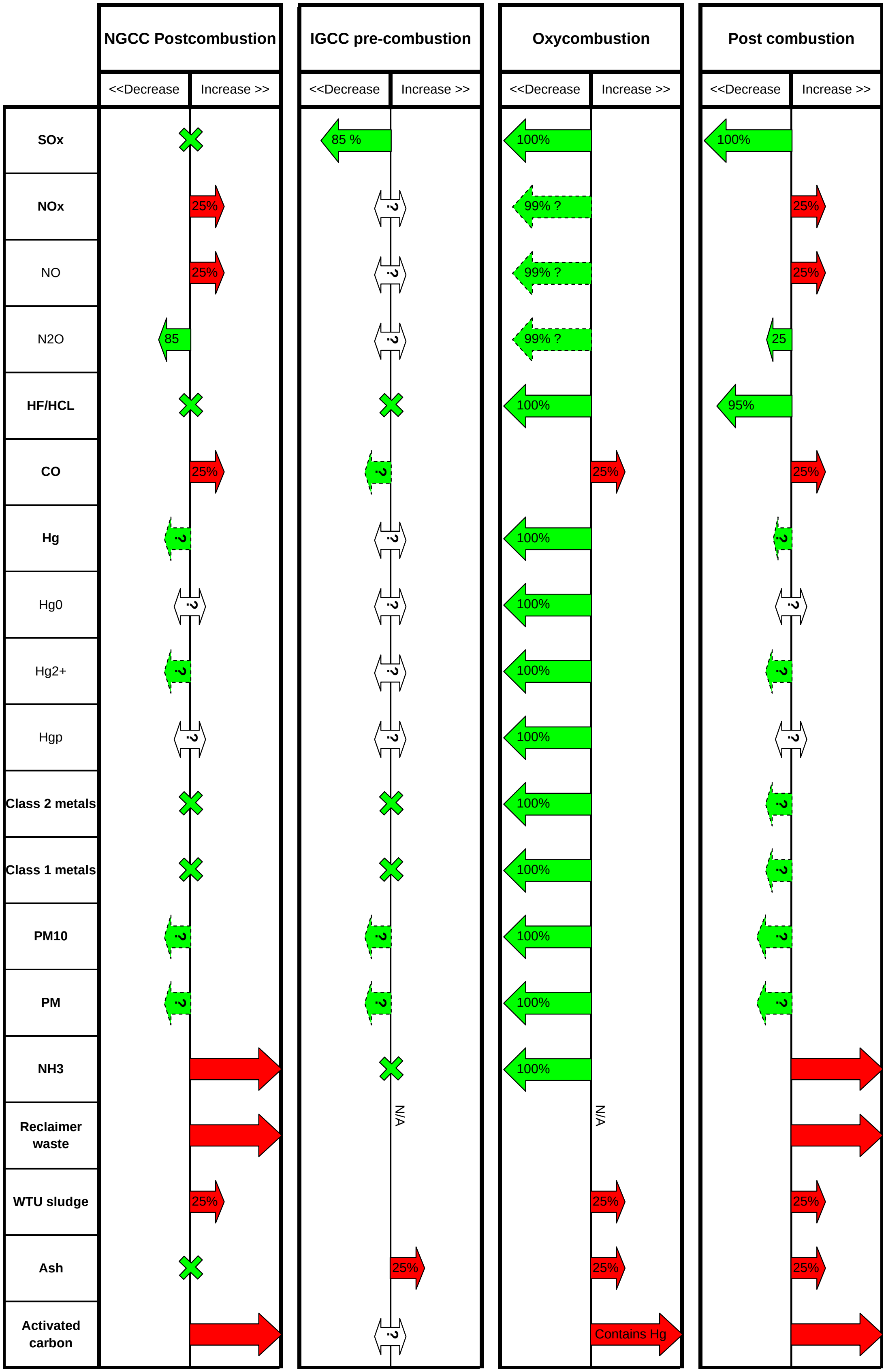
There is a significant increase in the amount of waste water production from post combustion coal plant due to the condensation of water out of the flue gases. No information was included in the study on the waste water streams expected from oxy-combustion. Experts pointed out that oxy-combustion process will produce a waste water stream containing sulphuric and nitric acids along with some mercury. Before discharge this stream will be treated for example by neutralization with caustic soda and for mercury extraction. Development of the clean up process for this stream is ongoing.

Overview of changes

Full details of the expected emission levels evaluated by the two techniques, (modeling and harmonization of figures published in literature) with and without CCS are included in the main report. Set out below in the form of a pictorial chart is an over view of the changes to emissions and wastes which each of the capture technologies will cause when applied to the baseline power plants. The indication is of the ***relative*** magnitude of emissions and wastes and does not indicate the actual size of the emissions. For some categories of emission the baseline plant already has essentially zero emissions and this is indicated by a green cross where this is the case A distinction is made between changes which are certain and those which are not. The arrows indicating the change have a dotted outline/contain a “?” symbol where there is currently uncertainty. Further work is needed to clarify all changes which are shown as uncertain. Most notable is the almost complete elimination of gaseous emission in the oxy-combustion process. Post combustion processes lower most emissions substantially but the exact extent is still subject to uncertainty. However there are small increases in NO and an introduction of a potentially substantial ammonia emission. There are also potentially other chemical emissions which are subject of a separate report. The extent of the ammonia emission is dependent on the additional scrubbing technology which is eventually deployed downstream amine absorbers.

The most notable change in solid/liquid wastes is the appearance of a new liquid waste from post combustion processes in the form of a stream of degraded solvent from the amine reclaimer. For oxy-combustion a new water stream containing sulphates and nitrates possibly containing some mercury is expected to be produced (not shown on the chart). Exactly how benign this stream can be made is not yet known. Ash from all of the coal fired processes increases in line with the increased fuel consumption.

Changes in emissions and wastes when CCS is applied



	NGCC Postcombustion	IGCC pre-combustion	Oxycombustion	Post combustion
	<<Decrease / Increase >>	<<Decrease / Increase >>	<<Decrease / Increase >>	<<Decrease / Increase >>
SOx	✗	← 85 %	← 100%	← 100%
NOx	→ 25%	↔ ?	← 99% ?	→ 25%
NO	→ 25%	↔ ?	← 99% ?	→ 25%
N2O	← 85	↔ ?	← 99% ?	← 25
HF/HCL	✗	✗	← 100%	← 95%
CO	→ 25%	← ?	→ 25%	→ 25%
Hg	← ?	↔ ?	← 100%	← ?
Hg0	↔ ?	↔ ?	← 100%	↔ ?
Hg2+	← ?	↔ ?	← 100%	← ?
Hgp	↔ ?	↔ ?	← 100%	↔ ?
Class 2 metals	✗	✗	← 100%	← ?
Class 1 metals	✗	✗	← 100%	← ?
PM10	← ?	← ?	← 100%	← ?
PM	← ?	← ?	← 100%	← ?
NH3	→	✗	← 100%	→
Reclaimer waste	→	N/A	N/A	→
WTU sludge	→ 25%		→ 25%	→ 25%
Ash	✗	→ 25%	→ 25%	→ 25%
Activated carbon	→	↔ ?	→ Contains Hg	→

Expert reviewer's comments

Reviewers raised a number of questions as to the completeness of the literature survey particularly in respect of data on IGCC and oxy-combustion processes. Some also considered that the treatment of these processes was a lot less thorough than for the pulverized coal plants. Reviewers also felt that there was far more emphasis on gaseous emissions and that the treatment of solid and liquid wastes should be more extensive. Most reviewers recommended improvements to make the study clearer and more easy to read. These comments were taken on board and a revision to address them as far as possible was undertaken.

Some reviewers challenged the method used to harmonise CO_2 capture percentage and the authors modified this in the final version. The Oxy-combustion process has an inherent high capture percentage and was not harmonized on thisattribute. Reviewers also pointed out where figures quoted seemed anomalous or incorrect and the authors reviewed and responded to these challenges in the final report. Some of these issues might be resolved if the authors database was available as part of the report. However their database forms part of their proprietary information and cannot be made generally available.

Some reviewers felt that too much emphasis was given to description of the methodologies rather than comparison of the results and this too was addressed. Despite these criticisms of the draft report most reviewers felt that the report was an extremely valuable synthesis of the available information on the effects of carbon dioxide capture processes on emissions and wastes of substances other than CO_2.

Conclusions

This report goes some way to quantify the changes which CCS will make in emissions and wastes other than CO_2 from power plant. A number of areas of uncertainty are revealed either due to lack of measurements or because processes are not yet fully developed.CCS processes in general offer reductions in gaseous emissions of most components but there are exceptions where small increases can be expected mainly related to increased fuel consumption. However solid and liquid wastes for all the processes show some increases and in some cases changes in nature. .

Recommendations

Further work needs to be done on all those areas flagged in the chart as being in some way uncertain. This work may need to be in the form of many more in depth measurement campaigns on pilot and demonstration capture plants but also some of the processes used to reduce or eliminate unwanted emissions and wastes need further development. Where gaseous emissions are highlighted as potentially increasing, attention needs to be given to the process selection and design to establish whether the increases can be mitigated or reversed. This work will need to be carried out by industry and research institutions and the role of IEAGHG should at present be limited to encouraging this work to be done, published in appropriate journals and presented at conferences and meetings.

Technical Sciences
Leeghwaterstraat 46
2628 CA Delft
P.O. Box 6012
2600 JA Delft
The Netherlands

www.tno.nl

T +31 88 866 22 00
F +31 88 866 06 30
infodesk@tno.nl

TNO report

| Final report

Emissions of Substances other than CO_2 from Power Plants with CCS

Date	20 September 2011
Author(s)	Eva Sanchez Fernandez Earl L.V. Goetheer Magdalena Jozwicka Toon van Harmelen Arjan van Horssen

Copy no	
No. of copies	
Number of pages	106 (incl. appendices)
Number of appendices	7
Sponsor	
Project name	
Project number	

Summary

This report summarizes the emissions and waste assessment performed by TNO on different power plant configurations with and without carbon capture. CO_2 Capture and Storage (CCS) is one of the possible solutions for carbon mitigation in fossil fuel power plants. Before its full demonstration at intermediate scale (by 2015) some aspects of its impact into the environment need to be investigated. IEA GHG has contracted TNO to investigate the effect of CCS on the emissions of substances other than CO_2 also emitted by power plants. There are two aspects that complicate this analysis:

- The scarcity of environmental data in relation to CCS, including data on emissions from solvent degradation products.

- Lack of harmony and/or standardisation and reliability in the existing data. This aspect adds one more difficulty to the comparison of technologies on a reliable basis.

The methodology for waste assessment has followed two approaches:

- Harmonization study: Consists of an statistical analysis of the emissions database created by reviewing the open literature. The emission database was harmonized prior to the assessment, in order to bring into line the reference basis of each data point and the reference basis of the cases under investigation. This is a top-down approach where the relative emissions are given for a specific group of plants and they are corrected for a pre-defined set of parameters that bring into a common line the reference basis.

- Modelling study: For a set of seven reference cases, plant performance and emissions were evaluated either with commercial software packages or with emission factors. The key difference with the harmonization is that the modelling performs a bottom-up approach. Starting with the definition of the different technologies, emissions are estimated based on source specific uncontrolled emission factors and the application of the best performance of emission controls.

Both approaches were used to estimate the emissions for the reference cases. Results from both approaches were collated and analysed for all cases. The double approach taken gives a broader perspective to the estimation of emissions. Harmonization results represent average performance of power plants, while modelling results represent the best performance available with state-of-the art commercial technology.

Harmonization has been found a useful tool for estimating relative emissions in those cases were technology is well established and much information regarding emissions is reported. Nevertheless, for cases that use relatively novel technology and much information is not available, harmonization might lead to results that contradict the expected performance.

On the other hand, modelling has been found the only possibility to cover the uncertainties on the emissions based on novel technology.. However, modelling is constrained to a pre-defined set of cases (mainly using pioneer technology) and does not cover situations of older operating technologies.

The final waste assessment combines the information from the two set of activities, highlights the lacking information and targets several parameters for further sensitivity analysis to cover uncertainties. Finally, the study analyses the consequences of including CCS technologies in state-of-the-art power plants.

Acronyms and abbreviations

SYMBOL	**Definition**
AP	Air pollutant
APC	Air pollutant control Unit
ASU	Air Separation Unit
BACT	Best Available Control Technology
BOLK	*'Beleidsgericht Onderzoeksprogramma Lucht en Klimaat'* – Dutch Policy Research Programme on Air and Climate. Study led by the Netherlands Environmental Assessment Agency (PBL) and financed by the Dutch ministry of Housing, Spatial planning and Environment
Cap.effliterature	CO_2 capture efficiency given in the literature [%]
CC	Carbon Capture
CCQ	Carbon Capture Quotient: Ratio of the specific emission factors of a given power plant with Carbon Capture and without Carbon capture respectively
CCQx,y,z	Carbon capture quotient for air pollution substance x, given energy conversion technology y and CO_2 capture technology z
CCS	Carbon Capture and Storage
CFcap_eff	Correction factor for capture efficiency [-]
CFCO2	Correction factor of CO_2 emissions to correct for the capture efficiency in the literature
CFcompr_press	Correction factor for compression pressure [-]
CFi	Correction factor for component i, (only applied to SO_2 and CO_2)
CFSO2	Correction factor of SO_2 emissions to correct for the S content in the coal [-]
CO_2	Carbon dioxide
CWC	Cooling water consumption
De-NOx	Unit operation to reduce the amount of NOx in flue gas
DOE	U.S Department of Energy http://www.energy.gov/
EBTF	European Benchmark Taskforce
EF	Emissions of pollutant i per unit electricity produced [kg/MWh]
EFccsx,y,z	Emission factor reported/estimated in the literature for air pollution substance x, energy conversion technology y and CO_2 capture technology z
EFi_corr	Emissions of pollutant i per unit electricity produced, corrected for fuel use and sulphur content in coal [g/kWh]
EFi_literature	Emissions of pollutant i per unit electricity produced, given in literature [g/kWh]
EFnoccsx,y,z	Emission factor for air pollution substance x and energy conversion technology y reported/estimated for the reference plant without CO_2 capture
EPA	United States of America Environmental Protection Agency (http://www.epa.gov/)
ESP	Electrostatic precipitator
FGD	Flue Gas Desulfurization
FP	Fuel penalty [MJ/kWh]
FrCO2_compr_press	Fraction of the fuel penalty assigned to the compression of CO_2
FU	Fuel use, primary energy input to generate electricity in [MJ/kWh]
FUcorr	Fuel use corrected for the compression pressure and capture efficiency [MJ/kWh]
FUliterature	Fuel use given in the literature [MJ/kWh]
FWI	Foster Weeler Italiana
GE	General Electric
Hg	Mercury

HRSG	Heat Recovery Steam Generator
IEA GHG	International Energy Agency Greenhouse Gas Research and Development Programme
IGCC	Integrated Gasification Combined cycle
IP	Intermediate pressure
LHV	Low heating value
LNB	Low NOx burners
LP	Low pressure
MEA	Monoethanolamine
NGCC	Natural gas combined cycle
NH_3	Ammonia
NOx	Oxides of nitrogen
OFA	Overfire air
Pin,orig	CO_2 compressor inlet pressure in the original literature [MPa]
Pout,orig	CO_2 compressor outlet pressure in the original literature [MPa]
ppmv	Parts per million volume
PWC	Process water consumption
R	Percentage of reduction of a given Air Pollutant in a specific Air Polutant Control
Scontent_literature	Sulphur content of the fuel found in the literature [%wt]
Scontent_ref	Sulphur content of the fuel in the reference case [%wt]
SCR	Selective catalytic reduction
SOx	Oxides of sulphur
TNO	Netherlands Organization for Applied Scientific Research
UEF	Emissions of pollutant per unit mass fuel in the absence of Air pollutant Controls [kg/ton coal]
USC PC	Ultra Supercritical Pulverized Coal
η	Plant efficiency based on LHV [%]

Contents

1 Introduction

1.1 Background information

Carbon Capture and Storage (CCS) is considered to be one of the short to mid term options in the portfolio of mitigation actions for stabilising acceptable concentrations of atmospheric greenhouse gas (GHG). The essence of CCS is to capture CO_2 from large point emission sources; transport and store this permanently (i.e. in depleted gas fields or deep reservoirs) [1]. There are basically three different routes for CO_2 capture, namely:

- post combustion capture: capturing CO_2 after the combustion process (separation of CO_2 from mainly nitrogen).
- pre combustion capture: capturing CO_2 after gasification and water gas shift of the subsequent syngas (separation of CO_2 from mainly hydrogen).
- oxyfuel: combustion with pure oxygen. The flue gas will contain predominantly CO_2 and water vapour.

Moreover, CO_2 capture can also be applied to industrial processes such as cement production, refineries, steel manufacturing and many others. There is a strong political and environmental push towards early demonstration of carbon capture and storage. CO_2 capture has been relatively well-studied in terms of CO_2 emissions reduction, power generation efficiency and carbon avoidance costs. However, many studies do not address clearly the effect that CO_2 capture might have on the emission levels of other pollutants originating from the fuel, combustion process or the CO_2 capture process itself.

1.2 Purpose of this study

There are concerns and uncertainties related to the impact which CCS may have on the environment. CCS technologies require additional energy for CO_2 separation and compression. This means that more fuel is required to meet the same energy outcome. As a result, it is possible that proportionally more attendant pollutants such as: SOx, NOx, PM, NH_3, VOC[1] and heavy metals are emitted into air, soil and water. Other effects of CCS technologies can be foreseen. One example is the application of post-combustion capture, which requires high SOx removal conditions and likely also high NO_2 removal conditions. These specific requirements will minimize the emissions of these pollutants to very low levels. Moreover, this specific technology may also cause the increase of ammonia emissions to higher levels than that normally emitted by the De-NOx facilities in conventional fossil fuel power plants. In general, it can be stated that emission is strongly dependent on the technology used for CO_2 capture.

Clarifying the environmental impact of carbon capture technologies requires a prior evaluation of the effect that these technologies might have on the mentioned emissions. Moreover, any possible emission or waste arising from the capture process needs to be considered. Although it is widely accepted that it is important to

---

[1] SOx - sulphur oxides, NOx – nitrogen oxides, PM- particulate matter, NH_3- ammonia, VOC-

evaluate the CO_2 capture process effect on emissions, including direct solvent emissions and its degradation products, such a total analysis has not yet been performed. There are two aspects that complicate this analysis:

- The scarcity of environmental data in relation to CO_2 capture, including data on emissions from solvent degradation products.
- Lack of harmony and/or standardisation and reliability in the existing data. This means differences in development stage of the technology, type of technology, fuel characteristics, plant size, plant configuration (influenced by emission standards locally in place [2]) and timing of the study. These aspects add one more difficulty to the comparison of technologies on a reliable basis.

All concerns mentioned above, have created the need to study the non-CO_2 emissions from power plants equipped with CO_2 capture. IEA GHG has contracted TNO to investigate the emissions and waste generated in different types of power plants with and without CO_2 capture technologies. This study aims to analyze and quantify the effects that various CO_2 capture technologies have on emissions and waste generated.

1.3 Approach and scope of the project

1.3.1 Approach and methodology

A systematic and rigorous methodology for waste evaluation has been applied to a selected number of coal fired power plants and a natural gas fired power plant. Two types of information sources were available in the project to assess the environmental performance of power plants with CO_2 capture:

- First, a growing body of knowledge is available in the open literature, based upon laboratory studies, desk and design studies, measurements at pilot and demonstration plants. Moreover, TNO and the University of Utrecht have accomplished several studies on the impacts of CO_2 capture technologies on air pollution in the Netherlands (BOLK study) [3;4]. This gives a substantial base for clarifying the non-CO_2 emissions profile for different reference plants. In agreement with IEA GHG the database derived from these studies was set as the starting point for this study.
- Second, process simulation tools (such as Aspen Plus®) and several technical assessments of power plants were available to model explicitly carbon capture plants and evaluating the performance of power plants with carbon capture. However, many flue gas contaminants (specially the trace contaminants) are not included in commercial simulating packages. These components were added to the mass balances by estimating their emission factors for each unit in the power plants.

The prediction of the process simulations can be compared to the average emissions existing in the BOLK database for several components. This combination (literature input and process simulation) was used to evaluate emissions of non-commonly reported contaminants. Since two types of information sources are used, two different types of activities were carried out in parallel during this study: Harmonization and Modelling. Figure 1.1 shows a scheme of the work flow consisting of the main steps in the project.

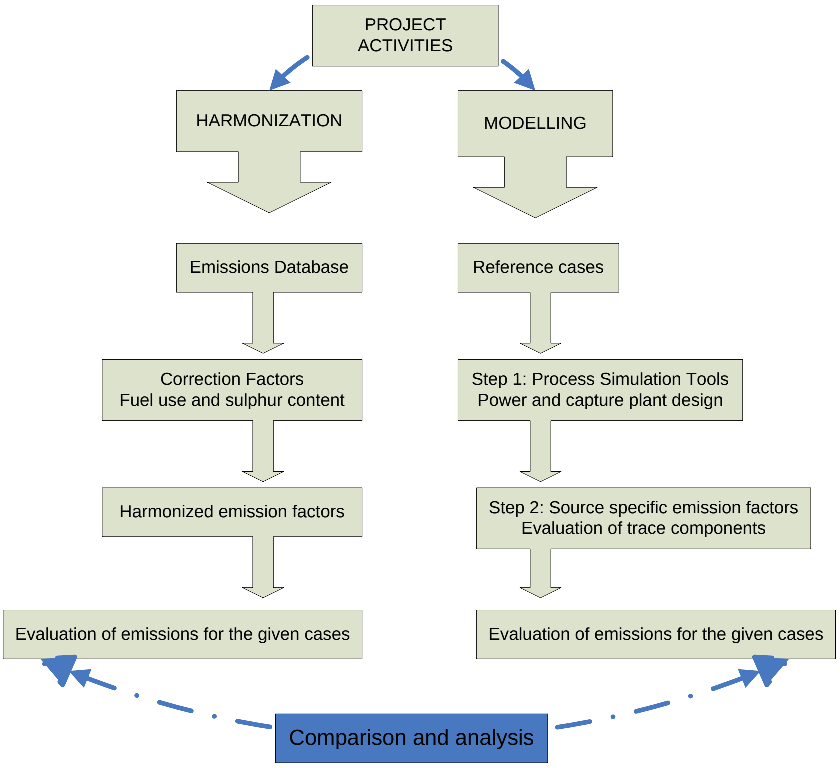


Figure 1.1 Scheme of methodology used in this project.

Harmonization activities consisted of reviewing the public domain information on emissions, harmonizing the available data and evaluating emissions for different reference plants with and without carbon capture. The harmonization step is necessary to compare different data and technologies. Previous projects have taught us that data are sometimes incomparable if input parameters have not been harmonized properly. For instance, the coal quality and the performance of the desulphurisation unit have to be known in order to be able to compare the SOx emissions of plants. For this reason the harmonization step is crucial. The harmonization methodology will be described in more detail in section 2.1.

Modelling activities consisted of process simulations to evaluate the basic performance of the power plants and estimation of emission factors for each unit in the power plant. Based on the emission factors, trace components and interactions between capture solvents and gas impurities could be added to the mass balance. Finally, the models were used to estimate the emissions and waste generation of all power plant cases studied.

The study finished with the overall review of the non-CO_2 emissions of power plants with and without carbon capture. The results from the harmonization and the modelling activities were compared. When possible, sensitivity analyses were performed on the most uncertain parameters in order to evaluate their impact into the overall waste generation.

1.3.2 Scope of the study

The focus of the study is directed on the power plant integrated with the capture plant, excluding transport and storage. Furthermore, safety issues, including fugitive emissions, and emissions that result from fuel preparation were not included in the scope of this project. The considered emissions were those emitted to air of substances in the flue gas that originate from the gas feed to the capture unit and emissions to land and water that originate from the power plant or the CO_2 capture plant. To be more specific, emissions of non-CO_2 substances, such as: SOx, NOx, PM, NH_3, VOC and heavy metals into air were analysed. Life cycle emissions are outside the scope of the project, as well as specific emissions directly stemming from solvents.

Emissions and waste data for the above mentioned components have been provided for three reference plants without CO_2 capture and four reference plants with CO_2 capture. The selection of the reference plants was made based on the state-of-the-art technologies for power generation and CO_2 capture. For this purpose, IEA Greenhouse Gas R&D Programme (IEA GHG) has issued reports that evaluate the power generation with and without CO_2 capture from coal fired power plants. These reports also include an evaluation of water usage in the selected power stations. The following lines give a brief description of the cases considered:

- Case 1A: USC PC Boiler reference case, based on standard ultra supercritical design, 750MWe nominal power output without limitation on water usage. This case is based on IEA GHG previous studies [5;10].

- Case 1B: USC PC Boiler reference case, based on standard ultra supercritical design, 750MWe nominal power output, with CO_2 capture and without limitation on water usage. This case is based on IEA GHG previous studies [5;10].

- Case 2: USC PC oxyfired boiler reference case. Based on standard ultra supercritical design, 750MWe nominal power output, with CO_2 capture and without limitation on water usage. Based on IEA GHG previous study [6].

- Case 3A: IGCC plant based on GE gasifier, 830MWe gross power output without limitation on water usage. This case is based on IEA GHG previous study [7].

- Case 3B: IGCC plant based on GE gasifier, 830MWe gross power output, with CO_2 capture and without limitation on water usage. This case is based on IEA GHG previous study [7].

- Case 4A: NGCC plant based on an F-class gas turbine, 423MWe nominal power output. This case is based on the European Benchmark Task Force (EBTF) study [8] and modelling work done by TNO for the present study. Details on the model and process description can be found in Appendix F.

- Case 4B: NGCC plant based on an F-class gas turbine, 423MWe nominal power output with CO_2 capture. This case is based on the EBTF study [8] and modelling work done by TNO for the present study. Details on the model and process description can be found in Appendix F.

1.4 Reference cases

Table 1.1 shows the basic characteristics of the reference power plants investigated in this study. The reference coal fired power plants were made available by IEA GHG for the present study [5;6;7]. Assumptions regarding the coal reference cases have been taken from previous evaluations worked by IEA GHG [9]. The NGCC cases (cases 4A and 4B) were modelled and executed by TNO based on the technical criteria reported by the European Benchmark Task Force (EBTF) [8] and modelling work performed with Aspen Plus ®. Appendix A shows a summary of the technical assumptions and Appendix F shows a description of the Aspen Plus ® model. In all cases, assumptions regarding fuel composition are in line with the documents provided by IEA GHG [5;6;7;9;10].

Table 1.1 also shows a description of the type of emission controls included in each case. A full description of these cases can be found in the mentioned studies [5-7].

The performance of the difference cases is summarized in Table 1.2. The basic performance parameters (e.g. the plant efficiency, net output, etc.) are the result of process simulations and its description can be found in references [5-7] for cases 1A to 3B or in Appendix F for cases 4A and 4B. The values presented in Table 1.2 were used for the standardization of the literature data and as reference for the waste assessment.

1.4.1 Ultra supercritical pulverized coal boiler (USC PC). Cases 1A and 1B

The block diagrams for each case can be found in Appendix B. Case 1A consists of an Ultra-Supercritical Pulverized Coal (USC PC) plant, fed with bituminous coal and not provided with CO_2 capture unit. Case 1B is the same plant type integrated with CO_2 capture unit. Plant location is coastal for both cases. Cooling system is a once through design that uses sea water.

The main parts of the plant for these cases are:

- Mitsui-Babcock boiler pulverized fuel ultra supercritical design.
- De-NOx Plant
- ESP
- Flue Gas Desulphurization Plant

- CO_2 capture and compression units (only present in case 1B)

The boiler is equipped with low NOx burners and is fitted with SCR for NOx abatement. Limitation of SOx emissions is accomplished with forced oxidation limestone / gypsum wet FGD system. In case 1A, flue gas desulphurization is provided to reduce the sulphur dioxide level in the flue gas from the boiler to around 70 ppm @ 6%O_2 v/v (dry). However, in case 1B flue gas desulphurization is provided to reduce the sulphur dioxide level in the flue gas from the boiler to around 10 ppm @ 6%O_2 v/v dry (a level which does not exceed the inlet requirement of the carbon dioxide absorption plant). This unit was designed in previous studies [5; 10].

The CO_2 Amine Absorption unit is based on monoethanol amine (MEA) scrubbing technology and consists of three main units: Direct contact cooler (DCC), absorber and stripper. The capture unit is designed with split flow and solvent heat integration to reduce the reboiler consumption. This is a common design provided by Fluor and a full design description can be found in [5]. The stripper reboilers are heated by condensing the steam extract from the IP/LP cross over in the power island. Condensate at saturation conditions is returned to the power island deaeration system. Overhead vapour from the stripper is cooled with recycled condensate from the boiler island. The remaining cooling duty is achieved with sea water. Carbon dioxide from the stripper is compressed to a pressure of 74 bara by means of a four stage compressor. The compression includes interstage cooling (with both recycled condensate from the power island and trim cooling with sea water) and knockout drums to remove and collect condensed water. The carbon dioxide is dehydrated to remove water to a very low level and is finally delivered at a pipeline pressure of 110 bara.

In the original design, some of the circulating amine is periodically sent to the reclaimer, where it is distilled with sodium carbonate to break down some of the heat stable salts (HSS), which are formed from the reaction of trace impurities with the MEA solvent. The heavy residues remaining after this batch regeneration are pumped away for disposal. MEA is made up into the system from the amine storage tanks. For the present study, a mass balance around the reclaimer unit has been performed considering continuous operation of the reclaimer unit. It was considered that the operation of the reclaimer should maintain the concentration of HSS in the process to a maximum concentration of 1%wt. Details on the reclaimer mass balance can be found in Appendix D.

1.4.2 *Ultra Supercritical pulverized coal boiler (oxy-firing). Case 2*

This is a pulverized coal, ultra supercritical steam plant converted to oxyfuel fired operation. Design characteristics, utility and heat and mass balances have been taken from the IEA GHG case described in reference [6]. The following paragraphs briefly describe plant main units. Block Diagram is given in Appendix B. For a full description of each unit, the reader is referred to the study report issued by IEA GHG.

Coal is pulverized and fed into the boiler. Two streams of recycle flue gas are required for the oxy-combustion system:

- Primary recycle, which passes through the coal mills and transports the PC to the burners. The water content in this stream needs to be reduced for adequate drying of the fuel.
- Secondary recycle, which provides the additional gas ballast to the burners to maintain temperatures within the furnace at similar levels to air firing.

The flue gas exiting the boiler is treated in order to remove particulates in the ESP unit. The gas is split in two to form the secondary recycle, which returns to the burners via the Gas / Gas heater and the CO_2 remaining stream. The CO_2 remaining stream is cooled and dried and split again into two streams: the primary recycle, which is sent back to the mills and the CO_2 product stream, which is further purified to meet the specifications for geological disposal applications. Although it is possible to use the same SOx, NOx and Hg removal technology as in conventional coal combustion, the carbon dioxide purification and compression unit employed in this study is based on a purification process proposed by White et al [11] and commercialized by Air Products and Chemicals Inc. Instead of exploiting selective catalytic reduction and wet limestone gypsum flue gas desulfurization, the proposed process uses two successive water-wash columns. SOx removal process takes place in the first water-wash column at 15 bara. It separates out all the SO_2 and SO_3 as sulfuric acid, as well as almost half of the remaining water content in the flue gases. This process is catalyzed by NO_2. After the de-sulphurization unit, the flue gases are compressed to 30 bara and introduced into the next water-wash column. The NO is rapidly converted to NO_2 at pressures around 30 bara and then is removed as nitric acid.

The result obtained from the Air Products cleaning process is that all the SO_2 and about 90% the NOx contained in flue gas and generated in the USC PC oxyfuel combustion process is removed and a stream of SO_2-free and NOx-lean carbon dioxide is obtained. Such stream is then sent to the sections of CO_2 inert removal and compression.

1.4.3 Integrated Gasification Combined Cycle (IGCC - GE gasifier). Cases 3A and 3B

Cases 3A and 3B refer to two GE IGCC power plants, fed with bituminous coal. Case 3A is not provided with a CO_2 capture unit. Case 3B is provided with a CO_2 capture unit. Plant description, process schemes and performance have been taken directly from reference study report [7].

The main features of the GE IGCC plant are:
- High pressure GE Gasification
- Coal Water Slurry Feed
- Gasifier Quench Type
- CO Shift and CO_2 removal (only in case 3B)

The Gasification Unit employs the GE Gasification Process to convert feedstock coal into syngas. Facilities are included for scrubbing particulates from the syngas, as well as for removing the coarse and fine slag from the quench and scrubbing water.

Syngas from the gasification section is contaminated with acid gases, CO_2 and H_2S, and other chemicals, mainly COS, HCN and NH_3. COS is converted to H_2S in the hydrolysis reactor. The acid gas removal (AGR) is based on the Selexol process.

The Sulphur Recovery (SRU) is an O_2 assisted Claus Unit, with Tail gas catalytic treatment (SCOT type) and recycle of the treated tail gas to AGR. Gas Turbine power augmentation and syngas dilution for NOx control are achieved with injection of compressed N_2 from ASU to the Gas Turbines.

1.4.4 Natural gas combined cycle (NGCC). Cases 4A and 4B

For both cases, the power plant is located inland and consists of one gas turbine (Siemens SGT5-4000F) equipped with dry low NOx burners, Selective catalytic reduction (SCR), steam turbine, generator, HRSG and water treatment equipment. Water cooling is done with draft cooling tower.

Besides the above mentioned units, case 4B has a CO_2 capture unit integrated into the power plant. The CO_2 Amine Absorption unit is also based on MEA scrubbing technology (as in case 1B). Nevertheless, the capture unit has a simpler design than that of case 1B and includes no split flow or MEA heat integration. The reason for choosing a simpler design is that complexity of control and operation is significantly reduced. In return, this design has slightly higher steam requirements in the stripper. The stripper reboilers are heated by condensing the steam extract from the IP/LP cross over in the power island in the same manner as in case 1B. However, there is no integration of the boiler island condensate in this design. Therefore, overhead vapour from the stripper is cooled directly with cooling water. Also interstage cooling during compression is done with cooling water. The other units in the capture plant are designed in a similar manner to case 1B.

Table 1.1 Summary of cases investigated in this study

Case	**1A**	**1B**	**2**	**3A**	**3B**	**4A**	**4B**
Type	**USC PC w/o CC**	**USC PC w CC**	**USC Oxyfuel**	**IGCC w/o CC**	**IGCC w CC**	**NGCC w/o CC**	**NGCC w CC**
Steam Cycle bar(a)/ºC/ºC	290/600/620	290/600/620	290/600/620			124/561/234	124 /561/ 234
Gas Turbine	NA	NA	NA	Advanced F class	Advanced F class	Advanced F class	Advanced F class
Boiler type	Supercritical PC	Supercritical PC	Supercritical PC	GE	GE	NA	NA
Oxidant	Air	Air	95% O_2	95% O_2	95% O_2	Air	Air
NOx Controls	Low NOx Burners & OFA & SCR		Air Products	Dilution with N_2		Low NOx Burners & SCR	
PM Controls	ESP	ESP					
H_2S controls	NA	NA	NA	Selexol	Selexol	NA	NA
SOx /Sulphur control	FGD (Wet Scrubber, Limestone)		Air Products	Claus	Claus	NA	NA
CO_2 separation	NA	MEA		NA	Selexol	NA	MEA
Fuel Type	Eastern Australian Bituminous coal					Natural Gas	Natural Gas

Table 1.2 Basic performance parameters of the reference plants

Parameter	Units	1A USC PC w/o CC	1B USC PC w CC	2 USC PC oxyfuel	3A IGCC(GE) w/o CC	3B IGCC(GE) w CC	4A NGCC w/o CC	4B NGCC w CC
Coal Flow rate (air dry)	t/h	239.8	266.3	209.1	303	323.1	56.1	56.1
Coal LHV	kJ/kg	25870	25870	25870	25870	25869	46502	46502
Thermal Energy (based on coal LHV (A)	MWt	1723.2	1913.7	1502.0	2177	2322	724.5	724.5
Gross Electricity Out put (D)	MWe	831	827	737	988.7	972.8	430.3	430.3
Power plant Auxiliaries (E)	MWe	73.3	78.3	54	162.2	203.5	7.7	7.7
Additional consumption due to CO_2 capture (F)	MWe		83.1	151.6		39		66
Net Electric Output (C=D-E-F)	MWe	757.7	665.6	531.4	826.5	730.3	422.6	356.6
Gross electrical efficiency (D/A*100)	% [LHV]	48.2	43.2	49.1	45.4	41.9	59.4	53.6
Net electrical efficiency (C/A*100)	% [LHV]	44.0	34.8	35.4	38.0	31.5	58.3	49.2
Specific fuel consumption	MWt / MWe	2.074	2.875	2.827	2.634	3.018	1.71	2.03
Specific CO2 emissions	kg/MWh	743	117	85	818	152	354	41.9
Cooling water consumption[2]	t/MWh	138.6	240.5	176.7	146.9	185.2	45.6	82.7
Specific water consumption[3]	t/MWh	0.104	0.410	0.063	0.126	0.411	1.02[4]	1.21

---

[2] For the cases with a once through cooling system (Cases 1 to 3) cooling water consumption indicates the sea cooling water supply. For the cases with cooling towers (Case 4), cooling water consumption indicates the cooling water make up.

[3] Specific water consumption indicates the consumption of raw water.

[4] Factor estimated for NGCC plants from [36] DOE study

2 Methodology

The emissions and waste assessment combines information retrieved from two types of activities:

- Literature review and harmonization
- Modelling of the reference cases

The next sections explain the details of each activity. Due to the specific characteristics of each reference case, some information was lacking with respect to the two activities. In some reference cases, there was no information found in the literature regarding specific components or technologies. Moreover, the literature database is restricted to air emissions. Therefore, liquid and solid waste was only estimated via modelling activities. For other reference cases, there is not sufficient knowledge about interactions and behaviour of specific contaminants to model emissions. In this situation, for higher level of confidence, experimental work is needed.

The final emissions and waste assessment combines the information from the two set of activities, highlights the lacking information and targets several parameters for sensitivity analysis to better understand the effect of any uncertainties.

2.1 Harmonization methodology

This study started with reviewing the open literature (conference proceedings, technical reports and peer reviewed journal articles) on the emissions of power plants (with and without CO_2 capture) and existing data of operating power plants. An emissions database was created based on the BOLK studies [3, 4], containing 176 cases from 37 data sources, with diverse levels of information. The underlying literature references are in Appendix G. The cases were derived from a wide variety of power plants with different kind of fuels and efficiencies. In order to compare data from various literature sources on an equal footing, harmonisation of key important parameter values is necessary.

Harmonization is the application of correction criteria to the database in order to bring into line the basis of each case in the database. The harmonization methodology used in this project was based on the application of correction factors, derived from literature. Correction factors are specific factors that act on the emission factors or on performance parameters, in order to correct the deviation of a key technology performance parameter with respect to a given criteria. The harmonization methodology for the correction of SO_2 emissions (related to the sulphur content of the coal) and the correction for the fuel use (due to variation in the compression pressure) was derived from the BOLK study [4]. An additional correction for the CO_2 capture efficiency, resulting in a corrected fuel use and a corrected CO_2 emission is developed within this project. The literature results on energy use and CO_2 emissions for oxyfuel are not corrected to the set efficiency of 90% CO_2 capture. This efficiency does not reflect the efficiencies mentioned in literature, which are up to 100%. Figure 2.1 shows the work sequence for the harmonization methodology.

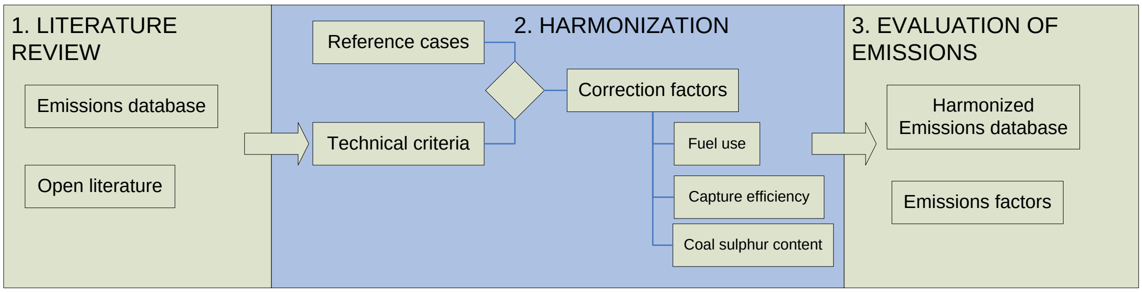


Figure 2.1 Work flow of the harmonization methodology

Technical criteria were agreed with IEAGHG at the beginning of the study. Appendix A shows a list of all technical criteria that are the basis for evaluating the performance of the reference cases. Correction has been applied for the following performance parameters and relative emission factors:

1. Fuel use: harmonisation to a CO_2 compression pressure of 110 bar and a CO_2 capture efficiency of 90%;
2. Emission factors: harmonisation to a CO_2 capture efficiency of 90% and a sulphur content of 0.95 wt% (dry basis)

The values for the key parameters subject to harmonization are shown in Table 2.1. This table shows the criteria for harmonization and the range of values that these parameters take in the emissions database.

Table 2.1 Criteria for harmonization of the literature database

Technical criteria	**Units**	**Value for this study. Source [9]**	**Range found in emissions database**
Coal type	[-]	Bituminous Eastern Australia	Different coal types
Sulphur content in coal	%wt dry	0.95[5]	0.95 – 1.5
CO_2 Capture Removal	[%]	90%	80% - 100%
CO_2 product conditions			
Temperature	ºC	<30	25 - 30
Pressure	Bar	110	80 - 200

---

[5] Corresponds to a calculated specific sulphur content of 0.333 g/GJ for the given LHV of 25.87 MJ/kg (as received) and a moisture content of 9.5 wt% (as received)

Table 2.2 Model for harmonization of fuel use and emissions

Eq.	Equations, factors description and units		
1	$FU_{corr} = FU_{literature} + \left(1 + Fr_{CO_2\_compr\_press} * \left(CF_{compr\_press} - 1\right)\right) * FP * CF_{Cap\_eff}$		
	FU_{corr}	-	Fuel use corrected [MJ/kWh]
	$FU_{literature}$	-	Fuel use given in the literature [MJ/kWh]
	$Fr_{CO_2\_compr\_press}$	-	Fraction of CO_2 compression pressure in fuel penalty [-]
2	$CF_{compr\_press} = \dfrac{\ln\left(\dfrac{11\ MPa}{P_{in,orig}}\right)}{\ln\left(\dfrac{P_{out,orig}}{P_{in,orig}}\right)}$		Based on previous studies [12]
	CF_{compr_press}	-	Correction factor for compression pressure [-]
	$P_{in,orig}$	-	CO_2 compressor inlet pressure in the original literature [MPa]
	$P_{out,orig}$	-	CO_2 compressor outlet pressure in the original literature [MPa]
	FP	-	Fuel penalty [MJ/kWh]
3	$CF_{Cap\_eff} = \dfrac{90\ \%}{Cap.eff_{literature}}$		
	CF_{Cap_eff}	-	Correction factor for capture efficiency [-]
	$Cap.eff_{literature}$	-	CO_2 capture efficiency given in the literature [%]
4	$EF_{i\_corr} = EF_{i\_literature} * CF_i$		
	EF_{i_corr}	-	Emission factor pollutant i, corrected [g/kWh]
	$EF_{i\_literature}$	-	Emission factor pollutant i, literature [g/kWh]
	CF_i	-	Correction factor for component i, (only applied to SO_2 and CO_2)
5	$CF_{SO_x} = \dfrac{S_{content\_ref}}{S_{content\_literature}}$		
	CF_{SO_x}	-	Correction factor for SO_2 emissions [-]
	$S_{content\_ref}$	-	Sulphur content fuel in reference case [%wt]
	$S_{content\_literature}$	-	Sulphur content fuel found in the literature [%wt]
6	$CF_{CO_2} = CF_{Cap\_eff}$		
	CF_{CO_2}	-	Correction factor for CO_2 emissions

The model applied for the correction of these parameters is summarized in Table 2.2. Derivation of this model can be followed in Appendix C. All emissions were corrected for the harmonized fuel use (equation [1] in Table 2.2).

The sulphur dioxide (SO_2) emission factors were adjusted based on fuel sulphur content. It was done by standardizing the sulphur content in coal to the sulphur content in the coal of the reference cases (Bituminous coal from Eastern Australia for all technologies: PC, IGCC and Oxyfuel [9]). SOx removal efficiencies of Flue Gas Desulphurisation (FGD), Acid Gas Removal (AGR) and CO_2 capture units were assumed to remain constant. For oxyfuel PC plants, SOx emissions largely depend on how the CO_2-rich gas is treated before being compressed and transported to the storage site. Some reports do not include CO_2-rich gas purification units within the system boundary, while other reports do [13;14;15]. It has been suggested that SOx should be removed to meet the CO_2 transport pipeline specifications (e.g., [16]).

The CO_2 emission factors were adjusted to the given capture efficiency of 90%. With the exception of the oxyfuel case (section 5.2).

Other emission factors could not be harmonised, because of its complexity (eg NOx) or lack of information on air pollutant control technologies. Therefore, the emission factors of NOx, PM, Hg and NH_3 have not been corrected.

All emission factors are expressed in g/kWh. Most literature references use this unit to express the emissions, as it is most relevant for power plants. Power plants reported in literature have nevertheless a large variation in efficiency. It is important to notice that the emission factors are not corrected for this variation in efficiency of the power plant.

2.2 Modelling methodology

The modelling methodology is based on the systematic accounting of waste generated by the power plant and capture plant (mass balance). Various engineering tools have been used for such accounting. The selection of the appropriate tool depends on the contaminant evaluated. The overall procedure is depicted in Figure 2.2 and comprises two steps that make use of different tools.

In a first step, process simulations and engineering calculations are used to evaluate the basic performance of the system and the mass flow of basic components that are commonly reported by commercial software. This part of the study was not done within this project, because it was based on previous IEA GHG studies [5;6;7] (with the only exception of the NGCC cases). In this step the following characteristics are evaluated:

- For the power plant, the mass flow for fuel and air are calculated. The net electricity output is also calculated. The flue gas flow that is treated in the capture plant is also given with its basic components, which are O_2, N_2, CO_2, H_2O, SO_2 for coal combustion, O_2, N_2, CO_2, H_2O, SO_2, H_2S, CO, COS for coal gasification and O_2, N_2, CO_2, H_2O for natural gas combined cycle.

- For the capture plant, the energy and steam requirement for solvent regeneration are calculated. Also the treated flue gas flow and product stream are calculated with its basic components.

In a second step, uncontrolled emission factors (source dependent) and removal efficiencies of the air pollutant control technologies listed in Table 1.1 were used to estimate the emissions of other components. The key difference with the harmonization is that this is a bottom-up approach where the influence of each air pollutant control technology can be accounted for. Modifications to a specific unit and parameters that describe the unit performance can be singularly modified and the influence on the overall emissions can be assessed.

Components evaluated at this step are divided into three categories:

- Basic gas components: In this category SOx and NOx emissions are divided into its gases (SO_2, SO_3, NO, NO_2, N_2O). NOx, and SOx gases are normally reported in the literature and not modelled, with the only exception of SO_2. The harmonization results show an estimate of these emissions (SO_2 and NO_x as a bulk figure). At this stage, an estimate of the different gases is given based on the boiler technology (dry-bottom for all USC cases) or gas turbine. CO is also a component that falls in this category.[6]

- Trace metals: In this category all the trace metals reported for the type of coal selected are included.

- Generated components: In this category all components that are generated by the control technologies are included. These are: gypsum, effluent from power plant, effluent from capture plant, heat stable salts, filters, activated carbon and ammonia.

Mass and utility balances developed in the prior stage were used as a basis for the estimation. The accounting of mass flows and energy has been done on the basis of the block diagrams reported in Appendix B. Then, the final estimate for the flows of the described components is calculated as follows:

$$F_i = (C - U) \cdot E_i \cdot \prod_{1}^{CS} (1 - R_i) \qquad [7]$$

Where Fi is the mass flow of component i emitted (kg/s), C is the flow of coal / fuel to the boiler as fired (ton/s), U is the unburned coal (ton/s), E_i is the specific uncontrolled emissions factor for component i (kg/ton coal) and R_i is the removal efficiency of component i in a given air pollution control system (CS).

This methodology has been systematically applied to all the cases. Nevertheless, for oxy-fired boilers and gasification no emission factors where found to describe the trace components. Therefore, for cases 2 and 3A and 3B the second step of the modelling methodology could not be fully applied.

---

[6] No emission factors are reported for gasification. In this case, the emission factor also includes pollutant control removal efficiencies

The specific uncontrolled emissions factors (E_i) and the removal efficiencies (R_i) for air pollution control systems are discussed in detail in the following sections.

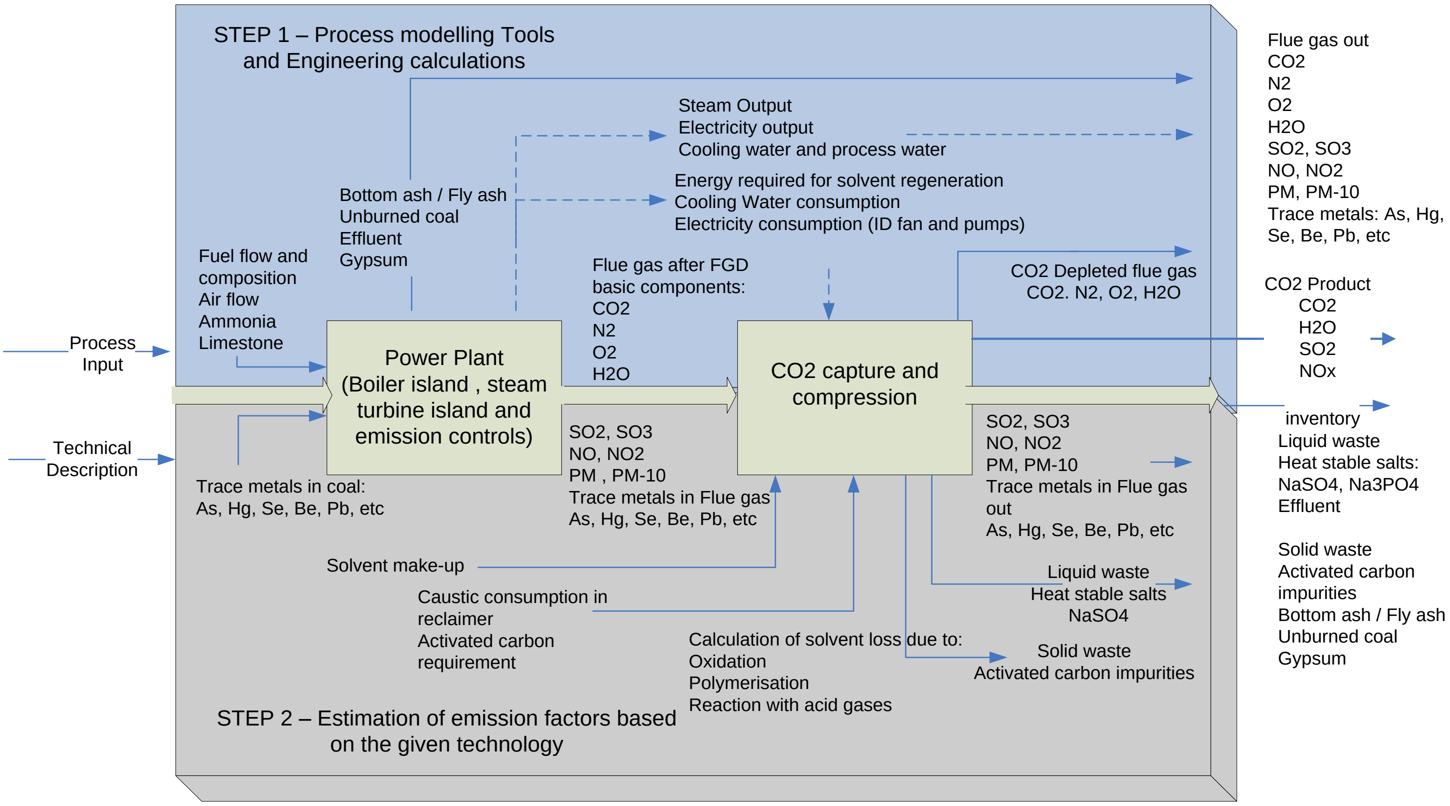


Figure 2.2 Work flow for the modelling activities (evaluation of emissions and waste inventory)

2.2.1 *Coal combustion in pulverized coal boilers*

2.2.1.1 *Uncontrolled emission factors*

2.2.1.1.1 *Basic components*

Gaseous SOx from coal combustion are primarily sulphur dioxide (SO_2), with a much lower quantity of sulphur trioxide (SO_3) and gaseous sulphates. NOx emissions from coal combustion are primarily nitric oxide (NO), with only a few volume percent as nitrogen dioxide (NO_2). Nitrous oxide (N_2O) is also emitted at a few parts per million, but it has not been considered in this study. The concentration of NOx depends on several things (temperature, N_2 and O_2 concentrations in the flame and residence time in the boiler). Therefore, the concentration might vary to a great extent. Emission factors for uncontrolled emissions used in this study are shown in Table 2.3.

Table 2.3 Emission factors for bituminous coal (PC-boiler dry bottom, wall –fired)

Emission factors	**Units** (based on coal)	**Source: [17]**
Emission factor for CO_2	kg/t	32.930C[7]
Emission factor for CO	kg/t	0.227
Emission factor for SO_2	kg/t	17.104S[8]
Emission factor for SO_3	kg/t	0.126S
Emission factor NO_2	kg/t	0.272
Emission factor for NO	kg/t	3.371
Emission factor for HCl	kg/t	0.544
Emission factor for HF	kg/t	0.068
Emission factor for particulate matter (PM)	kg/t	4.535A[9]
Emission factor PM-10	kg/t	11.260

Particulate matter (PM) composition and emission levels are a complex function of boiler firing configuration, boiler operation, pollution control equipment, and coal properties. In pulverized coal systems, combustion is almost complete; thus, the emitted PM is primarily composed of inorganic ash residues. Coal ash may either settle out in the boiler (bottom ash) or entrained in the flue gas (fly ash). The distribution of ash between the bottom ash and fly ash fractions directly affects the PM emission rate and depends on the boiler firing method and furnace type (wet or dry bottom). Table 2.3 shows the emission factors for a dry-bottom PC- boiler.

2.2.1.1.2 *Trace metals*

Trace metals are also emitted during coal combustion. The quantity of any given metal emitted, in general, depends on the physical and chemical properties of the metal itself; the concentration of the metal in the coal; the combustion conditions; and the type of particulate control device used, and its collection efficiency as a function of particle size.

Some trace metals become concentrated in certain particle streams from a combustor (e.g., bottom ash, collector ash, and flue gas particulate) while others do not. Various classification schemes have been developed to describe this partitioning behaviour [17;18;19]. These classification schemes generally are based on volatility and condensability on ash particles and distinguish between:

- Class 1: Elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no small particle enrichment. Examples include manganese, beryllium, cobalt, and chromium.

---

[7] C is the weight percentage of carbon in the coal as fired

[8] S is the weight percentage of sulphur in the coal as fired

[9] A is the weight percentage of ash in the coal as fired

- Class 2: Elements that are enriched in fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size. Examples include arsenic, cadmium, lead, and antimony.
- Class 3: Elements which are emitted in the gas phase (primarily mercury and, in some cases, selenium).

Control of Class 1 metals is directly related to control of total particulate matter emissions, while control of Class 2 metals depends on collection of fine particulate. Because of variability in particulate control device efficiencies, emission rates of these metals can vary substantially. Because of the volatility of Class 3 metals, particulate controls have only a limited impact on emissions of these metals.

Various studies have been conducted to determine the emissions of trace metals during combustion of coal. Sloss and Smith (2000) published an extensive review on trace element emissions [18] and Apps (2006) has conducted a more recent review on the topic [19]. Some of the studies on trace metal emissions include measurements at pilot plant and operating facilities. One characteristic of many of these studies is the lack of accuracy in achieving a closed mass balance between metal inputs in coal and emerging streams from combustion. Apps [19] underlined some of the reasons behind this low accuracy, which include flaws in sampling methods, and flaws in analytical methods.

Therefore, any form of generalization on the emissions of trace metals is very challenging. In the present study, an example of trace metals emissions has been given (Appendix H) and used to analyze the impact of different Air pollution controls in the final emissions of metals (with focus on the CO_2 capture unit). However, these values are not intended as benchmark for the technologies analyzed (USC PC and IGCC).

2.2.1.1.3 Generated components

Pollution control systems contribute to the generation of waste. The type of waste and amounts will be analysed in each emission control system.

2.2.1.2 Air Pollutants Controls (APCs)

2.2.1.2.1 Particulate matter

Typical Control systems that reduce PM emissions are Electrostatic Precipitators (ESP), bag house and Wet Scrubbers. The efficiency of all control systems depends on the particle size distribution among other factors. Electrostatic precipitation technology is applicable to a variety of coal combustion sources and effective with particle sizes below 0.1 μm and above 10 μm. ESPs and Bag houses are capable of achieving 99.9% of particles removal efficiency. However, efficiency drops for particles with size between 0.1 – 1 μm. It also needs to be considered that fine particles generally carry more of the semi-volatile elements due to their large specific surface [18].

Wet scrubbers are applicable for PM as well as SO_2 control on coal-fired combustion sources. Scrubber collection is more efficient for particles in the order of 2 μm

All cases in this study incorporate an ESP to reduce the emissions of particulates. Table 2.4 shows the efficiency of this system based on data collected from coal fired plants and also the estimate from other studies.

Table 2.4 Efficiencies of PM controls in coal fired plants and values used in this study

Removal efficiencies for PM controls		**Value and reference**
ESP		
Particulate removal efficiency	%	75%[10] 99%[11] (*used*), 99.50%[12] 99.80%[13]
PM-10 removal efficiency	%	75%[10] 99.20%[11] (*used*)
SO_3 removal efficiency	%	50%[12] (*used*)
Trace metals class 1 (Cr, Co,)	%	99% (*used*) 99.2% - 99.3%[14]
Trace metals class 2 (Sn, Be, Ar, Pb)	%	75% (*used*) 81.0% - 97.4%[14]
Trace metals class 3 (Se, Hg)	%	0% (*used*) <20%[13]
Wet Scrubbers		
Particulate removal efficiency	%	**50%**[11]

In the present study, it was assumed that metals of class 1 will exhibit the same removal efficiency as the particulates. For the semi-volatile metals (class 2) that are generally condensed over the fine particles, it is anticipated that less removal efficiency will be achieved during operation due to the low resistivity of fine particles and lower ESP efficiency. Low removal efficiency is generally appreciated in volatile metals (class 3 metals). However, it should be noticed, that elements volatility and related condensation over the fines as well as the characteristics of the fly ash influence ESP performance. Due to the high complexity, these characteristics have not been considered for this model. For this reason, the lowest value for removal efficiency found in literature was used for the semi-volatile metals and no reduction of mercury was considered. These estimates represent the lower end of the efficiency range.

2.2.1.2.2 NOx controls

---

[10] Based on modelling and design study [20]

[11] Based on coal fired plant data. Fractional collection efficiencies greater than 99 percent for fine (less than 0.1 micrometer) and coarse particles (greater than 10 micrometers). Data show a reduction in collection efficiency for particle diameters between 0.1 and 10 micrometers. [16]

[12] Based on LCA study [21].

[13] Based on LCA study [22].

[14] Based on experimental studies on specific conditions that might not reflect the conditions of the reference case [19].

Several techniques are used to reduce NOx emissions from coal combustion. Combustion controls to avoid NOx formation are included in all types of boilers. The present cases use overfire air (OFA), low NOx burners (LNBs), and selective catalytic reduction (SCR). This combination of controls gives a removal of NOx between 85% to 95% [17]. The value of 95% was used in the present study. Although this combination is commercially available, it is not widely used in the industry.

2.2.1.2.3 *Flue Gas Desulfurization (FGD)*

Post combustion flue gas desulphurization (FGD) techniques can remove SO_2 formed during combustion by using an alkaline reagent to absorb SO_2 in the flue gas. To date, wet systems are the most commonly applied. Wet systems generally use alkali slurries as the SO_2 absorbent medium and can be designed to remove greater than 90 percent of the incoming SO_2. Depending of the alkali used the removal can be increased to 98% [17].

The lime and limestone wet scrubbing process uses a slurry of calcium oxide or limestone to absorb SO_2 in a wet scrubber. Control efficiencies in excess of 91 percent for lime and 94 percent for limestone over extended periods are possible [16]. The removal efficiency of the FGD unit should be increased when a capture unit is present in other to maintain solvent integrity. This can be done by changing the reagent to a sodium based alkali (i.e. sodium carbonate) or by adding a second FGD unit to the system [23]. Moreover, the Alstom Flow Pack can achieve the desire level of 10 ppmv of SO_2 necessary for capture technology [24]. For this study an efficiency of 98% was used to comply with the needs of the capture unit. This efficiency can be achieved with the Alstom Flow Pack (included in the description of case 1B) or with two wet scrubber systems in series.

The wet scrubber also induces the removal of other acid gases such as SO_3 and HCl. Some authors have reported removal efficiencies for these components based on experimental data. Table 2.5 shows the estimates for removal of components in the FGD unit.

Also some waste is generated from the FGD unit. Typical values based on design studies are [5]:

- 3.38 kg Gypsum / kg SO_2 removed (9.5wt% water content)
- 0.18 kg waste effluent / kg SO_2 removed

Table 2.5. Estimated removal efficiencies for an FGD unit of the wet scrubber type using limestone. Values differ for the cases with no capture and capture due to extra constrains from the solvent system

Removal efficiency		**No Capture**	**References**	**With Capture**	**References**
Ash removal efficiency	%	50	[17]	50	[17]
SO_2 removal efficiency	%	90	[25], [21], [17]	98	[17], [25]
SO_3 removal efficiency	%	50	[25], [17] [26][15]	54	This study
HCl removal efficiency in FGD	%	90-95	[17]	95	[25]
Trace metals class 1 – class 2	%	50	This study	50	This study
Trace metals class 3 [Hg^{2+}]	%	80-95	[25]	80-95	[25]
Limestone to sulphur ratio	molCa / molS	1.03 1.04	[21] [23]	1.03 1.04	[21] [23]

2.2.1.2.4 *CO_2 capture unit*

The cases 1B and 4B make use of a post-combustion MEA capture system. The capture unit is designed to capture 86-90% of the CO_2 included in the flue gas stream. The main parameters that control the performance of this unit are (among others) the MEA concentration, lean and rich loadings of the solvent, specific requirement of regeneration heat, MEA make-up requirement and efficiencies of pumps and compressors. The above mention parameters are modelled or retrieved from previous work. Table 2.6 shows a summary of the performance parameters of the capture units of cases 1B and 4B. Description of the capture unit can be found in the references [5;6;7;8].

Table 2.6 Performance parameters of the capture unit

Performance parameters		Case 1B Source: IEA GHG	Case 4B Source: TNO
CO_2 capture efficiency	[%]	86	90
MEA concentration	%wt	Fluor formulation	30
Lean and Rich loadings of the solvent	mol_{CO2}/mol_{MEA}	Not disclosed	0.26 – 0.5
Specific requirement of regeneration heat	GJ/ton CO_2	3.2	4.1

Amines have been applied to refinery and natural gas sweetening industries since the 60's of the last century. Based on operational experience, there are known causes of solvent loss like oxidative degradation induced by oxygen, irreversible reaction with acid gases and thermal losses.

Most commercial formulations include an oxidation inhibitor to avoid excessive degradation of the solvent. This reaction has been studied by several authors. The reaction produces primarily ammonia and aldehydes as intermediates (according to reaction 8). Aldehydes can be further oxidized to form carboxylic acids. Analysis of samples taken from amine units in refinery installation show concentrations of

---

[15] Based on experimental values

formate in the range of 1000ppm, concentrations of oxalate in the range of 500 ppm and lower concentrations of acetate and glycolate [27;28].

$$MEA + O_2 \Rightarrow Aldehyde + NH_3 \qquad (8)$$

The amount of MEA degraded depends on the type of corrosion inhibitors that suppliers include in the solvent formulation. Some studies suggest that this rate ranges from 0.29kg/tCO_2 to 0.73kg/tCO_2 for flue gas containing 5% of O_2 approximately [29;30]. Experimental studies on MEA degradation rates show the dependence of this rate with solvent concentration, CO_2 loading, SO_2 and O_2 concentrations in the gas phase [31]. Experiments show higher degradation rate than the above mentioned. One of the possible reasons can be, that the experimental degradation rate is derived for MEA solutions which do not include corrosion inhibitors... Nevertheless, this experimentally derived degradation rate can be used to estimate the influence of SO_2 and O_2 concentration in flue gas. Appendix D shows in detail the variation of MEA degradation rates with increasing O_2 concentration in flue gas.
For this study the geometric mean of the range suggested in [29] was taken as nominal loss (0.46kg/tCO_2). Further more, it is also assumed that 50% of the reaction produces formaldehyde (reaction 8) and the other 50% produces acetaldehyde (reaction 8). In both cases 1 mol of ammonia is produced per mol of MEA degraded. These assumptions are in line with similar studies [32]. Also, these studies have suggested that acid gases (SO_2, NO_2) induce degradation similar to that of oxygen [32]. In this case, the primary degradation product from the reaction is ammonia. Known products of the reaction of SO_2 with MEA are isothiocynatoethane and tetrahydrothiophene [25]

The carboxylic acids formed due to oxidative degradation react further with MEA to form heat stable salts (HSS. These components are strong salts with amine molecules that can no longer be regenerated in the stripper. An example of HSS formation is given in equation 9.

$$HCOOH + MEA \Rightarrow [MEAH^+][HCOO^-] \qquad (9)$$

The interactions between acidic impurities in the flue gas and amines have also been described for MEA by several authors. MEA undergoes reactions with NO_2 and SO_2 that are not reversible under standard operation.. Rao and co-workers considered that due to its strong acid nature, SO_2, SO_3, NO_2, and HCl are very likely to form heat stable salts (HSS) with MEA [33]. The HSS formation of SO_2 and MEA was checked experimentally during recent pilot tests that showed that 75% of the SO_2 absorbed by MEA is removed as sulphate salt [25] [34]. These products lead to operational problems and need to be treated in a separate heat exchanger called reclaimer. The concentrated impurities are collected at the bottoms of the reclaimer and have to be disposed as hazardous material, contributing to generate waste in the process. The extension to which the salt formation takes place can be estimated from stoichiometry and acid gas removal efficiency. SO_3 and HCl are also likely to form heat stable salts with MEA. However, very little information has been found in the literature that allows the estimation of the effect of these components in the MEA solution. Table 2.6 shows typical removal efficiencies for acid gases found in literature and the likelihood of HSS formation. The reaction stoichiometry used in the present study is shown in the following reaction scheme:

$$SO_2+H_2O + 2MEA \rightarrow 2MEAH^+ + SO_3^{2-} \quad (10)$$

$$2NO_2 + H_2O + 2MEA \rightarrow MEAH^+ + NO_2^- + MEAH^+ + NO_3^- \quad (11^a)$$

$$3NO_2 + H_2O + 2MEA \rightarrow 2MEAH^+ + 2NO_3^- + NO \quad (11^b)$$

$$HCl + MEA \rightarrow MEAH^+ + Cl^- \quad (12)$$

$$HF + MEA \rightarrow MEAH^+ + F^- \quad (13)$$

This stoichiometry is in line with models used by others [32;33] with the exception of NO_2. Under absorption conditions it is more likely that NO_2 will be absorbed in the alkaline solution as a mixture of nitrous and nitric acid salts. Nitrous acid is not stable under acidic conditions when it is heated [35] and decomposes possibly leading to reaction 11^b. However, under alkaline conditions the reaction 11^a is more likely to take place.

Other forms of solvent loss are the reactions of carbamate polymerization. Rochelle (2001) and Korre and co-workers estimate oxidation and carbamate polymerization to account for 40 and 60 % of the solvent degradation respectively [36] [22].

Due to its volatility, some MEA is lost by evaporation in the absorber. These losses are minimized by adding washing stages on top of the absorber column. Typical value for MEA loss is 0.06kg/tCO_2 (for NGCC plant with water wash). Thermal degradation is only substantial for MEA at relatively high stripping temperatures. When the regeneration takes place at 120ºC, thermal degradation is not significant and it has been neglected for this study [32].

Trace metals might also be affected by the interaction with the solvent. Information describing the fate of these metals in the carbon capture unit is very scarce. In most pilot tests there are no measurements of trace contaminants. Those metals that concentrate in the particulates should be reduced as particulate matter is reduced. The capture unit consists of two gas/liquid systems: a Direct Contact Cooler and the absorber column. These units should reduce particulate matter as a wet scrubber. The assumed removal efficiencies are shown in Table 2.7

The fate of mercury in the scrubber is of particular interest, because of the toxic nature of this element. Mercury is present in the flue gas in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and condensed on fine particulates (Hg^p). Based on recent experimental studies, it is known that elemental mercury is not absorbed on MEA solutions [30]. Oxidizing agents, such the combined NaCl / NaOCl mixtures, remove elemental mercury by oxidation to Hg^{2+} and removal as $HgCl_2$. Nevertheless, these reactions take only place in acidic solutions. For this reason, they are not possible in combination with amine solutions [37].
On the other hand, the oxidized mercury is likely to be absorbed in MEA solutions [25] and traces of mercury in the order of 1-2 ppb have been detected in reclaimer waste analysis [38]. The mercury attached to the particulates is likely to follow the same removal as particulates. Table 1-6 shows the assumed removal efficiencies for this study.

Table 2.7 Estimated efficiencies for a MEA based capture plant

Removal efficiencies	**Value**	**Value used in this study**
CO_2 removal efficiency	90%	90%
SO_2 removal efficiency	99.5%	99.5% Partially removed as HSS
SO_3 removal efficiency	99.5%	50% Partially removed as HSS
NO_2 removal efficiency	25%[16]	25% Removed as HSS
HCl removal efficiency	95%	95% Removed as HSS
HF removal efficiency	95%	95% Removed as HSS
Particulate removal efficiency	50%	50%
Mercury removal efficiency [Hg^0]	8%	8%
Mercury removal efficiency [Hg^{2+}]	76%	76%
Trace metals Class 1	20%	20%
Trace metals Class 2	20%	20%

Regarding waste generation, a CO_2 capture unit produces three waste streams: reclaimer waste, spent carbon from the activated carbon system, filters elements from the slip-stream solvent filters.

- Spent carbon is assumed to be equal to the activated carbon consumption
- Waste generated by the filters is assumed to be equal to the particulates removed by the capture unit.
- Waste generated in the reclaimer is estimated by mass balance over the reclaimer

The heat stable salts and degradation products need to be removed periodically from the system. Generally, a side stream is taken from the lean hot solvent stream and treated in a separate heat exchanger. The criteria for the reclaiming process vary among different suppliers of technology. Table 2.8 shows different criteria, when suppliers of reclaiming technologies advise to start reclaiming. In parallel to the reclaimer, the filters and the activated carbon contribute to the elimination of degradation products. Normal design values for operational characteristics of the reclaimer are also listed in Table 2.8. The values of this Table are indicative values given by amine technology suppliers (ie Fluor Daniel). However, the actual waste generated depends on the flue gas composition and the plant operating conditions (including the emission control units).

For this study, a simple mass balance based was done around the reclaimer in other to estimate waste. The mass balance and assumptions are explained in Appendix D.

---

[16] This value is recommended in the literature [33]. However, it is recommended to check the NO_2 removal experimentally, since the acidity of NO_2 will probably lead to full absorption in MEA solutions

Table 2.8 Basic parameters for reclaimer and waste generation in MEA systems

Parameter	Value	Reference
Concentration of heat stable salts	1.2%wt	[28]
	500-2000ppm	[27]
Concentration of degradation products as a percentage of total active amine.	10%wt	[28]
NaOH consumption	0,13 kg / ton CO_2	[33]
Waste generated	0,003 m^3/ton CO_2	[39]

The CO_2 capture and compression unit generates two streams: The CO_2 product stream and the waste reclaimer stream. Typical composition of the CO_2 product stream is [25]:

- CO_2 >99.9%
- SO_2 34ppmw
- SO_3 <21ppmw
- NO_2 <7ppmw
- HCl <2ppmw
- Hg^{2+} <2ppbw

The above composition is based on a study under the assumption that 25% of the SO_2 captured is realised in the stripper. No experimental values (based on pilot campaigns) were found with this level of detail in the analysis of the CO_2 stream.

Typical composition of the waste stream from the reclaimer is given in appendix D.

2.2.2 Coal gasification in IGCC plants

With respect to uncontrolled emissions factors and emissions control technologies, coal gasification is not as well studied as the coal combustion. There are about 15 IGCC plants operating worldwide with sizes ranging from 40MWe to 545MWe, corresponding to Sarlux (Italy) [40]. Operating plants use different types of fuel such as coal, tar, pet coke and asphalt. Due to the scarcity of data based on bituminous coal, it has not been possible to derive uncontrolled emission factors for the specific gasifier and specific control technologies efficiencies selected for the reference case of this technology.

Table 2.9 shows a comparison of IGCC and PC technology in terms of combustion type and emission controls. Moreover, Table 2.10 shows the emissions factors for IGCC plants with emission control technologies for SOx, NOx, and PM. In IGCC, gasification takes place in a reducing atmosphere. Therefore, sulphur components are liberated as H_2S and COS. These components have been removed with refinery industry technologies for many years with removal efficiencies greater than 99%. Low levels of H_2S are burned in the gas turbine and become SO_2 in the exhaust. The NOx emissions are controlled by injecting N_2 at 1:1 ratio with syngas, as well as saturating the syngas stream with steam. Based on operating IGCC plants SOx emissions are comparable to the current state of the art PC plants, and NOx emissions and PM are lower.

Table 2.9 Technology comparison between PC boilers and IGCC

Components	**PC**	**IGCC**
Feedstock	[-]	Coal
Fuel	Coal	Syngas
Combustion	Coal in boiler	Syngas in turbine
Emission Controls	Post-Combustion clean-up of large volume gas	Pre-combustion clean-up of small volume of syngas
SO_2	Limestone-based FGD system	Amine / selexol system removes H_2S from syngas
NOx	Low-NOx burners, OFA, SCR	Syngas saturation and N_2 diluent
PM	ESP or bag house	Wet scrubber, high temperature cyclone, ceramic filter
Mercury	Activated carbon into flue gas	Pre-sulfide activated carbon beds in syngas streams

Table 2.10 Emission factors for IGCC plants

Emission factors (IGCC plants with emission controls)		Reference [40]		This study
		lb/MMBtu t	kg/t coal[17]	kg/t coal
SOx	Operating plants	0,1	1,241	0,124
	Newly design plants	0,01	0,124	
NOx	Operating plants	0,055	0,68	0,310
	Newly design plants	0,025	0,31	
PM	Operating plants	0,004-0,011	0,05-0,137	0,080
	Newly design plants	0,0063	0,08	

2.2.2.1 *Trace elements*

Trace element emissions in gasification systems are highly dependent on the gasification operating conditions and therefore on the gasifier type. For this reason, accurate data sources on trace metals emissions during gasification are very limited compared to the information already available for conventional boilers and evaluated during operation. The following paragraphs give a qualitative insight on the identification of emitted metals. However, it was not possible to derive a reliable estimate in the reference case mass balance.

Although most metals are trapped in the slag, some of them can be emitted in the vapour phase or condensed on the particulates. Therefore, the vaporization and condensation behaviour of metals is important in order to quantify their emissions. Information is available from thermodynamic models [18] and specific demonstration – scale IGCC plants [41]. Equilibrium studies have been used to identify chemical and physical forms of vapour trace elements likely to be formed during the gasification process. Sloss and co-workers published a review on the behaviour of trace elements in gasification systems [18]. More recent studies have also reviewed the fate of trace metals during gasification [19]. The following lines

---

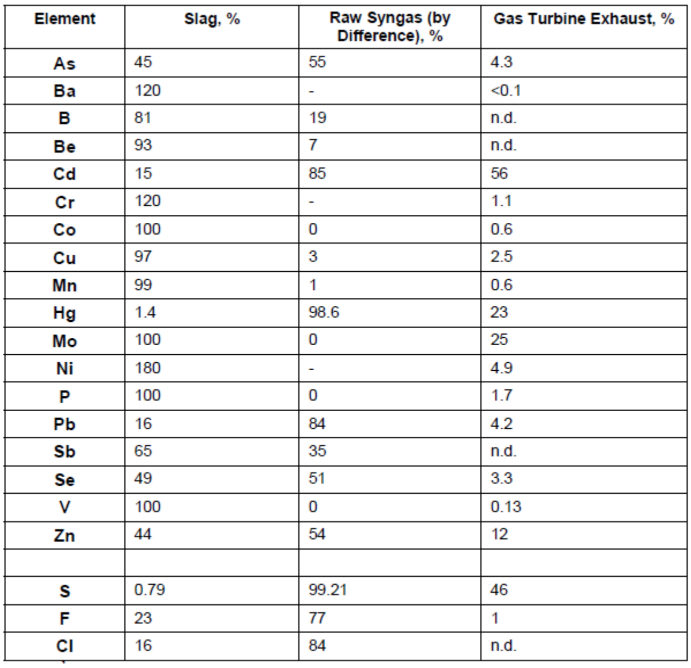
[17] Emission factors converted with Conversion was done with 1MMBtu <> 1,055GJ and an average LHV value for bituminous coal of 25,87 GJ/ton. Reference does not specify HHV or LHV

show one classification of metals. As in the case of conventional combustion, metals are classified in gasification regarding their condensing temperature [18]:

1. Co, Ni, Cr, V condensed at gasifier temperature 1000ºC
2. Zn, Cu, Mo condensed on cooling to 600ºC
3. Sn, Pb, Mn condensed on cooling to 400ºC
4. Hg, Se, As, Cd still vapour below 400ºC

Generally speaking, metal volatility is higher in gasification compared to air combustion, as reducing conditions are favourable to the formation of volatile reduced gaseous species of the trace elements, such as hydrides and carbonyls. Emissions of several metals have been investigated during a study in an IGCC plant operated by Louisiana Gasification Technology Inc. (LGTI) at Plaquemine (Louisiana). Table 2.11 is taken from Apps (2000) [19] and shows the partitioning of the studied metals. Numbers in Table 2.11 are indicative, since they had to be derived from the available information because necessary data for the evaluation was not disclosed in the study. The estimates in Table 2.11, despite the poor mass balance closures, suggest that some elements will be maily present in the gaseous phase. The order of volatility of the trace elements is Hg > Pb > Cd > As > Zn > Se > Sb > B > Be > Cu > Mn.

Table 2.11 distribution of trace metals in an IGCC plant. Data taken from [19]



Element	Slag, %	Raw Syngas (by Difference), %	Gas Turbine Exhaust, %
As	45	55	4.3
Ba	120	-	<0.1
B	81	19	n.d.
Be	93	7	n.d.
Cd	15	85	56
Cr	120	-	1.1
Co	100	0	0.6
Cu	97	3	2.5
Mn	99	1	0.6
Hg	1.4	98.6	23
Mo	100	0	25
Ni	180	-	4.9
P	100	0	1.7
Pb	16	84	4.2
Sb	65	35	n.d.
Se	49	51	3.3
V	100	0	0.13
Zn	44	54	12
S	0.79	99.21	46
F	23	77	1
Cl	16	84	n.d.

Moreover, during gasification the primary form of mercury that is produced is in oxidized state. For this reason, mercury removal is easier in IGCC plants than in PC plants. High levels of removal efficiencies are achievable (90%) with pre-sulfided carbon beds in the syngas stream. This system removes mercury in the form of mercury-sulphur complexes. The spent carbon is disposed once a year. Most IGCC plants plan to use this technology.

CO_2 capture is possible with amine solvents or Selexol. Partial capture is possible without any reworking of the technical detail of an IGCC plant. With respect to gas impurities, little is published on their interactions with the selexol solvent.

Table 2.12 Emission factors derive from IGCC plant data [42]

	Combined incinerator and turbine Stack		
	Emission rate	**Emission factor**	
	lb/h	**lb/10^6Btu**	**kg /MWh**
Criteria pollutants			
PM	25	0,0091	0,01
SO2	330	0,12	0,19
Nox	700	0,26	0,40
Ionic Species		lb/10^{12}Btu	kg /MWh
Chloride		740	1,15
Fluoride		38	0,06
Ammonia (as N)		440	0,68
Metals			
Antimony		4	6,2E-03
Arsenic		2,1	3,3E-03
Beryllium		0,09	1,4E-04
Cadmium		2,9	4,5E-03
Chromium		2,7	4,2E-03
Cobalt		0,57	8,8E-04
Lead		2,9	4,5E-03
Manganese		3,1	4,8E-03
Mercury		1,7	2,6E-03
Nickel		3,9	6,0E-03
Selenium		2,9	4,5E-03

2.2.3 *Natural gas fired turbines*

2.2.3.1 *Basic components*

Primary emissions during natural gas firing are NOx, carbon dioxide (CO_2) and nitrous oxide (N_2O) emissions. Trace to low amounts of hazardous air pollutants and sulphur dioxide (SO_2) are emitted from gas turbines. The later is related to the sulphur content in the gas, which is very low (H_2S is limited in pipeline regulations). PM emissions are negligible with natural gas firing. Methane (CH_4) is also present in the exhaust gas and is thought to be unburned fuel. Table 2.13 shows the uncontrolled emissions for natural gas fired turbines. PM emissions from turbines primarily result from carryover of non-combustible trace constituents in the fuel.

Table 2.13 Emission factors for stationary gas turbines (Source: [17])

	Uncontrolled[18]		Water steam injection	
Pollutant	lb/MMBtu	kg/t gas	lb/MMBtu	kg/t gas
NOx	0,32	7,080	0,13	2,876
CO	0,082	1,814	0,03	0,664
SO_2	0,0034	0,075		
Methane	0,0086	0,190		
VOC	0,0021	0,046		
PM (condensable)			0,005	0,104
PM (filterable)			0,002	0,042
PM (total)			0,007	0,146

2.2.3.2 *Trace components*

Available data indicate that emission levels of hazardous air pollutants (HAP) are lower for gas turbines than for other combustion sources. Table 2.14 shows the most significant trace pollutants.

Table 2.14 Trace components emissions

	Uncontrolled[13]	
NGCC	lb/MMBtu	kg/t
Acetaldehyde	4,00E-05	8,850E-04
Formaldehyde	7,10E-04	1,571E-02
Benzene	1,20E-05	2,655E-04

Regarding the APC's the NOx are controlled by water steam injection in the turbine or by the application of Low Burners and SCR. The efficiencies have been discussed in section 2.2.1.2.

---

[18] Uncontrolled emission factors from AP-42. Factors are derived for units operating at high loads (>80%). Conversion was done with 1MMBtu <> 1,055GJ and an average HHV value for natural gas on 51,473 GJ/ton (in line with IEA GHG technical criteria for Power plants assessments).

3 Results of harmonization studies

Based on the assumptions and method presented in section 2.1, all the reference cases were evaluated. The following sections describe the results of harmonization and its application to the reference cases.

3.1 Fuel use and fuel penalty

Table 3.1 presents the average plant efficiency (based on the Low Heating Value), fuel penalty and fuel use per CO_2 capture technology as found in the international literature. CCS power plants with the highest efficiencies have the lowest fuel penalties.

Table 3.1 Average plant efficiency, fuel use and fuel penalty per capture technology as found in the international literature.

Capture route	Power generator type	Plant efficiency [% LHV]	Fuel use [MJ/kWh]	Fuel penalty [%]	Fuel penalty [%points]
No-capture	IGCC	42	8.6	0	0
	NGCC	57	6.4	0	0
	PC	40	9.1	0	0
Post combustion	NGCC	49	7.4	18	8
	PC	31	11.8	37	9
Pre combustion	IGCC	35	10.4	24	7
Oxyfuel	NGCC	46	7.9	25	11
	PC	33	10.9	30	7

As described in Appendix C, fuel use was corrected for capture efficiency and compression pressure. The correction for compression pressure was applied to that part of the fuel penalty related specifically to CO_2 compression as shown in Table 3.2 and correction for CO_2 capture efficiency was applied on fuel penalty. The CO_2 compression pressure values found in the literature ranged between 80 and 200 bar.

Table 3.2 Fraction of fuel penalty related to CO_2 compression.

Fraction of fuel penalty related to CO_2 compression	average	min	max
Post combustion	30%	15%	71%
Pre combustion	29%	18%	77%
Oxyfuel	39%	15%	73%

Figure 3.1 presents the result of average raw (in red) and harmonised (in blue) fuel use per power generator type from the literature in MJ/kWh. Green bars have been plotted for the comparison as they represent the fuel use of the reference power plants. In the Figure, the 95% confidence intervals are indicated by the error bars and the number of cases used to calculate the average are given between the brackets (R: raw and H: harmonised). The confidence interval is calculated as twice the standard deviation, which is the typically reported 95% confidence interval for a standard normal distribution.

The effect of the harmonization of the raw literature data to the reference plant efficiency is illustrated by the comparison of the blue and red bars. The impact on the fuel use to standard CO_2 compression pressure and capture efficiency was very small; viz. the difference between the red and blue bars is small. Even the over-compensation of the fuel correction by assuming CO_2 to be an ideal gas did not lead to a large spread in results (discussed in Appendix C). Because of the little impact, no more effort was put in a more dedicated way to correct for the variance in compression pressure. Moreover, most cases already are based on a compressions pressure of 110 bar.

The efficiencies of the given reference plants are higher than the efficiencies of the power plants found in literature, even after harmonization. The only exception is the IGCC technology where the cases with and without CO_2 capture show lower efficiencies than the literature values (38 %LHV vs. 42 %LHV and 31.5 %LHV vs. 35 %LHV, for respectively the IGCC without and with CO_2 capture). The explanation for these differences is that the literature average includes different boiler types ranging from subcritical to ultra-supercritical (in the case of pulverized coal combustion) which ultimately leads to an averaged higher fuel consumption than the reference case (ultra-supercritical). In the case of IGCC, the literature average shows higher efficiency than the reference case (GE gasifier).

The fuel use of the oxyfuel case was not corrected. The corresponding harmonization to capture efficiency of 90% is useful for comparison with other technologies. However, such harmonization is not a realistic representation of the oxy – fuel technology where capture efficiencies up to 100% are possible. For this reason, no harmonization was applied to the oxyfuel case.

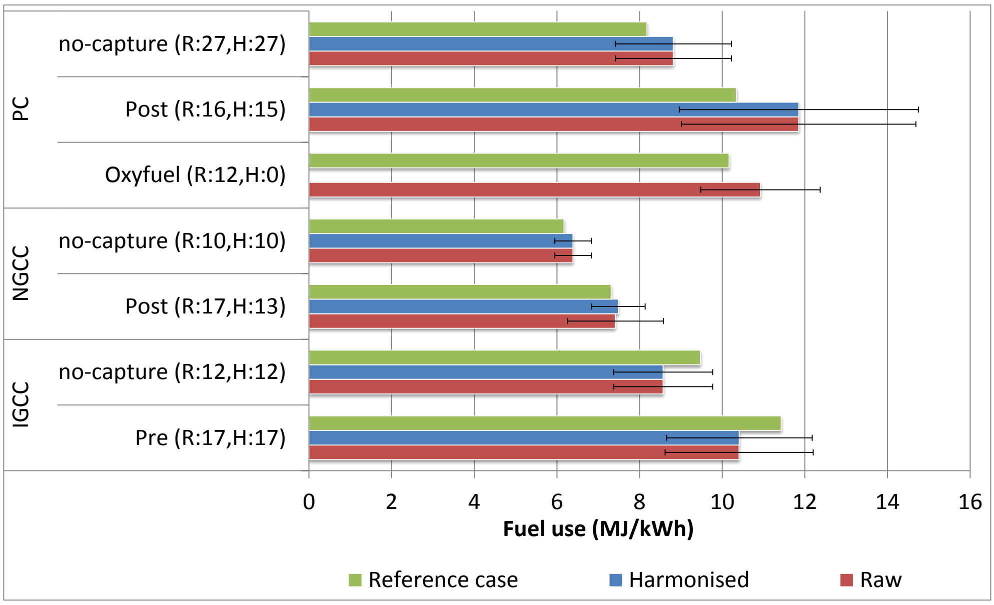


Figure 3.1 The average fuel use directly from literature (red), harmonised literature data (blue) and the reference cases (green) in [MJ/kWh], with between brackets the number of cases from literature (R) and after harmonization (H) shown per technology

3.2 Emissions

The following section presents graphs with the average emission factors per substance and per CO_2 capture technology (tables have been presented in the Appendix E. For each figure, the number of cases used for calculations is given between brackets. R (raw) means the number of cases directly from literature; H (harmonised) means the data could be harmonized with the available information in the literature source. When H is lower than R, specific information was lacking to calculate the correction factors. The figures include: raw literature (red) and harmonised (blue) emission factors. The figures provide the 95% confidence interval as approximated by twice the standard deviation.

The emission factors are presented in [g/kWh]. There is no correction for the efficiency of the power plants, which has a direct impact on the uncertainty ranges. The uncertainty ranges will be larger, because next to uncertainty of the emissions (per primary energy input) the variation in power plant efficiencies is added.

3.2.1 Carbon dioxide CO_2

The CO_2 emission factors and their 95% confidence intervals are presented in Figure 3.2. They depend on the type of the fuel, on the technology type, on the efficiency of the power plant and on the CO_2 capture and removal efficiency. The CO_2 emissions of the oxyfuel technology are not harmonized for the capture efficiency of 90% as given for the reference case. This would lead to a large increase in the CO_2 emissions as in literature the CO_2 capture efficiency is up to 100%. For the other technologies there are minor changes, except that the uncertainty interval decreases for the capture cases, due to set capture efficiency of 90%. The remaining uncertainty in the capture cases is caused by the variation in the efficiency of the power plants

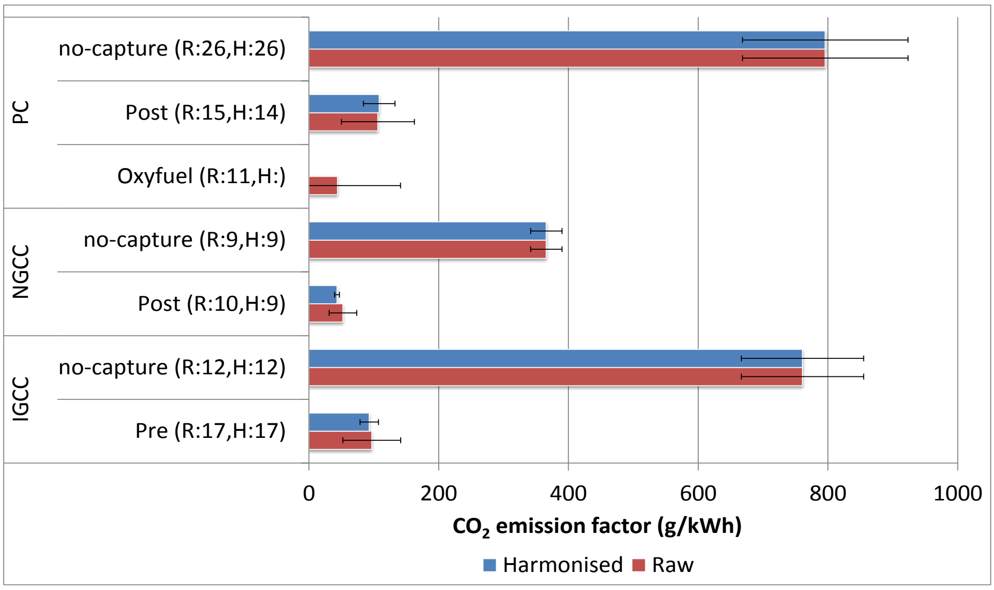


Figure 3.2 CO_2 emission factors from literature (red) and harmonised literature data (blue) in [g/kWh], with between brackets shown per technology the number of cases from literature (R) and after harmonization (H)

3.2.2 *Sulphur dioxide SOx*

Figure 3.3 summarizes the SOx emissions of the technologies with and without CO_2 capture. Harmonization, which means applying a linear correction between the SOx emissions and the S content in the coal, lowers the average SOx emissions. The type of coal defined in reference cases (Eastern Australian Bituminous coal) is relatively clean compared to the types used in the literature (ranges: 0.09 to 1.87 g/MJ)

The spread in the results remains large and will mainly be caused by a different degree of de-sulphurization by the FGD unit, which is not always explicitly mentioned in the literature sources. Generally speaking, there is a relation between the sulphur content in the coal, i.e. the SO_2 concentration before the cleaning process, and the cleaning efficiency. This relation was investigated as a sensitivity analysis study. For this purpose, the simplified models developed during this study were used. Chapter 4 shows the results of the sensitivity analysis.

The sulphur content of natural gas is very low, thus the SOx emissions are expected to be negligible.

PC plants without CO_2 capture show the highest SOx emissions. The emissions are significantly reduced by applying a post combustion process. For this process a high SOx removal is desired to prevent a reaction of SOx with the solvent in the capture unit. Some literature references show a zero emission for the oxyfuel process (with co-sequestration as well as with a FGD unit) other references do show some emissions. The IGCC process shows a low level of SOx emissions because of the efficient cleaning of the syngas prior to combustion.

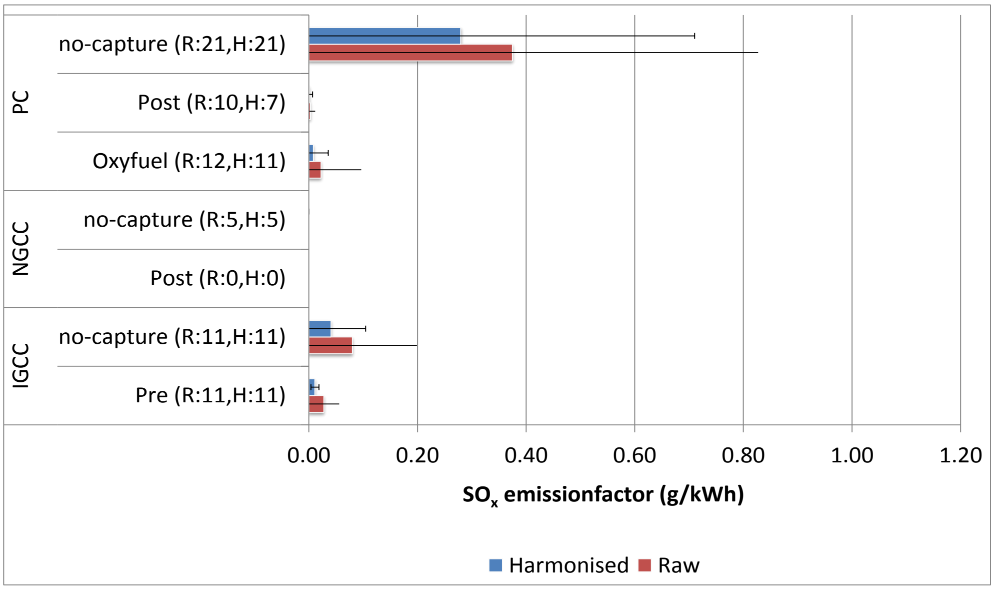


Figure 3.3 SOx emission factors from literature (red) and harmonised literature data (blue) in [g/kWh] , with between brackets shown per technology the number of cases from literature (R) and after harmonization (H)

3.2.3 *Other emissions: NOx, PM, NH_3, Hg.*

No specific harmonisation is applied for the rest of the emissions, except the correction for the fuel use. Amount of data available in the literature on the emissions and emission reduction technologies of particulate matter PM, NH_3 and NOx were insufficient to perform a harmonisation of parameters. An example is the NOx substances, whose emission level and distribution (NO, N_2O and NO_2) are directly influenced by the type of technology (boiler, De-NOx technology). When the technology type is not mentioned, the literature data are difficult to harmonise.

Figure 3.4 shows the raw (red), harmonised (blue) NOx emissions. The NOx emissions show a large standard deviations (95% confidence interval). For PC plants NOx emissions are clustered around two values, respectively 0,25 and 0,6 g/kWh. For the post combustion capture cases this kind of distribution is not visible. The values are related to the literature sources and can not be assigned to a parameter as technology, efficiency or coal type.

The distribution of NOx emissions in the IGCC cases, with and without CO_2 capture, is directly related to literature sources, with each its specific technologies and assumptions. No generic relation can be observed.The oxyfuel cases show values of zero (mainly co-sequestration cases) and of 0.3 g/kWh (on average).

For the post combustion CO_2 capture technology the NOx emissions per kWh increase due the fuel penalty. The NO_2 part (5-10% of NOx) is assumed to be partly removed by reaction with the amine based solvent. NOx emissions from the oxyfuel concept are expected to be low, but are highly dependent on the treatment and purification within the concept.

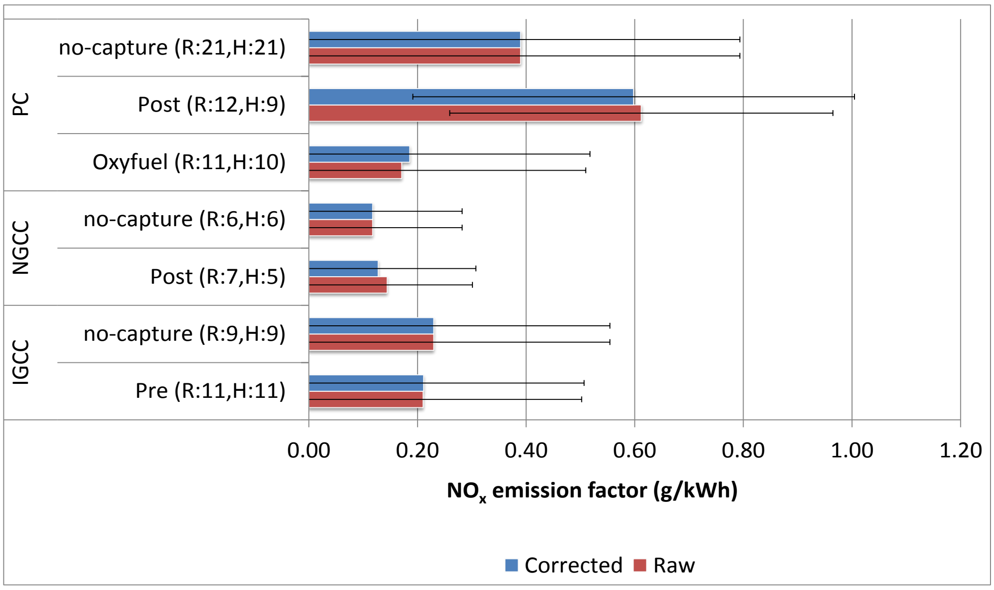


Figure 3.4 NOx emission factors from literature (red) and harmonized literature data (blue) in [g/kWh], with between brackets shown per technology the number of cases from literature (R) and after harmonization (H)

Figure 3.5 presents the emission factors of particulate matter (PM).The PM emission from NGCC are considered negligible in most studies. For coal fired oxyfuel power plants PM emissions are estimated to be lower compared to conventional pulverized coal fired power plants. The already low PM emissions for IGCC power plants are not expected to be significantly affected due to the application of pre-combustion capture and thus will result in an increase due to the efficiency penalty.

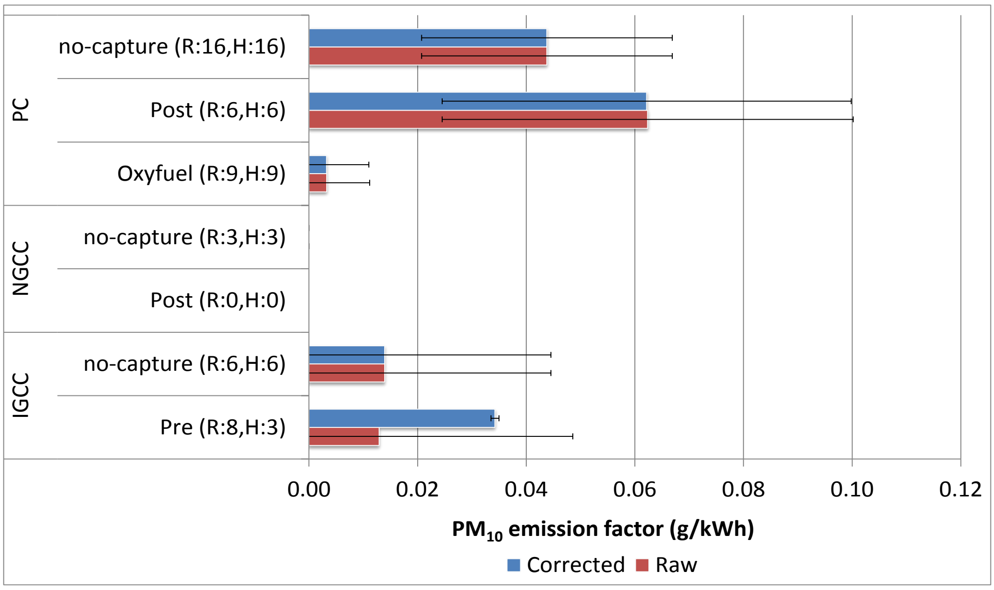


Figure 3.5 PM_{10} emission factors from literature (red) and harmonised literature data (blue) in [g/kWh], with between brackets the number of cases from literature (R) and after harmonization (H) shown per technology

Figure 3.6 shows the mercury emissions, which are only emitted by coal fired plants. The emissions seem to increase due to the fuel penalty for post- and pre-combustion carbon capture. The increase in case of the post combustion process seems to be relatively large. All cases originate from two literature references, of which only one mentions both the emissions for the capture and the no capture plant. The increase within this reference is less then than the average of all cases, and in line with the fuel penalty of approximately 40%. This indicates that the mercury emissions are directly related to the primary fuel input.

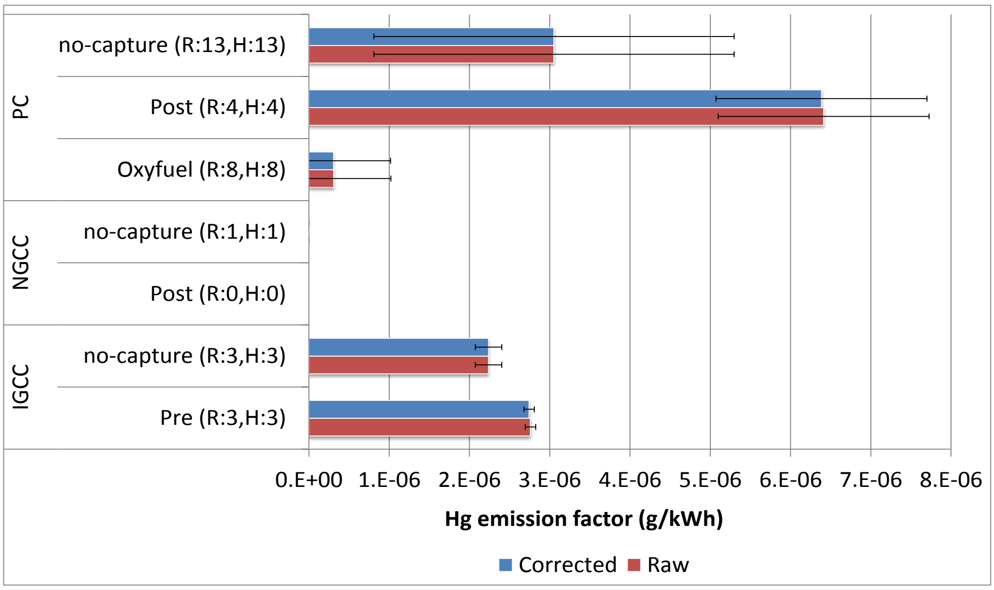


Figure 3.6 Hg emission factors from literature (red) and harmonised literature data (blue) in [g/kWh] , with between brackets the number of cases from literature (R) and after harmonization (H) shown per technology

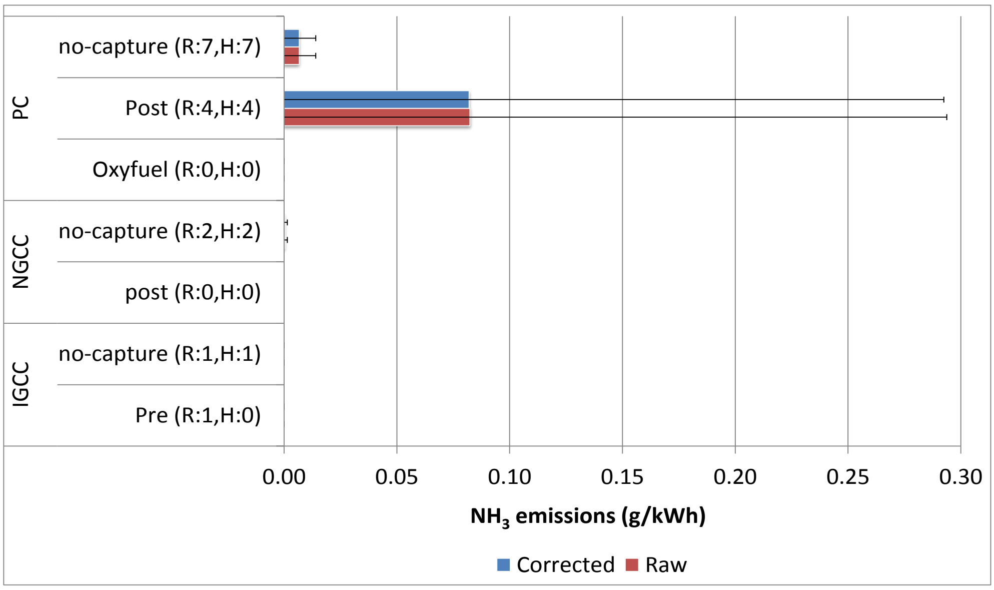


Figure 3.7 NH_3 emission factors from literature (red) and harmonised literature data (blue) in [g/kWh], with between brackets the number of cases from literature (R) and after harmonization (H) shown per technology

Figure 3.7 presents the ammonia (NH_3) emission factors. The majority of the available data are based on coal fired power plants. NH_3 emissions are expected to increase significantly due to post combustion capture, but the uncertainties are large. The increase in NH_3 emissions is caused by the degradation of amine based solvents that may be used in post-combustion capture. Additional scrubbers can reduce the NH_3 emissions to a large extent. Whether or not additional measures are applied in the literature cases is not taken into account in the database. The NH_3 emissions in the no-capture plants are caused by NH_3 slip from the SCR (De-NOx) unit.

No data on NH_3 emissions from NGCC post combustion capture were found in the literature. The emissions from the NGCC plants without capture are smaller because NO_x emissions are already lower and less De-NOx capacity (with associated NH_3 slip) will be needed.

No quantitative estimations on the effect of carbon capture on VOC emissions were found in literature. They are not reported in this report. VOC emissions can increase or decrease due to pre-combustion carbon capture. It is unknown whether and to what extent they are affected by the post and oxyfuel combustion processes [3].VOC emissions for coal fired power plant are in the order of 10 mg/kWh [58].

3.2.4 Analysis of specific USC technology

Three of the reference cases described in section 1.2 are equipped with Ultra Supercritical (USC) boiler. Available emission data for this specific boiler technology are scarce and sometimes non-existing (see the number of cases between the brackets). Obviously more information could be derived including data for other PC technologies, such as: PC/Supercritical and PC/Subcritical. The comparison of the emission factors estimation for both PC/all cases and PC/USC cases is presented in Table 3.3. The calculated emission factors for USC technology are within the range of uncertainties but based upon a much lower number of cases. Therefore, it was decided to use the whole spectrum of PC technologies.

Table 3.3 Comparison of USC technologies and the average of all cases (between brackets the number of cases).

Reference case			Plant efficiency [%LHV]	Fuel use [MJ/kWh]	CO_2 [g/kWh]	SO_x [g/kWh]	NO_x [g/kWh]	PM_{10} [g/kWh]	Hg [g/kWh]	NH_3 [g/kWh]
no-capture	1A	all cases	41.1% (27)	8.82 (27)	796 (26)	0.28 (21)	0.39 (21)	0.044 (16)	3.1E-06 (13)	6.7E-03 (7)
		USC	43.9% (9)	8.21 (9)	735 (9)	0.30 (6)	0.36 (6)	0.040 (5)	2.7E-06 (4)	3.5E-03 (1)
Post-combustion	1B	all cases	30.8% (16)	11.87 (15)	108 (14)	0.0013 (7)	0.60 (9)	0.062 (6)	6.4E-06 (4)	8.2E-02 (1)
		USC	34.1% (5)	10.57 (5)	97 (5)	0 (1)	0.50 (2)	0.046 (2)	5.5E-06 (1)	- (0)
Oxyfuel	2	all cases	33.1% (12)	10.96 (11)	102 (11)	0.0085 (11)	0.19 (10)	0.003 (9)	3.1E-07 (8)	- (0)
		USC	35.6% (4)	10.24 (3)	93 (3)	0.0117 (3)	0.20 (3)	0.004 (2)	3.5E-07 (2)	- (0)

4 Results of modelling studies

The following sections show the results of the modelling activities. Different models (as described in chapter 2) have been applied to seven different cases (described in chapter 1). The oxyfuel case is addressed separately in Chapter 5.

4.1 Emissions

Based on the methods and assumptions described in section 2.2, all the reference cases were evaluated. However, due to the different levels of information available for the various technologies, there are some exceptions to the general methodology described in section 2.2. The following lines cover in detail these exceptions:

- Hydrogen halides (HCl and HF): Evaluation of HCl and HF based on equation 7 in section 2.2 was not applied to the following cases: Case 2, Case 3A and Case 3B. The reason for that is the non-applicability. There are studies that evaluate the distribution of chlorine and fluorine in gasification plants [41;42]. However, these figures are not specific for the type of gasifier of Cases 3A and 3B. For this reason. The figures for chlorine and fluorine emissions are not given here and are discussed in section 2.2.2.
- Ammonia: For the cases which make use of SCR for NOx reduction, some ammonia is expected to be realised to the atmosphere during operation (ammonia slip). The final amount emitted depends on the technology used and operating conditions. The models used do not have a closed mass balance for the SCR unit since the final operating conditions and guarantees are given by the suppliers of the technology only. For cases 1A and 4A the ammonia slip was evaluated during the literature review and harmonization and has been discussed in section 3.2.3. For cases 1B and 4B the harmonized value for ammonia slip was taken and increased with the contribution from solvent degradation. Formation of ammonia during amine scrubbing has been addressed in section 2.2.1 and the estimation procedure is fully described in Appendix D.
- Trace metals (Hg): Evaluation of trace metals based on equation 7 in section 2.2 was not applied to the following cases: Case 2, Case 3A and Case 3B. There are studies that evaluate the distribution and partition of metals gasification plants [section 2.2.2]. However, these figures are not specific for the type of gasifier and conditions of Case 3A and 3B. Moreover, available experimental data show a very poor mass balance closure. For this reason. The figures for trace metals emissions are not given here and are discussed in section 2.2.2 and 3.2.3.

Table 4.1-A Emissions to air for the reference cases (power plants w/o and with of CO$_2$ capture). (NE, Not Evaluated; NA, Not Applicable)

Basic components	Units	**CASE 1A**	**CASE 1B**	**CASE 3A**
		USC PC w/o CC	**USC PC w CC**	**IGCC (GE) w/o CC**
CO$_2$	kg/MWh$_{net}$	739	93	818
Sulfur components (SOx)	kg/MWh$_{net}$	0.27	7.7E-04	0.05[19] 0.08[20]
SO$_2$	kg/MWh$_{net}$	0.26	6.5E-04	NE
SO$_3$	kg/MWh$_{net}$	0.02	1.2E-04	NE
Nitrous components (NOx)	kg/MWh$_{net}$	0.08	0.10	0.11[18] 0.39[19]
NO$_2$	kg/MWh$_{net}$	0.01	6.0E-03	NA
NO	kg/MWh$_{net}$	0.08	9.8E-02	NA
Other acid gases				
CO	kg/MWh$_{net}$	0.07	9.0E-02	0.24[19]
HCl	kg/MWh$_{net}$	9E-03	5.4E-04	NA
HF	kg/MWh$_{net}$	0.001	6.8E-05	NA
Particulate mater PM (total)	kg/MWh$_{net}$	0.05	0.03	0.03[18] 0.03[19]
PM-10	kg/MWh$_{net}$	0.01	5.6E-03	NA
Ammonia	kg/MWh$_{net}$	NE	1.1E-01	NE

Table 4.1-B Emissions to air for the reference cases (power plants w/o and with of CO$_2$ capture). (NE, Not Evaluated; NA, Not Applicable)

Basic components	Units	**CASE 3B**	**CASE 4A**	**CASE 4B**
		IGCC (GE) w CC	**NGCC w/o CC**	**NGCC w CC**
CO$_2$	kg/MWh$_{net}$	152	354	42
Sulfur components (SOx)	kg/MWh$_{net}$	0.0115	1.0E-02	5.9E-05
SO$_2$	kg/MWh$_{net}$	NE	1.0E-02	5.9E-05
SO$_3$	kg/MWh$_{net}$	NE		
Nitrous components (NOx)	kg/MWh$_{net}$	0.3915	0.03	0.03
NO$_2$	kg/MWh$_{net}$	NA	1.34E-03	1.2E-03
NO	kg/MWh$_{net}$	NA	0.03	0.03
Other acid gases				
CO	kg/MWh$_{net}$	0.2515	0.09	0.10
HCl	kg/MWh$_{net}$	NA		
HF	kg/MWh$_{net}$	NA		
Particulate Matter				
PM (total)	kg/MWh$_{net}$		9.7E-05	5.7E-05
PM-10	kg/MWh$_{net}$	NA		
Ammonia	kg/MWh$_{net}$	NE	NE	0.04

---

[19] *From emission factors (see section 2.2)*

[20] *From process modeling [6]*

Tables 4.1 A and B show a comparison of the studied cases based on state-of-the-art technologies.

Modelling results show that for the given set of cases, USC technologies have the highest SOx emissions compared to lower amounts in IGCC technologies and negligible amounts for NGCC and oxyfuel technologies (as will be discussed in Chater 5). However, when plants are equipped with capture units the SOx emissions for USC technology are drastically decreased to levels below IGCC emissions.

Regarding NOx emissions, the lowest amounts are emitted by the NGCC and oxyfuel technologies. IGCC and USC are comparable. Since NO does not interact with amine solvents, NOx emissions increase for post-combustion CO_2 control technologies due to the reduction in power efficiency.

In the case of IGCC, modelling results show that NOx emissions are equal for IGCC power stations with and without CO_2 capture. In this case, NOx emissions can be reduced by diluting the feed to the gas turbine with N_2. This control measure is sufficient to compensate the efficiency drop due to the auxiliary consumption of the capture unit. Therefore, NOx emissions are equal for IGCC power stations with and without CO_2 capture.

Regarding particulates, IGCC has lower PM emissions compare to USC. NGCC might have PM emissions due to particle carry over with the fuel. In this case, emissions depend entirely on the type of fuel used. Based on the emission factors (section 2.1.2) for gas turbines, the uncontrolled emissions for NGCC cases (4A and 4B) are 1.9E-02 kg/MWh_{net} (w/o CC) and 1.1E-02 (w CC). When the normal removal efficiencies of ESP controls are applied, emissions are reduced to the levels shown in Table 4.1-B. It should be noticed that the selected efficiency will decrease for very fine particles.

Finally it should be highlighted that based on operating IGCC plants, SOx emissions are comparable to the current state of the art USC PC plants, and NOx emissions and PM are lower. Estimates for the currently operating IGCC plants are:

- SOx 0.46 kg/MWh_{net}
- NOx 0.25 kg/MWh_{net} - 0.11 kg/MWh_{net} (with SCR)
- PM 0.05 kg/MWh_{net}

The trace metals were also estimated for the USC cases. Table 4.2 shows the emissions of these metals for the USC cases (Cases 1A and 1B). Results show that emissions for most metals are similar for the cases with and without carbon capture. This is due to the fact that the percentage reduction of trace metals in the CO_2 capture unit is in the same order of magnitude to the percentage reduction in net power output in the power plant. Therefore, no variation is observed in the emissions of trace metals. However, recent pilot studies [43] show a deeper reduction in fine particulates and metals for the CO_2 capture unit. Experiments were performed with a 30%wt MEA solution at 90% CO_2 capture removal present in flue gas from the coal fired station at Esbjerg (Denmark). Table 4.3 shows the monitored trace elements, at the inlet and outlet streams of the absorber. The indicated reduction in particulates is approximately 50%. The values measured at the outlet stream were below detection limit. However, the reduction is anticipated to be deeper (due to the deeper reduction in trace metals).

Table 4.2 Emission of trace components to air for USC cases

Trace metals	**Units**	**Case 1A USC PC w/o CC**	**Case 1B USC PC W CC**
Arsenic	kg/MWh$_{net}$	5.2E-05	5.2E-05
Cadmium	kg/MWh$_{net}$	1.7E-06	1.7E-06
Chromium	kg/MWh$_{net}$	4.0E-07	4.0E-07
Cobalt	kg/MWh$_{net}$	1.2E-07	1.2E-07
Lead	kg/MWh$_{net}$	5.2E-06	5.2E-06
Manganese	kg/MWh$_{net}$	4.0E-07	4.0E-07
Nickel	kg/MWh$_{net}$	6.4E-05	8.1E-05
Selenium	kg/MWh$_{net}$	5.3E-04	6.7E-04
Zn	kg/MWh$_{net}$	1.5E-02	1.9E-02
Copper	kg/MWh$_{net}$	1.1E-04	1.4E-04
Total mercury	kg/MWh$_{net}$	5.7E-06	5.3E-06

Table 4.3 Emission of trace components measured at the inlet and outlet of a 30%wt MEA operated absorber [43]

Compound	**Unit**	**Inlet absorber**	**Outlet absorber**
CO2	mg/Nm^3	13.2	1.7
CO	mg/Nm^3	9.8	12.4
HCl	mg/Nm^3	0.06	<0.04
HF	mg/Nm^3	0.04	<0.04
SO2	mg/Nm^3	14.4	1.5
Nox	mg/Nm^3	27.5	34.4
TOC	mg/Nm^3	<2	<2
Particulate	mg/Nm^3	2.1	<1.2
Al	μg/Nm^3	75	<2
Ca	μg/Nm^3	88	<1
Fe	μg/Nm^3	49	<1
Si	μg/Nm^3	140	<8

4.2 Generated waste

Water use, solid waste and waste water were well studied in prior studies [5;6;7]. Results showed that when post-combustion is applied to USC technology, the waste water generation increases drastically due to the effluents of the capture plant. The largest source of waste water is the water condensed from flue gas in the

DCC contact cooler. Other sources are the blown down water flows during compression and drying of the CO_2 product.

Table 4.4-A Generated waste for the power plant reference cases

Generated waste	**Units**	**Case 1A USC PC w/o CC**	**Case 1B USC PC w CC**	**Case 3A IGCC GE w/o CC**
Particules in ESP	kg/MWh$_{net}$	19	24	NE
Gypsum	kg/MWh$_{net}$	15	21	NA
Furnace bottom ash/ Coarse slag	kg/MWh$_{net}$	9.6	12	86.6
Fly ash / Fine slag	kg/MWh$_{net}$	29.0	37	36.1
Mill rejects	kg/MWh$_{net}$	0.7	0.8	NA
Sludges from WWT	kg/MWh$_{net}$	1.0	1.2	2.4
Reclaimer waste	kg/MWh$_{net}$	NA	3.291	NA
Activated carbon	kg/MWh$_{net}$	NA	0.063	NA
Waste water	kg/MWh$_{net}$	19	375	10
Raw Materials				
Cooling water consumption	t/MWh	138.6	240.5	146.9
Specific water consumption	t/MWh	0.104	0.410	0.126
MEA make up	kg/tCO_2		1.765	
Activated carbon make up	kg/tCO_2		0.075	

Table 4.4-B Generated waste for the power plant reference cases

Generated waste	**Units**	**Case 3B IGCC GE w CC**	**Case 4A NGCC w/o CC**	**Case 4B NGCC w CC**
Particules in ESP	kg/MWh$_{net}$	0	NA	NA
Gypsum	kg/MWh$_{net}$	0	NA	NA
Furnace bottom ash/ Coarse slag	kg/MWh$_{net}$	104	NA	NA
Fly ash / Fine slag	kg/MWh$_{net}$	44	NA	NA
Mill rejects	kg/MWh$_{net}$	0	NA	NA
Sludges from WWT	kg/MWh$_{net}$	3	NE	NE
Reclaimer waste	kg/MWh$_{net}$		NA	1.17
Activated carbon	kg/MWh$_{net}$	NA	NA	0.025
Waste water	kg/MWh$_{net}$	19	NE	NE
Raw Materials				
Cooling water consumption	t/MWh	185.2	45.6	82.7
Specific water consumption	t/MWh	0.411	1.01	1.21
MEA make up	kg/tCO_2		NA	1.79
Activated carbon make up	kg/tCO_2		NA	0.075

On the other hand, IGCC technology allows the re-use of waste water within the power plant. Main waste water streams can be recycled back and be re-used in the gasifier.

All coal cases produce a solid waste in the form of ash or slag. The relative emission of this solid waste increases when carbon capture is applied (post or pre combustion) due to the drop in power plant efficiency. Contaminants in this waste and moisture differ depending on technology. Previous studies give a qualitative composition of the slag [5-8].

4.2.1 Reclaimer waste

Reclaiming of the amine system is necessary for having a smooth operation of the capture plant. Thermal reclaiming is the most common approach for MEA reclaiming. In this study the waste generated by the reclaimer was estimated by calculating the mass balance around this unit. Appendix D shows the details of the estimation of reclaimer waste for cases 1B and 4B. One of our findings by going through the literature was that most studies over estimate the performance of the reclaimer. In an ideal case, most of the free amine present in the slip stream sent to this unit is recovered and sent back to the system. However, the units operating in refinery industries show a very high content of free amine in the reclaimer bottoms. This issue wastes the valuable amine [27]. Specific application of this technology for flue gas is not well reported in the literature.

On the other hand there are still uncertainties on the degradation rate of MEA. Although, there are experimental studies published in the literature [31], the degradation rates predicted lead to higher MEA loss than the reported by suppliers (1.6-3.1 kg/tCO_2; [39]).

Table 4.4 shows that the coal case produces more reclaimer waste than the NGCC case per unit electricity produced. However, per ton of CO_2 captured the generated waste is comparable (3.94 kg/tCO_2 in the coal case and 3.47 kg/tCO_2 in the NGCC case). This is due to the fact that the dominant formation of HSS is related to oxidative degradation products. Both reference cases used the same rate for oxidative degradation. However, flue gas from NGCC plants contains more oxygen than the one from USC plants. Therefore, the dependence of the degradation rate with oxygen concentration was taken from [31] and introduced in the mass balance.

4.3 Sensitivity analysis

The results presented in this chapter, have considered one set of fixed specifications. The following lines indicate the effect of the deviations of the given specifications. The most important parameters investigated are:

- Coal sulphur content: Quantitative analysis has been conducted for cases 1A and 1B. Regarding IGCC and oxy-combustion cases, there is not sufficient information for quantitative analysis. In the case of oxyfuel combustion, the SOx removal is catalyzed by the presence of NOx. Therefore, it is expected that all the SOx will be removed regardless the coal sulphur content. However, the state of the technology development dos not allow for a quantitative evaluation. Chapter 5 analyzes qualitatively the impact of SOx variations in flue gas.

- Oxygen content: Oxygen content was varied from 4% to 13% v/v and the effect on solvent degradation was analyzed. This is important for natural gas cases.

4.3.1 Coal sulphur content. USC PC cases

This study has analyzed the effect on emissions for a specific coal containing 0.95%wt (as received) sulphur. Sulphur content might vary among different coal type and sources. Regarding the pulverized coal cases with post combustion capture, coal sulphur content was varied independently in the model, while maintaining constant the FGD removal efficiency.

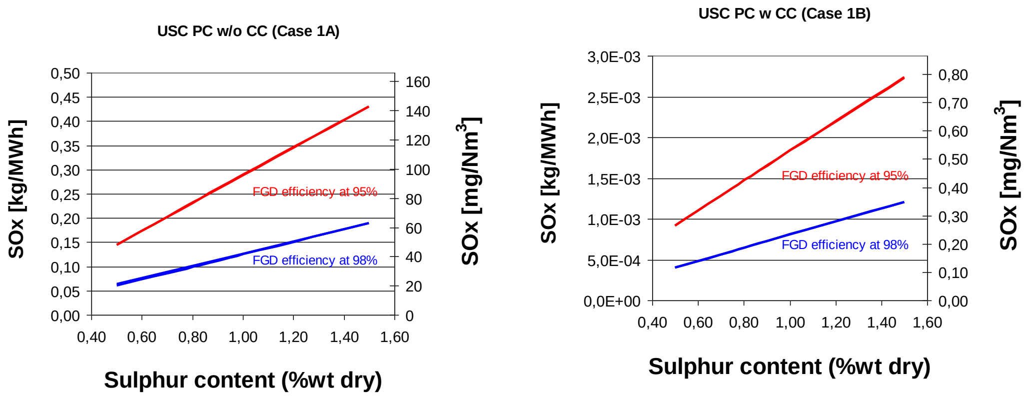


Figure 4.1 Emissions of SOx as a function of coal sulphur content.

Figure 4.1 shows the emissions of sulphur dioxide as a function of sulphur coal for two different situations: one represents the case where the FGD removal efficiency is 95% and the other represents the case where the FGD removal is 98%. As expected, the final SOx emissions depend on the removal efficiency of the FGD unit. It is important to notice that the SOx content in flue gas is limited to 10ppmv as a requirement for the CO_2 capture unit. For sulphur contents above 1% wt (dry), the FGD unit incorporated in the reference cases is not capable of reducing SOx to acceptable levels. Therefore, extra cleaning steps would need to be considered in the design, for cases with higher sulphur content.

Figure 4.2 shows the effect that higher sulphur content has in the flows of waste generated for the case with CO_2 capture. The reclaimer waste increases with increasing coal sulphur content. However, the generated waste per unit electricity produced dos not increase dramatically (3,2 – 3,4 kg/MWh). For the conditions explored, the major solvent loss and generated waste is related to the oxidative solvent degradation and polymerization.

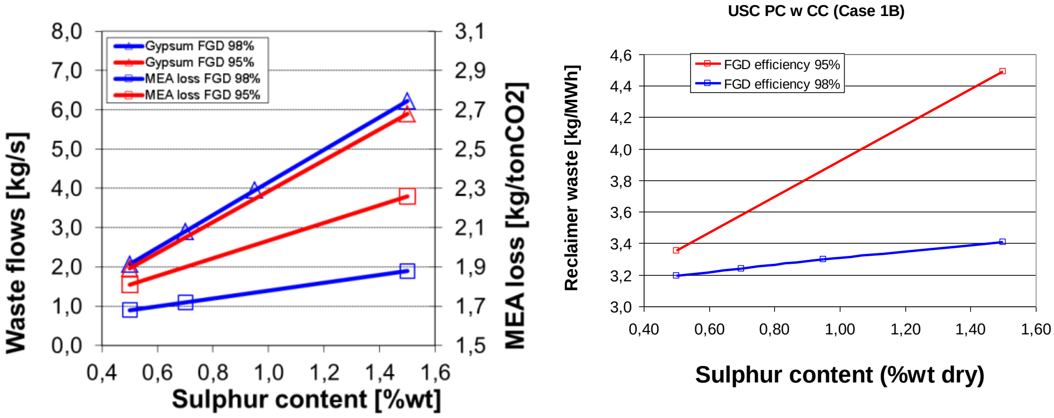


Figure 4.2 Generated waste flows for case 1B (USC PC w CC) as a function of coal sulphur content.

4.3.2 *Oxygen content. NGCC cases*

Figure 4.3 shows the MEA degradation and the waste generated as a function of O_2 concentration in the flue gas for case 4B. According to these authors the rate increases power 2.8 with the dissolved oxygen concentration in the solvent. This leads to a substantial increase in the solvent degradation and the waste generated. Nevertheless, it is important to notice that this degradation rate was derived from experiments on a raw solvent without corrosion inhibitors.

Results show that at 4% O_2, the waste produced is comparable to that reported in the literature. However, for the NGCC case, the O_2 concentration is 13% which would lead to a waste consumption of $0.008m^3/tCO_2$ and a MEA loss of almost $6kg/ton\ CO_2$.

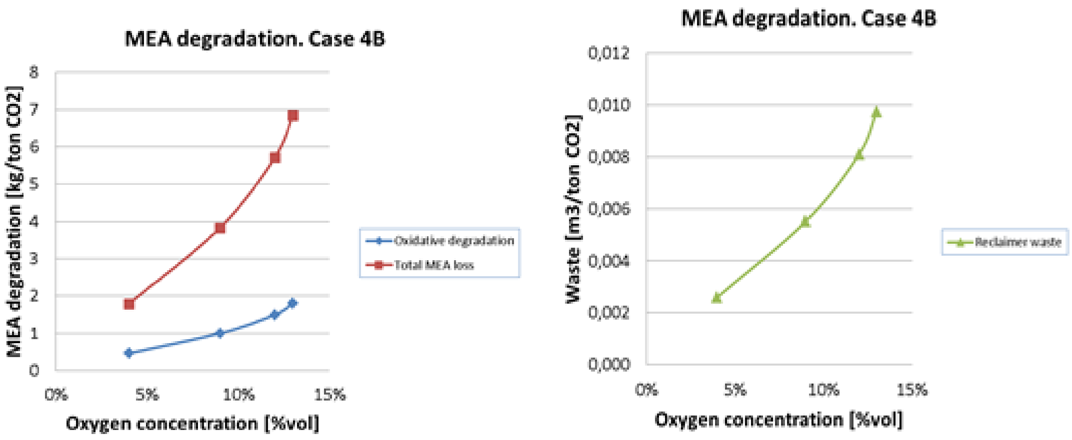


Figure 4.3 Sensitivity analysis on the MEA degradation rate

5 Overall waste assessments: comparison and analysis

Emissions for different power plants have been estimated following two different approaches: Harmonization of literature (results presented in Chapter 3) and Modelling (results presented in Chapter 4). The following sections compare and analyze the results from both approaches. Waste generation was directly estimated from models. Therefore there is no possible comparison.

Oxyfuel technology was also analyzed in this study based on reference case 2. Due to the characteristics of this technology, harmonization to 90% capture was not applied since it does not reflect the reality of this technology. Therefore, results are presented here without harmonization.

5.1 USC PC cases (Reference cases 1A and 1B)

5.1.1 Basic components

Table 5.1 shows harmonization and modelling results for the USC PC coal cases. In the case of SOx there is a relative good agreement between modelling results and harmonization results. Emission factors for SO_2 were reported in the harmonization study at 0.30 kg/MWh_{net}, which corresponds to a concentration of 99 mg/Nm^3. Nevertheless, newly build power plants have a stricter goal in SOx emissions. EBTF [8] selected 85mg/Nm^3 as emission limit, which is the average of the range given by the BAT [40]. Harmonization results show that on average most power plants need to decrease their emissions on SOx or that newly built plants designs need to incorporate lower targets for SOx.

The modelling results are based on 95% removal efficiency for wet scrubbers using limestone. However, other systems, such as dual alkali systems, give higher removal rates (up to 98%). If this removal efficiency is applied to case 1B, the concentration in the flue gas entering the CO_2 capture unit would be 34mg/Nm^3, concentration slightly above the limit for the amine operation (10ppmv or 29mg/Nm^3 @6% O_2). Therefore, modifications on the design presented for the reference cases need to be introduced if the coal is changed to another type with higher sulphur content. The effect of CO_2 capture on SO_2 emissions is predicted by both methods accordingly.

Table 5.1 Emissions to air for cases 1A and 1B. USC PC power plant without & with CO_2 capture.

Basic components	Units	Modelling 1A	Modelling 1B	Database[21] Harmonization 1A	Database[21] Harmonization 1B	Units	Modelling 1A	Modelling 1B
CO_2	kg/MWh$_{net}$	739	93	735	97	mg/Nm^3	NA	NA
SOx	kg/MWh$_{net}$	0.27	7.7E-04	NA	NA	mg/Nm^3	91	0.22
SO_2	kg/MWh$_{net}$	0.26	6.5E-04	0.30	0	mg/Nm^3	85	0.19
SO_3	kg/MWh$_{net}$	0.02	1.2E-04	NA	NA	mg/Nm^3	6	0.03
NOx	kg/MWh$_{net}$	0.08	0.104	0.36	0.50	mg/Nm^3	28	30
NO_2	kg/MWh$_{net}$	0.01	0.006	NA	NA	mg/Nm^3	2.1	1.7
NO	kg/MWh$_{net}$	0.08	0.098	NA	NA	mg/Nm^3	26	29
Acid gases								
CO	kg/MWh$_{net}$	0.07	0.09	NA	NA	mg/Nm^3	24	26
HCl	kg/MWh$_{net}$	0.009	5.4E-04	NA	NA	mg/Nm^3	3	0
HF	kg/MWh$_{net}$	0.001	6.8E-05	NA	NA	mg/Nm^3	0.4	0
Particulates								
PM (total)	kg/MWh$_{net}$	0.05	0.03	NA	NA	mg/Nm^3	16	9
PM-10	kg/MWh$_{net}$	0.01	0.006	0.04	0.046	mg/Nm^3	3	2
Ammonia	kg/MWh$_{net}$		0.107	0.004	0.08	mg/Nm^3		31
Total mercury	kg/MWh$_{net}$	5.7E-06	5.3E-06	2,7E-06	5,5E-06	mg/Nm^3	1,9E-03	1,5E-03

The NOx emissions estimated from the modelling study are much lower than the estimates from the harmonization study (0.36kg/MWh$_{net}$; equivalent to 119 mg/Nm^3). The reason for this difference lies in the different approaches taken. The harmonization value represents an average of the harmonized emissions database, which includes mainly operating power stations, new permitted installations and recent desk studies. The modelling value represents the result of one pioneer technology on NOx reductions. The combination LNB & OFA & SCR is seen as one of the Best Available Technologies (BAT) for reducing NOx emissions in coal fired stations. Although this combination is commercially available, it has not been widely demonstrated as a combined technology. The removal efficiency might vary in operation from 85% to 95%. Figure 5.1 shows the variation on the NOx levels for cases 1A and 1B when only the NOx reduction efficiency is changed. The emissions will vary between 28 and 84 mg/Nm^3, which are still below the emissions target for the present project (100mg/Nm^3). On the other hand, the harmonization result (119mg/Nm^3) indicates that there are a substantial number of power stations emitting relatively high concentrations of NOx. This will have implications if post-combustion capture technologies are retrofitted to these systems.

---

[21] *Results of Database harmonization for USC specific cases*

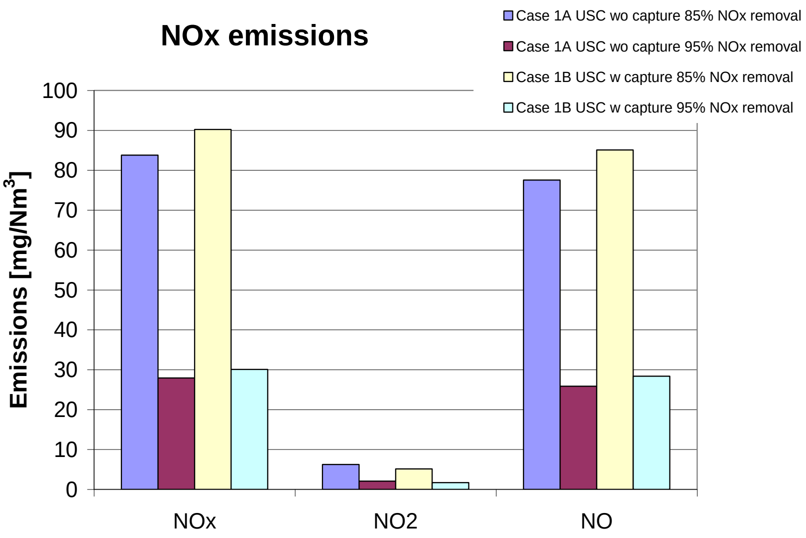


Figure 5.1 NOx emissions vs efficiency removal of NOx control

When carbon capture is added, only the NO_2 reacts partially with the amine solvent. For this reason the NOx emissions increase when the power plant is equipped with CO_2 capture. Harmonization predicts a larger rise in emissions. This is only related to the dispersion in power plant efficiencies existing in the emissions database.

NO_2 interaction with amines, mainly secondary amines, might lead to the formation of potential hazardous components (nitrosamines), solvent degradation and heat stable salts formation. Nevertheless, due to these interactions some authors also suggest that suppliers will also require levels of NOx in the order of 10ppmv [25]. The mentioned NOx controls are capable of reducing the NOx level to 13ppmv. This reduction is not needed in practice for environmental reasons.

In the same line, the particulates value is higher for the 10 micron particulates. This is due to the wide variation on the emissions control performance. On the other hand, the result for the power plant integrated with capture suggests no removal of particulates in the capture unit. This is due to the lack of measured data in pilot plants. Since no correction is applied to the harmonized PM emissions, the relative emission factor increases when the fuel penalty is included. However, part of the particulates will be washed in the direct contact cooler (DCC) and the absorption column of the capture unit.

The results on the basic components show that the parametric model is in agreement with the harmonized values from literature with respect to SOx and ammonia. In other cases, differences can be explained by the technology assumptions of the reference cases. The models have been used for estimates of other components outside literature. The results on the trace components show a limited impact of CCS technology in the relative emission factors for heavy metals.

Most of the metals that are enriched in the fly ash will be captured in the downstream filters (ESP). Moreover, part of the these metals is also captured in the carbon capture unit. This study assumed a reduction of 20% of the mass flow of these metals in the capture unit. This reduction is compensated by the fuel penalty, resulting in the same relative emissions as in the case with no carbon capture.

Mercury is a volatile metal that is present in the flue gas. Part of the emitted mercury absorbs in the unburned carbon in fly ash and will be removed in the ESP and the capture unit in the same way as the above mentioned metals. The condensate of the DCC unit in the capture plant might contain low amounts of mercury that will be sent to the waste water treatment [5]. The fraction of mercury that does not absorb in the fly ash will be present in flue gas as elemental mercury or as oxidized mercury. The oxidized mercury solubilises in the alkaline solutions used in the FGD and capture units. However, the elemental mercury is not soluble in these solutions and will not be removed. The removal of mercury depends on the distribution of this metal into the three possible forms. Based on the assumptions of this study (distribution taken from [22]) the relative emissions of mercury are slightly lower with carbon capture than without it.

Harmonization studies showed a different prediction (see Figure 3.6). It was discussed in section 3.2.3 that due to the large standard deviation, no firm conclusion can be drawn from harmonization studies on the removal of mercury.

5.2 Oxyfuel combustion. Results and analysis

Oxyfuel combustion is seen as one of the major options for CO_2 capture for future clean coal technologies. Although it has only been demonstrated for relatively small scale, it is seen as a short term technology suited for near-zero emissions and it has potential to retrofit existing boilers. The main advantages of this technology (as highlighted in several recent reviews [44;45] are:

- Industry is familiar with the technology (lower risk than CO_2 capture)
- Could be allowed in new plant design for retrofit at a later time
- Lower NOx emissions relative to conventional air-combustion

On the other hand, oxyfuel combustion requires an oxygen separation plant and it has significantly reduced efficiency compared to USC PC technology.

Oxyfuel combustion produces a raw CO_2 product containing mainly water vapour, oxygen, nitrogen and argon as contaminants. In principle, direct liquefaction of this stream will approach near zero emissions (ie 100% CO_2) removal. However, this possibility has not been demonstrated. There are also acid gases in this stream such as SO_2, SO_3, HCl and NOx produced as by-products of combustion and there is debate about necessary purification to acceptable CO_2 purities [44]. Due to the specific characteristics of oxyfuel technology, harmonization to 90% CO_2 capture is not applicable. For this reason, the average values of emissions found in literature are presented here without any harmonization on CO_2 capture.

Table 5.2 shows the emissions to the atmosphere of this case for both methodologies applied in the present study. The following sections analyse the different air pollutants in more detail.

Table 5.2 Emissions to air for Case 2. USC PC under oxyfuel conditions

Basic components	Units	CASE 2 Model	CASE 2 Literature average (min – max)
		USC PC oxyfuel	**USC PC oxyfuel**
CO_2	kg/MWh_{net}	85	44 (0-147)
Sulfur components SOx	kg/MWh_{net}	0.00	
SO_2	kg/MWh_{net}	0.00	0.01 (0-0.10)
SO_3	kg/MWh_{net}	0.00	
Nitrous components NOx	kg/MWh_{net}	0.03	0.19 (0-0.38)
NO_2	kg/MWh_{net}	NE	NE
NO	kg/MWh_{net}	NE	NE
Other acid gases			
CO	kg/MWh_{net}	NE	NE
HCl	kg/MWh_{net}	NE	NE
HF	kg/MWh_{net}	NE	NE
Particulate Matter			
PM (total)	kg/MWh_{net}	0.00	
PM-10	kg/MWh_{net}	NE	3.25E-03 (0-0.01)
Ammonia	kg/MWh_{net}	NA	NA

5.2.1 CO_2 Emissions

During oxyfuel combustion concentrations higher than 95% (dry basis) are possible. However, in reality concentrations are lower due to air leakage into the boiler. In order to deliver a CO_2 stream with acceptable quality, post-combustion treatment of this stream is necessary. The modelling study provided by IEAGHG and revised during the 2009 FWI predicts emissions of $85 kg/MWh_{net}$ for the reference case. The source for all gaseous emissions is the vent stream from the inert removal unit. The concentration of CO_2 in the vent stream and the total amount vented depends on the following main factors:

- Specifications of the CO_2 product stream
- CO_2 emissions
- Economic considerations

This study sets the CO_2 purity to 95% mol basis or above. Other components in the CO_2 stream are impurities (NOx), water vapour and inter gases (N_2, Ar, O_2). Water vapour is removed by adsorption on desiccants and inert gases are removed by phase separation between the liquid CO_2 and the insoluble gas impurities after cooling to -55ºC. The partial pressure of CO_2 in the vented inert is determined by considering the CO_2 purity specifications and the need to reduce the vented CO_2 to an economic minimum.

In literature a broader range of CO_2 emissions has been found, ranging from 0 to 147 kg/MWh_{net}. When the data are fitted to a normal distribution average CO_2 emissions are 44 kg/MWh. The variations found in literature are related to:

- Specifications of the final CO_2 product
- Type of boiler and steam cycle

Specifications on the CO_2 final purity vary upon study. Depending on the initial O_2 purity used for combustion, oxy-combustion will result in CO_2 purities around 83.4% to 87.2% (mol basis, wet). In order to increase CO_2 purity, the inert gases need to be removed. This results in emissions of CO_2 and other air pollutants (NOx, SOx) to the atmosphere. The specifications might vary depending on the final application of the CO_2 product and the source and location of the study. For instance, the study published by DOE [15] shows a 3-fold increase in CO_2 emissions when the specifications vary from 87% to 95% (mol basis, wet).

The type of boiler and power cycle also contribute to the variation in the CO_2 emissions found in literature. Another example from DOE study shows an 80% reduction on CO_2 emissions from a super-critical to an ultra-supercritical boiler.

5.2.2 SO_2 emissions

SO_2 emissions under oxyfuel conditions have been found to be lower than that in air combustion [44]. The reason suggested in previous studies is sulphur retention by the fly and bottom ash. Nevertheless, the necessary flue gas recycle to the boiler increases the concentration of SO_2 in the flue gas. According to modelling studies, if FGD is not installed before the primary and secondary flue gas recirculation the SO_2, SO_3 and HCl concentrations in flue gas will be significantly increased (up to six times that found in air-combustion for coals with 2% dry sulphur content) [46].

Measurements at the Clean Coal Test Facility (CCTF) of Doosan Babcok in Scotland show that the concentration of SO_2 in oxyfuel raw flue gas is only approximately 3 times higher than that of air-firing flue gas [48]. When emissions are expressed per energy unit the emissions of SO_2 are about 25% lower for oxyfuel than for air-firing. However, measured emissions are lower than that expected from mass balances. This fact indicates that SO_2 is being removed from the system. Most likely it is being adsorbed on the fly ash.

Recent studies have also suggested the use of an FGD unit to ensure that an oxycombustion facility is not more susceptible to corrosion than an air-fired combustion facility [15]. The objective of this FGD unit would be to decrease SO_2 in the flue gas recycle that is acceptable from corrosion perspective.

Nevertheless, this is only an operational risk. Other studies show that SO_2 and NOx can be virtually completely removed from the flue gas in the compression plant (see section 1.4) leading to no emissions to the environment. The result obtained from the Air Products CO_2 purification package is that all the SO_2 and about 90% of the NOx is removed. White et al [47] have investigating the factors that influence the removal of SO_2 in this configuration. The following parameters affect the removal of SO_2:

- Pressure in each washing step
- Residence time
- Ratio SO_2/NOx

Their findings show that high conversions are possible for SO_2. The presence of NOx catalyzes the oxidation reaction of SO_2 to SO_3 which is further removed as H_2SO_4 in the presence of water. At SO_2/NO_2 ratios of approx. 2.8, conversion is above 95% and at ratios of around 4 conversion decreases to 85%.

5.2.3 NOx emissions

NOx generated by the combustion process is significantly lower under oxyfuel firing (factor 2) than for air firing. [44]. The remaining NOx can be significantly decreased in the flue gas / CO_2 stream compression plant [48].

5.2.4 Emissions of trace elements and mercury

Gas phase concentration of volatile elements (Hg, Se and probably As) are expected to be higher under oxyfuel firing conditions. White and co-workers [48] have investigated mercury emissions during the first testing campaigns of the Oxycoal – UK project at the sour compression set-up at Imperial College (London), although they have not reported them. However, in the liquid samples all the mercury was present in the condensate from the first flue gas cooler. Mercury content was found to be negligible in all vessels located after the first compression step. Ideally, this will result in no mercury emissions.

In literature, the average value found is 3.06E-07 kg/MWh (0 – 8.2E-07 kg/MWh).

In practice a mercury guard bed will usually be required to protect the aluminium cold box of the inert removal unit against corrosion caused by mercury.

5.2.5 Liquid and solid waste

The waste generated from the oxyfuel case is presented in Table 5.3

Table 5.3 Emissions to air for Case 2. USC PC under oxyfuel conditions

Generated waste	**Units**	**Case 2 USC PC Oxyfuel**
Furnace bottom ash	kg/MWh_{net}	9.8
Fly ash	kg/MWh_{net}	39.1
Sludges from WWT	kg/MWh_{net}	25.8
Waste water	Kg/MWh_{net}	265
Raw Materials		
Cooling water consumption	t/MWh	176.7
Specific water consumption	t/MWh	0.063

5.3 IGCC cases (Reference cases 3A and 3B)

The results from harmonization studies and modelling studies are compared in table 5.4. SOx emissions results are comparable for case 3A (no carbon capture). SOx emissions are lower for IGCC plants that incorporate deep sulphur removal than for the USC cases.

Regarding the modelling of NOx emissions, Table 5.4 shows two results. The first one based on newly design IGCC plants (based on the emission factors described in section 2.2.2). The second one is based on the modelling of cases 4A and 4B. Said reference cases only include pre-combustion NOx controls, which consist of diluting the feed to the gas turbine with nitrogen. However, newly designs for IGCC plants plan to incorporate post-combustion SCR technologies to further reduce the NOx emissions. As shown in this study, SCR in IGCC plants reduces the emissions for case 3A from 0.39 kg/MWh to 0.11 kg/MWh, level comparable to the best performance of the USC cases. Nevertheless, it is important to highlight that the use of SCR in coal IGCC systems is not yet guaranteed. Problems might arise in the form of ammonium sulphate deposits in the HRSG causing corrosion and plugging. For this reason SCR requires high sulphur removal to reduce sulphate formation to low levels. The new build IGCC plants are also designed with deeper sulphur removal to accommodate the SCR. These emission controls result in a substantial reduction in emissions for IGCC.

Harmonization results show a different trend than the modelling. Emissions of IGCC plants without pre-combustion capture are in agreement with the modelling results of case 3A. However, when pre-combustion capture is incorporated the relative NOx emissions decrease. For NOx emissions, it was not possible to harmonize the data base to the reference cases description. The result is an average of all possible technologies to reduce NOx, which might include pre and post combustion controls (at different dilution factors). This explains the difference in trend.

Table 5.4 Relative emission factors for IGCC cases

Basic components	Units	Modelling	Database	Units	Modelling

				Harmonization				
		3A	3B	3A	3B		3A	3B
CO_2	kg/MWh_{net}	818	152	761	93	mg/Nm^3	NE	NE
SOx	kg/MWh_{net}	0.05[22] 0.08[23]	0.01[23]	NE	NE	mg/Nm^3	10	1
SO_2	kg/MWh_{net}	NE	NE	0.04	0.01	mg/Nm^3		
SO_3	kg/MWh_{net}	NE	NE	NA	NE	mg/Nm^3		
NOx	kg/MWh_{net}	0.11[22] 0.3[238]	0.39[23]	0.23	0.21	mg/Nm^3	49	46
NO_2	kg/MWh_{net}	NA	NA	NA	NE	mg/Nm^3		
NO	kg/MWh_{net}	NA	NA	NA	NE	mg/Nm^3		
Acid gases								
CO	kg/MWh_{net}	0.24[23]	0.25[23]		NE	mg/Nm^3	30	29
HCl	kg/MWh_{net}	NA	NA	NA	NA	mg/Nm^3		
HF	kg/MWh_{net}	NA	NA	NA	NA	mg/Nm^3		
Particulates								
PM (total)	kg/MWh_{net}	0.03[22] 0.03[23]	0.03[23]			mg/Nm^3	4	4
PM-10	kg/MWh_{net}	NA	NA	0.01	0.03	mg/Nm^3		
Ammonia	kg/MWh_{net}	NE	NE	NA	0	mg/Nm^3		

5.4 NGCC cases (Reference cases 4A and 4B)

Results from harmonization studies and modelling studies are summarized in Table 5.5. SOx emissions are negligible with NGCC. Nevertheless, depending on the quality of the gas, some sulphur might be present in the fuel to the gas turbine. During combustion, sulphur produces very small amounts of SOx.

NOx emissions are over predicted by the harmonization study. This reflects the wide variety of NOx control performance for NGCC plants. SCR can be incorporated in gas turbines as a post-combustion control of NOx emissions. However, the use of SCR depends on the legislation of each country. For most cases water steam injection and the use of low NOx burners is sufficient to reduce emissions to acceptable levels. Harmonization studies suggest that this is the most applied case worldwide. However, the modelling results show that NOx emissions can be further reduced with the incorporation of SCR technology.

---

[22] From emission factors (see section 2.2.2)

[23] From process modeling [6]

Table 5.5 Emissions for NGCC cases

		Modelling		Database Harmonization			Modelling	
Basic components	Units	4A	4B	4A	4B	Units	4A	4B
CO_2	kg/MWh_{net}	354	42	366	43	mg/Nm^3		
SOx	kg/MWh_{net}	1,0E-02	5,9E-05			mg/Nm^3	2,2	0,0
SO_2	kg/MWh_{net}	1,0E-02	5,9E-05			mg/Nm^3		
SO_3	kg/MWh_{net}					mg/Nm^3		
NOx	kg/MWh_{net}	0,03	0,03	0.12	0.13	mg/Nm^3	5,8	6,2
NO_2	kg/MWh_{net}	1,3E-03	1,2E-03	NA	NE	mg/Nm^3	0,3	0,2
NO	kg/MWh_{net}	0,03	0,03	NA	NE	mg/Nm^3	5,5	5,9
Acid gases								
CO	kg/MWh_{net}	0,09	0,10			mg/Nm^3		
HCl	kg/MWh_{net}					mg/Nm^3		
HF	kg/MWh_{net}					mg/Nm^3		
Particulates								
PM (total)	kg/MWh_{net}	9,7E-05	5,7E-05			mg/Nm^3	4,2	0,0
PM-10	kg/MWh_{net}					mg/Nm^3		
Ammonia	kg/MWh_{net}		0,04			mg/Nm^3		8,5

5.5 Future technology developments for CO_2 capture

This study has evaluated emissions for different types of power plants based on state-of-the-art technologies. Nevertheless, new technologies are being developed with the aim of reducing capture costs. Emerging technologies include processes that show (either in the laboratory or in the field) potential to significantly reduce the cost of CO_2 capture. However, technologies with high potential for cost reduction also require more time to commercialization.

Next to the amine and physical solvents considered in this report, second generation CO_2 capture technologies will include advanced amine systems. Third generation technologies include membrane systems and solid sorbents. Table 5.6 shows the most relevant technologies that are currently under development and its application to different power plants. Due to future environmental implications, some of these systems will be analyzed in the following sections in more detail.

Table 5.6 Innovative CO_2 capture techniques. Application to different power plants. Colours indicate different atages in technology delevolment: 2nd generation (Green), 3rd generation (Blue)

Technique		USC PC	IGCC	Oxyfuel	NGCC
Membranes	O_2/N_2		√	√	
	CO_2/N_2	√			
	CO_2/H_2		√		
Solvents	Amine based solvents	√			√
	Aminoacids based solvents	√			√
Sorbents		√	√		

5.5.1 *USC PC and NGCC technology. Future improvements*

Different process developers and technology suppliers are pursuing improvements to amine systems for post-combustion capture. There are several possibilities to improve current amine technology:

- Modified packing materials that reduce pressure drop and improve contacting
- Increased heat integration to reduce energy requirements
- Additives that reduce corrosion and allow higher amine concentrations
- Amine systems or mixture of amines that exhibit higher CO_2 absorption capacity

The last three topics mentioned focus on reducing the energy consumption of the capture unit. Table 5.7 shows a qualitative comparison between two different types of new amine systems. The number of amine technology providers is much broader than the ones selected for table 5.7 (among others: Hitachi, HTC, Fluor, CB&I Lummus, BASF). However, a full evaluation of all possible technologies is outside the scope of this study. Instead, two different systems have been selected to show the impact on emissions of future amine technologies. The first is an amine based system licensed by Mitsubishi Heavy Industries (MHI) and referred to as KS-1. The second is an aminoacid based system developed by Siemens. An indication of the regeneration energy for each system is given in table 5.7. It is important to notice that these numbers are only indicative, and that the final energy duty will depend on flue gas impurities and integration philosophy between the capture unit and the host power plant.

As indicated, new solvents have the potential to reduce the regeneration energy by 15-20% compared to MEA (reduction depends on integration aspects). This will result in lower emissions of all air pollutants per unit electricity. The process licensed by MHI also includes a deep de-sulphurization unit which reduces the levels of SOx to less than 0.1ppmv before the capture unit. Therefore, the reduction on SOx emissions is expected to be deeper.

On the other hand, amino acid salts have negligible vapour pressure. Due to this fact, solvent losses to the environment are fully minimized. Moreover, amino acids are more resistant to oxidative degradation than conventional amines, fact that will contribute to decrease the generation of waste in the reclaimer unit. Due to these characteristics, amino acids are seen as more environmental friendly than amines. However, in terms of regeneration energy, amine based systems (such as KS-1) are still more efficient.

Table 5.7 Comparison between to advanced amine technologies (amine based and aminoacid based)

	Solvent system	
Parameter	**KS-1 (MHI)**	**Siemens**
Regeneration energy [GJ/tonCO_2]	2,6[24]	2,7[25]
Solvent basis	Amine	Amino acid
Solvent degradation	Low	Very low
Solvent loss	Low	Negligible
SOx emissions	Very Low	Low
PM emissions	Low	Low
NOx emissions	Low	Low
Trace metals emissions	Low	Low
Reclaimer waste	Low	Very Low
Other waste (FGD, ESP)	Low	Low

5.5.2 IGCC technology. Future improvements

Solvent absorption is the current technology option for capturing carbon dioxide from syngas. However membrane technology offers advantages with respect to current technology. Membranes have in general a good prospective and high potential to increase the efficiency of IGCC plants with Pre-combustion capture. Membranes are also more environmental friendly than solvent applications and are easy to scale-up.

There are many strategies for the application of membranes in IGCC. A recent review by Scholes and co-workers [51] summarizes the implementation possibilities in three different paths:

1. Stand alone membrane technology
    i. Retention of hydrogen
    ii. Retention of carbon dioxide
2. Integrated with water gas shift reactor

IGCC capture systems with membranes are being investigated in different projects worldwide. There are different materials being investigated for pre-combustion application, such as metallic membranes, ceramic membranes and polymeric

---

[24] Reference [49]
[25] References [50]

membranes. Metallic and ceramic membranes are the preferred choice for this application due to their higher mechanical and chemical resistance. However, there are a number of issues to be address before this technology can be considered competitive with solvent absorption process (mainly membrane stability and resistance to syngas impurities). A major burden for assessing the impact of membranes in IGCC plants is the lack of pilot trials which demonstrate the performance at real industrial conditions. The current focus on this topic is still on developing membrane materials and evaluating performance and economics.

The most studied is the application of metallic membranes and membrane reactors. Application of highly selective Pd based membrane reactors results in a pure hydrogen stream, which is sent to the combined cycle and a rich CO_2 retentate. Mainly all the gas impurities are retained in this stream, which will contain CO, non-permeated H_2, CH_4 and H_2S as main components. Moreover, other impurities such as COS will be also present although they are often not addressed in the research studies. The emissions will then depend on the further treatments of this stream.

One possibility is the catalytic combustion of this stream to recover energy by generating steam. Then, the stream is condensed to separate water. The SOx formed might be removed with normal limestone scrubbers. Other possibility is the cryogenic separation of CO_2 and H_2S, which will be compressed for storage.

5.5.3 Mercury removal

Mercury speciation is essential for its removal from flue gas. Mercury is generally present as elemental mercury (Hg^0) or oxidized as mercury chloride ($HgCl_2$) or mercury oxide (HgO). The dominant species are Hg^0 and $HgCl_2$ based on industrial experience [57]. Also, the presence of Cl_2 enhances the oxidation of mercury. Under reducing conditions also the chlorides are more dominant. The oxidized forms are easier to remove by scrubbing technologies, since they are more soluble in the solutions used in the desulphurization or CO_2 capture units.

Elemental mercury (Hg^0) might also condense on particulates. However, the extension of this phenomenon is very limited. This is reflected in the low Hg removal efficiency observed in ESP devices, since this unit will only remove the mercury adsorbed on particulates.
There are different possibilities for mercury removal which may be classified into two categories:

- Dry separation (adsorption of mercury)
- Wet scrubbing (absorption of mercury)

The focus on the first category is on adsorption of mercury on adsorptive materials. Activated carbon is well know for its affinity to different trace metals, including mercury. Control of mercury can be achieved by activated carbon injection and recovery of the carbon particles in the downstream filters or by carbon filter beds. The following lines list possibilities of improving mercury removal [57]:

- Adsorption of mercury on unburnt carbon in fly ash

- Activated carbon derived from coal
- Iodine-impregnated or sulphide-impregnated carbon
- Enhance properties of activated carbon

The wet scrubbing methods focus on conversion of elemental mercury to its soluble form for further scrubbing. Possibilities for conversion are:

- Carbon based catalyst
- Oxidizing agents (used upstream the FGD unit or in the scrubber): for instance aqueous hypochlorite

FGD itself can remove mercury above 17% efficiency removal.

6 Conclusions and recommendations

This study has evaluated the emissions and waste generation of seven power plants with and without CO_2 capture. The methodology assessment has followed two approaches:

- Harmonization study: Consists of a statistical analysis of the emissions database created by reviewing the open literature. Said emission database was harmonized prior to the assessment, in order to bring into line the reference basis of each data point and the reference basis of the cases under investigation. This is a top-down approach in which the relative emissions are given for a specific group of plants and they are corrected for a pre-defined set of parameters that bring into line the reference basis.

- Modelling study: For a set of seven reference cases, plant performance and emissions were evaluated either with commercial software packages or with emission factors. The key difference with the harmonization is that the modelling performs a bottom-up approach. Starting with the definition of the different technologies, emissions are estimated based on source specific uncontrolled emission factors and the application of state-of-the-art emission controls

Both approaches were used to estimate the emissions for seven reference cases. On the other hand, the waste generated was estimated from the models’ mass balance.

Regarding emissions, both approaches provide valuable insight in the impact of carbon capture in the emissions related to the power sector. In general, harmonization value represents an average of the emissions of plants in operation for those cases that are more conventional in the power industry (i.e USC PC and NGCC). In other cases, harmonization value represents an average of the studies on emissions published in the literature. The modelling value represents the estimated emissions of the selected cases based on the performance predicted by commercial models and the estimation of emission control efficiencies commercially available.

Table 6.1 shows the emissions of the different power plants. The estimated waste for all cases is presented in Table 6.2. The following lines analyze the various conclusions derived from the study.

Ultra supercritical pulverized coal:

In the case of the USC PC power plants there is a very good agreement in the estimates of CO_2 emissions. This is straight forward when the boiler type and the capture percentage removal are fixed. In the case of sulphur emissions, the coal sulphur content had to be corrected in the database. SO_2 emissions results are in good agreement within the accuracy of the methods used. The impact of carbon capture in this type of power plants is clear: SO_2 is significantly reduced together with the reduction in CO_2 emissions.

With respect to NOx emissions, the same trend has been observed for both USC PC and NGCC power plants. The impact of CO_2 capture predicted by both methodologies is clear. NOx emissions increase due to the deployment of CO_2 capture approximately to the same extent as the increase in fuel use.

Moreover, estimates for hydrogen halides (HCl and HF) have been derived for the USC PC case following the modelling methodology. Confirmation on these estimates via the literature database was not possible due to the lack of relevant data at the scale and plant type defined in this case. For this reason, these values are indicative and should be carefully used. However, the impact of CO_2 capture on these emissions is certain. HCl and HF decrease substantially when CO_2 capture is integrated into the power plant. This is due to the acidic nature of these gases and the alkalinity of the solvent. This impact is also corroborated by recent pilot studies [43]. Nevertheless, more thorough measurements are needed in order to give an accurate estimate on the extension of this reduction.

Particulates have been a case of contradiction between the literature database (which predicts and increase in particulates emissions due to CO_2 capture) and the modelling (which predicts a decrease in particulates and fines when the capture technology is integrated). The pilot studies mentioned above, also indicate a substantial reduction in particulates and fines. One of the possible reasons for the poor estimate given by the literature database is the use of out-dated studies. The contacting efficiency of current packing materials used for CO_2 absorption is high enough to justify the decrease in particulates and fines emissions. This fact is also related to the reduction in trace metals emissions. Trace metals were estimated in this study by the application of models only (with the exception of mercury). The model assumed an efficiency of 50% in the reduction of particulates, fines and trace metals associated with them. This assumption is inline with the efficiency of a wet scrubber. However, structure packing will give at least a 98% reduction (also derived from pilot studies). Therefore, deployment of CO_2 capture will result in a substantial reduction in the emissions of particulates, fines and trace metal associated with particulates, such as Fe, Si, and As.

Mercury emissions were estimated via both methodologies. Results are also contradictory. It is evident by specific research that elemental mercury is not absorbed in alkaline solutions and that only oxidized mercury is fully dissolved in these solutions. Moreover, elemental mercury can be adsorbed in the fly ash and char and be removed in the units that control particulates (ESP, FGD, CO_2 absorber, etc). However, there are many factors that have an effect in the oxidation state of mercury. The model used an assumption in the distribution that results in a slight decrease in mercury emissions but there is a substantial degree of uncertainty in this assumption that can not be checked with pilot studies since this element is generally not monitored. It is highly recommended to include this type of measurements in future test campaigns. Mercury can be removed in flue gas by injecting activated carbon and recovering it in the down stream filters (for coal fired power plants).

Ammonia emissions increase when CO_2 capture (based on amine technology) is integrated into power plants. Ammonia slip from the SCR is very low compare to the ammonia generated due to amine degradation (the values for all PC cases in the literature database is lower than the estimated by the model). It should be noticed that the model does not contain the effect of washing sections (normally two units). The degradation rate of the solvent is an important parameter that has a direct effect in ammonia emissions. This rate needs to be consulted with the supplier of the amine technology.

Table 6.1-A Final emission factors for the cases. (H) means harmonization result. (M) means modelling result. When only one result is present, either information is missing or a supported choice has been made.

Basic components	**Units**	**1A USC PC w/o CC**	**1B USC PC w CC**	**2 USC PC Oxyfuel**
CO_2	kg/MWh_{net}	735^{H} – 739^{M}	93^{M} – 97^{H}	85^{M}
SO_2	kg/MWh_{net}	0.26^{M} - 0.30^{H}	0.00^{H} - $6.5E\text{-}04^{M}$	0.00^{H}-0.01^{M}
NOx	kg/MWh_{net}	0.08^{M} - 0.36^{H}	0.10^{M} - 0.50^{H}	0.03^{M}-0.19^{H}
PM (total)	kg/MWh_{net}	0.05^{M}	$3.0E\text{-}02^{M}$	0.00^{M}
PM-10	kg/MWh_{net}	0.01^{M} - 0.04^{H}	$5.6E\text{-}3^{M}$ - 0.046^{H}	0.00^{M}-$3.25E\text{-}3^{H}$
Ammonia	kg/MWh_{net}	3.5E-3	0.08 - 0.11	

Table 6.1-B Final emission factors for the cases. (H) means harmonization result. (M) means modelling result. When only one result is present, either information is missing or a supported choice has been made.

Basic components	**Units**	**3A IGCC GE w/o CC**	**3B IGCC GE w CC**	**4A NGCC w/o CC**	**4B NGCC w CC**
CO_2	kg/MWh_{net}	761^{H}-818^{M}	93^{H} - 152^{M}	354^{M}- 366^{H}	42^{M}-43^{H}
SO_2	kg/MWh_{net}	0.04^{H}-0.05^{M}	0.01^{M}- 0.01^{H}	0.00^{H}-$1.0E\text{-}02^{M}$	0.00^{H}-$5.9E\text{-}05^{M}$
NOx	kg/MWh_{net}	0.11^{M} - 0.23^{H}	0.21^{H} - 0.39^{M}	0.03^{M}-0.12^{H}	0.03^{M}-0.13^{H}
PM (total)	kg/MWh_{net}	$0.03^{(H)}$-0.014^{M}	0.03^{M}- - 0.034^{H}	$9.7E\text{-}05^{M}$	$5.7E\text{-}05^{M}$
PM-10	kg/MWh_{net}			0.00^{H}	0.00^{H}
Ammonia	kg/MWh_{net}			$3.7E\text{-}4^{H}$	0.04^{M}

Regarding liquid and solid waste, it has been found that CC will increase the generated waste. On one hand, waste increases due to the extra fuel use when CC is integrated in the plant. On the other hand, more waste is generated by the reclaimer unit of the capture plant. As a direct result of this study, it has been found some gaps in the literature, regarding the actual degradation of amine in commercial formulations. An attempt has been done to estimate the actual waste generated by the reference cases based on literature values for conventional amine solutions.

Ultrasupercritical pulverized coal under oxy-firing conditions:

For the oxyfuel case, the number of estimates that could be taken is considerably reduced due to the development stage of the technology. Based on the results, comparison can be done between the modelling results of the case provided by IEA and the values from the literature database, which contain mainly similar studies to the one provided. The variation observed in the emissions of all air pollutants (including CO_2) is related to the specifications and purity of the final CO_2 product. For a given purity of 95% (mol basis) the CO_2 stream needs to be treated in order to separate inert. This process leads to emissions of other pollutants that increase when the CO_2 specifications are tightened.

The higher values in the CO_2 emissions range corresponds to a case which makes use of an ITM (transfer membrane for O_2/N_2 separation) which delivers higher oxygen purity >99% but also has higher penalty to the host power plant (fact that is reflected in the higher specific emissions of CO_2)

Depending on the purification system selected for the CO_2 stream some amounts of SO_2 and NOx could be vented to the atmosphere. However, the purification system selected for this case virtually leaves the CO_2 stream with zero content of SO_2. In contrast, the water condensate generated during compression will contain acids and most of the volatile metals (i.e. mercury) and needs to be treated accordingly to its quality.

IGCC power plants:

As in the previous cases, there is a good agreement between the two estimate types regarding CO_2 emissions. As shown in table 6.1, there is no impact of CC in the NOx emissions per unit electricity. There is a reduction on the SOx emissions due to the integration of CO_2 capture.

NGCC power plants:

NGCC plants have less emissions to the atmosphere than the other power plants. For the reference plants analysed, both methodologies were in good agreement when predicting CO_2 emissions. SOx emissions are negligible. Regarding NOx, emissions of these pollutants are over predicted by the harmonization study. De-NOx controls were estimated to reduce the NOx emissions to 0.03kg/MWh for the reference plant.

Results also show high values of waste generated for the NGCC case in comparison with the coal case. More research is needed to establish the real waste generated by commercial amine solvents. Another point of attention is the operation of thermal reclaimers. Based on units operating in refinery, it is known that thermal reclaimers tend to waste valuable amine. Possibilities for reducing waste could be the use of Ion Exchange systems, which are commercially available [36].

Finally, it is important to highlight the differences in the methodologies adopted. Harmonization has been found a useful tool for estimating relative emissions in those cases were technology is well established and much information regarding emissions is reported. On the other hand, modelling has been found the only possibility to better understand the uncertainties on the emissions of novel technology (with scarce published information).

Table 6.2-A Final waste factors for the cases.

Generated waste	**Units**	**1A USC PC w/o CC**	**1B USC PC w CC**	**2 USC PC Oxyfuel**
Particules in ESP	kg/MWh$_{net}$	19	24	NA
Gypsum	kg/MWh$_{net}$	15	21	NA
Furnace bottom ash/ Coarse slag	kg/MWh$_{net}$	9.6	12	9.8
Fly ash / Fine slag	kg/MWh$_{net}$	29.0	37	39.1
Mill rejects	kg/MWh$_{net}$	0.7	0.8	NA
Sludges from WWT	kg/MWh$_{net}$	1.0	1.2	25.8
Reclaimer waste	kg/MWh$_{net}$	NA	3.291	NA
Activated carbon	kg/MWh$_{net}$	NA	0.063	NA
Waste water	kg/MWh$_{net}$	19	375	265
Raw Materials				
Cooling water consumption	t/MWh	138.6	240.5	176.7
Specific water consumption	t/MWh	0.104	0.410	0.063
MEA make up	kg/tCO$_2$	0	1.765	NA
Activated carbon make up	kg/tCO$_2$	0	0.075	NA

Table 6.2-B Final waste factors for the cases.

Generated waste	**Units**	**3A IGCC GE w/o CC**	**3B IGCC GE w CC**	**4A NGCC w/o CC**	**4B NGCC w CC**
Furnace bottom ash/ Coarse slag	kg/MWh_{net}	86.6	104	NA	NA
Fly ash / Fine slag	kg/MWh_{net}	36.1	44	NA	NA
Sludges from WWT	kg/MWh_{net}	2.4	3	NE	NE
Reclaimer waste	kg/MWh_{net}	NA	NA	0	1.17
Activated carbon	kg/MWh_{net}	NA	NA	0	0.025
Waste water	kg/MWh_{net}	10	19	NE	NE
Raw Materials					
Cooling water consumption	t/MWh	146.9	185.2	45.6	82.7
Specific water consumption	t/MWh	0.126	0.411	1.01	1.21
MEA make up	kg/tCO_2			0	1.79
Activated carbon make up	kg/tCO_2			0	0.075

7 References

[1] IPCC (2005). IPCC Special Report on Carbon Dioxide Capture and Storage.

[2] WHO (2006). Air quality guidelines. Global update 2005,

[3] van Harmelen, T., Koornneef, J., van Horssen, A., Ramirez, A., van Gijlswijk, R. (2008). The impacts of CO2 capture technologies on transboundary air pollution in the Netherlands. Utrecht, The Netherlands, TNO Built Environment and Geosciences and University of Utrecht.

[4] van Horssen, A., Kuramochi, T., Jozwicka, M., Koornneef, J., van Harmelen, T., Ramirez, A. (2010). The impacts of CO2 capture technologies in power generation and industry on greenhouse gases emissions and air pollutants in the Netherlands. Utrecht, The Netherlands, TNO Built Environment and Geosciences and University of Utrecht.

[5] Sobacchi, L., Cotone, P., Arienti, S. (2010). Water usage and loss of power in plants with CO2 capture. USC PC cases.

[6] Sobacchi, L., Cotone, P., Arienti, S. (2010). Water usage and loss of power in plants with CO2 capture. Oxy-PC cases.

[7] Sobacchi, L., Cotone, P., Arienti, S. (2010). Water usage and loss of power in plants with CO2 capture. IGCC cases.

[8] EBTF. European Benchmarking Task Force. Common framework definition document and Test cases 2010

[9] Personal communication from Abu-Zahra, M.A. (IEA GHG)

[10] IEA GHG Improvement in power generation with post-combustion capture of CO2. Report number: PH4/33 (2004)

[11] Allan, R.J., White, V., Miller, E.J. Purification of carbon dioxide. European patent application EP 1 790614 A1. 2006

[12] Hendriks, C., Wu, Z., Neele, F., 2009. CCS economic evaluation tool - Including Rijnmond case study. Ecofys, Utrecht, the Netherlands.

[13] Andersson, K., 2007. Combustion tests and Modelling of the oxyfuel process- an overview of research activities at Chalmers University, Sweden., 2nd International Oxy-Combustion Network Meeting IEA GHG, Alstom Power, Windsor, Connecticut, USA.

[14] Davison, J., 2007. Performance and costs of power plants with capture and storage of CO2. Energy 32, 1163.

[15] DOE, NETL, 2007. Pulverized Coal Oxycombustion Power Plants -Volume 1: Bituminous Coal to Electricity.

[16] de Visser, E., Hendriks, C., Barrio, M., Molnvik, M.J., de Koeijer, G., Liljemark, S., Le Gallo, Y., 2008. Dynamis CO2 quality recommendations. International Journal of Greenhouse Gas Control.

[17] AP-42 ((accesed 2009)). "Compilation of Air Pollutant Emision factors." Us Environmental protection Agency; Office of Air quality Planning and Standards an dOffice of Research and Development: Washington, DC, Volume 1: Stationary Point and Area Sources.

[18] Sloss, L.L. and Smith, I.M. Trace elements emissions. Clean Coal Centre report number CCC/34, 2000

[19] Apps, J.A. A review of Hazardous Chemical species Associated with CO2 Capture from Coal-fired power lants and their potential fate during CO2 geologic storage. Ernesto Orlando Lawrence Berkeley National Laboratory. 2006

[20] DOE/NETL-2007/1281 “Cost and performace baseline for fossil energy plants. Volume 1: Bituminous Coal and Natural Gas to Electricity. Final Report (2007)

[21] Odeh, N. A. and T. T. Cockerill (2008). "Life cycle GHG assessment of fossil fuel power plants with carbon capture and storage." Energy Policy **36**(1): 367-380.

[22] Korre, A., Z. Nie, et al. (2010). "Life cycle modelling of fossil fuel power generation with post-combustion CO2 capture." International Journal of Greenhouse Gas Control **4**(2): 289-300.

[23] Carl R. Bozzuto, N. y. N., Gregory N. Liljedahl, Mark Palkes,John L. Marion,David Vogel, J. C. Gupta (2001) Engineering Feasibility And Economics Of CO2 Capture On An Existing Coal-Fired Power Plant. NETL DOE **1**, 271

[24] Agonis, R., Nolin, K., Schreyer, D. (2003). FlowPacTM - 'Pump-less'High efficiency FGD Scrubber. "Mega" symposium, Washington, DC.

[25] Lee, J. Y., Keerner, T.C., Tang, Y. (2009). "Potential Flue Gas Impurities in Carbon Diosxide Streams Separated from Coal-fired Power Plants." Journal of the Air & Waste Management Association **59**: 725-732.

[26] Srivastava, R.K., Jozewick, W. (2001) “Flue Gas desulphurization: the state of the art; Journal of the Air & Waste Management Association 51, 1676-1688: 725-732.

[27] Cummings, A. L., Smith, G.D., Nelsen, D.K. (2007). Advances in Amine Reclaiming - Why Ther is No Excuse To Operate a dirty Amine System. Laurence Reid Gas Conditioning Conference.

[28] Thitakamol, B., Veawab, A. and Aroonwilas, A. (2007) “Environmental impacts of absorption-based CO2 capture unit for Poast-combustion treatment of flue gas from coal-fired power plant” ." International Journal of Greenhouse Gas Control I 318-342.

[29] Goff, G. S. (2005). Oxidative degradation of aqueos monoethanol amine in CO2 capture proesses: Iron and copper catalysis, inhibition, and O2 transfer. Austin, USA, University of Texas.

[30] Goff, G.S. and Rochelle, G.T. (2004) “Monothanol amine Degradation: O2 Mass Transfer effects under CO2 capture conditions”. Industrial & Engineering Chemistry Research **43**(24): 6400-6408.

[31] Uyanga, I.J., Idem, O. “Studies of SO2 and O2-induced degrdation of aqueous MEA during CO2 capture from Power plant flue gas streams”. Industrial & Engineering Chemistry Research **46**: 2558-2566.

[32] Veltman, K., B. Singh, et al. (2010). "Human and Environmental Impact Assessment of Postcombustion CO2 Capture Focusing on Emissions from Amine-Based Scrubbing Solvents to Air." Environmental Science & Technology **44**(4): 1496-1502.

[33] Rao, A. B. and E. S. Rubin (2002). "A Technical, Economic, and Environmental Assessment of Amine-Based CO2 Capture Technology for Power Plant Greenhouse Gas Control." Environmental Science & Technology **36**(20): 4467-4475.

[34] Abu-Zahra, M.A., Feron, P., Alix, P, Biede, O., broutin, P., Jong, H., Kittle, J., Knudsen, J., Raynal, L. Vilhelmsen, P., Jensen, J.N.”Development of Post-combustion capture of CO2 within the Castor integrated project: First result from the pilot plant operation using MEA. Presented at the 3rd international conference on Clean Coal Technologies for Out future. CCT 2007, Sardegna, Italy May 2007.

[35] Ingale, N. D., I. B. Chatterjee, et al. (2009). "Role of nitrous acid decomposition in absorber and bleacher in nitric acid plant." Chemical Engineering Journal 155(3): 851-858.

[36] Rochelle, G. “CO2 capture by aqueous absoprtion/stripping opportunities for better technology. In: 2001 Conference Proceedings of Workshop on Carbon Sequestration Science. National Energy Technology Laboratory. 2001

[37] Cui, Z., A. Aroonwilas, et al. (2010). "Simultaneous Capture of Mercury and CO2 in Amine-Based CO2 Absorption Process." Industrial & Engineering Chemistry Research **49**(24): 12576-12586.

[38] Strazisar, B. R., Anderson, R.R., White, C.M. (2003). "Degradation Pathways for monoethanolamine in a CO2 Capture Facility." Energy & Fuels **17**: 1034-1039.

[39] Chapel, D.G., Ernest, J., Maritz, C.L. „Recovery of CO2 from flue gases: commercial trends. Canadian society of chemical engineers annual meeting (1999) fluor daniel reference

[40] Weeks, A. (2007). “ Advanced coal technology Development Can Be Supported under Existing Clean Air act Permiting Frameworks: why IGCC, for

example, is BACT for new cola-fueled EGUs. U.S. EPA's Advanced Coal Technologies Working Group

[41] Ratafia-Brown,J., Manfredo, L., Hoffmann, J., Ramezan. M. Major environmental aspects of gasification-based power generation technologies. National Energy Technology Laboratory. 2002

[42] Williams, A., Wetherold, B., Maxwell, D. Trace substance Emissions from a Coal-fired gasification plant. DOE report DOE/PC/93253 T3 (1996) Prepared by Radian International LLC.

[43] Knudsen J. Results from test campaigns at the 1 t/h CO2 post-combustion capture pilot-plant in Esbjerg under the EU FP7 CESAR project. Presented at the PCCC1 in Abu Dhabi.

[44] Buhre, B.J.P., Elliot, L.K., Sheng, C.D., Gupta, R.P., Wall, T.F. Oxyfuel combustion technology for coal-fired power generation. Progress in Energy and Combustion Science 31 (2005) 283-307.

[45] Wall, T, Liu, Y., Spero, C., Elliot, L., Khare, S., Rathman, R., Zeenathal. F., Moghtaderi. B., Buhre, B., Sheng, C., Gupta, R., Yamada, T., Makino, K., Yu, J. An overview on oxyfuel coal combustion – State of the art research and technology development. Chemical engineering research and design. 87 (2009) 1003-1016

[46] Liu, H., Shao, Y. Prediction of the impurities in the CO2 stream of an oxy-coal combustion plant. Applied Energy 87 (2010) 3162-3170.

[47] White Purification of CO2 stream Energy procedia

[48] Doosan Bacokc report Development of mercury emissions controls

[49] Yagi, Y. Mimura, T., Iijima, M. Improvements of carbon dioxide capture technology from flue gas. Mitsubishi Heavy Industries. Downloaded from: http://uregina.ca/ghgt7/PDF/papers/nonpeer/183.pdf

[50] Scheneider, R., Schramm, H. Environmental friendly and economic carbon capture from power plant flue gase: The Siemens PostCap TM technology. Presentation at PCCC1. Abu Dhabi (2011). Downloaded from: http://www.ieaghg.org/index.php?/technical-programme.html

[51] Scholes, C.A., Smith, K.H., Kentish, S.E., Stevens, G.W. CO2 capture from pre-combustion processes – Strategies for membrane gas separation. International journal of greenhouse gas control 4 (2010) 739-755.

[52] Supap, T., Idem, R., Tontiwachwuthikul, P.Saiwan, C. "Analysis of monoethanol amine and its oxidative degradation products during CO2 absorption form flue gases: A comparative Study of GC-MS, HPLA-RID, and CE-DAD analytical techniques and possible optimum combinations" Industrial & Engineering Chemistry Research **45** 2437-2451.

[53] Vevelstad, S.J., Eide-Haugmo, I., Silva, E.F., Svendsen, H.F. “Degradation of MEA; a theoretical study” GHGT-10 Energy procedia (2010)

[54] Lepaumier, H., Silva, E.F., Einbu, A., Grimstvedt, A., Knudsen, J.N., Zahlsen, K., Svendsen, H.F. “Comparison of MEA degradation in polt-scale with lab-scale experiments” GHGT-10 Energy procedia (2010)

[55] European Commission, 2006. Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for Large Combustion Plants.

[56] Koornneef, J., Ramirez, A., van Harmelen, T., van Horssen, A., Turkenburg, W., Faaij, A. (2010). The impact of CO2 capture in the power and heat sector on the emission of SO2, NOx, Particulate Matter, Volatile Organic Compounds and NH3 in the European Union, Atmospheric Environment 44 (2010) 1369-1385.

[57] Zhao, L.L., Rochelle, G.T. Mercury absorption in Aqueous Hypochlorite. Proceedings of the EPRI-DOE-EPA combined Utility Air Pollutnat Control Symposium. Washington, DC (1997)

[58] Nexant Inc. (2006). Environmental Footprints and Costs of Coal-Based Integrated Gasification Combined Cycle and Pulverized Coal Technologies. U.S. Environmental Protection Agency.

8 Signature

Delft, <datum>	Placeholder
<naam afdelingshoofd> Earl L.V. Goetheer Toon van Harmmelen Arjan van Horssen Magdalena Jozwicka	Eva Sanchez Fernandez
Head of department	Author

Appendix A Technical Criteria of the assessment

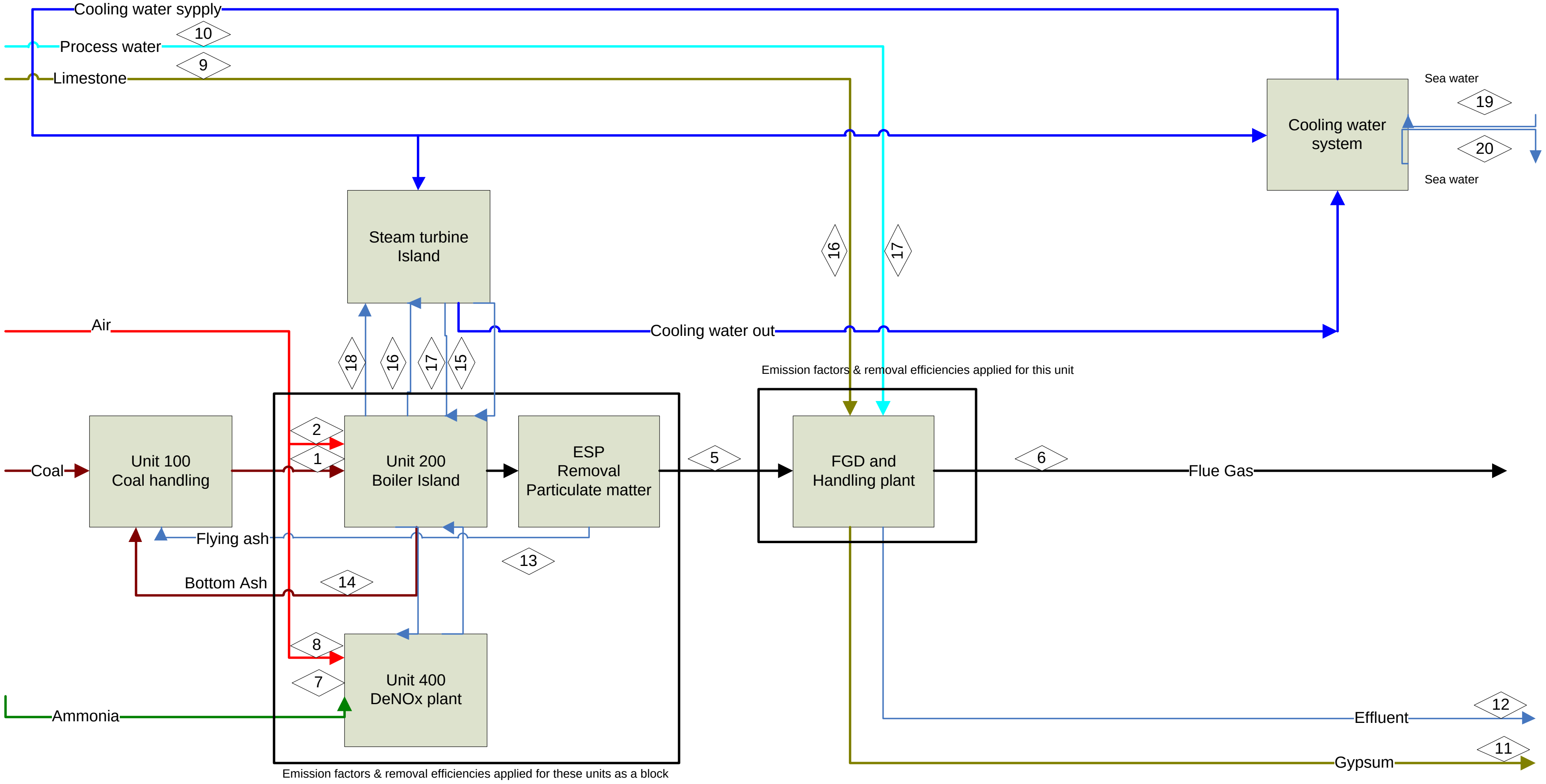
	IEA technical criteria	**EBTF criteria**	**Additional Information**
Plant location			
Country	Netherlands	Northern EU	
Plant site	Coastal	Inland	
Site condition	Clear, level no special civil work	NA	
Seismic risk	Negligible	NA	
Ambient conditions			
Temperature (dry-bulb average) ºC	9	10,8	*15ºC is average ambient temperature*
Max temp ºC	30	NA	
Min temp ºC	-10	NA	
Humidity	60	60	
Pressure	101,3	101,3	
Plant capacity			
Net Power output	800 Mwe	800 Mwe	
Raw material and product delivery			
Coal and limestone	Rail	Rail	
Natural gas delivery	pipeline	pipeline	
Storage capacity			
Ash disposal			
Cooling water system			
Type	once-through sea water cooling	Natural draft cooling towers	
Inlet temperature ºC	12	18,2	
Max Temperature out ºC	19	33,2	
Coal analysis			
Coal type	**Eastern Australia, open cast bituminous**	**South African Douglas Premium 2**	
Proximate analysis			
Moisture (as received) wt%	9,5	8	
Ash (as received) wt%	12,2	14,15	
Volatile Matter (as received) wt%		22,9	
Fixed carbon (as received) wt%	78,3	54,9	
Total Sulfur (as received) wt%		0,52	
Ultimate analysis [dry]			
Carbon (dry) wt%	71,38	72,3	
Hydrogen (dry) wt%	4,85	4,1	
Oxygen (dry) wt%	7,76	5,9	
Nitrogen ((dry) wt%	1,56	1,7	
Sulphur (dry) wt%	0,95	0,56	
Chlorine (dry) wt%	0,03	0,01	

Ash (dry) wt%	13,5	15,4	
Carbon (dry ash free) wt%	82,5	85,5	
Hydrogen (dry ash free) wt%	5,6	4,8	
Oxygen (dry aash free) wt%	8,97	7,0	
Nitrogen (dry ash free) wt%	1,8	2,0	
Sulphur (dry ash free) wt%	1,1	0,7	
Chlorine (dry ash free) wt%	0,03	0,0	
HHV (as-received) MJ/kg	27,06	26,2	
LHV (as-received) MJ/kg	25,87	25,2	
Hardgrove index	45		
Ash analysis wt%			
SiO_2	50	45,0	
Al_2O_3	30	30,0	
Fe_2O_3	9,7	3,0	
CaO	3,9	7,5	
TiO_2	2	2,0	
MgO	0,4	1,2	
Na_2O	0,1	0,2	
K_2O	0,1	0,4	
P_2O_5	1,7	2,0	
SO_3	1,7	3,5	
Ash fusion temp (reducing) ºC	1350		
Natural gas analysis			
Methane, vol%	89	89	
Ethane, vol%	7	7	
Propane, vol%	1	1	
Butane, vol%	0,1	0,1	
Pentane, vol%	0,01	0,009	*+ 0.001 Hexane*
CO_2, vol%	2	2	
Nitrogen, vol%	0,89	0,89	
Pressure, MPa	7	7	*10ºC*
HHV, MJ/kg	51,473	51,473	
LHV, MJ/kg	46,502	46,502	
Efficiency basis for presentation of results			
Standard basis	LHV	LHV	
Sensitivity basis	HHV	NA	*possible to include*
Emission limits			
SO_2, mg/Nm^3 (6%O_2)	100	85	*for gas turbines @ 3% oxygen 35mg/Nm^3 SO_2 and 50 mg/Nm^3 NOx*
NOx, mg/Nm3 (6% O_2)	100	120	
Particulates, mg/Nm^3 (6% O_2)	10	8	
CO_2 Capture			
CO_2 capture %	>=90	90%	
CO_2 Maximum impurities (vol basis)			
H_2O	500ppm	500ppm	
N_2/Ar	4%	4%	
O_2	100ppm	100ppm	

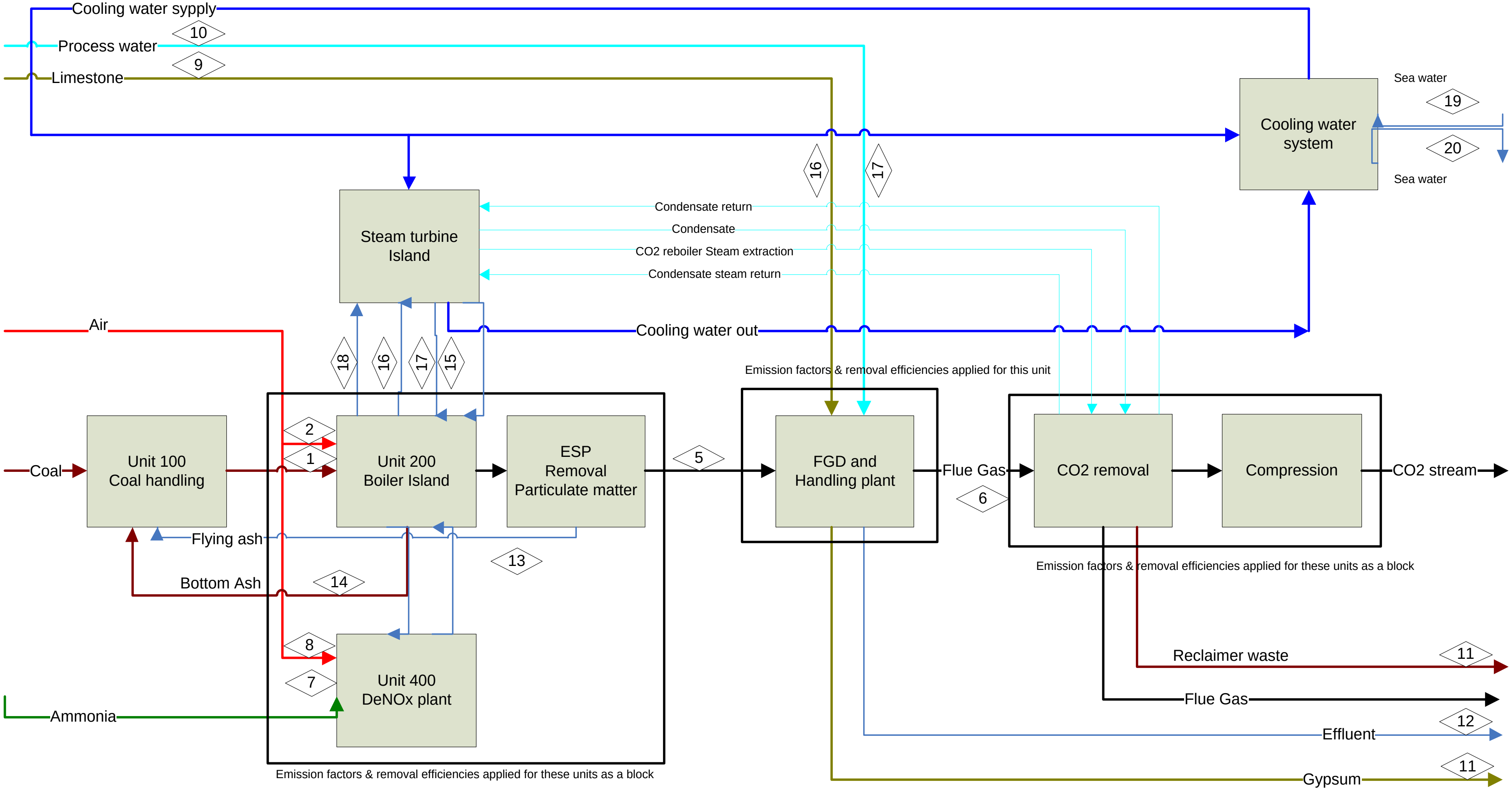
CO	0,20%	0,20%	
CH_4 and other hydrocarbons	4%		
H_2S	200ppm	200ppm	
SO_2, mg/Nm^3 (6%O_2)	100ppm	100ppm	
NO_2	100ppm	100ppm	
Total non-condensables	4%	4%	
CO_2 conditions - pipeline transport			
Pressure, MPa	11	11	
Maximum temperature [ºC]	30	30	

Appendix B Block Diagrams of the reference cases

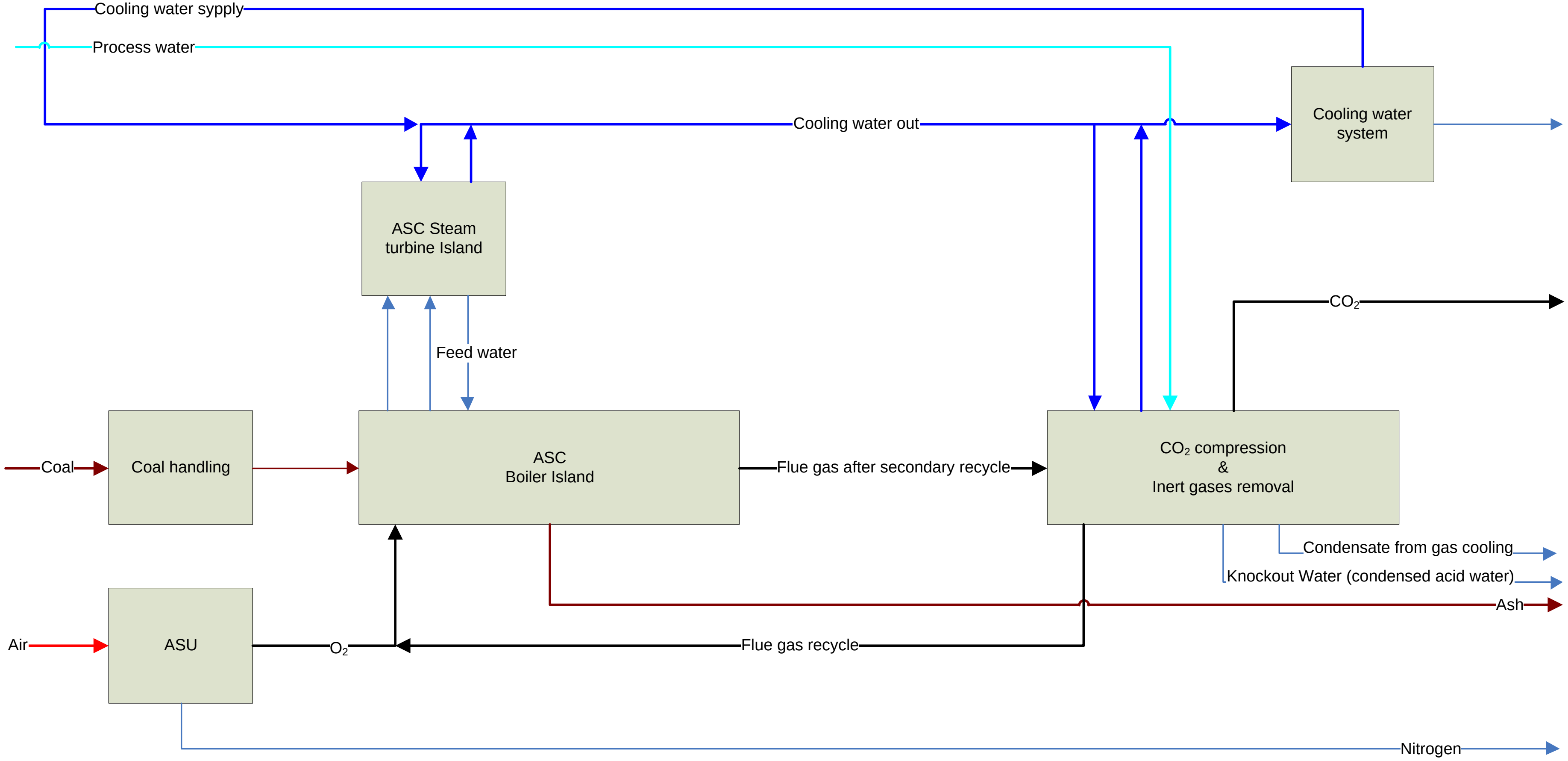
Case 1A USC PC power plant without carbon capture (Stream numbers in agreement with reference study [5])



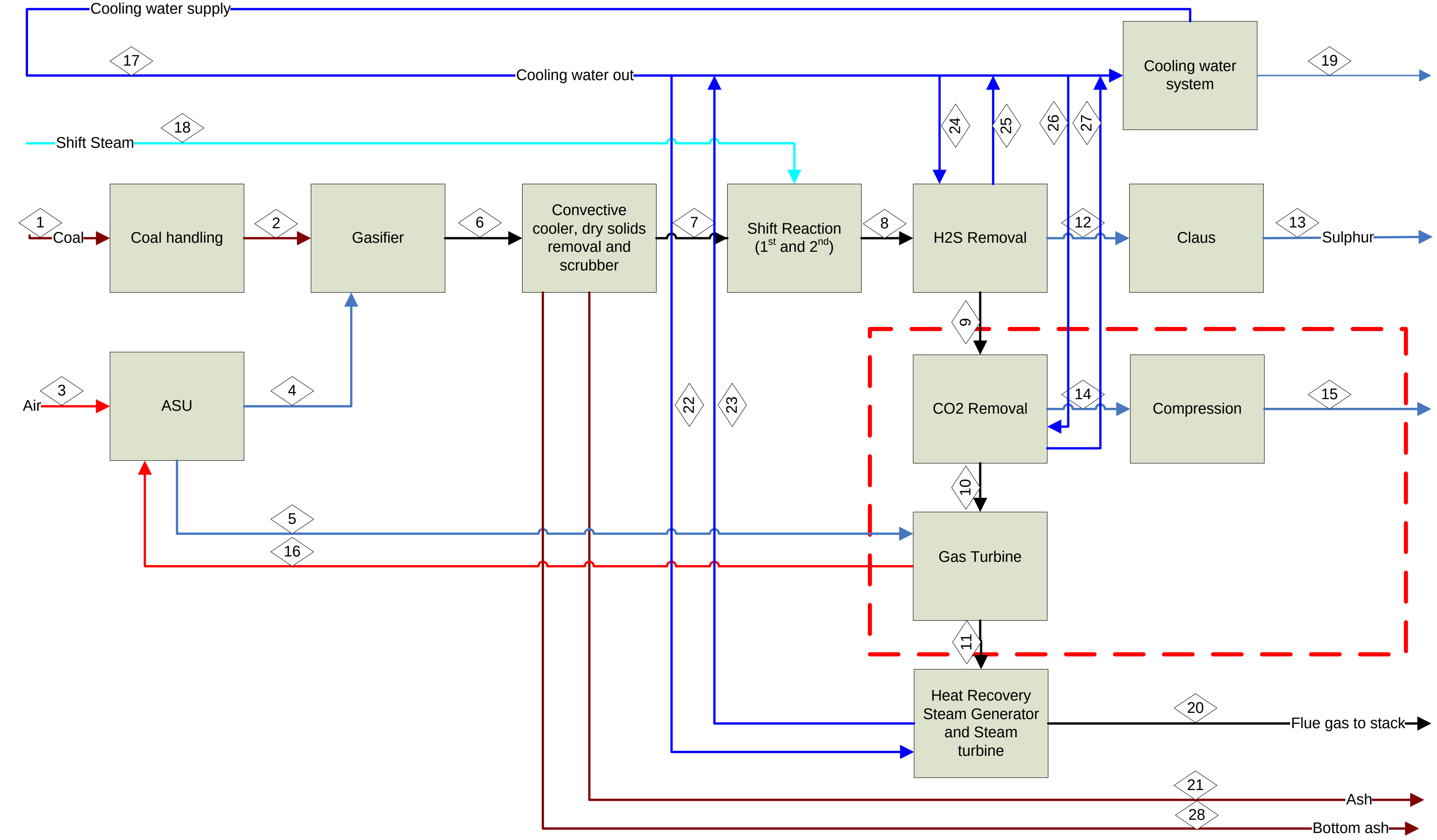
Case 1B USC PC Power plant with capture (Stream numbers in agreement with reference study [5])



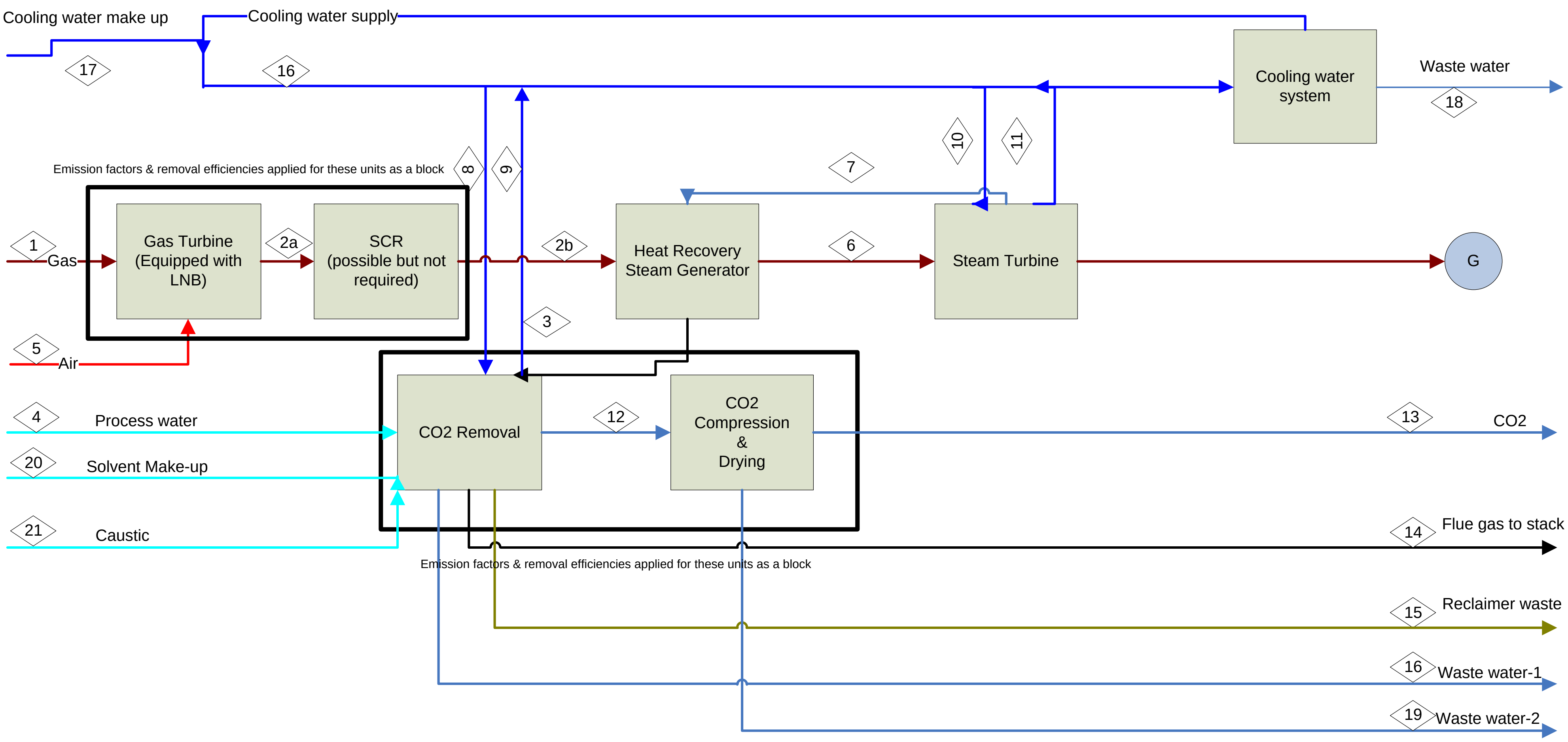
Case 2 USC oxyfired Power plant



Case 3B IGCC with capture (emissions factors taken on the whole plant)



Case 4B NGCC Power plant with carbon capture



Appendix C Harmonization Methodology. Correction model

C.1 Correction for Fuel Use

A fossil fuel power station burns fossil fuels such as: coal, natural gas or petroleum (oil) to produce electricity. The chemical energy stored in fossil fuels and oxygen of the air is converted successively into thermal energy, mechanical energy and, finally, electrical energy. To correct for the different efficiencies of these conversion processes, all energy streams are expressed in units of primary fuel input (MJ) using the fuel use factor:

$$FU = \frac{3.6}{\eta} \left[\frac{MJ}{kWh} \right] \qquad \text{Eq.1}$$

Where:

FU - Fuel Use [MJ/kWh]

η - plant efficiency [LHV]

Obviously, power plant with CO_2 capture unit uses more energy thus burns more fuel than the power plant without CCS. Energy is needed to separate and compress CO_2 to pressures required for transport. This energy consumption results in a reduction of the overall power plant efficiency. This reduction is called the efficiency penalty or energy penalty.

Fuel use had to be corrected to be consistent with the reference cases: compression pressure (110 bar) and for CO_2 capture efficiency (90%). The correction for compression pressure was applied to that part of the fuel penalty related specifically to CO_2 compression and correction for CO_2 capture efficiency was applied on fuel penalty.

C.1.1 Correction for the CO_2 compression pressure

Power consumption for CO_2 compression is assumed to be proportional to the natural logarithm of (outlet pressure/inlet pressure). The power consumption for CO_2 compression is corrected by using the following equation, based on the compression work for an ideal gas. In this case, the gas compression power requirement is proportional to the logarithm of outlet/inlet pressure ratio [11]:

$$CF_{compr\_press} = \frac{\ln\left(\frac{11\ MPa}{P_{in,orig}}\right)}{\ln\left(\frac{P_{out,orig}}{P_{in,orig}}\right)} \qquad \text{Eq.2}$$

Where:

$P_{in,orig}$ - CO_2 compressor inlet pressure in the original literature [MPa]

$P_{out,orig}$ - CO_2 compressor outlet pressure in the original literature [MPa]

For those literature sources were the inlet pressure was not specified, it is assumed to be 0.1013 MPa (1.013 bar) for post combustion and oxy-combustion capture routes, and 1 MPa (10 bar) for pre-combustion capture, unless otherwise indicated in the literature.

The equation above is valid for ideal gasses. Therefore, deviations are expected when CO_2 becomes supercritical fluid. This will lead to an overestimation of the correction for the fuel use. Figure C-1 shows the comparison between the correction factor estimated according to equation 2 and the correction factor derived from simulation results of a 4-stage compression train with intercooling, which delivers the CO_2 stream at 110 bara, starting at 1.7 bara (as described in [8]). The correction factor derived from simulation results is calculated by the ratio of compression power consumption of a given situation to the compression power consumption of the reference case.)

The left part of the figure shows the deviations in power consumption (directly related to fuel used) when the initial pressure is maintained constant at 1.7 bara (reference) and the outlet pressure varies from 110 bara (reference) to 80 bara.

The right part of the figure shows the deviations in power consumption when the initial pressure is varied from 1.7 bara (reference) to 4 bara and the outlet pressure varies from is maintained at 110 bara (reference).

In both cases, the estimate from the simulation in Aspen Plus® and the estimated correction factor are shown. As expected, the correction factor applied is valid for the correction of the inlet pressure (ie lower pressures) and deviates (maximum of 6%) at higher pressures.

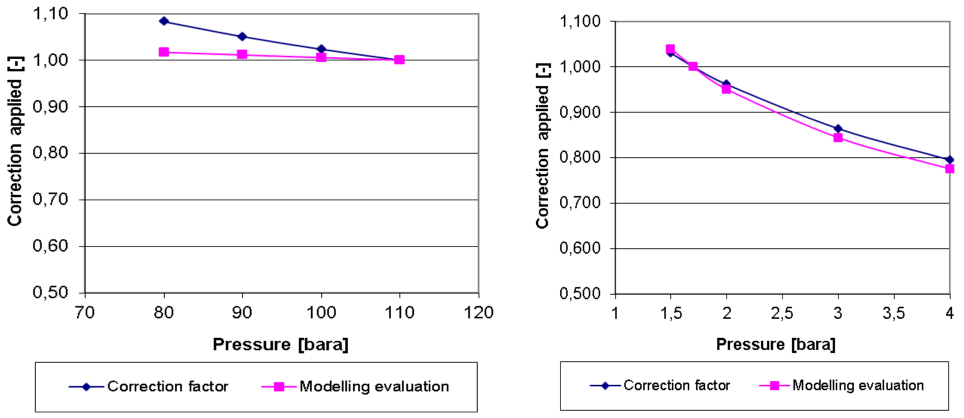


Figure C-1 Analysis of the compression pressure correction factor. Correction factor is compared to the simulation results of a 4-stage compression scheme with intercooling (based on Aspen Plus® software), described in [8]. The left figure shows the variation of the delivery pressure while maintaining constant the inlet pressure. The right figure shows the variation of the inlet pressure while maintaining constant the delivery pressure.

Because of the limited impact on the results in this study (see results of harmonization) no more effort was put in a more dedicated way to correct for the compression pressure.

C.1.2 Correction for the CO_2 capture efficiency

CO_2 capture efficiency represents the theoretical ability of capturing certain amount of CO_2 by particular technology. Given a capture efficiency of 85-95%, CCS can avoid CO_2 emissions to the atmosphere by about 80-90% compared to a plant without CCS. To compare the different types of capture plants on a similar basis, the capture efficiency needs to be kept constant. In the literature reviewed, the capture efficiency was usually about 90%. Consequently, the capture efficiency was set at a constant value of 90%:

$$CF_{Cap\_eff} = \frac{90\%}{Cap.eff_{literature}} \qquad \text{Eq.3}$$

Where:

$Cap.eff_{literature}$ - CO_2 capture efficiency given in the literature [%]

Finally, fuel use was corrected according to the equation (Eq.4):

$$FU_{corr} = FU_{literature} + \left(1 + Fr_{CO_2\_compr\_press} * \left(CF_{compr\_press} - 1\right)\right) * FP * CF_{Cap\_eff}$$

Where:

FU_{corr} - Fuel use corrected [MJ/kWh]

$FU_{literature}$ - Fuel use given in the literature [MJ/kWh]

$Fr_{CO_2\_compr\_press}$ - Fraction of CO_2 compression pressure in fuel penalty [-]

CF_{compr_press} - Correction factor for compression pressure [-]

FP - Fuel penalty [MJ/kWh]

CF_{Cap_eff} - Correction factor for capture efficiency [-]

C.2 Correction for Emissions

All emissions were corrected for the harmonized fuel use calculated as described in the previous paragraph.

The sulphur dioxide (SOx) emissions were standardised to the reference cases. The SOx emissions were adjusted based on sulphur content in the fuel. It was done by standardising the sulphur content in coal to the sulphur content in the coal of the reference cases (Bituminous coal from Eastern Australia for all technologies: PC, IGCC and Oxyfuel [9]). SOx removal efficiencies of Flue Gas Desulphurisation (FGD), Acid Gas Removal (AGR) and CO_2 capture units were assumed to remain constant. For oxyfuel PC plants, SOx emissions largely depend on how the CO_2-

rich gas is treated before being compressed and transported to the storage site. The correction factor for sulphur dioxide has been calculated using the Eq.5:

$$CF_{SO_x} = \frac{S_{\mathrm{content\_ref}}}{S_{\mathrm{content\_literature}}} \qquad \text{Eq.5}$$

Where:

$S_{\mathrm{content\_ref}}$ - Sulphur content fuel in reference case = 0.346 [g/MJ (LHV)]

$S_{\mathrm{content\_literature}}$ - Sulphur content fuel found in the literature

Then the emission factor for SOx was recalculated according to the formula:

$$\mathrm{EF}_{\mathrm{SO_2}} = EF_{\mathrm{SO_2}\_literature} * \mathrm{C}F_{SO_x} \qquad \text{Eq.6}$$

Other emissions could not be harmonised because of its complexity (NOx) or lack of information on pollutant control technologies. Thus emissions of NOx, PM, Hg and NH_3 have been corrected only for fuel use every where were possible.

Appendix D Thermal reclaiming of amine systems

MEA is known to degrade with different impurities in flue gas. The reactions lead to degradation products and formation of HSS. The following reactions show how the possible HSS are formed. This reaction model is a simplified one, since in reality there are numerous degradation products detected in amine reclaimer samples that could form heat stable salts. The following model is a parametric model that aims to quantify the influence of gas impurities in the waste generated by the reclaimer unit. Therefore, only a reduced number of components were taken into account.

$\mathrm{MEA} + a\mathrm{O_2} \rightarrow 2\ \mathrm{HCOOH} + \mathrm{NH_3}$ [1]

$\mathrm{MEA} + a\mathrm{O_2} \rightarrow \mathrm{CH_3COOH} + \mathrm{NH_3}$ [2]

$\mathrm{HCOOH} + \mathrm{MEA} \rightarrow [\mathrm{MEAH^+}][\mathrm{HCOO^-}]$ [3]

$\mathrm{CH_3COOH} + \mathrm{MEA} \rightarrow [\mathrm{MEAH^+}][\mathrm{CH_3HCOO^-}]$ [4]

$\mathrm{SO_2}+\mathrm{H_2O} + 2\mathrm{MEA} \rightarrow 2\mathrm{MEAH^+} + \mathrm{SO_3^{2-}}$ [5]

$2\mathrm{NO_2} + \mathrm{H_2O} + \mathrm{MEA} \rightarrow \mathrm{MEAH^+} + \mathrm{NO_2^-} + \mathrm{MEAH^+} + \mathrm{NO_3^-}$ [6]

$\mathrm{HCl} + \mathrm{MEA} \rightarrow \mathrm{MEAH^+} + \mathrm{Cl^-}$ [7]

$\mathrm{HF} + \mathrm{MEA} \rightarrow \mathrm{MEAH^+} + \mathrm{F^-}$ [8]

Oxidative degradation is the main form of MEA loss in a capture process. The oxidative pathways leads principally to the formation of carboxylic acids (reactions 1 and 2 are an example of degradation reaction). Oxidative pathways have been studied by several authors [29;30;52;53;54]. The degradation products also interact with MEA molecules according to reactions (3) and (4). Estimation of MEA loss is done trough the following equations:

$$MEA_{loss}^{ox} = R_{O2} \cdot \frac{m_{CO2}}{1000} \cdot (2.5) \qquad [9]$$

$$MEA_{loss}^{acid} = \left(\frac{2 \cdot f_{SO2}}{Mw_{SO2}} \cdot m_{SO2} + \frac{2 \cdot f_{SO3}}{Mw_{SO3}} \cdot m_{SO3} + \frac{f_{NO2}}{Mw_{NO2}} \cdot m_{NO2} + \frac{f_{HCl}}{Mw_{HCl}} \cdot m_{HCl} + \frac{f_{HF}}{Mw_{HF}} \cdot m_{HF} \right) \cdot Mw_{MEA} \qquad [10]$$

$$MEA_{loss}^{pol} = \frac{60}{40} MEA_{loss}^{ox} \qquad [11]$$

Where,

MEA_{loss}^{ox}	kg/s MEA losses due to oxidation
MEA_{loss}^{acid}	kg/s MEA losses due to irreversible reactions with acid gases
MEA_{loss}^{pol}	kg/s MEA losses due to carbamate polimerization reactions
R_{O2}	kg MEA /ton CO_2 specific degradation rate (0.46kg/tCO_2 for the reference case)
Mw_{MEA}	kg/kmol molecular weight of MEA
f_i	% removal rate of component i

m_i	kg/s mass flow of component I into the CO_2 capture unit
Mw_i	kg/kmol molecular weight of component i

Estimation of heat stable salts formation follows from the removal rates and stoichimetry of the reactions:

$$HSS_{loss}^{ox} = R_{O2} \cdot \frac{m_{CO2}}{1000} \cdot \left(Mw_{formate} + 0.5 \cdot Mw_{acetate} \right) \qquad [12]$$

$$HSS_{loss}^{acid} = \sum \left(\frac{f_i \cdot MwHSS^{i}}{Mw_i} \cdot m_i \right) \qquad [13]$$

HSS_{loss}^{ox}	kg/s of HSS formed due to oxidation products
HSS_{loss}^{acid}	kg/s of HSS formed due to irreversible reactions with acid gases
R_{O2}	kg MEA /ton CO_2 specific oxidation degradation rate
f_i	% removal rate of acid gas i
m_i	kg/s mass flow of acid gas i into the CO_2 capture unit
Mw_i	kg/kmol molecular weight of acid gas i
$MwHSS^{i}$	kg/kmol molecular weight of the resulting HSS with acid gas i
$Mw_{formate}$	kg/kmol molecular weight of formate
$Mw_{acetate}$	kg/kmol molecular weight of acetate

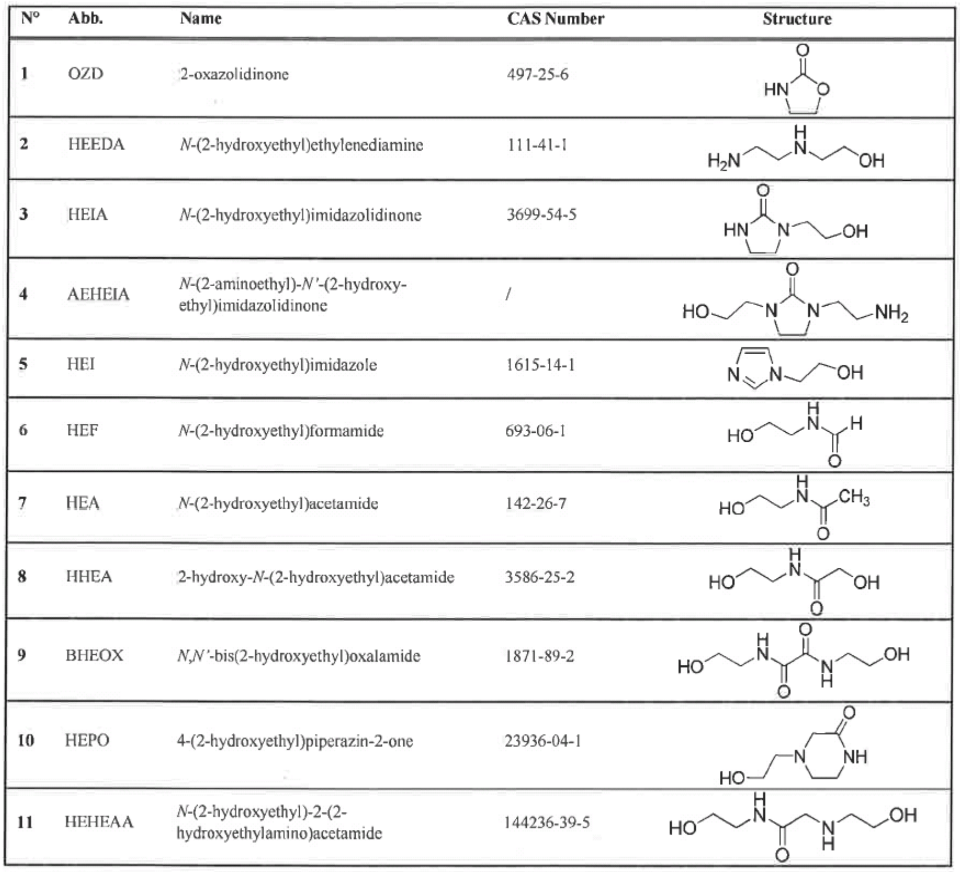
In the case of SO_2, it was assumed that 75% is recovered as HSS. The other fraction will lead to degradation products or will be emitted in the CO_2 stream. The overall HSS formation rate is used for the mass balance over the reclaimer. For the mass balance the software Aspen Plus ® was used to simulated the conditions of the lean stream leaving the reboiler. The table below shows the main performance characteristics of the capture plant and the lean solvent conditions for case 1B.

Table D.1 Performance of the capture plant

Parameter	Unit	Value
CO_2 Product (dried)	kg/s	172.7
MEA concentration	%wt	30
Removal Eff CO_2	[%]	90
Lean loading	mol/mol	0.271
Rich loading	mol/mol	0.464
Lean Solvent Rate	m^3/ton CO_2	24.0
Boiler Heat Required	GJ/ton CO_2 produced	3.20
Cooling water Required	m3/ton CO_2 produced	**73.65**
Lean Feed Temp	(^oC)	40
Lean stream conditions		
Flow Lean	kg/s	3762
Flow Lean	kmol/s	156
MW	kg/kmol	24.1
Density	kg/m^3	908
Composition of lean solvent		

MEA	%mol	12%
CO_2 app	%mol	3%
H_2O	%mol	85%

MEA degradation leads to many degradation compounds. Figure D.1 (taken from [52]) summarizes the most common products of degradation reactions.



N°	Abb.	Name	CAS Number	Structure
1	OZD	2-oxazolidinone	497-25-6	
2	HEEDA	*N*-(2-hydroxyethyl)ethylenediamine	111-41-1	
3	HEIA	*N*-(2-hydroxyethyl)imidazolidinone	3699-54-5	
4	AEHEIA	*N*-(2-aminoethyl)-*N'*-(2-hydroxy-ethyl)imidazolidinone	/	
5	HEI	*N*-(2-hydroxyethyl)imidazole	1615-14-1	
6	HEF	*N*-(2-hydroxyethyl)formamide	693-06-1	
7	HEA	*N*-(2-hydroxyethyl)acetamide	142-26-7	
8	HHEA	2-hydroxy-*N*-(2-hydroxyethyl)acetamide	3586-25-2	
9	BHEOX	*N,N'*-bis(2-hydroxyethyl)oxalamide	1871-89-2	
10	HEPO	4-(2-hydroxyethyl)piperazin-2-one	23936-04-1	
11	HEHEAA	*N*-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide	144236-39-5	

Figure D.1 Summary of the degradation compounds

Table D.1 shows an analysis of a reclaimer sample taken from the IMC Chemicals Facility in Trona, California. This facility has been performing CO_2 capture from flue gas since 1978 [28;38].

Table D.1 List of chemicals in process waste from reclaimer

Chemicals	**Units**	**Concentration**
Na	%wt	0,0821
K	%wt	0,0018
Ca	%wt	0,00013
Fe	%wt	0,00011
Cu	%wt	0,00001
Zn	%wt	0,00002
Al	%wt	0,00004

Se	%wt	0,00174
Ar	%wt	0,00017
Fl	%wt	0,15
Cl	%wt	4,9
Br	%wt	0,008
SO_4^{2-}	%wt	0,025
NO_3^-	%wt	0,31
NO_2^-	%wt	0
PO_4^{3-}	%wt	0,023
Absorption solvent, other HSS,corrosion inhibitors	%wt	94,45

Table D.3 shows the ratio of individual HSS to the total amount of salts [28].

Table D.3 Ratio of individual HSS to the total amount of HSS

Component	Fraction (%wt)
Formate	87
Acetate	4,6
Thiosulphate	1,2
Thiocyanate	6,8
Oxalate	0,2
Sulphate	0,2
Corrosion inhibitor	500ppm

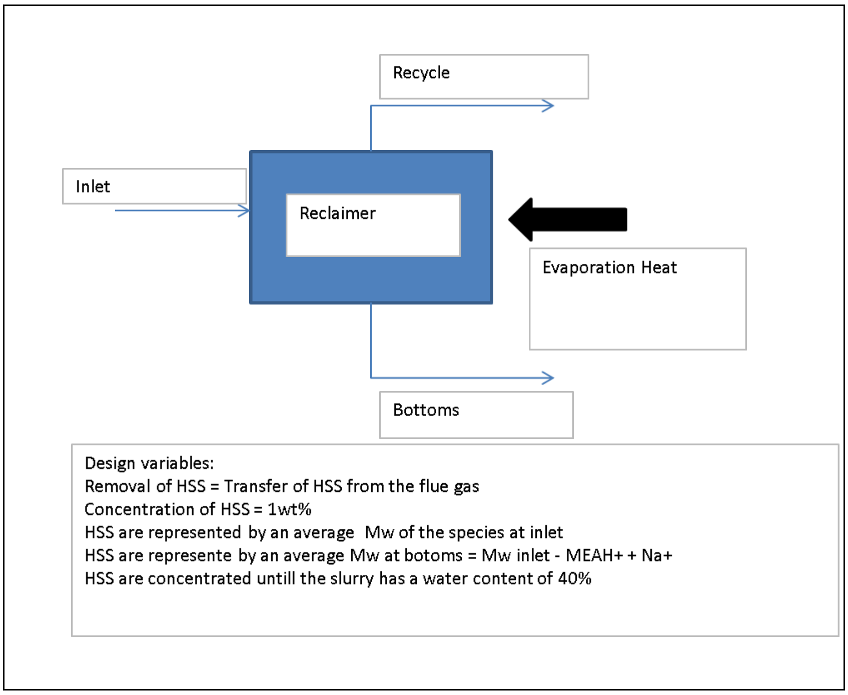
The reclaimer is periodically discharged to empty the accumulated salts. In principle, the concentration of the amine in the reclaimer should be as low as possible. Nevertheless, in many thermal reclaimers the concentration of amine is still high, transforming the thermal reclaimer more into a feed and bleed system [27]. For refinery thermal reclaimers, the concentration of MEA could be as high as 82molMEA/molHSS in the system and as low as 1molMEA/molHSS in the bottoms of the reclaimer.

The following assumptions were taken for the mass balance:

- The concentration of salts in the inlet stream to the reclaimer is assumed to be 1% wt.
- Fraction of the lean stream reclaimed : fixed to match the HSS formation rate
- Concentration factor in the reclaimer: fixed to deliver a slurry containing 40%wt water
- Concentration of free amine in the system: 60mol MEA / mol HSS
- Concentration of free amine at the bottoms: 1molMEA/molHSS
- All the HSS are kept in the reclaimer bottoms

- For simplicity, an average molecular weight of the HSS was used. At the reclaimer's inlet the average was taken on the components shown in the reaction scheme. When the oxidative degradation is assumed to be 0.46kg/ton CO_2, the predominant component was the HSS of formate (in agreement with the distribution shown in table D.2). For the polimerization products, mass is calculated assuming the molecular weight of 2-oxazolidinone (87 g/mol)

Figure D.2 shows the basic scheme of the reclaimer



Design variables:
Removal of HSS = Transfer of HSS from the flue gas
Concentration of HSS = 1wt%
HSS are represented by an average Mw of the species at inlet
HSS are represente by an average Mw at botoms = Mw inlet - MEAH+ + Na+
HSS are concentrated untill the slurry has a water content of 40%

Figure D.2 Scheme of the mass balance around the reclaimer

Table D.3 Results of the reclaimer mass balance for the base case 1B

Parameter	**Units**	**Inlet**	**Bottoms**	**Recycle**
Flow to reclaimer	kg/s	33	0.65	32
	kmol/s	1.3664	0.020	1.345
HSS-Na+	%mol	0%	14%	0%
MEA	%mol	12%	14%	12%
CO_2	%mol	3%	0%	3%
H_2O	%mol	84%	73%	85%
Molecular weight	kg/kmol	24.1	32.52	24.03

The energy associated with this reclaiming is 60MWth, approximately 0.3GJ/ton CO_2 for case 1B

Oxidative degradation rate depends on Temperature, oxygen concentration in the flue gas, MEA concentration, SO2 concentration in the flue gas and CO_2 loading [31]. The following reaction rate has been derived experimentally:

$$-r_{MEA} = k_0 e^{(45300/RT)} \cdot [MEA]^{1.91} \cdot [CO_2]^{-0.33} \cdot \left([SO_2]^{3.42} + [O_2]^{2.78}\right)$$

Where ($-r_{MEA}$) is the MEA rate degradation in mol/Lh and all the concentrations except for SO_2 are solvent concentrations in mol/L. Dissolved oxygen concentration was studied in [31]. The concentration taken for SO_2 is the gas phase concentration.

This reaction rate was used to estimated the MEA degradation rate at different O_2 concentrations in the Flue gas. The figure below show the results:

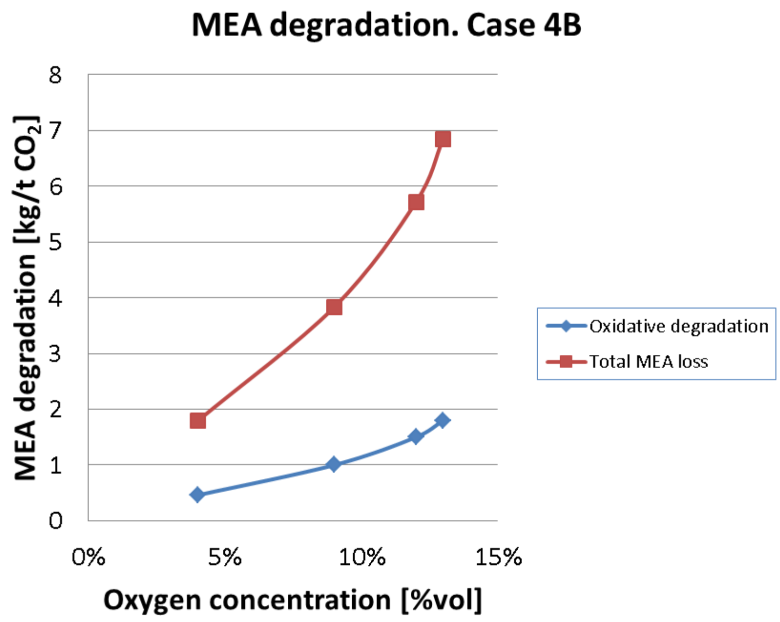


Figure F.3 MEA degradation as a function of oxygen concentration in flue gas (case 4B)

According to this results, the reference value taken (0.46kg/ton CO_2) is valid for an oxygen concentration of 4% (case 1B). For case 4B the MEA degradation would be significantly larger (1.5kg/ton CO_2).

Appendix E Carbon Capture quotients

Carbon Capture Quotients (CCQ's) are used to calculate the ratio between a power plant with and without CCS. The CCQ indicates the relative increase or decrease in the emission factor of a substance or fuel use due to the application of a certain capture technology. In case of emissions the equation is as follows [1]:

$$CCQ_{x,y,z} = \frac{EF_{CCSx,y,z}}{EF_{noCCSx,y}} \qquad \text{Eq.1}$$

Where:

$CCQ_{x,y,z}$	-	Carbon capture quotient for air pollution substance x, given energy conversion technology y and CO_2 capture technology z
$EF_{CCSx,y,z}$	-	Emission factor reported/estimated in the literature for air pollution substance x, energy conversion technology y and CO_2 capture technology z
$EF_{noCCSx,y}$	-	Emission factor for air pollution substance x and energy conversion technology y reported/estimated for the reference plant without CO_2 capture

The CCQ's are calculated for every individual literature case in which both CCS and no CCS data are given. The CCQ is both calculated for the raw as on the harmonised emission factors.

The CCQ's are useful to calculate the emissions of a CCS plant when the emissions of the non-CCS power plant are given. The emissions can be calculated by:

$$E_{CCS} = E_{non\_CCS} \cdot CCQ_{fuel\_use} \cdot CCQ_{emissions} \qquad \text{Eq.2}$$

Carbon Capture Quotients (CCQ)

CCQ's have been calculated from both the harmonised and raw literature emission data and later they have been used to estimate the final emission factors. As already mentioned the CCQ indicates the relative increase or decrease in the fuel use or in the emission factor of a substance due to the application of a certain capture technology. It has been performed for: CO_2, SO_x, NOx, PM_{10}, NH_3 and Hg. The results of this calculation are shown in table E.1. The numbers of cases which were use for calculating the average are also given.

Table E.2 presents an overview of the harmonised emission factors for CO_2, SO_2, NOx, PM_{10}, VOC, NH_3, Hg and CO. Further in this section graphs are shown to illustrate these emission factors. The large range of the values (large standard deviation) can be explained by different phases of the projects (demo vs commercial), different processes and technologies (i.e. water cooling, different solvents/sorbents), different flue gas cleaning technologies or sometimes even lack of De-NOx or de SOx.

Table E.1 CCQ for: fuel use, CO_2, SOx, NOx, PM_{10}, NH_3, and Hg, in brackets number of cases used to calculate the average is given. (h=harmonised)

		fuel	fuel(h)	CO_2	CO_2(h)	SOx	SOx(h)	NOx	NO_x(h)	PM_{10}	PM_{10}(h)	NH_3	NH_3(h)	Hg	Hg(h)
Post	NGCC	1.17 (13)	1.17 (13)	0.14 (9)	0.12 (9)	- (0)	- (0)	1.22 (5)	1.22 (5)	- (0)	- (0)	- (0)	- (0)	- (0)	- (0)
	PC/all cases	1.37 (15)	1.37 (15)	0.14 (14)	0.13 (14)	0.00 (7)	0.00 (7)	1.29 (9)	1.29 (9)	1.31 (6)	1.31 (6)	8.36 (4)	8.32 (4)	1.44 (4)	1.44 (4)
	PC/USC	1.31 (5)	1.31 (5)	0.14 (5)	0.13 (5)	0.00 (1)	0.00 (1)	1.19 (2)	1.19 (2)	1.20 (2)	1.20 (2)	- (0)	- (0)	1.40 (1)	1.39 (1)
Pre	IGCC	1.24 (17)	1.24 (17)	0.13 (17)	0.12 (17)	0.62 (11)	0.62 (11)	1.03 (11)	1.03 (11)	1.24 (3)	1.23 (3)	- (0)	- (0)	1.23 (3)	1.23 (3)
Oxyfuel	PC/all cases	1.30 (11)	1.29 (11)	0.06 (11)	0.12 (11)	0.07 (11)	0.07 (11)	0.61 (10)	0.61 (10)	0.08 (9)	0.08 (9)	- (0)	- (0)	0.07 (8)	0.07 (8)
	PC/USC	1.30 (3)	1.30 (3)	0.07 (3)	0.12 (3)	0.11 (3)	0.11 (3)	0.60 (3)	0.59 (3)	0.09 (2)	0.09 (2)	- (0)	- (0)	0.09 (2)	0.09 (2)
no-capture	NGCC	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	PC/all cses	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	PC/USC	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	IGCC	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Table E.2 CO_2, SOx, NOx, PM_{10}, , NH_3, and Hg final (harmonized) emissions [g/kWh] from power plants with and without CO_2 capture, in brackets number of cases used to calculate the average is given.

		Reference case	Plant efficiency [% LHV]	Fuel use [MJ/kWh]	CO_2 [g/kWh]	SO_2 [g/kWh]	NOx [g/kWh]	PM_{10} [g/kWh]	Hg [g/kWh]	NH_3 [g/kWh]
PC	no-capture/ all cases		41,1%	8,82	796	0,28	0,39	0,044	3,1E-06	6,7E-03
	no-capture /USC	1A	43,9%	8,21	735	0,30	0,36	0,040	2,7E-06	3,5E-03
	Post /all cases		30,8%	11,87	108	0,0013	0,60	0,062	6,4E-06	8,2E-02
	Post /USC	1B	34,1%	10,57	97	0	0,50	0,046	5,5E-06	
	Oxyfuel /all cases		33,1%	10,96	102	0,0085	0,19	0,003	3,1E-07	
	Oxyfuel /USC	2	35,6%	10,24	93	0,012	0,20	0,004	3,5E-07	
ICC	no-capture	3A	42,2%	8,57	761	0,041	0,23	0,014	2,2E-06	0
	Pre	3B	34,8%	10,42	93	0,011	0,21	0,034	2,7E-06	
NGCC	no-capture	4A	56,4%	6,39	366		0,12			3,7E-04
	Post	4B	48,8%	7,48	43		0,13			

Appendix F Description of NGCC cases (Reference cases 4A and 4B)

This section briefly describes the NGCC cases (reference cases 4A and 4B). The technical assumptions were taken from the Common framework document of the European Benchmarking Task Force [8].The reference power plant is located inland, assumed 20 meters above sea level. The main equipment, such as gas turbine, steam turbine, generator, HRSG and water treatment is located indoor. Switchyard is included. With respect to the power plant, in this case the main equipment consists of only one gas turbine (Siemens SGT5-4000F) equipped with dry low NOx burners, steam turbine, generator, HRSG and water treatment equipment. Water cooling is done with draft cooling tower. The plant yields 430MWe gross. When the auxiliaries are taken into account the net electricity is reduced to 422.5MWe net. CO2 emissions for this case are 354g/kWh (based on net electricity). The overview of heat and mass balances is shown in table F.1

Table F.1 Overview of overall heat and mass balance

Parameter	**Unit**	**Value**
GT shaft power	MW	289.2
ST shaft power	MW	145.7
Gross electricity output	MW	430.3
Total net power output	MW	422.5
HP turbine inlet steam conditions	bara / °C	123.8 / 561
IP turbine inlet steam conditions	bara / °C	30.1 / 561
LP turbine inlet steam conditions	bara / °C	4.2 / 234
Auxiliary power consumption	%	1.80
Final feed water temperature	^oC	33
Fuel flow	kg/s	15.6
Net full load plant efficiency	% LHV	58.29
CO_2 emissions at full load	kg/s	41.54
CO_2 emitted	g/kWh	354

F.1 Design of capture unit

The CO_2 capture plant consists primarily of three large vessels; the direct contact cooler, the absorber and the stripper. The direct contact cooler decreases the temperature of the flue gas to a suitable absorption temperature. The absorber facilitates the capture of CO_2 by providing large surface areas for solvent-flue gas contact. The stripper regenerates the solvent releasing the CO_2 for compression and storage. At the conditions of the absorber, the CO_2 is chemically bound to the MEA solvent. A blower is required to overcome the additional pressure drop from the absorber. After passing through the absorber, the flue gas passes through a water wash section to balance water in the system and to remove any solvent droplets or solvent vapour carried over and then leaves the CO_2 capture plant. The "rich" solvent, which contains the chemically bound CO_2, is then pumped to the top of a stripper, via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (120 ºC) and slightly elevated pressure. Heat is supplied to the stripper from a reboiler; this heat is required to heat the solvent, generate stripping gas/vapour and provide the required desorption heat for removing the chemically bound CO_2. The steam necessary to supply this heat must be extracted from the power plant, the steam is suitably conditioned (through pressure reduction and attemperation) for reboiler use. The extraction of this steam leads to a significant thermal energy penalty to the host power plant.

The capture process technical data and performance are determined by simulation using Aspen Plus ® commercial software. Figure F.1 shows the Aspen flow sheet used for the NGCC cases.

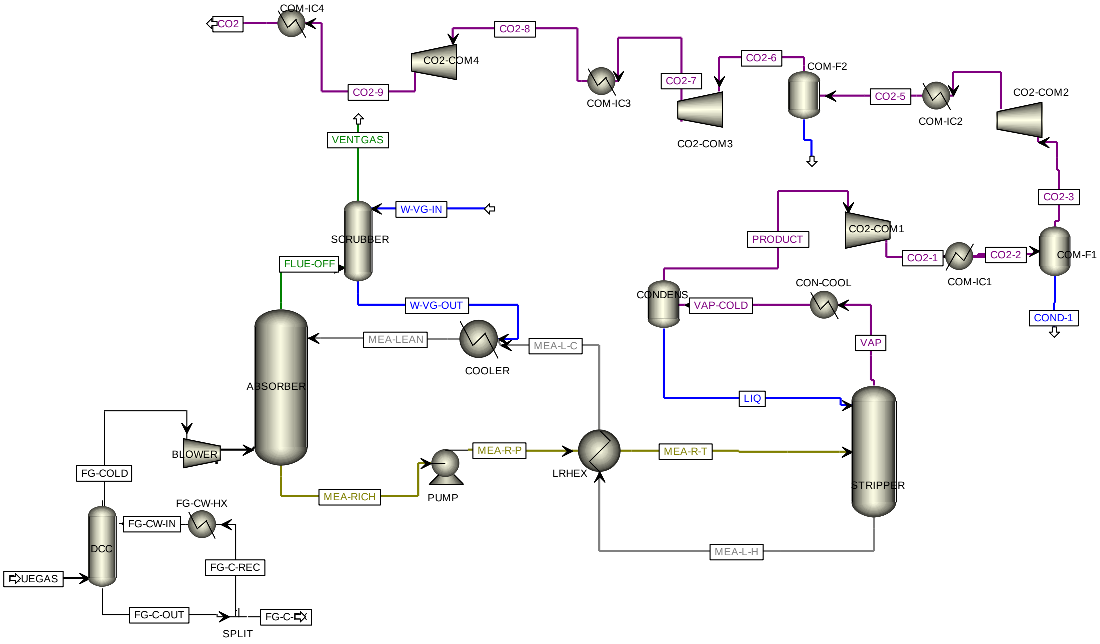


Fig. F.1 – Basic Aspen Process flow sheet

The absorption process is modelled with two unit operations: absorber and water wash section. Both unit operations are simulated with the ASPEN RadFrac® model. This model assumes a sequence of equilibrium stages. The rich solvent coming from the absorber is pumped to the stripper via the lean-rich heat exchanger. This heat exchanger is designed on the basis of a fixed overall heat transfer coefficient and a temperature approach of 5 ºC (cold in-hot out approach). The stripper is simulated again with the ASPEN Radfrac® model. The top two stages serve as a washing section.

The vapour leaving the stripper is condensed at 40 ºC. The condensate is separated from the gas in a flash vessel (40 ºC, 1.6 bara) and recycled back to the stripper at the top stage (water reflux). The CO_2 product gas, once separated from the condensate, is compressed in three stages and includes intercooling after every stage. After the final compression and intercooling stage, the CO_2 is already a supercritical fluid. The final conditions of the product stream are 25 ºC and 110 bara.

The main operational characteristics of the capture plant are summarized in table F.2. Table F.3 shows the thermal and electrical requirements of the capture plant. The electrical output falls due to the thermal energy requirements of the stripper reboiler, ultimately reducing steam available to the LP cylinders and hence reducing gross electrical output. The conditions of the steam going to the reboiler are 134ºC saturated. Steam is extracted from the IP/LP cross over pipe. The auxiliary power consumption is also increased by the compression system, blower and pumps.

Table F.2 - Specific performance parameters of the capture process

Parameter	Unit	VALUE
Removal efficiency	%	89
Flue gas flow rate	kg/s	690.65
CO_2 feed content	mol. %	3.88%
CO_2 captured	t/hr	134.07
Solvent Concentration	wt-%	30%
Lean solvent flow rate	m^3/s	0.87
Solvent specific demand	m^3/tCO_2	23.41
CO_2 rich loading	mol CO_2/mol MEA	0.46
CO_2 lean loading	mol CO_2/mol MEA	0.26
Net cyclic loading	mol CO_2/mol MEA	0.209
Regeneration energy requirement	MWth	149
Regeneration energy specific requirement	GJ/t CO_2	4.01
Cooling water requirement	m^3/hr	9864
Cooling water specific requirement	m^3/tCO_2	73.58

Table F.3 - Thermal and electrical requirements of the capture plant

	VALUE
Thermal (MWth)	
Reboiler Heat	149
Stripper Condenser cooling	65
Lean liquid cooling	37
Flue gas cooling	46
Compressor cooling	24
Electric power (MWe)	
Compressors	13
Pumps	3.6
Blower	7.4

Installation of an amine scrubber downstream of the power plant results in a loss in overall plant performance. Based on the thermal requirements shown in Table F.3, an evaluation of heat integration with the power plant was done. Results are shown in table F.4.

Table F.4 – Comparison of cases with and without capture			
PARAMETER	UNIT	Without capture	With capture
Gross electricity output	MWe	430.3	388.3
Auxiliary power consumption (power plant)	MWe	7.7	31.7
Net electricity capture	MWe	422.5	356.6
Efficiency	%	58.29	49.16
CO2 Emitted	Kg/MWh	354	41.9

Appendix G Trace metal emission factors in PC boilers

Experimental determination of trace metals in a 500Mw wall-fired boiler fuelled with bituminous coal and equipped with Low NOx Burners, OFA and ESP. Results are taken from [16] (reference 46 of AP-42 section 1.1 background documentation) and are based on 3 test runs.

Table G.1 Emissions factors for trace metals

Trace metals	Unit	Value
Antimony	kg/t	NA
Arsenic	kg/t	1,32E-03
Berylium	kg/t	3,74E-05
Cadmium	kg/t	4,34E-05
Chromium	kg/t	2,53E-04
Cobalt	kg/t	7,85E-05
Lead	kg/t	1,32E-04
Manganese	kg/t	2,53E-04
Nickel	kg/t	2,05E-04
Selenium	kg/t	1,69E-03
Zn	kg/t	NA
Copper	kg/t	3,53E-04
Thalium	kg/t	NA
Vanadium	kg/t	4,94E-04
Barium	kg/t	1,69E-03
Silver	kg/t	NA
Mercury	kg/t	5,81E-05
