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Carbon dioxide capture — Carbon dioxide capture systems, technologies and processes

National foreword

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Carbon dioxide capture — Carbon dioxide capture systems, technologies and processes

Capture du dioxyde de carbone — Systèmes de capture du dioxyde de carbone, technologies et processus

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Foreword

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The committee responsible for this document is ISO/TC 265, *Carbon dioxide capture, transportation, and geological storage*.

Introduction

Carbon capture and storage (CCS) is a technology to mitigate climate change. Many demonstration projects have been conducted worldwide, and CO_2 capture is an important process in CCS and is cost and energy intensive.

CO_2 capture in power industry could be classified through pre, post and oxy combustion. Technologies such as chemical and physical absorption, adsorption, and membrane separation are currently under development and are in various stages of maturity from commercial (110 MW)[1] large-scale demonstrations to laboratory-scale evaluation, and should be delivered at low cost and low energy consumption.

The objectives of this Technical Report are to specify and review existing capture technologies, equipment and processes and comprehend CO_2 capture systems so that this Technical Report can provide stakeholders with the guidance and knowledge necessary to develop a series of standards for CO_2 capture and build consensus on this standardization work in advance.

This Technical Report describes CO_2 capture systems based on published papers and other documents and then summarizes the different issues deemed most important by ISO/TC 265. This includes the following:

- boundary for CO_2 capture systems;
- technologies, equipment and processes;
- CO_2 streams, gas streams and emissions, processes and waste products;
- evaluation procedures for capture performance;
- safety issues on each capture system;
- reliability issues on each capture system;
- management system.

Carbon dioxide capture — Carbon dioxide capture systems, technologies and processes

1 Scope

This Technical Report describes the principles and information necessary to clarify the CO_2 capture system and provide stakeholders with the guidance and knowledge necessary for the development of a series of standards for CO_2 capture. This Technical Report also covers technologies, equipment and processes specific to CO_2 capture from the viewpoints of the international standardization for the implementation of CCS.

The purpose of this Technical Report is to provide guidance for the development of an ISO document related to CO_2 capture as part of a CCS chain. This Technical Report covers CO_2 capture systems applicable to CO_2 emission sources and their respective boundaries, as well as capture technologies, equipment and processes. In addition, it can be used for the development of International Standards under TC 265.

The following issues are to be excluded from this Technical Report:

- industrial use of CO_2;
- compression of CO_2 (not described in detail);
- terminologies not used in this Technical Report.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
absorbent
substance able to absorb liquid or gas

3.2
affinity
tendency of substances to react with each other

Note 1 to entry: Also defined as the decrease in Gibbs energy on going from the reactants to the products of a chemical reaction.

[SOURCE: IUPAC Compendium of Chemical Terminology]

3.3
air separation unit
unit separating oxygen, nitrogen and other inert gases from air which delivers the reqired oxygen for gasification or combustion applications in the context of CCS

3.4
alkanolamine
chemical compound that carries hydroxy (–OH) and amino ($–NH_2$, –NHR, and $–NR_2$) functional groups on an alkane backbone

3.5
amine
chemical compound consisting nitrogen atoms bound to hydrogen and/or carbon atoms having the general formula R_3N

3.6
amino acid
any of a class of organic compounds in which a carbon atom has bonds to an amino group, a carboxyl group, a hydrogen atom and an organic side group

3.7
antioxidant
substance that inhibits oxidation or reactions promoted by oxygen, peroxides, or free radicals

3.8
Brayton cycle
thermodynamic cycle that describes the workings of a constant pressure heat engine such as gas turbine engine

3.9
capital cost
sum of direct equipment costs to capture CO_2 which is also known as investment cost or first cost

[SOURCE: IPCC Special Report on Carbon Dioxide Capture and Storage]

3.10
capital requirement
sum of direct equipment costs and indirect costs to capture CO_2

3.11
catalyst
substance that increases the rate of reaction without itself being consumed in the reaction

3.12
CCS energy consumption
total energy used for the development and operation of a CCS project

3.13
chemical absorption
process in which CO_2 is absorbed by chemical reaction

3.14
circulating dry scrubber
type of semi-dry FGD using hydrated lime as chemical reagent which is based on a circulating bed reactor set up to desulfurize the flue gas

3.15
clinker
mass of incombustible matter fused together

3.16
CO_2 capture
separation of CO_2 in such a manner as to produce a concentrated stream of CO_2 that can readily be transported for storage

3.17
CO_2 capture rate
ratio of the captured CO_2 mass flow rate at CO_2 capture system to the inlet CO_2 mass flow rate to CO_2 capture system

3.18
CO_2 processing unit
group of processes used in the purification of the CO_2 rich gas to a desired CO_2 specification

Note 1 to entry: Also known as compression and purification unit (CPU), CO_2 purification unit (CPU), cryogenic purification unit, gas processing unit (GPU).

3.19
critical pressure
vapour pressure at the critical temperature

3.20
critical temperature
temperature above which liquid cannot be formed simply by increasing the pressure

3.21
decarboxylation reaction
chemical breakdown of compounds containing carbonates

3.22
degradation
act or process of chemical which makes its functional effectiveness or chemical purity decrease towards the failure to meet the performance of the plant through physical and chemical breakdown or reaction with other substances

3.23
dehydration
process of removing water from a stream or material

3.24
demineralized water
demin water
water of which the mineral matter or salts have been removed

Note 1 to entry: Sometimes designated as demin water.

3.25
demister
device, often fitted with vapour-liquid separator vessels, to enhance the removal of liquid droplets or mist entrained in a vapour stream

3.26
desorption
release of CO_2 from absorbent or adsorbent

3.27
direct quench
process where hot gas is cooled by injection of water, cool gas or water immersion

3.28
effluent
flow of waste material discharged into the environment

3.29
equilibrium
state of balance between opposing forces or actions that is either static or dynamic

3.30
flash gas
gas separated from a liquid by pressure reduction

3.31
flue gas
gases produced by combustion of a fuel that are normally emitted to the atmosphere

3.32
flue gas condenser
process of removing water from the flue gas by cooling

3.33
flue gas desulfurization
equipment normally used in the removal of SO_x in the flue gas by using chemical reagents

3.34
flue gas processing unit
unit of processes used to remove different criteria pollutants (SO_x, NO_x, PM, etc.) from flue gas of boilers or fired heaters

Note 1 to entry: Also known as environmental island, air quality control system (AQCS), gas quality control system (GQCS).

3.35
forced oxidation wet flue gas desulfurization
type of wet FGD using limestone as chemical reagent

3.36
gas turbine
machine in which a fuel is burned with compressed air or oxygen and mechanical work is recovered by the expansion of the hot products

3.37
gasification
reaction that coal, biomass, petroleum coke, or natural gas is converted into a syngas composed mainly of carbon monoxide (CO) and hydrogen (H_2)

3.38
gasifier
reactor in which coal, biomass, petroleum coke, or natural gas is converted into a syngas composed mainly of carbon monoxide (CO) and hydrogen (H_2)

3.39
membrane
permeable solid material that selectively separates the components of a fluid mixture

3.40
mist
stream of liquid in the form of very small drops

3.41
nitrosamine
any of various organic compounds which are characterized by the grouping NNO

3.42
nitramine
any of various organic compounds which are characterized by the grouping NNO_2

3.43
off-gas
gas that is produced as a by-product of a process

3.44
oxy-combustion
oxyfuel combustion
process involving combustion of a fuel with pure oxygen or a mixture of oxygen and re-circulated flue gas

3.45
oxy-CFB boiler
CFB boiler using technology based on oxyfuel combustion with recycled flue gas

3.46
oxy-PC boiler
PC boiler using technology based on oxyfuel combustion with recycled flue gas

3.47
particulate emission
solid and liquid particles that are by-products of combustion entrained in flue gas exiting the stack of a fossil fueled boiler

3.48
permeability rate
quantity of flow of gas (or liquid) through a membrane per unit of time and area

3.49
permeance
measure of gas actually flowing through a membrane per unit of pressure differential

Note 1 to entry: In general, it is expressed in gas permeance units (GPU).

Note 2 to entry: 1 GPU = 10^{-6} cm^3(STP)/scm^2(cmHg).

3.50
physical absorption
process where a solvent absorbs a gas physically with pressure and without chemical reaction

3.51
post-combustion capture
capture of carbon dioxide from flue gas stream produced by fuel air combustion

3.52
power output
electricity which is produced or supplied from a power plant

3.53
pre-combustion capture
capture of carbon dioxide following the processing of the fuel before combustion

3.54
pressure swing adsorption
method of separating gases using the physical adsorption of one gas at high pressure and releasing it at low pressure

3.55
pulverized coal
finely ground coal

3.56
pulverized coal boiler
utility boilers using pulverized fuel or coal as fuel

3.57
pulverized fuel
finely ground solid fuels such as coal or biomass

3.58
quench
to cool hot gas suddenly

3.59
radiant quench design
design of the process where hot gas is cooled by radiant cooler

3.60
reaction rate
speed of a chemical reaction

3.61
reclaimer
process or unit that regenerates deteriorated absorbent

3.62
recycled flue gas
flue gas recycled to moderate the combustion temperature

3.63
regenerator
see *stripper* (3.79)

3.64
reliability
ability of an item to perform a required function, under given environmental and operational conditions and for a stated period of time

[SOURCE: ISO 8402]

3.65
retrofit
modification of the existing equipment to upgrade and incorporate changes after installation

[SOURCE: IPCC Special Report on Carbon Dioxide Capture and Storage]

Note 1 to entry: See IEA Technology Roadmap: Carbon Capture and Storage.

3.66
saturation
point of a solution condition at which a solution of a substance can dissolve no more of that substance and additional amounts of it will appear as a separate phase at the stable condition

3.67
scrubber
gas liquid contactor device, normally used to remove gaseous and solid emissions from flue gas streams

3.68
selectivity
degree that one substance is absorbed in comparison to others

[SOURCE: US Department of Energy/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, February 2013]

3.69
shift conversion
see *shift reaction* (3.71)

3.70
shift converter
reactor in which the water-gas shift reaction, $CO + H_2O = CO_2 + H_2$, takes place

3.71
shift reaction
chemical formation of carbon dioxide and hydrogen from carbon monoxide and water

3.72
sludge
semi-liquid (or semi-solid) residue or solids separated from suspension in a liquid in industrial processes and treatment of sewage and waste water

3.73
slurry
thick, flowable mixture of solids and a liquid, usually water

3.74
solute
dissolved substance in a solution

3.75
solvent
liquid substance capable of dissolving CO_2

3.76
sorbent
substance that absorbs CO_2 or to which CO_2 is adsorbed

3.77
sour shift (reaction)
shift reaction without removing H_2S or COS

3.78
steam reforming
catalytic process in which a hydrocarbon is reacted with steam to produce a mixture of H_2, CO and CO_2

3.79
stripper
gas-liquid contacting device, in which a component is transferred from liquid phase to the gas phase

Note 1 to entry: Can also be referred to as “regenerator” or “desorber”.

3.80
sweet shift (reaction)
shift reaction after removing H_2S or COS

3.81
syngas
synthetic gas produced through gasification process

3.82
treated gas
gas finally discharged from the CO_2 capture process in the emission side after being processed to have a lower CO_2 concentration than the feed gas

3.83
waste water
water for which there is no use in the process anymore

3.84
water gas shift
see *shift reaction* (3.71)

4 Symbols and abbreviated terms

%RH	% relative humidity
AAS	Amino acid salt
ACI	Activated carbon injection
AEP	American Electric Power
AGR	Acid gas removal
AIGA	Asian Industrial Gas Association
AOD	Argon-oxygen decarbonization
AQCS	Air quality control systems
ASME	American Society of Mechanical Engineers
ASU	Air separation unit
A-USC	Advanced ultra-supercritical
BAC	Booster air compressor
BAHX	Brazed aluminium heat exchanger
BAT	Best available technology
BF	Blast furnace
BFG	Blast furnace gas
BFW	Boiler feed water
BOF	Basic oxygen furnace (also known as LD or converter)
BOFG	Basic oxygen furnace gas (also known as LDG or CG)
BOP	Balance of plant
BOS	Basic oxygen steelmaking
BREF	Best available technology reference document
BSF	Boiler simulator furnace
BTG	Steam and power generation unit
BTX	Benzene, toluene and xylene (also known as Benzole)
CalEPA	California Environmental Protection Agency
CAP	Chilled ammonia process
CAPEX	Capital expenditure
CAS	Chemical abstract service
CCF	Cyclone converter furnace
CCS	Carbon capture and storage
CCUS	Carbon capture, utilization and storage
CDA	Circulating dry absorber
CDQ	Coke dry quenching
CDS	Circulating dry scrubber
CEMS	Continuous emission monitoring system
CERC	Cambridge Environmental Research Center
CFB	Circulating fluidized bed
CFR	US Code of Federal Regulations
CG	Converter gas (also known as BOFG or LDG)
CGA	Compressed Gas Association
CIS	Commonwealth of Independent States
CISWI	Commercial and industrial solid waste incinerators
COG	Coke oven gas

COSHHHSE	Control of substances hazardous to health under health and safety executive
CPU	CO_2 processing unit, compression and purification unit, CO_2 purification unit or cryogenic purification unit
CSIRO	Commonwealth Scientific and Industrial Research Organization
CTL	Coal to liquids
CW	Cooling water
DAF	Dry ash free
DCAC	Direct contact and after cooler
DCC	Direct contact cooler
DCCPS	Direct contact cooler polishing scrubber
DP	Dew point
DRI	Direct reduction ironmaking
DSI	Direct sorbent injection
EAF	Electric arc furnace
EHS	Environmental, health and safety
EHSM	Environmental, health and safety management system
EIA	Environmental impact assessment
EIGA	European Industrial Gas Association
EOP	Electricity output penalty
EOR	Enhanced oil recovery
EPA (USEPA)	US Environmental Protection Agency
ESP	Electrostatic precipitator
ETP	Energy technology perspectives
EU	European Union
FBC	Fluidized bed combustion
FCV	Flow control valve
FD fan	Forced draft fan
FEED	Front end engineering design
FEGT	Furnace exit gas temperature
FF	Fabric filter or bag filter
FGC	Flue gas condenser
FGD	Flue gas desulfurization
FMECA	Failure mode and effects critical analysis
FOH	Forced outage hours
FOR	Forced outage rate
FTA	Fault tree analysis
GBFS	Granulated blast furnace slag
GCCSI	Global Carbon Capture and Storage Institute
GGBFS	Granulated ground blast furnace slag
GGH	Gas-gas heat exchanger
GHG	Greenhouse gas
GHGT	Greenhouse gas control technologies conference
GOX	Gaseous oxygen
GPU	Gas processing unit
GQCS	Gas quality control system
GTCC	Gas-fired combined cycle

GTL	Gas to liquids
HAZOP	Hazard and operability
HBI	Hot briquetted iron
HC	Hydrocarbons
HGI	Hard grove index
HM	Hot metal (also known as pig iron)
HP	High pressure
HRC	Hot rolled coil
HRM	Hot rolling mill (also known as HSM)
HRSG	Heat recovery steam generator
HS	Hot stove
HSE	Health, safety and environment
HSM	Hot strip mill
IARC	International Agency for Research on Cancer
ID fan	Induced draft fan
IEA	International Energy Agency
IFA	International Fertilizer Industry Association
IFC	International Finance Corporation
IGCC	Integrated coal gasification combined cycle
IP	Intermediate pressure
IPCC	Intergovernmental panel on climate change
ISO	International Organization for Standardization
JCR	Jumbo coke reactor (also known as SCS)
JT	Joule-Thomson
LCOE	Levelized cost of electricity
LDG	Linz-Donawitz gas (also known BOFG or CG)
LFO	Light fuel oil
LHV	Lower heating value
LIN	Liquid nitrogen
LM	Ladle metallurgy
LNG	Liquefied natural gas
LOI	Loss on ignition
LOX	Liquid oxygen
LP	Low pressure
LTEL	Long-term exposure limit
MAC	Main air compressor
MCR	Maximum continuous rating
MDT	Mean downtime
MHX	Main heat exchanger
MP	Medium pressure (also referred to as IP)
MTBF	Mean time between failures
MTPY	Million tonnes per year
MTTR	Mean time to repair
NAFTA	North American Free Trade Agreement (include USA, Mexico and Canada)
NEDO	New Energy and Industrial Technology Development Organization
NFBF	Nitrogen free blast furnace

NG	Natural gas
OBF	Oxy-blast furnace (oxygen blown blast furnace)
OBF-PG	OBF processed gas
OBF-TG	OBF raw top gas
OFA	Overfire air
OFO	Overfire oxygen
OHF	Open hearth furnace
OHSAS	Occupational health and safety assessment series
OPEX	Operating expenditure
OPERA	Operational problem analysis
OREDA	Offshore reliability data
OSHA	US Occupational Safety and Health Administration
Oxy-CFB	Oxyfuel combustion — circulating fluidized bed
Oxy-PC	Oxyfuel combustion — pulverized coal
PC	Pulverized coal (also known as powdered coal)
PCC	Post combustion capture
PCI	Pulverized coal injection
PF	Pulverized fuel
PFD	Process flow diagram
PGAN	Pressurized gaseous nitrogen
PHA	Process hazard analysis
PM	Particulate matter
POH	Period of hours
PSA	Pressure swing adsorption
PSM	Process safety management
R&D	Research and development
RCRA	Resource conservation and recovery act
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RFG	Recycled flue gas
RIST	Research Institute of industrial science and technology
SC	Supercritical
SCGH	Steam coil gas heater
SCR	Selective catalytic reduction
SCS	Single chamber system (also known as JCR)
SDA	Spray dry absorber
SDI	Sorbent direct injection
SDS	Safety data sheet
SEC	Specific energy consumption
SECARB	Southeast regional carbon sequestration partnership
SM	Secondary metallurgy
SMR	Steam methane reformer
SNCR	Selective non-catalytic reactor
SPC	Specific power consumption
SR	Smelting reduction
STEL	Short-term exposure limit
STP	Standard temperature and pressure

SWIFT	Structured what-if checklist
TC 265	Technical committee 265
TCM	Technology Center Mongstad
tcs	Tonne of crude steel
TDL	Target detection limit
TGR	Top gas recycle
thm	Tonne of hot metal
tls	Tonne of liquid steel
TPD	Tonnes per day
TR	Technical Report
TRT	Top gas recycle turbine
TSA	Temperature swing adsorber
TWA	Time–weighted average
ULCOS	Ultra-low CO_2 steelmaking
USC	Ultra-supercritical
VLE	Vapour-liquid equilibrium
VOC	Volatile organic compounds
VPSA	Vacuum pressure swing adsorber
WESP	Wet ESP
WGS	Water gas shift (reaction)
WHO	World Health Organization
WID	Waste Incineration Directive
WSA	World Steel Association
ZR	Zero reformer

5 Carbon dioxide (CO_2) capture system

5.1 General

In 2011, the global CO_2 emission (as reported in References [12] and [228]) was around 33,8 gigatonnes. The power generation sector was responsible for nearly 40 %; while the other industrial sector was responsible for 26 % of the CO_2 emissions.

Table 1 briefly summarizes the breakdown of the emissions from each sector in 2011. IEA has reported that to achieve the greenhouse gas mitigation goal for the 2DS (two-degree scenario) or 450 ppm scenario, CCS is needed to capture both energy- and process-based emissions, that is, it is important to be deployed widely not only in the power generation sector but also in various energy intensive industrial sectors.[11]

Table 1 — Global CO_2 emissions in 2011

CO_2 Emission Sources	% of total CO_2 emission	Remarks
Power	39 %	fossil fuel power plant as large CO_2 stationary sources
Transport	20 %	
Industry	26 %	iron and steel production, cement production, chemicals, refining and so forth as large CO_2 stationary sources
Buildings	8 %	
Agriculture and others	7 %	
NOTE See Reference [12].		

CO_2 capture is the first part of the CCS chain. The CO_2 capture system consists of technologies, processes and equipment that enable the separation, capture and processing of CO_2 from gas streams (e.g. natural gas, syngas, process off-gas, flue gas) and make it suitable for transport and storage.

CO_2 can be captured from different stationary point sources such as: fossil fuelled power plants, steel works, cement and lime production, chemicals and petrochemicals processes, pulp and paper mills, natural gas processing plants, oil refineries and fuel conversion plants (i.e. gas to liquids or coal to liquids).

At present, the capture of CO_2 is an established commercial process of different industries such as natural gas processing, ammonia and urea production. Generally, the CO_2 captured from these processes are either released to atmosphere or used as raw materials in the production of other chemicals (i.e. urea, precipitated calcium carbonates) or sold as commodities to the EOR and food industries.

On the other hand, the capture of CO_2 from power plants and other energy intensive industries such as steel and cement, are now being developed and/or demonstrated with the purpose of mitigating CO_2 emissions through CCS.

Table 2 lists large-scale integrated projects for CCS and/or EOR that are operational or under construction and/or commissioning (i.e. execute). The list, provided by The Global CCS Institute, shows projects that capture and store CO_2 amount greater than 0,4 Mtpa, for gas-fired power plants and industrial processes, or greater than 0,8 Mtpa for coal-fired power plants.

Table 2 — Large-scale integrated projects for CCS and/or EOR

Project Name	Project Life Cycle Stage	Country	CO_2 Capture Capacity (Mtpa)	Operation Date	Industry
Val Verde Natural Gas Plants	Operate	USA	1,3	1972	Natural gas processing
Enid Fertilizer CO_2-EOR Project	Operate	USA	0,7	1982	Fertiliser production
Shute Creek Gas Processing Facility	Operate	USA	7,0	1986	Natural gas processing
Sleipner CO_2 Storage Project	Operate	Norway	0,9	1996	Natural gas processing
Great Plains Synfuel Plant and Weyburn-Midale Project	Operate	Canada	3,0	2000	Synthetic NG production
In Salah CO_2 Storage	Operate	Algeria	—	2004	Natural gas processing
NOTE See Reference [13].					

Table 2 *(continued)*

Project Name	**Project Life Cycle Stage**	**Country**	**CO_2 Capture Capacity (Mtpa)**	**Operation Date**	**Industry**
Snøhvit CO_2 Storage Project	Operate	Norway	0,7	2008	Natural gas processing
Century Plant	Operate	USA	8,4	2010	Natural gas processing
Air Products Steam Methane Reformer EOR Project	Operate	USA	1,0	2013	Hydrogen production through SMR
Coffeyville Gasification Plant	Operate	USA	1,0	2013	Fertiliser production
Lost Cabin Gas Plant	Operate	USA	0,9	2013	Natural gas processing
Petrobras Lula Oil Field CCS Project	Operate	Brazil	0,7	2013	Natural gas processing
Boundary Dam Integrated CCS Project	Operate	Canada	1,0	2014	Power generation
Agrium Fertiliser Plant using Alberta Carbon Trunk Line (ACTL)	Execute	Canada	0,3–0,6	2015	Fertiliser production
Illinois Industrial CCS Project	Execute	USA	1,0	2015	Chemical production
Quest Project	Execute	Canada	1,08	2015	Hydrogen production through SMR
Uthmaniyah CO_2 EOR Demonstration Project	Execute	Saudi Arabia	0,8	2015	Natural gas processing
Gorgon Carbon Dioxide Injection Project	Execute	Australia	3,4–4,0	2016	Natural gas processing
Kemper County Energy Facility (formerly Kemper County IGCC Project)	Execute	USA	3,0	2016	Power generation
Abu Dhabi CCS Project (formerly Emirates Steel Industries CCS Project)	Execute	UAE	0,8	2016	Iron and steel production
Petra Nova Carbon Capture Project (formerly NRG Energy Parish CCS Project)	Execute	USA	1,4	2016	Power generation
North West Sturgeon Bitumen Refinery using Alberta Carbon Trunk Line (ACTL)	Execute	Canada	1,2–1,4	2017	Hydrogen production through Lurgi Gasification Process
NOTE See Reference [13].					

5.2 Classification of CO_2 capture systems

As illustrated in Figure 1, CO_2 capture system could be classified according to three different capture routes.

a) Post-Combustion CO_2 Capture: Separation of CO_2 from combustion flue gas.

b) Pre-Combustion CO_2 Capture: CO_2 removal from syngas obtained from gasification prior to its combustion[1].

c) Oxyfuel Combustion with CO_2 Capture: Combustion of the fuel in nearly pure oxygen and recycled flue gas to produce a flue gas with highly concentrated CO_2 ready for further processing and purification to a desired CO_2 specification.

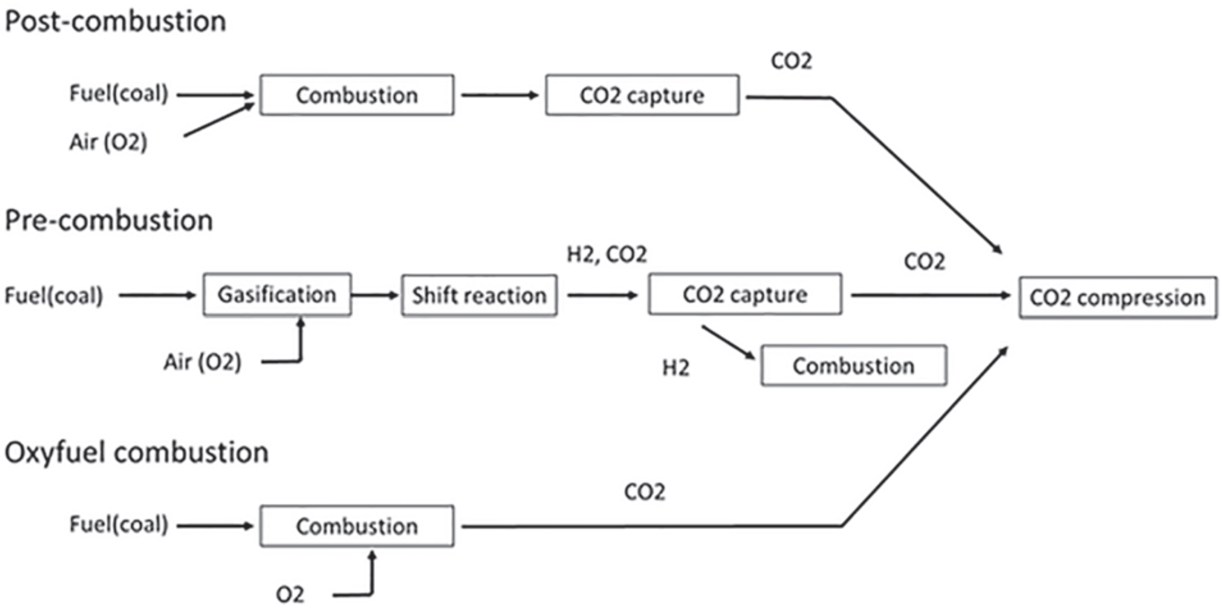

Figure 1 — Different CO_2 capture routes for coal-fired power plant

Detailed description and types of technologies, processes and equipment used in these capture routes applied to power generation industry are presented in Clauses 7, 8 and 9, respectively.

On the other hand, CO_2 capture system could also be classified according to the types of CO_2 separation and capture technologies used. This is presented in Figure 2 and explained briefly in Clause 6.

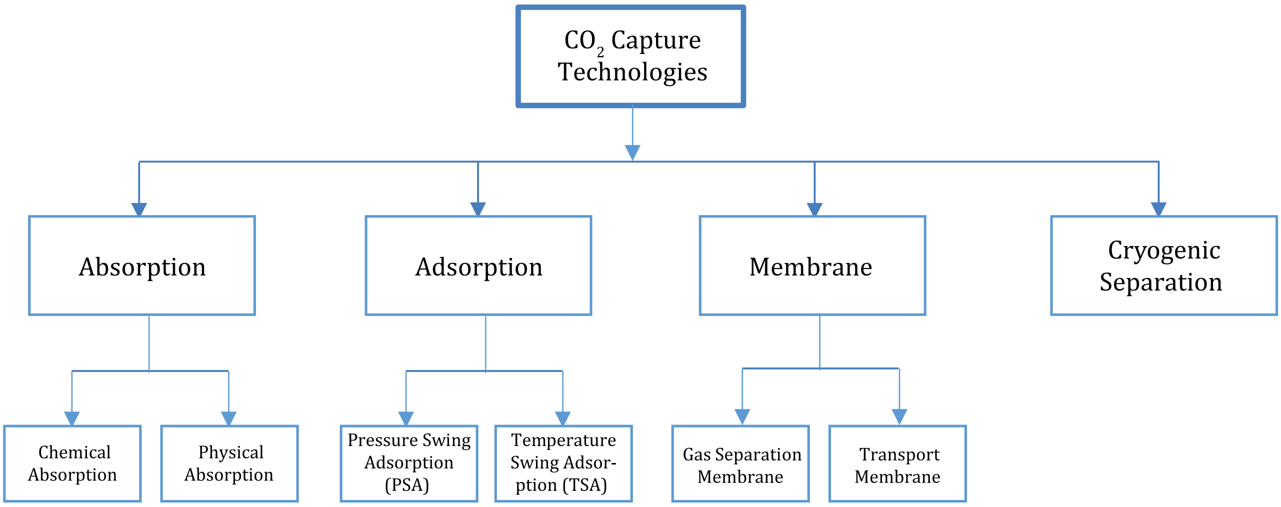

Figure 2 — Types of CO_2 capture technologies

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[1] Pre-combustion CO_2 capture is not limited to gasification. This could be used as well in natural gas processing when CO_2 is captured before its combustion in power plant or other appliances. Also for off-gases from SMR, ATR or others, removing the CO_2 before combustion.

For power generation industry, the use of both classifications is straightforward and well-defined. For industrial CO_2 capture, it is preferable to use technologies as the basis for classification. In fact, the definitions of post-, pre- and oxy-combustion are typically referred to power generation and, in some cases, might not be suitable to properly describe an industrial capture system if combustion process is not included.

5.3 System boundary

The system boundary of interest includes the host plant (i.e. power plant or industrial processes) and the CO_2 capture system, up to the point where CO_2 enters the pipeline (i.e. entry point to the CO_2 transport). It should be noted that CO_2 compression is included in the boundary of the CO_2 capture system; however, this is not discussed in detail in this Technical Report.

For post-combustion CO_2 capture, the CO_2 capture system is not integrated into the host plant; thus, system boundary of the capture system could be clearly defined. This could start from the point where the flue gas is taken and enters the flue gas quencher or other flue gas pre-treatment unit. It ends at the point where CO_2 exits from the CO_2 compression flange and enters the CO_2 pipeline. A more detailed discussion of the boundary system for post-combustion capture is presented in 7.1.

For pre-combustion CO_2 capture, the CO_2 capture system could be partially integrated into the host plant. There are several variations depending on the technology selected, the defined CO_2 specifications and the capture rate. The boundary between the host plant and the CO_2 capture system for pre-combustion capture is not well defined but could be distinguished. Generally, the CO_2 capture system includes the shift reactor, the acid gas removal unit and the CO_2 compression unit. However, it should be clearly noted that incorporating CO_2 capture in IGCC power plant could also impact other parts of the host plant. A more detailed discussion of the boundary system for pre-combustion capture is presented in 8.2.

For oxyfuel combustion CO_2 capture, the CO_2 capture system is fully integrated with the host plant. The system boundary for the CO_2 capture system could not be defined and could not be distinguished. Thus, the whole power plant should be considered as the system boundary, including the air separation unit, boiler, flue gas processing and CO_2 processing unit. Furthermore, it should also be noted that CO_2 compression is integrated into the CO_2 processing unit. A more detailed discussion of the boundary system for oxyfuel combustion with capture is presented in 9.1.

In conclusion, the boundary of the CO_2 capture system and the host plant could vary depending on the CO_2 capture technology selected; and the variation to the boundary system could also be site specific. A possible approach in defining the boundary system for a particular project is by using the definition of the project scope as specified in the FEED study.

6 Review and documentation

6.1 General

The following topics will be discussed with regard to the capture technologies applicable to each source:

a) system boundaries;

b) technologies, equipment and processes;

c) CO_2 stream, gas streams and emissions, process and waste products;

d) evaluation procedure for capture performance including energy penalties (parasitic losses) and other issues;

e) safety issues and environment impact assessment;

f) reliability issues;

g) management system, including interfaces

   1) between capture plant and emission source, and

   2) with other Working Groups of TC 265.

“System boundaries” is defined as facility boundaries to be described respectively for the above-mentioned CO_2 capture systems based on each of the capture technologies.

“Technologies, equipment and processes,” including outlines of the capture technologies, required equipment and processes are described. Equipment and processes refer to a series of equipment and processes required to implement the aforementioned technologies. Each technology requires unique equipment and processes, which will be discussed in each clause.

“Carbon dioxide stream, gas streams and emissions, process and waste products” will provide information regarding main gas streams containing CO_2, remaining gas streams after CO_2 was captured, especially in pre-combustion capture or industrial gas production, and emissions and waste products from gas streams that occur during those processes. This subclause will also provide information related to chemical compounds occurring in capture processes or chemical compounds in waste materials arising out of such processes.

The treatment of emissions and chemical compounds or waste products that occur in capture processes should, at a minimum, comply with the regulations on the treatment, release, and disposal of chemical substances in respective countries and regions. They should be made innocuous or decreased to the prescribed value or below by incineration or other processes before they are released into the environment.

“Evaluation procedure for capture performance” will provide unique performance parameters and indicators for the capture technologies, to be used as common indicators for comparing the performances of different capture technologies. Information necessary for the relative evaluation should be provided.

“Safety and reliability issues” will describe manifested and potential issues related to safety that are specific to each capture technology and relevant to the goal of disseminating and promoting CCS. Health, safety and environment (HSE) issues will be discussed from the perspectives of facilities, operations, occupational safety and hygiene, and environment. For example, potential emissions and areas of occurrence will be described.

It should be noted that any equipment and facilities related to capture plant must comply with existing laws and regulations in each country or region.

In addition to compliance with laws and regulations relating to chemical processes and others in each country and region, it may be necessary to apply risk scenario analyses such as FMECA, HAZOP, FTA, SWIFT, and OPERA. Since each of these methods has both advantages and disadvantages,[7] it may be necessary to recommend the most appropriate method(s) for capture processes.

One of the common issues in capture technologies related to HSE is exposure to CO_2. The most probable routes of human exposure to CO_2 are inhalation or skin contact. The need for a risk-based approach is clear from the following two descriptions. CO_2 and its products of degradation are not classified as a toxic substance; are non-hazardous on inhalation, are non-irritant and do not sensitize or permeate the skin. However, chronic effects on humans follow from long-term exposure to airborne CO_2 concentrations of between 0,5 % and 1 % resulting in metabolic acidosis and increased calcium deposits in soft tissues. The substance is toxic to the cardiovascular system and upper respiratory tract at concentrations above 3 %. The product risk assessment process is therefore necessary as with any other chemical use to determine the risk and establish the necessary risk management processes.[3] Other than CO_2, substances such as amine, oxygen, and hydrogen also need to be considered.[10]

Incidentally, no management systems specific to CCS have been established so far. However, as a future item, there is a need to consider the development of management systems in association with the following:

- ISO/TC 176, *Quality management and quality assurance* — for the quality control of personnel, equipment, facility, work environment, etc. for the processes up to CO_2 compression;
- ISO/TC 69, *Applications of statistical methods* and IEC/TC 56, *Dependability* — for reliability and sampling;
- ISO/TC 207, *Environmental management*, ISO/TC 146, *Air quality* and ISO/TC 147, *Water quality* — for environmental management.

Life cycle assessment (LCA) and end-of-life management need to be considered as a management tool of CO_2 capture system.

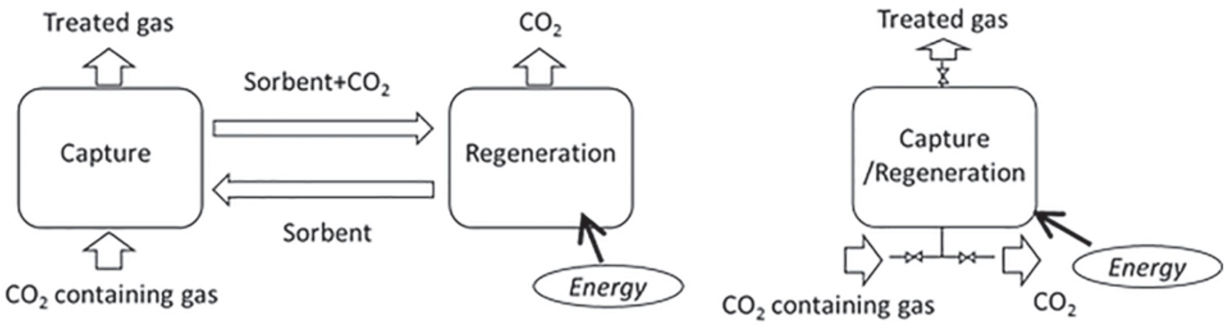
6.2 Separation processes

There are three general separation processes of CO_2 capture that are integrated into the CO_2 capture route (see Reference [3], Figure 3.2). These details are described in subsequent subclauses.

6.2.1 Separation with sorbents/solvents

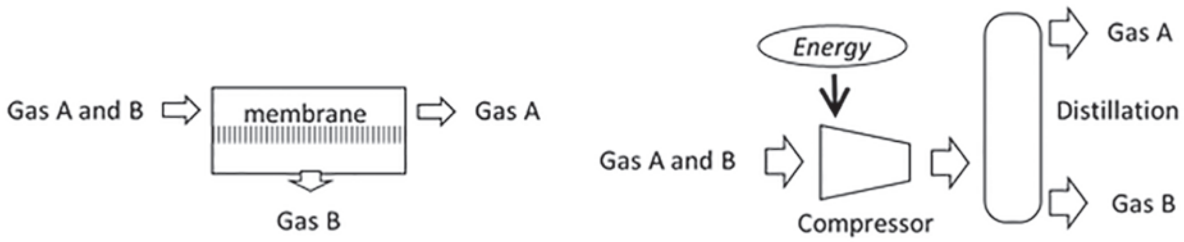
The separation is achieved by passing the CO_2-containing gas in intimate contact with a liquid absorbent or solid sorbent that is capable of capturing the CO_2. In the general scheme of diagram a) in Figure 3, the sorbent loaded with the captured CO_2 is transported to a different vessel, where it releases the CO_2 (regeneration) after being heated, after a pressure decrease or after any other change in the conditions around the sorbent. The sorbent resulting after the regeneration step is sent back to capture more CO_2 in a cyclic process. In some variants of this scheme the sorbent is a solid and does not circulate between vessels because the sorption and regeneration are achieved by cyclic changes (in pressure or temperature) in the vessel where the sorbent is contained or by a replacement of sorbent inventory. A make-up flow of fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses.

The general scheme of Figure 3 governs many important CO_2 capture systems, including leading commercial options like chemical absorption and physical absorption and adsorption.



a-1) Separation with sorbent/solvent (Continuous flow type)

a-2) Separation with sorbent (Semi-batch type)



b) Membrane separation

c) Cryogenic distillation

Figure 3 — General scheme of main separation processes of CO_2 capture

Emerging processes based on new liquid sorbents, or new solid regenerable sorbents are being developed with the aim of overcoming the short comings of the existing systems such as high energy requirement, degradation, high investment, and so on. One common problem of these CO_2 capture systems is that the flow of sorbent between the vessels in Figure 3 a) is large because it has to match the huge flow of CO_2 being processed in the power plant. Therefore, equipment sizes and the energy required for sorbent regeneration are large and tend to translate into an efficiency penalty and added cost. Also, in systems using expensive sorbent materials there is always a danger of escalating cost related to the purchase of the sorbent and the disposal of sorbent residues. Good sorbent performance under high CO_2 loading in many repetitive cycles is obviously a necessary condition in these CO_2 capture systems.

Chemical absorption and physical absorption are well-known as CO_2 separation process with liquid absorbents.

The chemical absorption uses solvents (absorbents) that react chemically to gas to selectively capture target substances. Materials such as amines and potassium carbonate are used in liquid absorbents. Generally speaking, the chemical absorption method is suited for reducing the concentration of CO_2 from tens of percentage points to around 0,1 %, or down to tens of ppm if necessary.

Figure 4 shows a schematic process flow of the chemical absorption method. This approach consists of two major components: the absorber that captures the target substances and the regenerator (stripper) that recycles the absorbent by adding heat to strip the absorbed substances from it. The absorbent circulates between the absorber and regenerator, repeating the absorption and stripping of CO_2.

Many of chemical absorption methods utilize heat to regenerate the solvent.

A typical technology of the chemical absorption method is called amine absorption, which has such a long history and successful track record that it can be considered a mature technology in the gas refining sector. Many CCS projects use the chemical absorption method for CO_2 capture.

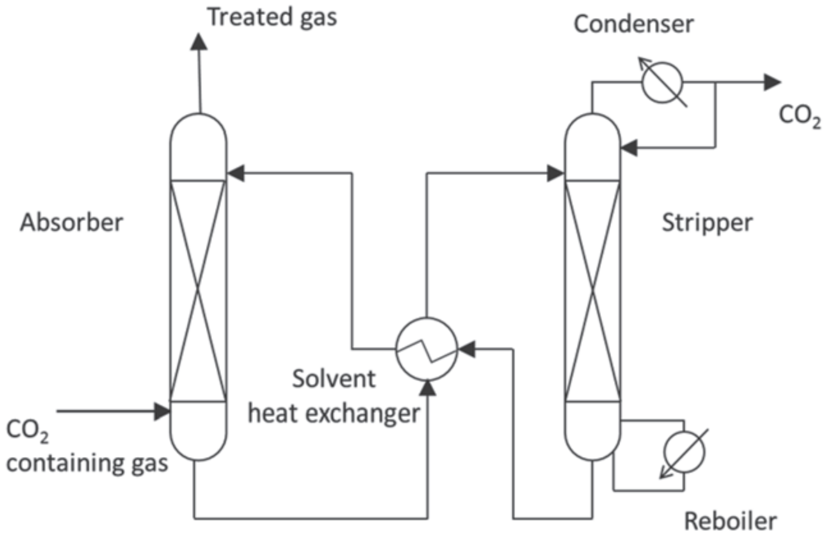


Figure 4 — Schematic flow of chemical absorption

Annex A shows several examples of the chemical absorption processes.

The physical absorption takes advantage of differences in solubility (without chemical reactions) into the absorbent to physically capture the target gas components, including CO_2. A variety of absorbent products are used, including methanol, propylene glycol and propylene carbonate. This technology is mainly used for the production of syngas-based chemical products as a syngas purification technology and is recently applied to the capture process of IGCC.

A schematic flow chart of the physical absorption process is shown in Figure 5.[8] As with the chemical absorption method, the system consists of a couple of primary components: an absorber, which absorbs target gas components such as CO_2, and a flash drum and a regenerator, which reduce the pressure or use heat to strip the absorbed gas compounds from the absorbent to regenerate the absorbent. In the physical absorption method, the solubility of gas components in the absorbent is almost directly proportional to the partial pressure of the vapour phase (Henry’s law). In addition, solubility increases as the temperature decreases. Thus, it follows that the higher the operating pressure of the absorber and the lower the operating temperature, the more effective the capture of target gas components.

The physical absorption method of industrial application is also a mature technology with a long history.

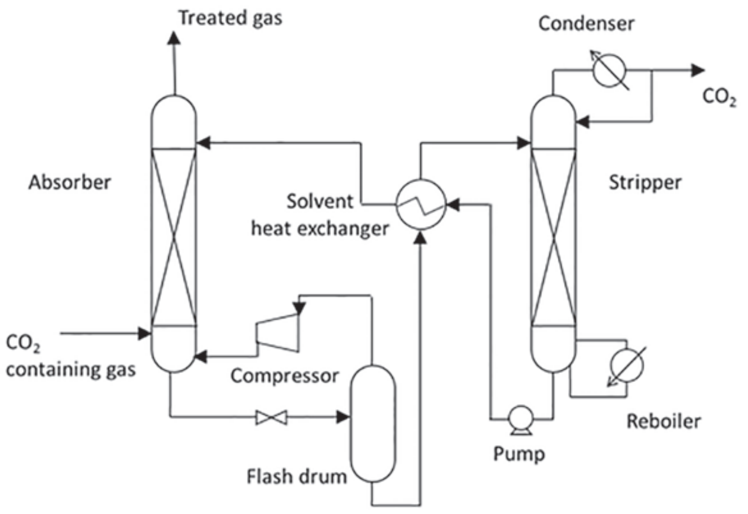


Figure 5 — Flow chart of the physical absorption method

Pressure swing physical adsorption and temperature swing chemical adsorption are known as typical CO_2 separation process with sorbents. Pressure swing adsorption (or sorption) (PSA or PSS) is a technology in which CO_2 is physically adsorbed into the pores of solid sorbent. Once the pressure is lowered, the adsorbed CO_2 is released and captured.

Temperature swing adsorption (or sorption) (TSA or TSS) is a technology in which CO_2 is chemically adsorbed to solid sorbent.

Promising results have also been reported with CO_2 removal from flue gas utilizing a combination of PSA and TSA (PTSA).

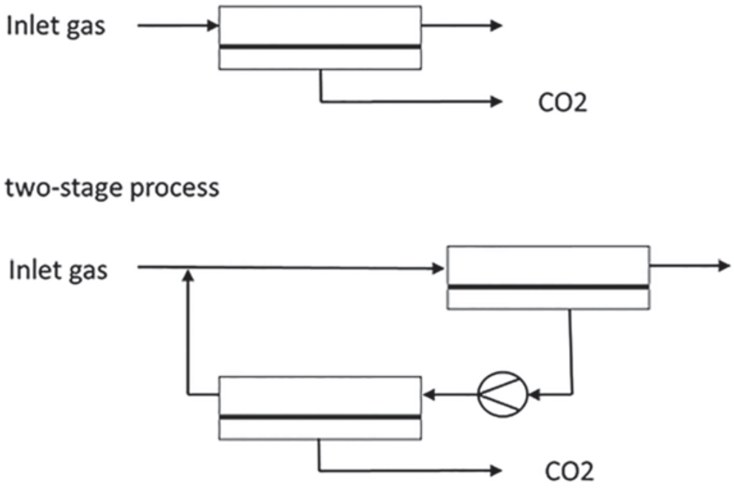
6.2.2 Separation with membranes

The membrane separation process is a gas separation technology that takes advantage of the differences in the membrane permeability rates among gas components. Because this process separates CO_2 by using as a driving force the pressure difference between the CO_2 inclusive feed gas side and the permeate gas side of a membrane, very little energy is required to separate CO_2 from a high-pressure gas. It is therefore especially effective when the feed gas is at high pressure and contains a high-concentration CO_2.

Membranes in Figure 3 b) are specially manufactured materials that allow the selective permeation of a gas through them. The selectivity of the membrane to different gases is intimately related to the nature of the material, but the flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high-pressure streams are usually preferred for membrane separation. There are many different types of membrane materials (polymeric, metallic, ceramic) that may find application in CO_2 capture systems to preferentially separate H_2 from a fuel gas stream, CO_2 from a range of process streams or O_2 from air, with the separated O_2 subsequently aiding the production of a highly concentrated CO_2 stream. Although membrane separation finds many current commercial applications in industry (some of a large-scale, like CO_2 separation from natural gas), they have not yet been applied for the large scale and demanding conditions in terms of reliability and low-cost required for CO_2 capture systems. A large worldwide R&D effort is in progress aimed at the manufacture of more suitable membrane materials for CO_2 capture in large-scale applications.

A flow chart of the membrane separation process is shown in Figure 6.[9] The CO_2 inclusive feed gas is introduced upstream, and CO_2 is separated to the lower pressure side through a membrane. To improve the capture rate, a two-stage process recycling permeate gas is adopted.

The membrane separation process has been used widely in natural gas refineries where the feed gas contains a high concentration (20 %) of CO_2. Research and development on the membrane separation in the IGCC process is also underway.



NOTE Top: Single-stage process; Bottom: Two-stage process.

Figure 6 — Schematic flow of membrane separation process

6.2.3 Separation by cryogenics or flash evaporation

A gas can be made into a liquid by a series of compression, cooling and expansion steps. Once in liquid form, the components of the gas can be separated in a flash or distillation column. In the case of air, this operation is currently carried out commercially on a large scale. Oxygen can be separated from air following the scheme in Figure 3 c) and be used in a range of CO_2 capture systems (oxyfuel combustion and pre-combustion capture). Refrigerated separation can also be used to separate CO_2 from other gases. It can be used to separate impurities from relatively high purity CO_2 streams, for example, from oxyfuel combustion, and also for CO_2 removal from natural gas or synthesis gas that has undergone a shift conversion of CO to CO_2.

7 Post-combustion capture in the power industry

Post-combustion capture (PCC) is an important and fundamental technology in the context of carbon capture and storage (CCS). PCC is the process which separates CO_2 from a stream of flue gas after combustion, e.g. in a gas turbine or a coal-fired boiler, as well as raw gas, suitable for PCC, from other industrial sources, e.g. refineries, chemical plants.

Coal is an important low-cost fuel source for generating electricity in various regions of the world, especially developing nations. PCC could prove to be a critical technology for minimizing the CO_2 emissions generated by this industry.

7.1 System boundary

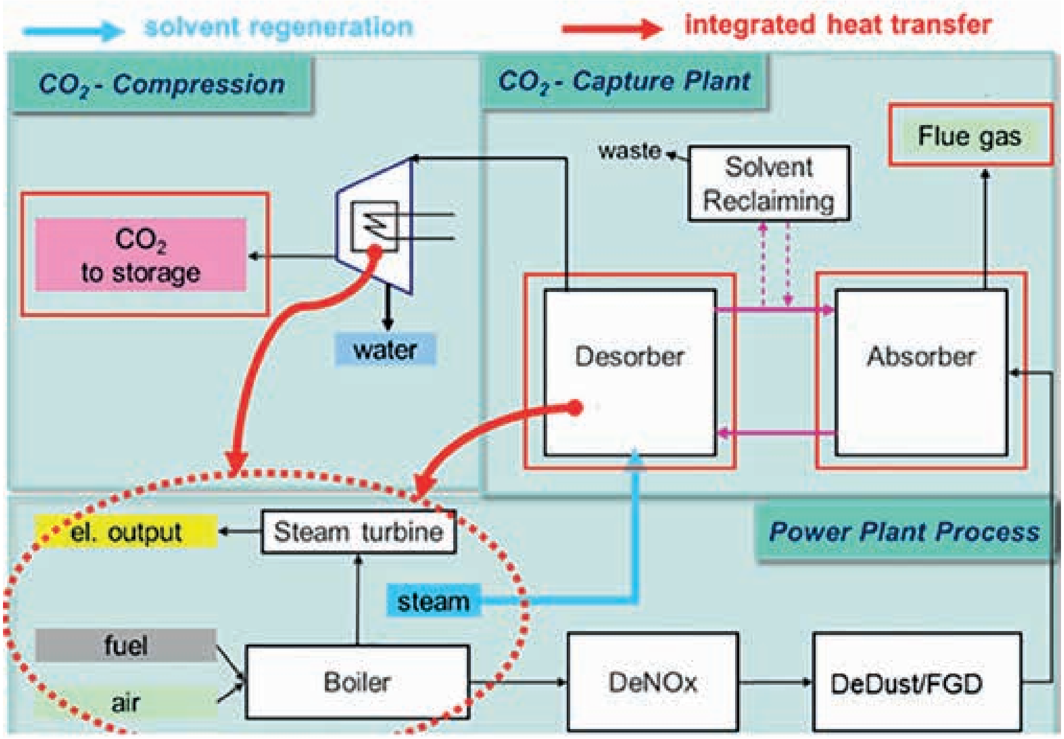
7.1.1 Boundary with power plant or other process stream (cooling water, steam, flue gas, product CO_2)

Figure 7 shows an example of the CO_2 capture processes deployed in a thermal power generation plant.[14] Figure 7 can be also applicable to the combustion type steam generation plant. Here, the chemical absorption method is used as an example. The captured CO_2, once compressed, is transported using pipelines and mobile carriers, such as ships and trains (not shown in Figure 7). After the CO_2 has been removed, the flue gas is released into the atmosphere. The underlying principle for CO_2 capture is the exothermic, reversible reaction between a weak acid such as CO_2 and a weak base such as an alkanolamine. The flue gas to be treated is contacted by the aqueous solution in an absorbing column or vessel where a soluble salt is formed from the reaction between the CO_2 and the base solution.

The flue gas, now depleted of CO_2, is then released to the atmosphere. The solution, enriched with the CO_2, is sent to a stripping column or vessel (desorber unit) where, by the addition of heat, the salt formation reaction is reversed and the CO_2 is released and the base solution is regenerated. The lean base solution is recycled to the absorber unit while the CO_2 is made ready for transportation by dehydrating, and if required, deoxygination and compressing it.

As shown in Figure 7, this subclause covers the flue gas path from the outlet of the flue gas desulfurization (FGD) to the outlet of the absorber unit of the CO_2 capture plant, the solvent system and the CO_2 path up to the outlet of the CO_2 compressor, regardless of the CO_2 capture process used. The associated utilities, waste water and waste products are shown in Figure 8. In some cases, flue gas pre-treatment is required and this should be included within the boundary of the PCC plant.

To support the PCC process, there are interconnections with the power or utility plants steam, cooling water system and other utilities installed (e.g. demin water, plant drainage, pressurized air and others) as shown in 7.4.2. The waste issue related to absorbent purification and/or recovery or total exchange, if cleaning is not possible, including solid waste, is noted in the following subclauses. Red arrow lines in Figure 7 show the possible integrated heat transferred from a capture and compressor part to power plant using the steam condensate of a power plant steam-water cycle, for example, to improve the power plant efficiency utilizing the waste heat in PCC plant.



NOTE See Reference [14].

Figure 7 — Schematic of a pulverized coal-fired power plant with a PCC system and other emission reduction equipment

Figure 8 shows a generic chemical absorption process in detail.[14] A part or all of the flue gas exhausted from the FGD equipment (only relevant for PCC at hard coal-fired power plants) may be routed through a pre-scrubber to adjust the temperature and humidity of the flue gas to fit the optimal conditions of the absorption process. The pre-scrubber may additionally be used to remove SO_2 in the flue gas. The flue gas is then routed to the absorber where CO_2 comes in direct contact with the solvent. The effect is that the vast majority of CO_2 is absorbed by the solvent and capture rates of 90 % are considered typical. After the CO_2 is removed, the remaining flue gas is released to the atmosphere. An additional washing step, utilizing a water scrubber installed at the top of the absorber to remove highly volatile substances such as process degradation product and absorbent, may be necessary to ensure that the flue gas released into the atmosphere is in a state that would be acceptable under an Environmental Impact Assessment (EIA). The solvent is returned to the system.

The CO_2-loaded (rich) absorbent is forwarded to the stripper (desorber or regenerator). In the desorption process the solvent is heated, by either Low Pressure (LP) or Medium Pressure (MP) steam depending on the process demand, and extracted from the power plant process to release the captured CO_2. The CO_2-free (lean) solvent is returned to the absorber to absorb CO_2 again. At the stripper gas outlet a mixture consisting of saturated CO_2 is exhausted. The condensate is collected and sent to both the lean solvent inlet at the absorber and the top part of the stripper.

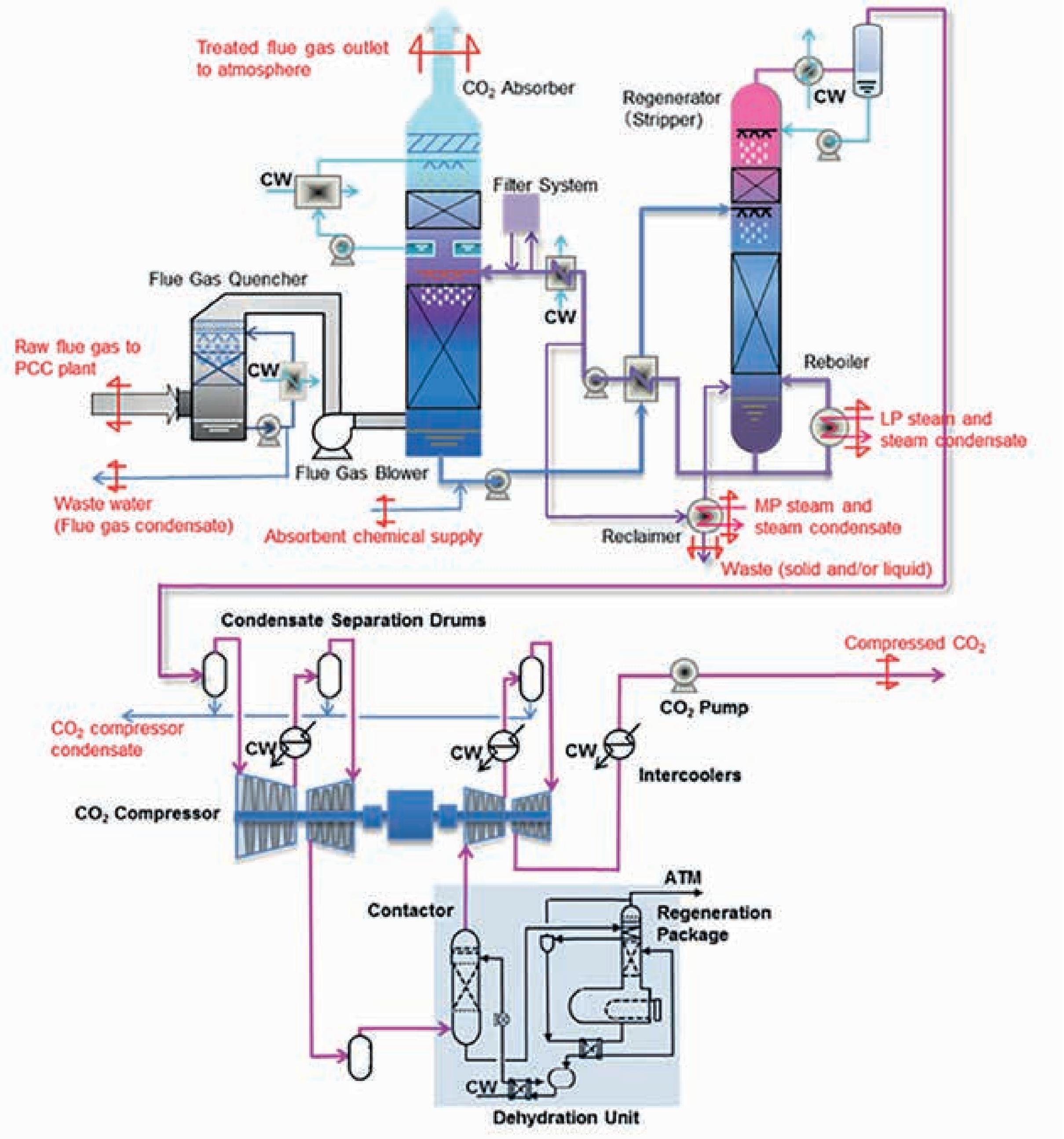


Figure 8 — Generic PCC process flow scheme

7.1.2 Boundary of the PCC plant

Boundary conditions have to be defined for further development of PCC technologies and projects. The following boundaries are considered for a PCC plant:

- raw flue gas to the PCC plant;
- required control and monitor signals to and from a hosted power plant;
- residual flue gas outlet to the atmosphere on top of the absorber or at the inlet flange of a separate stack;
- CO_2 outlet of the separate vent stack or top of the CO_2 absorber to the atmosphere in case of an unplanned disruption in the transport and/or storage chain of CO_2;
- flue gas condensate;
- CO_2 compressor condensate;
- demin water, potable water, firefighting water;
- plant drainage;
- pressurized air, inert gas (e.g. nitrogen);
- steam and steam condensate;
- cooling water supply and return;
- power supply;
- by-product and waste generation (solid and/or liquid);
- absorbent chemical supply.

7.1.3 Boundary with transport and storage of CO_2

The boundary between the PCC plant and the CO_2 transport and storage systems is the downstream flange of the CO_2 compressor.

To avoid backflow effects and to clearly separate battery limits, an open-close valve should be positioned upstream of the downstream flange.

7.2 Technologies, equipment and processes

The following process technologies[18] are currently available or under development for PCC:

- absorption processes based on chemical solvents;
- adsorption processes and membrane processes are described at the beginning of Clause 6.[14]

With respect to absorption processes based on chemical solvents, significant progress has been made in the application of the absorption processes to the flue-gas treatment in coal-fired power plants following the publication of the 2005 report on CCS by Intergovernmental Panel on Climate Change (IPCC).[14] An overview of this technology is included in 7.2.1 to 7.2.3. The detailed processes are described in References [18] and [19] as examples.

7.2.1 Chemical absorption process based on (alkanol-) amines (amine process) (A)

General explanation is provided in 7.1.1.

According to the International Energy Agency (IEA), notable developments in CCS between 2009 and 2013 include increased experience and confidence with CO_2 capture technologies.[18] It is believed that the following factors are partly responsible for these developments on CO_2 capture; these statements are partially applicable to all technologies not just amines.

a) Several PCC technologies have been tested at scales on slipstreams of up to 25 MWe, mainly from coal-fired power plants where the number of commercial references of the medium scale in industrial applications increased.[21][22]

b) As a result of improvements achieved in processes and absorbents, significant progress has been made in reducing the amount of heat needed per unit of captured CO_2. However, it should be noted that presented values by the technology suppliers are dependent on the specific plant design and operating conditions.[23] In some processes, a base unit of 2,5 GJ per tonne of captured CO_2,[23][24] or 1,0 tonne of LP steam per tonne of captured CO_2,[25] has already been achieved or projected. Currently, efforts are aimed toward 2,0 GJ per tonne of captured CO_2.[28]

c) Efforts have been made to reduce the performance penalty suffered by a power generation plant when the LP steam used in a PCC is supplied by the turbines of the power generation plant as a source of flue gas. Ways to reuse waste heat from both plants and find an optimal arrangement of the LP steam supply system were pursued so as to improve the efficiency of the power generation plant as a whole, including the PCC process.[21]

d) The attention of the EIA has been drawn to the amines contained in the gas streams that are emitted to the atmosphere after being treated by PCC facilities. Initially many research groups, primarily in Norway, have been conducting studies on this subject, resulting in evaluations and improvements of PCC processes such as zero amine emission system[28] to minimize emissions.[21]

e) During the CO_2 capture process the chemical absorbents may react with other contents of the flue gas, e.g. oxygen, NO_x and SO_x, to form heat stable salts which degrade the solvent performance. This may, over time, reduce CO_2 absorption efficiency. To maintain the solvents CO_2 capture capability during operation, reclaiming systems are used. The technology used for solvent reclaiming differs with the process and solvent used. Ammonia-based solvents are reported not to degrade in this manner and do not require reclaiming.

7.2.2 Chilled ammonia process (CAP) (B)

The Chilled Ammonia Process (CAP) treats flue gas from coal-fired power plants, natural gas combined cycle plants, and refinery cat crackers to capture CO_2. CAP consists of seven integrated unit operations.

a) Direct-contact cooler/heater to condition the primary flue gas stream by removing moisture and absorbing SO_2 (in DCC1) and to prepare the residual flue gas for atmospheric discharge by heating the gas and absorbing residual ammonia in the flue gas leaving the wash system (in DCH1).

b) Absorber system to capture CO_2 by reaction with a circulated ionic ammoniated solution.

c) Ammonia water wash system to capture residual ammonia saturating the flue gas discharged from the absorber system.

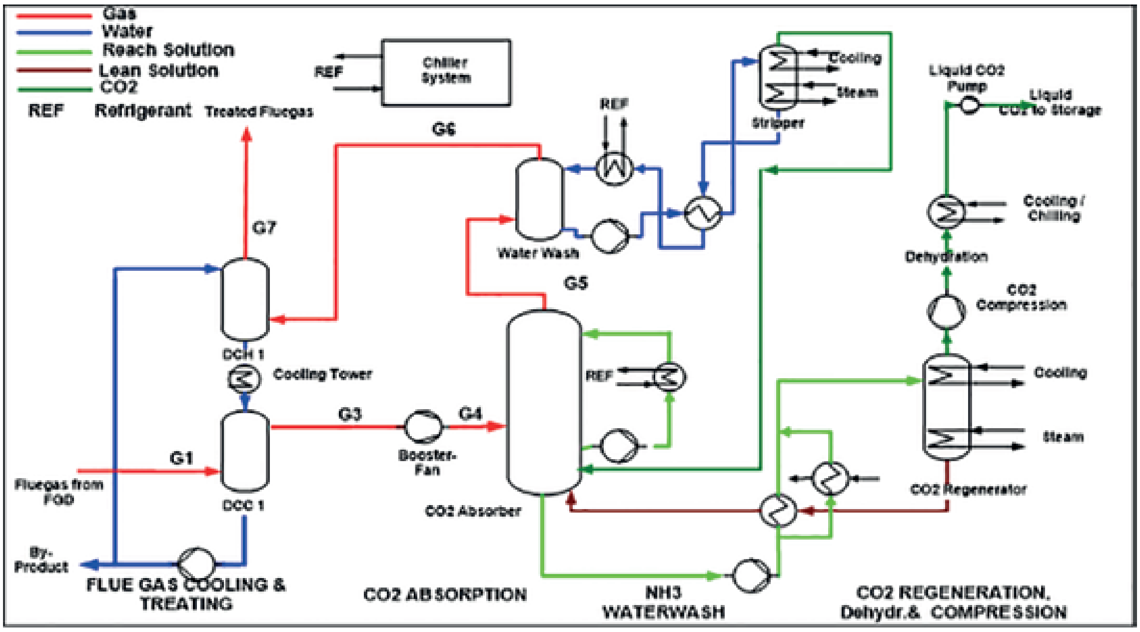
d) Regenerator system to release the CO_2 from the rich ammoniated solution and return the lean ammoniated solution to the absorber system for reuse.

e) Ammonia stripper system to release NH_3 from the wash water and returns it to the absorber system for reuse.

f) Separate stripper system (not described in Figure 9) for ammonia recovery from wash water and to limit salt accumulation (primarily ammonium sulfate) in the ammoniated ionic solution.

g) Compression system to permit transport of the product CO_2 for beneficial use or storage in a geologic storage formation.

CAP is illustrated in Figure 9.



NOTE See Reference [16].

Figure 9 — Simplified CAP process flow diagram

Details on the unit operations, including Flue Gas Conditioning, Regeneration, Appendix Stripper, CO$_2$ Dehydration and Compression and Refrigeration Systems should be referred to published information.[16]

7.2.3 Amino acid salts (AAS) process (C)

The AAS process uses the aqueous solution of amino acid salts as a solvent. Figure 10 shows the flow chart for PostCap2) of Siemens as an example. The equipment configuration is similar to that of a standard amine process.

As the chosen solvent has a very low vapour pressure, it is anticipated that it will cause less emissions from the absorber as the amine system does. In addition, amino acid salts are less susceptible to degradation by oxygen and heat and therefore will have less losses of solvent than the standard amine (MEA) process.[48]

Within the process deposits and solids could theoretically form through precipitation. This is addressed by respective design features and margins. No precipitation was reported during pilot plant operation.[17]

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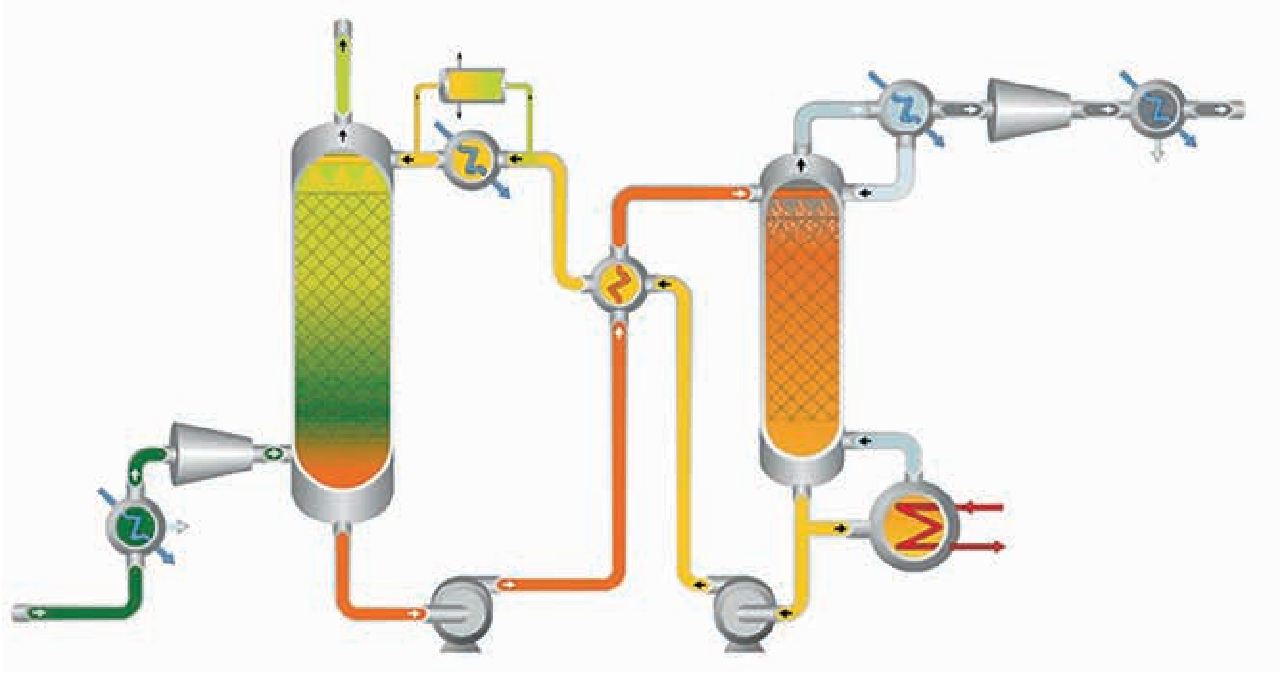
2) PostCap is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.



NOTE See Reference [48].

Figure 10 — Siemens PostCap AAS process

7.3 Carbon dioxide streams, flue gas streams and emissions, process and waste products

7.3.1 Flue Gas streams

7.3.1.1 PCC plant with coal-fired boiler and gas-fired combined cycle gas turbine (GTCC) with Heat Recovery Steam Generators (HRSG)

The composition of flue gas that is to be introduced into a PCC plant to capture CO_2 is largely a function of the fuel being combusted to generate electricity. In the coal-fired application shown in Figure 11, a Selective Catalytic Reaction (SCR) removes NO_x, Electrostatic Precipitator (ESP) removes particulates, and a flue gas desulfurization (FGD) removes SO_2.

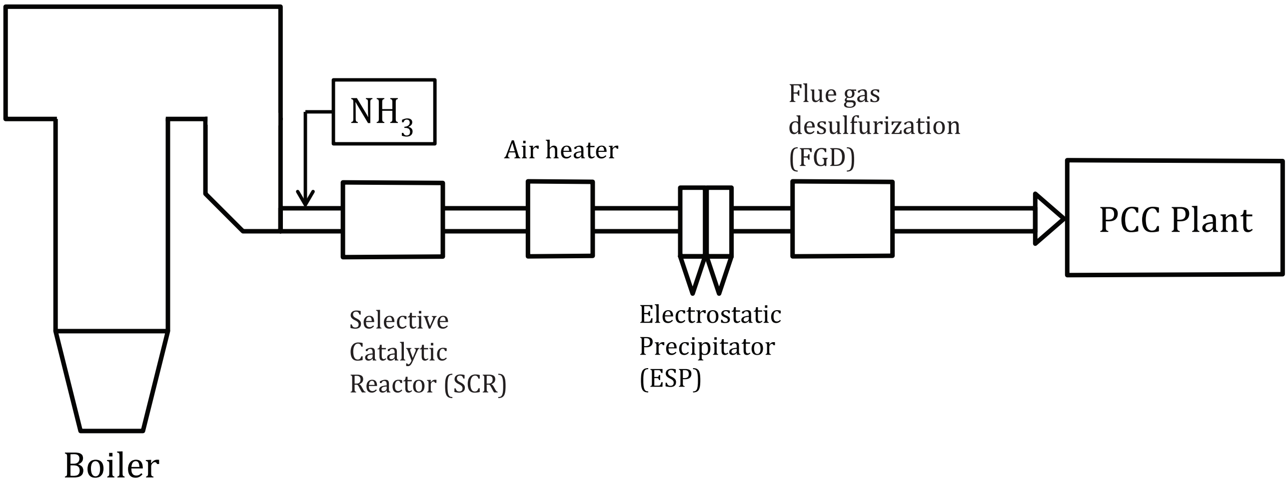


Figure 11 — Gas phase configuration of PCC plant for the coal-fired power plant

In the natural gas-fired application shown in Figure 12, catalytic beds promote the oxidation of CO into CO_2 and NO_x into N_2 and H_2O. Sulfur compounds are not present in natural gas and as a consequence are not generally found in the flue gas.

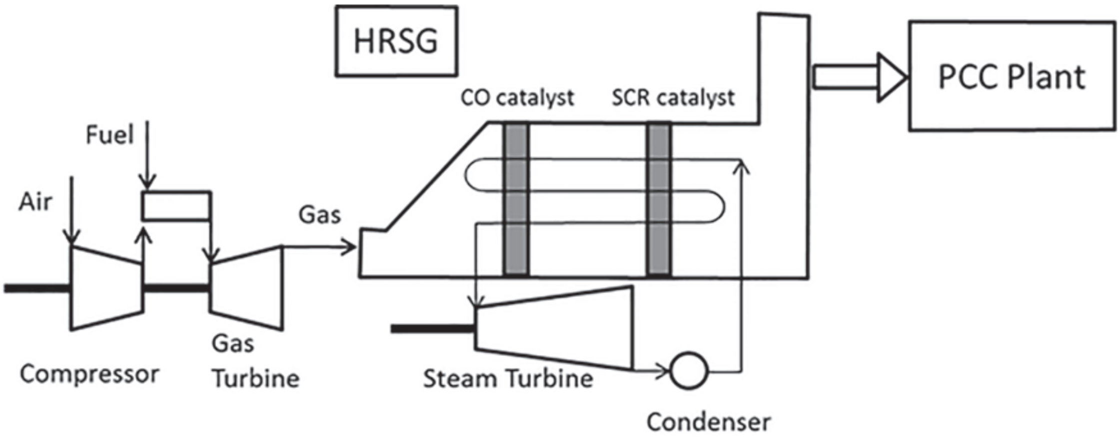


Figure 12 — Gas phase configuration of PCC plant for GTCC with HRSG

As the combustion type steam generation plant, the once-through steam generators (OTSG) for *in situ* oil sands production is an important and growing emissions source in the oil and gas industry and the fastest growing source of emissions in Canada. OTSG is very similar to HRSG fed by the hot combustion gas from the furnace or the gas turbine except for the steam generation section where typically the primary stage evaporates the fed water to an intermediate steam quality and the secondary stage completes the evaporation to a required level for injection into the ground without recycle of the generated steam as the feed water after utilization of its energy. Regarding CO_2 capture from the flue gas, the same concept mentioned above can be applied to OTSG.

7.3.1.2 Input capture plant

"Flue gas streams" in this context refers to the flue gases that occur as a result of the combustion of fossil fuels and that are emitted from such sources as boilers and gas turbines at thermal power plants and HRSGs at GTCC plants.

Currently specific to plants, FGD, CO/NO_x removal equipment and dust collecting equipment are installed to remove impurities (pollutant) pursuant to the relevant emissions regulations and the flue gases downstream of these purification systems are to be the subject gas streams within this Technical Report.

The properties (composition, temperature and impurities) of flue gas supplied to PCC plant varies significantly depending on the type of fuel used, the power plant type and the its system configuration. Generally further abatement of the pollutants, rather than the emission requirement at the conventional stack outlet, is favourable to ensure conditions which allow an efficient and cost-effective CO_2 capture through simplification of the flue gas pre-treatment part or the countermeasures inside the PCC plant, depending on the applied technology.

Particularly in the case of coal, the composition of impurities varies greatly according to its grade and mining location, and this may result in severe impacts related to the flue gas composition depending on the above purification systems performance.

The characteristics of flue gases from power plants are manifested in the flow rate, temperature, gas pressure, and composition (e.g. N_2, O_2, CO_2, H_2O, NO_x, SO_x, NH_3, mercury, soot, ash). There could be an obvious impact on the end-of-pipe CO_2 capture process design, even when the PCC plant is not installed to treat 100 % of the flue gas.

It is very important to clarify the flue gas properties fed to PCC plant in terms of a proper comparative evaluation of technology as explained in 7.4 and achievement of high reliability as explained in 7.6, as well as fulfillment of emission regulation and waste management explained in 7.3.3 and 7.3.6.

Flue gas conditions are a function of fuel type, combustion conditions and pre-existing environmental technologies.

The following are examples of flue gas compositions when natural gas or coal is used as fuel.

Example 1 — Natural gas-fired (B.1)

SINTEF, Emission Compound Toxicity Protocol, P152

Pressure: 1,01 Bar, Temperature: 20 °C to 45 °C (after flue gas quencher), Composition (N_2 76 mol%, O_2 13,8 mol%, CO_2 3,4 mol%, H_2O 6,8 mol%, NO_x 3 ppmv, NH_3 2 ppmv)

Example 2 — Coal-fired (B.2)

CSIRO, process modelling for post combustion capture plant, P91

Temperature: 104,5 °C, Composition (N_2 75,8 vol%, O_2 6,3 vol%, CO_2 10,1 vol%, H_2O 7,8 vol%, NO_x to 150 ppmv, SO_x to 200 ppmv, HCl ppmv)

The important parameters summarized below, which will impact the plant design as explained in the above, should be clarified and will be surveyed in the next step for indication of the typical ranges (minimum to maximum) respective to applied fuel type (coal, gas and LFO) so as to clarify the characteristics depending on the fuel type, including the effect of both combustion condition and existing environmental equipment.

- Flue gas flow rate
- Flue gas temperature
- Flue gas pressure
- Flue gas composition:
  - O_2
  - CO_2
  - H_2O
  - NO_x
  - SO_x
  - NH_3
  - CO
  - mist
  - dust

7.3.1.3 Output capture plant (treated gas)

There are treated flue gases which are discharged to the atmosphere from the PCC plant after impurities have been removed by purification equipment and the amount of CO_2 has been captured.

As treated flue gases are released into the atmosphere, there is a need to characterize the discharge in order to meet regulatory and permitting requirements that specify the concentrations of pollutants, including additional absorbent derived substances, to acceptable levels.

Although identified parameters that could impact the compositions of the treated gas should be surveyed if needed in the next step, according to the variety of the inlet flue gas to PCC plant as shown in 7.3.1.2, the properties of flue gases emitted from power plants are varying, as are the properties of treated flue gases. The concentration of CO_2 normally gets around 1 % in case of boiler flue gas application, however, this value varies depending on the capture rate of CO_2 from the flue gases and both SO_x and the solvent get in the order of ppm as shown in the Examples below. SO_2 is easy to be captured, while NO is not possible. Studies are underway to lower the concentrations of absorbent (amines), which is generated in PCC plant, in order to reduce the impact of their emissions.[26]

The parameters listed below, which characterize PCC plant output in the emission sides and have the obvious or possible impact on the plant design as explained in the above, should be clarified in terms of the requirement, if any, and should be surveyed in the next step for indication of the typical range respective to applied fuel type (coal, gas and LFO) so as to clarify the influence of the fuel type including the influence of both combustion condition and existing environmental equipment.

— Outlet gas flow rate

— Outlet gas temperature

— Outlet gas pressure

— Outlet gas composition:

  — O_2

  — CO_2

  — H_2O

  — NO_x

  — SO_x

  — NH_3

  — CO

  — mist

  — dust

  — VOC

  — absorbent

  — absorbent degradation product

  — organic compound

Trace components contained in the gases are discussed in 7.5.

The following are examples of flue gas compositions when natural gas or coal is used as fuel.

Example 1 — Natural Gas-Fired (B.1)

SINTEF, Emission Compound Toxicity Protocol, P152

Pressure: 1,01 Bar, Temperature: 20 °C to 45 °C, Composition (N_2 81,5 mol%, O_2 13,8 mol%, CO_2 0,6 mol%, H_2O 3 mol%, NO_x 2 ppmv to 20 ppmv, NH_3 <50 ppmv, amine <5 ppmv)

Example 2 — Coal-fired (B.2)

CSIRO, process modelling for post combustion capture plant, P91

Temperature: 27,65 °C, Composition (N_2 89,2 vol%, O_2 6,8 vol%, CO_2 0,9 vol%, H_2O 3,2 vol%, NO_x approx. 150 ppmv, SO_x <5 ppmv, HCl <5 ppmv, MEA <5 ppmv)

7.3.2 Composition of carbon dioxide streams

“Carbon dioxide streams” refer to the captured (purified) CO_2 gases leaving the regenerator and then compressing the remaining gases. The characteristics of carbon dioxide streams include flow rate, temperature, gas pressure, and composition (e.g. N_2, O_2, CO_2, H_2O, NO_x, SO_x, hydrocarbons, solvent components).

The specifications for the captured (purified) CO_2 are different depending on whether high-pressure pipelines or shipping, which requires cooling and liquefaction, is used as the mode of transportation. Therefore, the pressure and temperature follow the specifications set by individual plants. Variation in compression discharge (i.e. battery limits) pressure should meet pipeline requirements. This could be a changing condition depending upon the pipeline system requirements over time. Design consideration for pressure variation is needed.

To prevent equipment damage due to the corrosion of pipes and the solidification of moisture during cooling, the concentrations of water, oxygen, SO_x and NO_x are strictly controlled. To also ensure proper transportation and storage of the CO_2, it is necessary to consider the requirements in that respect. Currently, no universally agreed figures of the maximum value of water and oxygen exist and then the requirements also set by individual plants have to be followed utilizing the CO_2 purification process described below in the outline, if necessary. CO_2 specifications are provided by the pipeline operator.

Oxygen removal is accomplished by catalytic oxidation and is based on the reaction of hydrogen with oxygen with excess hydrogen to the downstream. The process and the respective equipment can be scaled up.

A number of suitable technologies for CO_2 dehydration already exist. Glycol-based systems utilizing triethylene glycol (TEG) and solid adsorption systems using the molecular sieve are the most likely technologies for implementation. The process and respective equipment can be scaled up.

There are several liquid agents available for use as a dehydration medium from a variety of different vendors, TEG is well known in the continuous process. In this process, lean TEG fed to the contactor absorbs the moisture in the raw CO_2 gas at the surface of the packing inside. Rich TEG with absorbed water is removed from the chimney tray of the contactor to be routed to the regeneration package for purification by the addition of heat and the stripping agent, if required, to produce lean TEG, which achieves the required purity for the dehydration performance and recycles to the contactor after cooling. Considerations in the process as minimum are

a) heat integration between the rich and the lean TEG for heat economy,

b) prevention of TEG entrainment as mist with dried CO_2 stream CO_2 gas velocity control with demister device in the contactor, and

c) prevention of TEG loss by controlling the operation temperature in the regeneration package.

Relatively small CAPEX/OPEX generally and the robustness to impurities in dehydrate gases are its merits compared with the solid sorbents. However trace TEG enters into the CO_2 stream.

Substances that are well suited as solid adsorption agents are inorganic silica gel, activated alumina and the molecular sieves, a material with very small holes of precise and uniform size. At least two fixed bed adsorbers, which are alternatively loaded or regenerated, are required. Solid adsorption systems can be used if significantly lower moisture contents are required.

The normal compression process, such as compressor inter-stage cooling with knockout vessels, reduces the gas equilibrium moisture content and could offload the dehydration unit, resulting in smaller dehydration systems. The CO_2 purification process will be operated at the pressure range within the multi-stage CO_2 compressor system and located between adequate steps of it as an economic optimization. Using multiple dehydration techniques in series of the system above is possible.

Invariably, the contact with the package vendors or the media vendors is required for the access to the cost and operation information with clarification of the required specification and the compositions of the CO_2 stream including impurities. Details on the characteristics of the various drying processes and their integration into the PCC system should be referred to published information.[26]

The important parameters summarized below, which characterize the CO_2 stream of PCC plant as explained in the above and have the obvious or possible impact on the plant design, should be clarified in terms of its requirement and should be surveyed in the next step in the typical range respective to applied fuel type (coal, gas and LFO) so as to understand its properties according to the variety of its requirement.

- CO_2 flow rate
- CO_2 temperature
- CO_2 pressure
- CO_2 composition:
  - CO_2
  - O_2
  - H_2O
  - NO_x
  - SO_x
  - NH_3
  - VOC
  - absorbent
  - absorbent degradation product
  - organic compound

This list only applies to PCC from combustion sources.

It is very important to highlight the item other-than-normal operation and the related consequences.

The following are examples of CO_2 compositions.

Example 1 — Coal-fired (B.2)

CSIRO, process modelling for post combustion capture plant, P91

Temperature: 23,2 °C, Composition (N_2 0 vol%, O_2 0 vol%, CO_2 98,2 vol%, H_2O 1,8 vol%, NO_x approx. 7,4 ppmv, SO_x <5 ppmv, HCl <5 ppmv, MEA <5 ppmv)

Example 2 — Coal-fired (B.3)

GHGT-11, Project Status and Research Plans of 500 TPD CO_2 capture and sequestration Demonstration at Alabama Power's Plant Barry, P.6344

Composition (N_2 210 ppm, O_2 + Ar 38 ppm, CO_2 >99,9 vol%)

Example 3 — Coal-fired (B.4)

GCCSI, ROAD CSS Non Confidential Feed Report, P34

Composition (N_2 1 mol%, CO_2 99,9 mol%, H_2O <30 ppmv)

Example 4 — Coal-fired[3]

IPCC, Special Report on Carbon Dioxide Capture and Storage (2005), P141

For coal-fired plants (SO_x <0,01 vol%, NO <0,01 vol%, N_2 + Ar + O_2 0,01 vol%)

For gas-fired plants (SO_x <0,01 vol%, NO <0,01 vol%, N_2 + Ar + O_2 0,01 vol%)

7.3.3 Solvent streams, reclaiming waste products

“Waste products” refer to those substances emitted from a CO_2 capture facility other than the aforementioned emissions described under 7.3.1.2 and CO_2 streams under 7.3.2. In the following subclauses, the term “solid waste” describes solid, semi-solid, liquids or contained gaseous material.[30] Primary examples include waste products generated when absorbents, adsorbents, or membranes to be used for CO_2 capture are recycled and cleaned, and used absorbents, adsorbents, and membranes, and waste detergent discharged from equipment cleaning.

7.3.3.1 Waste products (process effluent)

CO_2 capture technologies can be differentiated by the types of effluents they generate. For amine-based technologies, effluents are generated during the treatment of heat stable salts. For ammonia-based technologies, residual ammonia in the treated flue gas is neutralized with sulfuric acid to form ammonium sulfate, which can be utilized as a fertilizer, depending on the impurities concentration.

The function and necessity of a reclaimer in chemical absorption processes is described in 7.2.1.

Absorbents degrade with the elapse of operating time and need to be regenerated on a periodic basis. During this process, a portion of the absorbent, with impurities and degraded substances, is separated and disposed of as reclaimer waste according to federal, state and local regulatory requirements.

One of the following waste treatment methods is selected based on the circumstances at the plant:

a) off-site disposal contracted out to a waste disposal contractor;

b) on-site incineration using an incinerator;

c) on-site crystallization to obtain solid ammonium sulfate which can be sold as fertilizer (for ammonia-based process);

d) off-site shipment of ammonium sulfate liquid as feed for a fertilizer process (for ammonia-based process).

In general, a chemical analysis is performed on waste product (process effluents) to ensure that their range of characterization is consistent with the specification. While the characterization of waste product (process effluents) depends on regulation and recipient requirements, the following basic information is required:

— The physical properties and chemical composition of the waste.

— Waste category (product quality specification) or complete analysis data needed for legal classification of waste, hazardous or non-hazardous. For example, if it has any of the four characteristics (ignitable, corrosive, reactive, toxic) in 40 CFR Part 261, it is classified as a hazardous waste and if a US RCRA listed solvent is used in the process, the waste solvent would be a listed hazardous waste in US. If it displays one or more of the characteristics of hazardous properties (explosive, oxidizes, ignitable, irritant, harmful, toxic, carcinogenic, corrosive, infectious and mutagenic) listed in the Directive 2008/98/EC, Annex III, 12 December 2008, it is classified as hazardous waste in EU.[30]

— Total annual production.

— Selected method of transport for the selected waste disposal method.

— Safety Data Sheets (formerly known as “Material Safety Data Sheet [MSDS]”) of the component, if it is available.

In the amine-based technologies, since the waste has typically the heating values within range of those of lignite coals, firing it in the cement kiln or in the on-site pulverized coal power plant is a potential disposal option. However, the addition of the waste to the cement kiln would require additional testing to show that the kiln emissions would still comply with the applicable emission limits while using the waste as fuel. A pulverized coal power plant co-firing the waste would be subject to Commercial and Industrial Solid Waste Incinerator regulation (CISWI), whereas when the waste is considered a hazardous waste, then co-firing this material would be regulated as a hazardous waste combustor under the hazardous waste regulations of 40 CFR Parts 260 through 270 or state equivalent (whichever is more stringent) in the US. In EU co-firing any amount of reclaimer waste in the boiler furnace triggers the Waste Incinerator Directive (WID) without minimum threshold of the co-fired waste amount and is classified as waste incineration.[30]

For amine-based technologies, thermal reclaiming is the most robust solvent reclaiming method and the ion exchange solvent reclaiming or the elecrodialysis solvent reclaiming can be applicable depending on PCC technology. In the thermal reclaiming,[30] chemicals like alkalines such as NaOH may be used to support the regeneration of the solvent, which should be handled with care, and some sodium will be found in the waste product in this case. Residues from the reclaiming process are mostly harmless sulfates produced by neutralization (e.g. Na_2SO_4); however, in some cases, toxic degradation products such as nitrosamines and nitramines described in 7.5.3.2 may occur, which should be handled with caution.[47]

While amine and ammonia processes generally evaporate the solvent by use of steam utilizing the generated vapour for stripping of CO_2 in the stripper (desorber or regenerator) and disposing of the remaining components, the AAS process uses crystallization to separate the NO_x and SO_x from the solvent.

In these applications, solid waste management will become more important for the large-scale CCS plant. Therefore it is favourable to list up the outline of the composition and properties of the reclaimed waste product in the typical range. However, such information is very difficult to gather in the public domain.

Other waste products, such as the filter elements of the cartridge filter or the activated carbons beds in the absorbent line, which need man-hours for replacement, will need to be considered. In the event where the dust content in the flue gas going into the CO_2 absorber is relatively high, like coal-fired flue gas, an automatic filter systems may be necessary. The treatment method should be selected by identifying the composition and amount of waste.

7.3.3.2 Solvent streams

The solvent is pumped around in a loop between the absorber and the desorber. In principle, this is a closed loop, but it is not contained in a complete closed system. Solvent droplets and/or aerosols could leave the system at the absorber to the atmosphere or at the desorber to the CO_2 compressor, depending on the process and the demister performance, and have to be considered to minimize emissions and the need for the solvent refill.

Waste generated (process effluent) varies from one CO_2 capture technology to another.

The following are examples of the composition of liquid waste generated when amine absorbent is treated for regeneration.

Example 1 — (B.5)

CSIRO, process modelling for amine-based post combustion capture plant, P94

a) Reclaimer discharge (Sample A)
SO_4 4,8 %, NH_3 1 700 ppmw, NO_3 5 300 ppmw, absorbent content 46 %, pH 11,0

b) Reclaimer discharge (Sample B)
SO_4 15,5 %, NH_3 1 100 ppmw, NO_3 7 000 ppmw, absorbent content 33 %, pH 10,0

7.3.4 Waste (process) water streams

7.3.4.1 Waste (process) water sources

Water is generally produced when flue gas is cooled. Depending on upstream flue gas treatment, the water collected could be used as make-up water for cooling tower and other use. There are different waste water sources to be found in a PCC plant, water streams that have to be counted as separate streams, which could produce waste water to be discharged out of process as a result of condensation and separation occurring at several process steps and related equipment. These include:

- flue gas cooling;

  The flue gas cooler generates flue gas condensate that is affected by the composition of flue gas.

- CO_2 dehydration;

- reclaiming;

  Depending on the PCC technology, the waste water as hazardous waste water resulting from the absorption/desorption process may contain traces of Volatile Organic Compounds (VOC) and has to be treated accordingly. Treatment of this amount of water may be necessary.

- others.

Condensation of water occurs also in other parts of the process but the resulting stream is mixed into the solvent stream and therefore not seen as a separate stream to discharge out of the process.

7.3.4.2 Properties of waste (process) water

Waste (process) water treatment should comply with the local waste water effluent regulations and standards of the considered country and region. Characterization of each process water source is the necessary first step in the permitting process.

7.3.5 Emission determination and calculation

7.3.5.1 Emissions into the atmosphere

7.3.5.1.1 Emission release

The following ways of emission release are possible:

- Directly releasing the emissions into the atmosphere from PCC plant (top of the CO_2 absorber). Reheating to avoid immediate condensation is an option.
- Releasing the emissions using an existing stack, when the CO_2 absorber height is not high enough to clear the environmental quality standards in the flue gas temperature and the ground level concentration. In this case, the stack material and the mixing effect with the untreated gas should be checked due to the change in the treated gas properties.

These emissions could include a reuniting of captured CO_2 with the flue gas stream or there could be a separate stack for CO_2 product discharge.

7.3.5.1.2 Concentrations of emission components

Additional equipment for flue gas treatment to ensure compliance with the emission regulations, e.g. reduction of NO_x or SO_x content or dust in the flue gas, is generally considered as part of the power plant/industrial process. Any treatment of the benchmark flue gas that is required prior to introduction of the flue gas in the PCC facility should be included in the scope of the PCC technology provider. In special cases, e.g. revamp of existing plants, it may also be part of the PCC plant. In the PCC process, CO_2 is abated through the CO_2 capture process after the flue gas from the boiler/process and is treated by the aforementioned equipment.

For a GTCC power plant, there is also treatment with NO_x removal equipment and occasionally CO removal equipment. Both are catalyst systems not adding secondary pollutants to the flue gas except for NH_3 depending on the process used.

As a result, the evaluation method of conventional emission in case of PCC plant addition is necessary, taking into account the following positive PCC plant performance on the following flue gas contaminants:

- NO_x, SO_2, PM removal effect;
- NO_2 is partly absorbed but NO is not absorbed (separate measurement to identify NO and NO_2 may be necessary); SO_2, SO_3 absorbed;
- PM removal effect in flue gas cooler;
- NH_3 in process (7.2.1, 7.2.2, 7.2.3) removal effect;
- reduction of CO_2 flow rate according to the absorption rate as defined in 7.4.2;
- concentrations to be measured as CCS in and CCS out in g/GJ and as CCS outlet, the mass flow leaving the absorber should be evaluated.

Additional emission such as amine/amine degradation products (aldehyde, ammonia, etc.) are discussed in 7.5.

7.3.5.1.3 Emission regulations

In cases where there are no clearly defined emission regulations for PM, SO_x and NO_x leaving a CO_2 capture plant, it is suggested to express pollutants in g/GJ (fuel input), due to additional fuel fired. A requirement may be set as the mass of pollutants in total is not higher than that of the entering flue gas.

In addition, other substances related to CO_2 capture process is regulated by the existing regulations, such as VOC and ammonia, depending on the region and the technology.

In order to obtain an operating license for a PCC plant (as is generally required for such big plants), an EIA permit is required. General requirements following IFC General EHS guidelines as a minimum requirement should be considered and checked with local EIA regulations.[73]

7.3.5.1.4 Methods of calculating the concentrations of impurities

There have been methods developed for the conventional plants applicable to the measurements of the amounts and compositions of the flue gas, SO_x, NO_x and PM. These need to be adapted for the changed flue gas streams (O_2-ref. content, etc.).

Issues may be encountered when measuring trace or impurity components that are unique to the PCC system. Research is currently underway to develop simple and accurate measurement methods for such substances that are present as both gas and mist phase.[33][36]

7.3.6 Process by-products

Other than pressurized CO_2, which may improve the economy depending on the process, there can also be the following by-products produced in the specific process.

Examples of economically interesting by-products of some capture processes are $(NH_4)_2SO_4$ and K_2SO_4.

7.4 Evaluation procedure for capture performance

CO_2 capture from flue gases emitted by fossil fuel power stations, which are large stationary sources, is an effective means of reducing Greenhouse Gases (GHG). However, its economic viability is yet to be established and efforts toward its market application are currently underway. It is noted that mechanisms should be established to facilitate knowledge sharing from early CCS projects.

Based on this philosophy, among a number of project-specific Front End Engineering Design (FEED) of large-scale CO_2 capture and compression plant completed in recent years, only a few are in the public domain, including Longannet project of ScottishPower Ltd.,[31] Kingsnorth project of E.ON UK[31] and the Rotterdam Capture and Storage Demonstration Project (ROAD).[32] For FEED studies, overall capital cost estimation is supported by detailed engineering and provides sufficient accuracy to permit an informed business decision. Caution needs to be exercised in applying these public studies for a specific location and project. Considerable variability can be found in available plot space, utility capacity, current ducting layout and operating objectives.

On the other hand, new regulations, such as Directive 2009/31/EC on the geological storage of carbon dioxide, requires businesses of new large-scale coal-fired power plants (nominal electrical output of 300 MW or more) to conduct studies into presence or absence of appropriate storage site, technical feasibility and cost of transport equipment, technical feasibility and value of additional CO_2 capture facility (retrofit). Moreover, this philosophy also supports compliance with the above requirement in order to build a new large-scale coal-fired power plant, since, for supercritical pulverized fuel (PF) plant, the most developed capture retrofit options are post-combustion amine capture and oxyfuel combustion.[33]

Reflecting this background, developing a standard for the performance evaluation method of CO_2 capture technologies could help to achieve the following goals of CO_2 capture technologies:

- facilitating an objective evaluation of the current state of progress for better understanding and sharing of public knowledge;
- contributing to fair competition without hampering technological advancement;
- promoting the development of widespread application.

7.4.1 Clarification of the evaluation basis

In order to carry out a proper comparative evaluation, the evaluation basis and the definition of major performance values and the economic indexes should be clarified, as the reported figures could be site- or technology-specific and should therefore be normalized. In addition, the estimating methodology should be identified and applied uniformly across each plant design.

It is important to establish a common set of start and end points. To start, the flue gas properties such as flow rate, temperature, pressure and the composition (such as H_2O, CO_2, O_2, SO_x, NO_x, HCl and dust) should be established. Quality of the treated flue gas stream and the CO_2 product stream should be defined. Finally, a common list of utilities such as steam, steam condensate, cooling water, power, pressurized air, chemicals and industrial gases should be established. Modifying the basis set of utilities would need to be accommodated within the scope of the CO_2 capture system.

In addition, the following performance parameters affect the economic index and should be clarified before evaluation.

7.4.2 Basic performance

7.4.2.1 CO_2 capture efficiency and total mass of CO_2 captured

CO_2 capture efficiency (ηCO_2) is defined as follows:

$$\eta CO_2 = (fCO_{2in} - fCO_{2out})/fCO_{2in} \times 100 \quad (1)$$

where

$fCO_{2in,\ out}$ is the mass flow rate of CO_2 at CO_2 capture plant inlet and outlet (treated flue gas emission side) [in Nm^3/h].

$$fCO_{2in} = F_{in} \times CO_{2in}/100\ [Nm^3/h] \quad (2)$$

$$fCO_{2out} = F_{in} \times (1\text{-}CO_{2in}/100)/(1\text{-}CO_{2out}/100) - F \times (1\text{-}CO_{2in}/100)\ [Nm^3/h] \quad (3)$$

NOTE Since the outlet gas flow rate changes according to the CO_2 removal rate and the inlet gas flow rate, which is always constant, is based on and $fCO_{2out} = F_{out} \times CO_{2out}$ is not applied.

where

$F_{in,\ out}$	is the flue gas flow rate at CO_2 capture plant inlet and outlet (treated flue gas emission side) [Nm^3/h-dry];
CO_{2in}	is the CO_2 concentration in the flue gas at CO_2 capture plant inlet [vol%-dry];
CO_{2out}	is the CO_2 concentration in the flue gas at CO_2 capture plant outlet (treated flue gas emission side) [vol%-dry].

Total mass of CO_2 captured is defined as follows:

- The total mass of CO_2 captured is measured by the flow meter installed in the product CO_2 line (before CO_2 compression), corrected by the operating condition: (W_A).

In the operational data evaluation case, it is also recommended to check the following calculations:

- Total mass of CO_2 captured calculated from the absorbent side by the measurement of the dissolved CO_2 concentration (g/L) and the flow rate of absorption solvent (both the lean and rich solution): (W_B);
- Total mass of CO_2 captured calculated from the flue gas side by the balance calculations from the gas side in the above Formula (2) and Formula (3): (W_C).

If the difference among the value calculated from (W_A), (W_B) and (W_C) is within the acceptable level, the CO_2 balance is maintained correctly. Online analyzers have also been developed for the analysis of absorption solvent and it is possible to quickly perform the operation management.[34]

7.4.2.2 Properties of the captured CO_2 at CO_2 compression system outlet

7.4.2.2.1 CO_2 purity

In the chemical absorption processes, a CO_2 concentration (on a dry volumetric basis) of 99 % or more can be achieved.[35]

7.4.2.2.2 Concentrations of CO_2 impurities

The captured CO_2 contains moisture, oxygen and nitrogen as a by-product of the absorption/desorption process. Quality of CO_2 and content of other elements (H_2O, N_2, O_2) has to be defined with regards to transport and storage/usage requirements. Conditions required for the further processing of the CO_2 have to be given by the organization responsible for transport and storage. This includes CO_2 quality inclusive of allowable pressure content of other elements, e.g. H_2O, N_2 and O_2. If the requirements concerning the moisture and the oxygen concentrations from the transportation side and beyond are too stringent for the specifications to the CO_2 capture and compression systems, it may be necessary to install a dehydrator (moisture removal system) and/or an oxygen removal system.

7.4.2.2.3 CO_2 compressor system outlet port pressure

Coordination with the CO_2 transportation side based on CO_2 transportation mode and the actual specifications of the transportation is needed. Interface pressure and temperature of CO_2 capture equipment with CO_2 compression system is recommended to be defined in the specifications of the CO_2 compressor along with impacts on the evaluation of the power consumption of the CO_2 compressor.

7.4.2.2.4 Others

Captured CO_2 is the end product of the CO_2 capture and compression process and it is important to have quality control measures in place. CO_2 metering will be required in the system to measure plant performance, potentially as a means of demonstrating compliance with the requirement from the transportation and sequestration side and environmental regulations, as a total.

7.4.3 Utility consumption

7.4.3.1 LP (-MP) steam

The required steam for the desorption process is delivered by the power or industrial plant. The way the steam is extracted from water steam cycle depends on the local power plant operating conditions. Majority is LP and MP is required for some cases

The LP (-MP) steam required by the PCC plant can be extracted from the water-steam-cycle in the power plant. This requires modifications in the power plant steam cycle and results in a reduction of the power plant efficiency. In terms of power plant performance alone, it is favourable to lower the conditions of the extracted steam as much as possible.[32] In the case that the power plant is mature and the modification is restricted, or there is a necessity to avoid any impact of power plant operation, an additional gas- or oil-fired boiler can be installed with the existing open cycle gas turbine being modified with an HRSG to supply LP steam.[31] The water condensate of the PCC is discharged in the condensate system of the power plant.

7.4.3.2 Power consumption

For rotating machinery like pumps, blowers, compressors, electric motors and/or steam turbines using MP to HP steam can be used as the driver. When the steam turbine drive is selected, the outlet steam is used again as LP steam for PCC plant and its supply source needs to be considered. When an electric motor is used, a power generation penalty as an equivalent to the LP steam consumption in 7.4.3.1 may be incurred, depending on its electrical consumption. In any case, the shaft power consumption varies according to the model and efficiency of the compressor applied and the CO_2 product gas interface pressure at CO_2 capture unit outlet before CO_2 compression unit-inlet.

Ammonia systems typically have higher regeneration pressures than generic amine systems as the vapour pressure of the solvent with higher pressure heating steam for the reboilers, provides higher interface pressure of the captured CO_2 at CO_2 capture unit outlet. As a result, the design and number of stages of the compressor can vary significantly. In addition, a higher suction pressure reduces power demand.

Therefore, a separate assessment of the impact to the drive energy consumption needs to be performed for CO_2 capture plant part and CO_2 compression part, respectively.

7.4.3.3 Cooling medium (CW)

In the PCC plant, CW is used at several steps and its required amount depends on the capacity and the efficiency of the process applied. Feed and the return outlet temperatures of CW should be made clear, since it may affect process performance. When once-through water cooling is not viable, evaporative cooling towers or air coolers could be employed. If it is difficult to secure water, an air-cooling fan can be applied. For the chilled ammonia process, a chilled water system is needed to supplement CW to achieve the desired absorption temperatures. This utility is typically supplied by a refrigeration system using anhydrous ammonia as the refrigerant.

In either case, required power consumption used for providing CW or required chilled water should be included in the total power consumption in 7.4.3.2.

Waste heat integration using steam cycle condensate as cooling medium in the PCC coolers result in a reduction of the additional cooling duty associated with the PCC operation.

The steam extracted from the steam cycle for solvent regeneration reduces the cooling requirements of the turbine condenser, therefore offsetting some of the increase in cooling utility required by the PCC plant.

7.4.3.4 Demineralized water

In the PCC process, demineralized water is required for dilution of solvent, of the form received from production, to supplement and maintain on specification alkaline solution during operation as required for the process

7.4.3.5 Absorbent/solvent and other chemicals

Different types of chemicals, including absorbents, caustic soda or other alkaline used for desulfurization, sulfuric acid for ammonia neutralization, nitrogen, activated carbon and hydrogen used when necessary to de-oxidize, depending on the requirements of the process deployed have to be considered. Absorbents in particular have a major economic impact due to the large amounts in which they are consumed in the case of a large-scale PCC plant. Therefore, it is necessary to clarify the consumption amount, refill method, transporting method and to develop technologies to minimize the amount of consumption.

7.4.4 Operability (operational requirements)

Since PCC plant requires consequential amounts of LP steam and electricity, it is necessary to operate in collaboration with the hosted power stations and/or utility supply systems in order to achieve efficient operation. The following are the general operational requirements.

7.4.4.1 Load following (ramping speed)

While various scenarios of economical operations are possible, a PCC plant should be able to handle the capacity of the flue gas source (e.g. provided by the thermal power plant) and ideally not impose any restrictions on it. Furthermore the PCC plant should be able to adjust its operating load in accordance with a maximum load ramp up rate required, such as 5 %/min.

7.4.4.2 Partial load operation

The requirements of the flue gas source could make it necessary for PCC plant to operate at partial load and the stable operation at the specified partial load should be satisfied, solving the issues of a lower operating threshold such as a liquid distribution balance within the system. It has to be considered that flue gas composition may differ significantly in partial load operation, it is noted that the CO_2 concentration of the flue gas can change as the unit ramps up and down. In addition the NO_x content in the gas turbines is also known to vary.

7.4.4.3 Availability

The following is a definition of availability in PCC plant, although there are different ways to express it. Since it concentrates on the operational reliability, the periodic maintenance period related to the maintainability could be discussed separately.

$$\text{Availability} = (1\text{-FOR}) \times 100\ \% \tag{4}$$

$$\text{Forced Outage Rate (FOR)} = \frac{\text{FOH}}{\text{Period of Operation Hour (POH)}} \tag{5}$$

where

FOH is the number of hours a PCC plant is unable to treat the flue gas from the hosted power plant due to the inability of PCC plant to operate;

POH is the total period of hours for a PCC plant with calendar date basis, excluding the periodic maintenance period.

7.4.5 Economic evaluation index

Utility consumption (LP steam and electricity consumption) has a major impact on the economic performance of PCC plant and evaluated in subsequent subclauses.

7.4.5.1 Specific Energy Consumption (SEC) for PCC plant

SEC, which refers to the thermal energy consumption, is defined as:

$$\mathrm{SEC}\left[\frac{\mathrm{GJ}}{\mathrm{tCO_2}}\right]=\frac{\left\{\left(\text{supplied steam flow}\left[\frac{\mathrm{t}}{\mathrm{h}}\right]\times\text{steam enthalpy}\left[\frac{\mathrm{GJ}}{\mathrm{t}}\right]\right)-\left(\text{recovered steam condensate flow}\left[\frac{\mathrm{t}}{\mathrm{h}}\right]\times\text{condensate enthalpy}\left[\frac{\mathrm{GJ}}{\mathrm{t}}\right]\right)\right\}}{\text{captured CO}_2\text{ amount}\left[\frac{\mathrm{tCO_2}}{\mathrm{h}}\right]} \tag{6}$$

7.4.5.2 Specific power consumption (SPC) for CO_2 capture and compression

Specific power consumption (SPC) for CO_2 capture and compression is defined as:

$$\mathrm{SPC}\ [\mathrm{kWh/tCO_2}] = (\text{power consumption of PCC plant [kW]})/\text{captured CO}_2\text{ amount }[\mathrm{tCO_2/h}] \tag{7}$$

NOTE Power consumption of PCC plant includes CO_2 compression and related utility facilities.

7.4.5.3 Electricity output penalty (EOP)

Electricity output penalty (EOP), as defined below, is the unit output penalty by PCC technologies independent of fuel composition.[39]

$$\mathrm{EOP} = \text{Efficiency penalty/fuel specific emissions} \tag{8}$$

where

EOP	is the total net loss in plant output due to PCC plant, as indicated in Formula (9), in kWh/tCO_2;
Efficiency penalty	is calculated based on the extracted steam information, the heat balance of the steam turbine and the auxiliary power consumption required for PCC plant, in kWh/kWh$_{th}$;
Fuel specific emissions	are calculated based only on the fuel information, as shown in Reference [40], Annex B, in tCO_2/kWh$_{th}$.

$$\mathrm{EOP} = \frac{1\,000 \times \left[\text{loss of gross power output (MW)} + \text{PCC plant power consumption (MW)}\right]}{\mathrm{CO_2}\text{ captured amount }(\mathrm{tCO_2/h})} \tag{9}$$

Therefore, loss of steam turbine generator output by the steam extracted from a steam turbine and the unit cost of steam should be assessed using the heat balance data of the steam turbine. In determining the unit cost of the steam for the purpose of conducting economic evaluation, the efficiency and operating restrictions of the power plant need to be considered.[41][42]

The development of high-efficiency super-critical thermal power plant and GTCC plant, with very low levels of pollutants like NO_x, SO_x and PM makes the installation of such capture plants much more sustainable.[53]

The unit cost of steam based on individual configuration would be needed to calculate the running cost.

7.4.5.4 Levelized cost of electricity (LCOE)

To conduct a comprehensive economic evaluation including that of the investment cost, the Levelized Cost of Electricity (LCOE), the cost of CO_2 avoided and the costs of CO_2 captured or removed need to be considered. For details, see Reference [35]. The cost of CO_2 avoided is evaluated at full CCS chain; the increase in utility consumption by the CCS installation, which produces additional CO_2 emission, is also considered. Since various site-specific economic parameters, such as the investment cost, the owner's cost, the maintenance cost, the fuel cost, the discount rate and so on, are included in the evaluation of these three parameters, it is reported that there are significant differences in the methods employed by various organizations to estimate the cost of CCS systems for fossil fuel power plants. Such differences are often not readily available in publicly reported CCS cost estimates.[38] Therefore, it is necessary to develop a standard for this.

7.5 Safety issues

In general, facilities and equipment dedicated for the corresponding capture technology are designed and constructed in compliance with the existing and applicable international, regional and national standards such as ISO, OSHA, and ASME, and other specific company standards. In addition, compliances with the laws, regulations and requirements in the region or country where the plant is located provide additional securities for safety.

The safety issues relating to PCC technologies vary according to the capture processes and chemicals applied, which are listed in the IPCC Special Report on Carbon Dioxide Capture and Storage 2005, Figure 3.2[14] and 7.2 and 7.3, in addition to general safety issues common to those technologies. Some of the leading examples are listed below.

7.5.1 Safety categories

The safety categories for chemical substances include toxicity (e.g. acute toxicity, accumulating property, genetic toxicity and carcinogenicity), explosibility and inflammability.[43]

7.5.1.1 Toxicity

Ammonia and amine solutions can cause injury through unprotected skin contact and inhalation. There are well known protocols for the safe handling of these substances. In addition, it has been reported that some of nitrosamines, which are produced when amines react with NO_2, cause genetic toxicity or probably carcinogenic to humans.[49][50]

As Table 3 shows, CO_2 is not toxic at low concentrations, but its toxicity increases as its concentration rises. According to Control of Substances Hazardous to Health under Health and Safety Executive (COSHH HSE) of the UK, its occupational Long-Term Exposure Limit (LTEL) is 0,50 % at the Time-Weighted Average (TWA) of 8 h, while the occupational Short-Term Exposure Limit (STEL) is 1,5 %, at 15 min. Therefore, it is important to have safety measures in place to ensure that these limits are observed when operating a CO_2 capture system and handling captured CO_2.[44]

Table 3 — Exposure reactions to carbon dioxide

Concentration in air (% v/v)	**Effect**
1 %	Slight increase in breathing rate.
2 %	Breathing rate increases to 50 % above normal level. Prolonged exposure can cause headache and tiredness.
3 %	Breathing increases to twice the normal rate and becomes laboured. Weak narcotic effect, impaired hearing, headache, increase in blood pressure and pulse rate.
NOTE See Reference [44].	

Table 3 *(continued)*

Concentration in air (% v/v)	Effect
4 % – 5 %	Breathing increases to approximately four times the normal rate, symptoms of intoxication become evident and slight choking may be felt.
5 % – 10 %	Characteristic sharp odour noticeable. Very laboured breathing, headache, visual impairment and ringing in the ears. Judgement may be impaired, followed within minutes by loss of consciousness.
10 % – 15 %	Within a few minutes' exposure, dizziness, drowsiness, severe muscle twitching, unconsciousness.
17 % – 30 %	Within one minute, loss of controlled and purposeful activity, unconsciousness, convulsions, coma, death.
NOTE See Reference [44].	

7.5.1.2 Explosibility and inflammability

While aqueous solutions of ammonia and amines are not explosive or pyrophoric in nature, their pure form has low boiling points and high auto-ignition temperatures.

The typical operating conditions found in a PCC are several hundred degrees less than the auto-ignition temperature. In handling these compounds, these factors should be taken into consideration when designing a CO_2 capture system and setting up its operating conditions. Such risks are reduced or solved when aqueous solutions are used, since they are not inflammable as long as the concentration level is kept below a certain level.

7.5.2 Relevant equipment and manifestations

The following equipment and their behaviours are believed to pose safety risks in the CO_2 capture system, in case of troubles.

7.5.2.1 Pre-scrubbers

Pre-scrubbers are safety equipment that reduce SO_2 gases to very low levels using alkaline (NaOH, etc.) when necessary. The equipment should be handled carefully as it uses strong alkaline. In addition, due to the heavy metals, such as mercury, collected from flue gas at the same time, waste water treatment should comply with the local waste water effluent standards of the considered country and region.

7.5.2.2 Absorber

Depending on the nature of the absorbent used, a very small portion of absorbents or its components are emitted with the flue gas in the form of gas and/or mist from the absorber. Large portions of the mist can be removed using a demister installed inside the absorber or the water scrubber. Recently the presence of SO_3-induced aerosols with sub-micron dimensions has been shown to result in increased emissions of amines from the absorber.[45] There has been developed a countermeasure to reduce or avoid amine emission caused by SO_3 mist.[46]

In addition, it has been reported that the oxidative degradation of amines by oxygen in the flue gas cause the formation and accumulation of ammonia, aldehydes amines and their polymerized materials, and acid (formic acid and oxalic acid) within the absorbents, and some of these are emitted with the flue gas from the top of the absorber. Furthermore, amines and their degradation products in the absorbents react with NO_2 to produce nitramines and nitrosamines, which can be removed by the water scrubber and accumulate in the absorbents. Some reports claim that traces of the nitrosamine and nitramine are emitted with the flue gas from the absorber outlet.[47]

For an ammonia-based system, solvent degradation has not been experienced. Ammonia, in equilibrium with the treated flue gas, leaves the absorbers and is captured in an ammonia wash and neutralized with sulfuric acid in a direct contact heater prior to atmospheric discharge.

7.5.2.3 Water scrubber

The water scrubber is installed if required depending on the absorbent used to remove gases and mists, such as ammonia and amines, using water or acid to reduce and/or recover the emissions of these substances.[47]

7.5.2.4 Regenerator

The high temperature inside the regenerator causes thermal decomposition products to form and accumulate in the absorbent. When the absorbent is routed back to the absorber and comes into contact with the flue gas, portions of the thermal decomposition products may be released into the atmosphere through the absorber outlet together with the flue gas. They may also mix in with the captured CO_2. Solvent degradation has not been experienced in ammonia processes.

7.5.2.5 Reclaimer

Please refer to 7.3.3.1.

7.5.2.6 Waste water treatment systems

Waste water produced by CO_2 capture systems is subject to the waste water effluent regulations and treatment requirements applicable to the chemical production/power plants in each country and region. Normally there is no waste water from CO_2 absorber, if the acid wash is not applied. Ammonia systems are generally water neutral with residual water injected in the by-product system.

7.5.2.7 By-product systems

Ammonia systems produce an ammonium sulfate solution by contacting residual ammonia in flue gas with sulfuric acid.

7.5.2.8 CO_2 compressor systems

Using the CO_2 compressor, the CO_2 gas captured from the flue gas is compressed in several stages up to the prescribed pressure. The compressor is equipped with knock out vessels, heat exchangers such as an intercooler and a mist separator. The number and size of this equipment mainly depends on the suction pressure.

The complete compressor unit is often installed in an enclosure as a noise-control measure, and in some cases a liquefier is also installed. Large amounts of highly concentrated CO_2 are released outside the system during normal operational shutdowns as well as emergency shutdowns. It is essential that CO_2 be released into the atmosphere from a safe location in such cases. In addition, personnel safety should be ensured in the event of CO_2 emissions at high concentrations due to mechanical malfunctions or other incidents. In particular, countermeasures need to be established in case high-pressure CO_2 is released, as this may cause freezing and blockage.

7.5.2.9 Pipes, solvent storage tanks, etc.

The pipes and solvent storage tanks in CO_2 capture systems are subject to the regulations and treatment requirements applicable to the chemical production plants in each country and region.

7.5.3 Chemical substances and their behaviours

Chemical substances and their behaviours that should be subject to safety consideration are discussed below. Although Table 4 is not an exhaustive list, it compiles a list of substances and their CAS numbers[48] that are studied mainly in amine-based PCC plants.

Table 4 — Compounds that may be present in emissions from a PCC unit with amines

Class	Compounds[a]	CAS Numbers
PCC solvents	Monoethanolamine (MEA)	141-43-5
	Diethanolamine (DEA)	111-42-2
	2-Amino-2-methyl-1-propanol (AMP)	124-68-5
	Piperazine	110-85-0
	N-Methyldiethanolamine (MDEA)	105-59-9
Amines	Ammonia	7664-41-7
	Ethylamine	75-04-7
	Methylamine	74-89-5
	Dimethylamine	124-40-3
	Diethylamine	109-89-7
	N-Methylethylamine	624-78-2
	1-Propanamine	107-10-8
	1,2-Ethanediamine	107-15-3
Amides	Formamide	75-12-7
	Acetamide	60-35-5
	N-(2-Hydroxyethyl) formamide	693-06-1
	N-(2-Hydroxyethyl) acetamide	142-26-7
	N-Methylformamide	123-39-7
Aldehydes	Formaldehyde	50-00-0
	Acetaldehyde	75-07-0
	2-Aminoacetaldehyde	6542-88-7
	Hydroxyacetaldehyde	141-46-8
Alcohols	Ethanol	64-17-5
	1,2-Ethanediol	107-21-1
Acids	Formic acid	64-18-6
	Acetic acid	64-19-7
	Propanoic acid	79-09-4
	Butanoic acid	107-92-6
	Glycolic acid	79-14-1
Nitrosamines	*N*-Nitrosodimethylamine (NDMA)	62-75-9
	N-Nitrosodiethylamine (NDEA)	55-18-5
	N-Nitrosomorpholine (NMor)	59-89-2
	N-Nitrosopiperidine (NPip)	100-75-4
	N-Nitrosodiethanolamine (NDELA)	1116-54-7
	N-Nitrosopiperazine (NPz)	5632-47-3
	1,4-Dinitrosopiperazine	140-79-4

[a] The list is comprehensive based on literature information and possibilities of more compounds could not be ignored. This list does not contain compounds produced as a result of degradation in the atmosphere.

NOTE See Reference [48].

7.5.3.1 Chemical substances

As discussed in 7.5.2.2, some volatile substances contained in the absorbents may be released into the atmosphere together with the flue gas in the form of gas or mist particles, and as a result may mix with captured CO_2. The same applies to the additives in absorbents (e.g. antioxidants).

7.5.3.2 Degradation products

As discussed in 7.5.2.2 and 7.5.2.5, most of the substances low in volatility are emitted from the reclaimer as residues. However, highly volatile substances may be emitted into the atmosphere with flue gas as gas or mist, and may mix with captured CO_2.

7.5.3.3 Heat stable salts

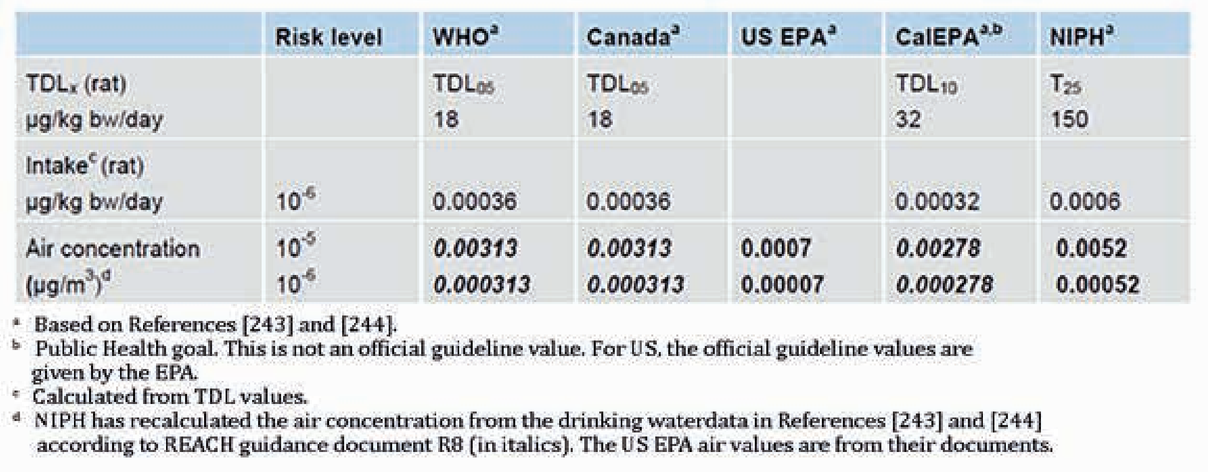
Heat stable salts generally have a low vapour pressure and are less prone to vapourization. Most of them are emitted from the reclaimer as residues.

7.5.3.4 Nitrosamines

Some nitrosamines cause acute toxicity, genetic toxicity, and/or probable carcinogenicity. Among those nitrosamines that may be produced in CO_2 capture systems, *N*-nitrosodimethylamine (NDMA) is categorized as "probably carcinogenic to humans" according to the International Agency for Research on Cancer (IARC). NDMA is categorized high class probable carcinogenicity and there is abundance of data available on cases involving acute toxicity, genetic toxicity and/or probable carcinogenicity. There are many types of nitrosamines that may be produced in CO_2 capture systems. Not all of them have the potential of causing acute toxicity, genetic toxicity, and/or probable carcinogenicity. If data are not available on a certain species regarding its toxicity, it should be handled with the assumption that it has the toxicity equivalent to NDMA.[49]

Table 5 and Table 6 show the allowable atmospheric concentrations of NDMA established by various organizations, assuming that there is an increase of the cancer rate of one person (patient) per 100 000 to 1 million after lifetime exposure (i.e. daily dose is taken or inhaled for approximately 70 years).[49]

Table 5 — Concentrations of NDMA in air, recalculated from the dose descriptors TDL_x and T25 by NIPH (in italics)[49]



	Risk level	WHO[a]	Canada[a]	US EPA[a]	CalEPA[a,b]	NIPH[a]
TDL_x (rat) µg/kg bw/day		TDL_{05} 18	TDL_{05} 18		TDL_{10} 32	T_{25} 150
Intake[c] (rat) µg/kg bw/day	10^{-6}	0.00036	0.00036		0.00032	0.0006
Air concentration (µg/m^3)[d]	10^{-5} 10^{-6}	*0.00313* *0.000313*	*0.00313* *0.000313*	0.0007 0.00007	*0.00278* *0.000278*	0.0052 0.00052

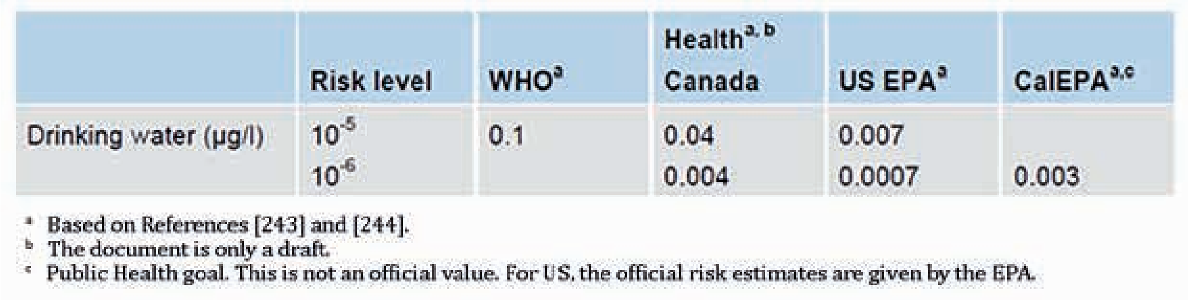
[a] Based on References [243] and [244].

[b] Public Health goal. This is not an official guideline value. For US, the official guideline values are given by the EPA.

[c] Calculated from TDL values.

[d] NIPH has recalculated the air concentration from the drinking waterdata in References [243] and [244] according to REACH guidance document R8 (in italics). The US EPA air values are from their documents.

Table 6 — Human cancer risk estimate of NDMA in drinking water[49]



	Risk level	WHO[a]	Health[a, b] Canada	US EPA[a]	CalEPA[a,c]
Drinking water (µg/l)	10^{-5}	0.1	0.04	0.007	
	10^{-6}		0.004	0.0007	0.003

[a] Based on References [243] and [244].
[b] The document is only a draft.
[c] Public Health goal. This is not an official value. For US, the official risk estimates are given by the EPA.

7.5.3.5 Nitramines

Very little data are available regarding the risks of acute toxicity, genetic toxicity, and/or carcinogenicity and the extent of the risks remain unclear. Data collection will be one of the major goals going forward in the future. Presently, the toxic assessment identical to that of nitrosamines may be conducted in some cases, to be considered a conservative risk estimate.[49]

7.5.3.6 Acid gases (SO_X, NO_X, CO_2) included in flue gases, heavy metals (mercury, etc.)

The flue gases and particulates emitted from thermal power stations are treated in compliance with the regulations of each country and region.[48] Specifically, acid gases and particles are reduced to the regulations or below by NO_X removal equipment, flue gas desulfurization equipment, and dust collecting equipment. Preferably, this treatment should take place on the emitted side (power plant or industrial process). When these devices are not installed, high concentrations of NO_X and SO_X enter into the CO_2 capture system. While a large portion of SO_X may be removed by the pre-scrubber, most of NO_X remains and is at risk of entering into the system from ducts or other components. For amine systems, as mentioned in 7.5.3.4 and 7.5.3.5 above, generally NO_2 can react with the solvent and lead to formation of nitramines and nitrosamines.

Highly volatile heavy metals, such as mercury, are not completely removed before reaching the flue gas desulfurization equipment,[43] and some of them are collected and accumulated by the PCC pre-scrubber. If they are not collected by the pre-scrubber, they enter into the CO_2 capture system and accumulate within the absorbents.[43] Depending on their concentration levels, these highly volatile heavy metals, if they enter into the CO_2 capture system, may negatively impact its operation and their behaviour should be closely monitored in the future.

7.5.3.7 High-concentration CO_2

The concentrations of CO_2 captured from the regenerator may be 99 % or above once moisture is removed and there are risks of leakage from pipes while it is being routed to the compressor. When large amounts of high-concentration CO_2 are to be released outside the system during normal operational shutdowns or emergency shutdowns, diffusion simulations may be necessary in some cases for safety reasons.

7.5.3.8 Anhydrous ammonia

Anhydrous ammonia supplies replacement solvent and is a refrigerant in ammonia-based PCC plants. Anhydrous ammonia is a hazardous material but a widely available chemical with well-known methodology for design and handling. This chemical is commonly found in power plants for use in Selective Catalytic Reduction (SCR) units.

7.5.3.9 Sulfuric acid

Sulfuric acid is used to neutralize residual ammonia solvent in ammonia-based PCC plants. Sulfuric acid is a hazardous material but widely available chemical with well-known methodology for design and handling. This chemical is commonly found in power plants for use in water treatment.

7.5.4 Environmental Impact Assessment (EIA)

To install a PCC system in a fossil-fired power plant or another industrial plant, under requirements of local regulations and standards, an EIA should be conducted to obtain construction and operation permits.

This assessment is necessary to evaluate the extent of direct emissions of solvent and solvent degradation products from the PCC system, as well as toxic substances generated in the atmosphere by the emitted solvent and its degradation products through photochemical reactions.

While nitrosamines are prone to decomposition through chemical reactions in the atmosphere, nitramines are considered to be relatively stable. Europe is leading the way in the development of EIA for amine emissions. For example, the Cambridge Environmental Research Center (CERC), NVE Corporation, and Commonwealth Scientific and Industrial Research Organization (CSIRO) have released exposure assessment models that take reaction rate into consideration.

While standards such as those in Table 5 and Table 6 are available, currently, specific data used for the evaluation criteria of nitrosamines and nitramines have not yet been established. In particular, very little data has been established with respect to nitramines.

Therefore, early establishment of EIA methods for amine emissions is desirable. In regard to the emission regulations, it should be stated that the emission levels leaving the PCC plant are of great interest, as the overall environmental impact of the PCC plant will form a key point in future plant acceptance.

Higher abatement of pollutants in combination with more fuel input to produce utilities for PCC plant are leading to higher emission levels per output (kg/h, kg/kWh), which need to be identified in detail. As a consequence, the relevant emission regulations need to be updated in that respect.

For an appropriate consideration of process/plant efficiency, it is recommended to change emission limit definitions from concentration-related figures to efficiency-related figures (from mg/Nm^3 to g/kJ_{fuel} or g/kWh_{el}).

Emission/Effluent limits for liquid and gaseous substances resulting from the solvent used in the absorption/desorption process have to be evaluated and defined, e.g. amines, NH_3, nitramines and nitrosamines. Based on the actual lack of commercial PCC plants with long-term and continuous operation license, an established set of requirements for such plants is not yet available.

The following topics should be also considered in the design, with regards to environmental impacts, based on similar plant handling similar chemicals.

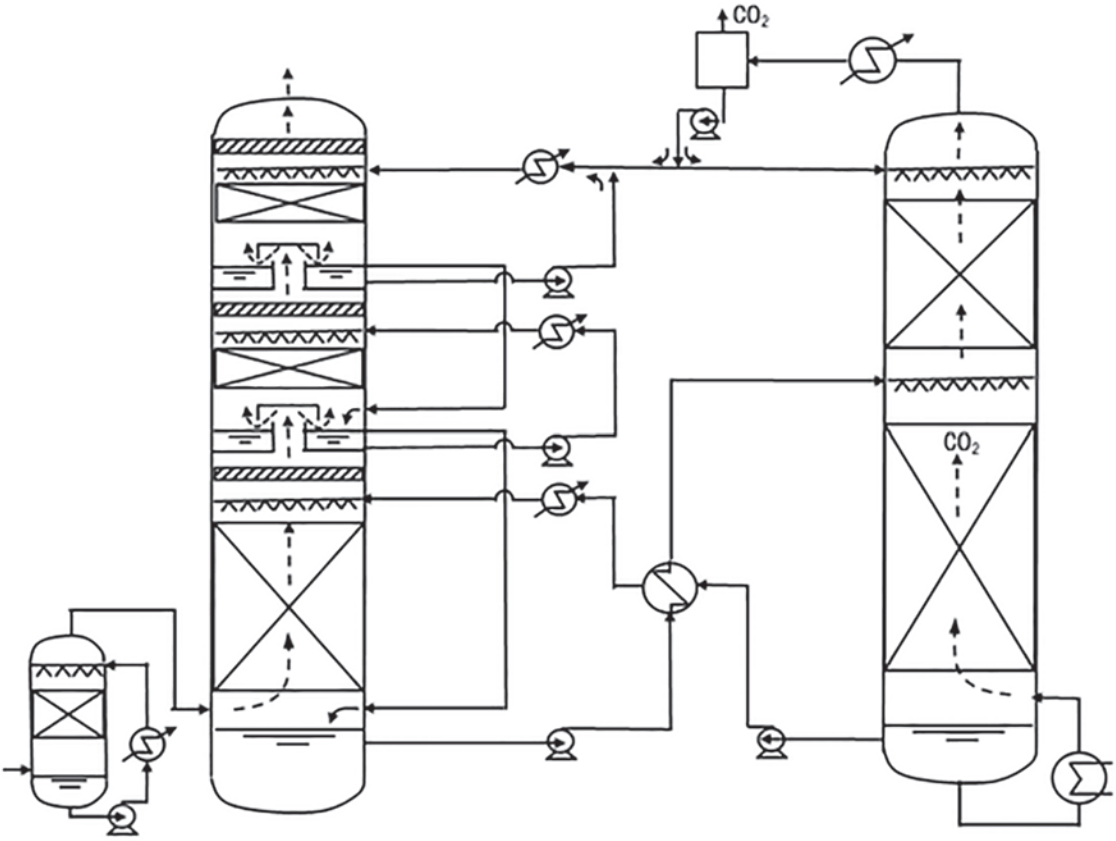
- Solvent leakages/spillages during the transport chain to/from the PCC plant and in the plant during operation with regards to soil and water
- Possible leakage/emission of other substances used in the process, e.g. chemical substance used in the flue gas scrubbers
- Ambient conditions, e.g. earthquakes, wind, rain, flooding

7.5.5 Preventive measures

A variety of measures have been introduced to the capture processes to maintain the safety of PCC systems. Examples of the technologies used are dicussed in subsequent subclauses.

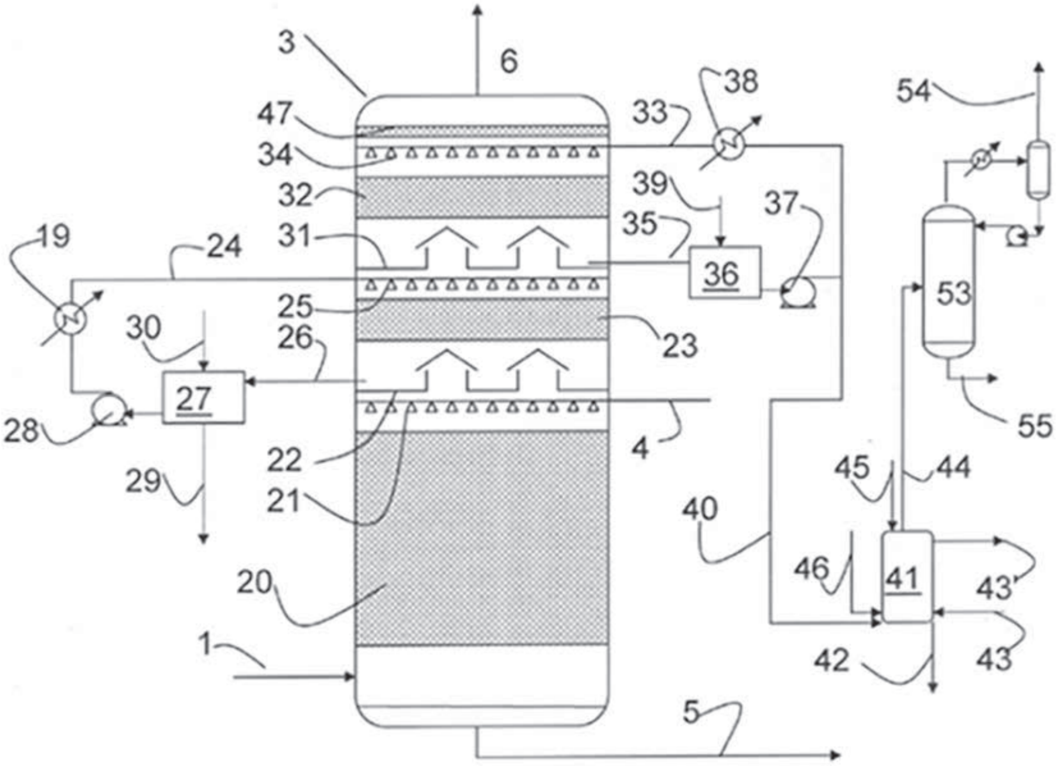
7.5.5.1 Washer

Atmospheric emissions may be reduced by removing and capturing gaseous amines and their decomposition products if applicable based on the used capture process. Using multiple process stages, as well as acid, is effective for improving the efficiency of removal process.[48] However, when their concentrations in the cleaning water increase, the water is routed back into the system. Therefore, it is necessary to treat decomposition products other than amines separately. Main processes are shown below (Figure 13 and Figure 14). In ammonia-based PCC systems, similar equipment is integrated into the overall design.



NOTE See Reference [48].

Figure 13 — Flow scheme showing two stages of washing on the top of absorber



Key

6	decarbonized gas exit
19	external cooler
20	absorber contact zone
21	liquid distributor
22	collector plate
23	washing zone
24	washing water line
25	water distributor
26	water line
27	water wash tank
28	pump
29	water bleed line
30	water make-up line
31	collector plate
32	acid washing zone
33	acid wash line
34	distributor
35	liquid collector line to acid wash tank
36	acid wash tank
37	pump
38	optional heat exchanger (heater or cooler)
39	acid makeup line
40	acid wash bleed line
41	amine reclaimer
42	non-volatile and solid waste discharge
43	condensing steam
44	reclaimed steam and amine exit
45	alkaline solution feed line
46	line to run reclaimer in batch mode
47	demister
53	fractionation column
54	ammonia disposal line
55	amine and water exit to the main solvent loop

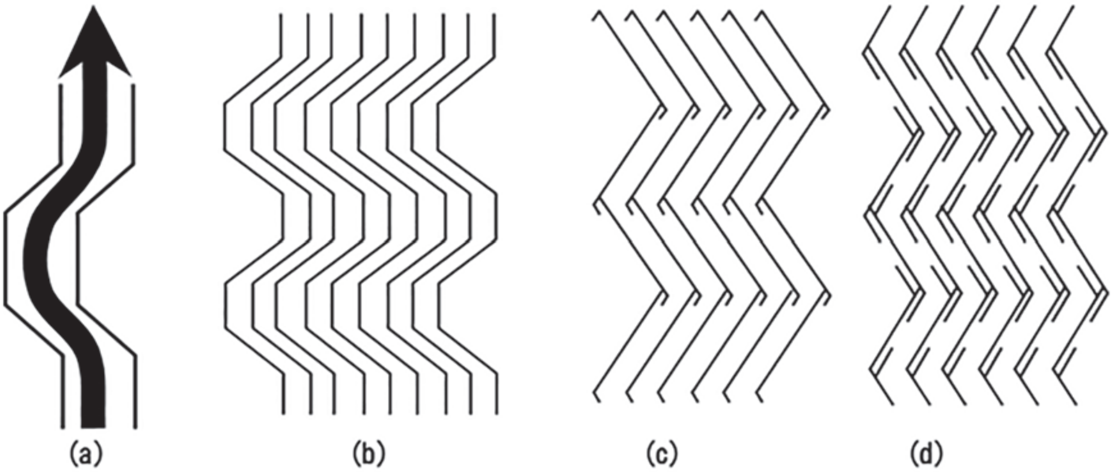
NOTE 1 Acid is added at the last washing stage to realize acid wash.

NOTE 2 See Reference [48].

Figure 14 — Modified absorption column with acid wash

7.5.5.2 Demister

The demister is effective for removing mists containing solvent and its degradation products. Examples of its structure are shown in Figure 15. The demister is installed above the absorber and (if applicable) the washer as well as the regenerator.[48] The demister is available in different geometrical designs. Mesh type mist eliminators are also used where applicable.



NOTE See Reference [48].

Figure 15 — Vane type demister

7.5.5.3 Adsorption

Gases containing amines and decomposition products are passed through a solid adsorbent layer of solid material to adsorb amines and prevent them from leaking outside the system. However, further development of adsorbents is needed.[48] For ammonia systems, residual ammonia is neutralized with sulfuric acid.

7.5.5.4 Ventilation

When a CO_2 capture system (or part of it) is installed indoors, various safety measures are implemented for potential leakage of absorbents and CO_2 from pipes and tanks. For example, such measures include installation of a ventilator.

7.6 Reliability issues

7.6.1 Need for reliability assessment

Considering the urgency of deployment of CCS as a greenhouse gas mitigation technology,[51] it is noted that there is a need to shift into a higher gear in developing large-scale CCS into a true energy option.[53]

a) The practical technologies for separating CO_2 from the flue gases at a power station, as well as those technologies for compressing CO_2 into a liquid-like state (dense phase) for transport and storage with operating experience of a certain scale in similar gas treatment experience, are ready for scale-up.[53]

b) Technical maturity of CO_2 capture technologies to-date varies from demonstration phase and pilot phase to lab or concept level. Some are used for similar gas treatment processes with small-to-medium commercial systems, as no large-scale commercial plant for flue gas treatment is in operation yet. However, Saskpower Boundary Dam Integrated CCS project (1 million tonnes per year of CO_2) from 139 MW net, lignite-fired power station for capture and sales is at the operational stage[54] and the large post combustion CO_2 capture system of KM CDR Process[3)], which has a CO_2 capture capacity of 4 776 tonnes per day from the coal-fired boiler for the enhanced oil recovery project in Texas, U.S.A, is in EPC stage and will start operation in 2016.[55]

c) The CCS system is still very costly and is yet to be economically viable. Therefore, the construction of a large-scale system is, at the current time, only economically feasible by the support of multiple funding sources. For example, the production cost of coal-fired power generation may be increased by 40 % ~ 63 %, to around 100 USD per megawatt hour (MWh) for commercial plants, by the addition of CO_2 capture technology.[53]

d) Efforts to improve and develop the CCS performance and decrease economic impact are currently under way and have the possibility of modifying the process.

Typically, rapid development can come with sustained technical problems, causing, for example, substantial reliability and maintenance issues, which would take some time to resolve.[53]

While impact in small plants may be limited, large-scale CCS plants (3 000 TPD ~ 5 000 TPD) based on amine technology have been discussed and may encounter major problems, such as absorbent leakage caused by corrosion resulting in escalating cost to purchase replacement absorbent and the disposal of absorbent residues.[56] In case of ammonia as a commodity chemical, it is less costly to replace. However, such issues can be solved through R&D, long time commercial experiences of the middle size units and long-term demonstration test result of the middle size unit. As a result, the impact on the budget cannot be ignored.

Reliability plays a key role in the cost-effectiveness of systems. Therefore, achieving high plant availability is vital to keep costs competitive.[58] Full-size plants are so large and expensive that an owner acting in a commercial environment cannot tolerate any technical failure.[51]

Since operational reliability is largely the outcome of reliability in design (maturity in technology), it is recommended that reliability in design assessment and review be performed as early as possible, for instance, when the technology is selected.[51]

7.6.2 Operational reliability

Reliability is defined as “the ability of an item to perform a required function, under given environmental and operational conditions and for a stated period of time” (ISO 8402), plant availability is the most commonly used reliability parameter.

a) Reliability is generally measured as Mean Time Between Failures (MTBF), which shows how frequently downtime occurs.

   MTBF = Total operating hours/number of failures

b) Maintainability is generally measured as The Mean Time to Repair (MTTR), which shows how quickly equipment can be made available after failure.

c) Availability has relationships with reliability and maintenance and is generally expressed in Formula (10).

$$\text{Operational availability} = \text{MTBF}/(\text{MTBF} + \text{MDT}) \tag{10}$$

Where Mean Downtime (MDT) includes MTTR and all other time involved with downtime, such as periodical maintenance as preventive inspection and corrective maintenance, including logistical delays.

Reliability needs to be evaluated and improved related to both availability and the cost of ownership due to the cost of spare parts, maintenance man-hours, transport costs, storage cost and part obsolete risks, etc. There is often a trade-off between the two. Achieving optimal performance would be

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3) KM CDR Process is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

challenging for premature technologies and it only becomes possible through technology optimization and maturity.

However, plant availability is often utilized as the same meaning as the reliability as shown in 7.4.4. Operation requirement, as the consequences for the downtime for a PCC plant might be minimal compared to a process that is fully integrated with the power plant, such as in a pre-combustion process, an oxyfuel combustion process[51] or the host power plant itself and fulfilment of the design performance is the main interest.

7.6.3 Reliability evaluation methods

Various quantification methods have been proposed to evaluate and improve the reliability of designs.[51] Here, "quantification" is defined as "the process of providing the evidence that the technology will function within specific limits or operating regime with an acceptable level of confidence." To conduct this assessment, it is necessary to gain a high level of understanding and knowledge regarding the processes and equipment. System designs should be examined from the perspective of reliability in order to satisfy with minimum requirements, as large-scale PCC commercial systems do not have a sufficient track record it is not easy to establish fault scenarios attributed to the PCC processes.

Various assessment methods, including Reliability and Maintenance (RAM) studies, are being proposed. However, not enough data are available to conduct a RAM study. Therefore, based on the assumption that the PCC system is a collection of equipment with a proven track record, the assessment will be conducted based on the data on mechanical and electrical malfunctions compiled from the experiences faced in general chemical and environmental plants such as OREDA.[52] In this circumstance, the debate often relates to the availability of redundant equipment.[51] As a result of this, critical equipment, with lack of redundancy, plays an essential role in process reliability since its failure results in a major economic failure of processes production margin for the owner. This in turn is due to the high cost and the limited availability of very reliable equipment for installation of redundant equipment.[20]

The basic data will be based on manufacturers' research and development efforts, pilot demonstrations and operating experiences. To understand or substantially improve reliability, availability and maintainability, it is preferable to be able to access precise, dependable data that document the factors that decrease reliability and availability in large-scale commercial plants. Currently, there are no formal mechanisms for acquiring this without direct contact with the technology supplier.

7.6.4 Parameters of reliability

7.6.4.1 R&D results and their operating experience on PCC plant

R&D results and operating experience are important parameters of a reliability assessment. Examples of mid-scale PC-fired electric power plants with a PCC process include MC Global Soda Ash Plant in the United States and two other plants. One of the most well-known commercial PCC facilities was the Bellingham facility in Massachusetts, US, however this facility terminated operations as of 2005. Similarly, a plant of Sumitomo Chemical Co., Ltd. and one other plant are listed as natural gas-fired facilities with PCC processes.[59]

One of the examples of PCC from natural gas reforming flue gas is the KM CDR Process developed by The Kansai Electric Power Co., Inc./Mitsubishi Heavy Industries, Ltd. Eleven mid-scale (around 450 TPD) plants using this process have been constructed and are currently in operation.[60]

The very first fully operating anthropogenic CO_2 CCS plant was a 300 TPD chilled ammonia facility installed at the AEP Mountaineer power station and operated successfully for 8 000 h while injecting CO_2 in two underground formations.[29] Another example of PC-fired power plants with PCC process is the 500 PD CO_2 Capture and Sequestration Demonstration Plant which applied KM CDR Process, as SECARB anthropogenic test with dedicated CO_2 pipeline and injection and monitoring systems has achieved 100 000 tonnes injected (as of 29 October 2013) to understand the integration of capture plant and injection field.[61] This plant is currently (2014) in operation at Alabama Power's Plant Barry.[62]

Up to this point, all amine-based PCC processes have been based on the monoethanolamine (MEA) process, with the exception of KM CDR Process which involves the use of other amines, not only MEA and reduces steam consumption, circulation rates and the consumption of chemicals in comparison with MEA-based processes.[63]

7.6.4.2 Scale-up

For significant cost reductions in CCS, the capacity should be increased in order to achieve economies of scale.[53] Any scale-up plans will require a steep learning curve. Therefore, to achieve large-scale applications of CCS, securing reliability is essential and appropriate criteria should be established in order to satisfy its evaluation. It is important to acknowledge that key component technologies of complete PCC plant have been deployed at scales large enough to meaningfully inform discussions about CCS deployment on large commercial fossil-fired power plants.[63]

a) Facilities that capture and separate CO_2 from high-pressure gas for natural gas processing include; Salah Natural Gas Production Facility (Algeria), Sleipner West Field (North Sea, Norway) and Snohvit LNG Project (Barents Sea, Norway). All of which have large-capacity facilities producing a few thousand tonnes of CO_2 per day. The CO_2 capture process has also been applied to large-scale fertilizer plants. The process technologies used to capture CO_2 have had a good track record in the gas processing, chemical and petroleum industries for more than 50 years.[64] The regenerator designs of above application are virtually identical to the PCC plant.

b) In contrast, PCC process targeting the flue gas requires treatment of a large amount of gas close to atmospheric pressure. Flue Gas Desulfurization (FGD) is performed in many large-scale plants currently in operation. This is particularly common with the packing layer inside the absorber with the application of scale prevention technologies and is most similar to PCC in that it treats a very large amount of gas at atmospheric pressure.[67] In general, the critical aspects of scale-up relate to the impact of surface/volume and height/diameter ratios on flow patterns, gas/liquid dispersion and heat transfer.[51]

c) In addition, large-scale heat exchangers and pressure vessels have been deployed at general chemical plants and their performance reliability has been confirmed. CO_2 compressors are installed downstream of natural gas processing facilities, mentioned above, and are also deployed on a large-scale basis in ammonia plants and a coal gasification plant.[65][66]

Since there are no commercial CCS plants yet, the integrated function of large-scale components in the manner required for large-scale CO_2 reduction has no references. Nevertheless, common scale-up experiences indicate that large-scale PCC plants can be designed, built and operated in the required manner.

7.6.4.3 Parameters relating to flue gas composition and process design

Although the capital cost reductions, solvent degradation, solvent volatility and other such parameters are secondary to the prime issue of reduction in parasitic load on the host power plant imposed by the PCC process itself,[68] the control of degradation and corrosion has in fact been an important aspect in the development of absorption processes over the past few decades.[56] Some degradations and corrosion are attributed to the processes themselves and are hard to distinguish, presenting issues for advancing large-scale deployment. The following are the main issues commonly reported.

7.6.4.3.1 Information required for reliability assessment

a) Foaming

Foaming in solvent systems may cause system malfunctions by the generation of flooding that leads to an off spec product, lost production and solvent losses. Therefore, a better management system of solvent properties is necessary.

b) Prevention of corrosion of materials and degradation of solvents

Better management of corrosion issues for PCC technologies to reduce solvent degradation and to optimize absorber feed gas composition, which reduces concentration of nitrogen oxide and sulfur dioxide in flue gas as much as possible, is required as with item d) below.[69]

c) Fouling in the process equipment

Efficiency decreases due to fouling of heat exchangers, etc. Filters and other counter-measures may be required to address soot in absorbents.

d) Impurities in the flue gas

A wide variety of impurities contained in the flue gas, especially from coal-fired plants, may affect reliability and the cost of the PCC process depending on their concentrations and types. Some impurities require a long-term assessment for their impact. For this reason, a long-term operability and reliability test is useful to demonstrate the efficiency of the process and to confirm the effectiveness of the countermeasures which are commercially viable.

7.6.4.3.2 Operability (load following operation)

Some reports show that control (operability) issues may have a significant impact on reliability on this kind of plant and particular attention need to be paid to the load following performance of the plant.

CO_2 capture systems, hosted by other non-power plant, are generally based on a constant load operation and the optimum load values proposed for economic performance. However, PCC plants will need to be able to withstand load changes on demand and operate flexibly following the variability of electricity demand[70] and to fulfil the electric grid reliability requirements[71] due to the prime issue of considerable parasitic load on the host power plant imposed by the PCC process itself.[68] Therefore, it is necessary to validate the control system logic and reliability to ensure load shifting[72] so as to prevent the CO_2 capture system from having a negative impact on the power plant.

7.6.4.3.3 Information required for reliability assessment

While many bench-scale and pilot-scale tests have been performed, it is difficult to expect technology suppliers to disclose information on their technologies. Then, dedicated R&D efforts supported by governments and industry, sharing of experiential learning and research efforts can facilitate improvements in reliability.[53] However, since no large-scale commercial systems are available at present, it is necessary to specify data that will be used as the basis of reliability evaluation, examples listed below.

a) Clear record of operating conditions and performance including the flue gas source, presence of impurities, operating duration and processes deployed.

b) Clearly identified troubles, its causes and countermeasures, such as any additional equipment needed to maintain the solution quality as a result of the formation of degradation products, corrosion products and at the presence of particles [56] to avoid operational problems.

c) Data on long-term operation including the operational load, the operational conditions and the load following performance. Due to the lack of experience on coal-fired flue gas on a commercial scale, the operational data collected during this demonstration project can be utilized to design and develop the process on a full scale.[62]

d) Performance and reliability of CO_2 compressor system.

7.7 Management system

7.7.1 Management system between capture plant and emission source

For each PCC, an Environmental Health and Safety (EHS) aspect identification and evaluation is recommended to be prepared. EHS document management is pursuant to ISO 9000 and many of those system components comply with international management system requirements such as ISO 14001 and OHSAS 18001 or regional emission regulations (air pollution prevention, water pollution prevention, waste treatment, etc.). Key elements of EHS Management system (EHSMS) are the “check” of performance; furthermore, at the same time it is preferred to meet ISO 14000, OHSAS 18000 and the corresponding sustainability specifications/standards. For all the EHS aspects, the legal requirements, risks and operational mitigation measures have to be considered. For all EHS aspects, monitoring plans need to be developed. Records also need to be kept.

The following are examples for key elements of EHS management system.

- EHS aspects
- Environmental aspects:
  - Accidents/incidents with environmental impacts
    - For all systems possible accidents to be identified
    - Special focus on compressor system (gas leak)
  - Consumption of energy — primary/secondary energy
    - Inventory of energy consumption to be established (if possible energy management to be applied)
    - Insulation to be optimized
  - Consumption of resources
    - Optimization of fuel input (plant efficiency)
    - Consumption of absorbents to be minimized
    - Optimizing consumables
    - Optimized layout
  - Usage of water (fresh/waste water)
    - Optimizing cooling water demand
  - Use of land
    - Optimization of plant footprint
  - Disposal/waste management
    - Optimization of absorbent usage
  - Emissions to air
    - Amines and resulting reaction products

    - Reduction of pollutants NO_x, SO_x, PM, NH_3
  - Hazardous waste disposal
    - Sludge from reclaimer, discharged absorbent
  - Noise emissions
    - Noise concept
  - Soil contamination
    - Delivery and storage of chemicals
    - Leaks scenario
    - Spills from accidents (water from firefighting, etc.)
- Health and Safety hazards aspects:
  - Air quality, e.g. dust, air conditioning, inadequate ventilation
    - Absorber/desorber (regenerator) venting
  - Gas leak hazard
    - Detection of gas leaks (e.g. CO_2)
    - Selection of materials and equipment
  - Hazardous substances, e.g. carcinogens
    - Amines exposure in work areas
    - Insulation materials during construction
  - Plant and equipment hazard
    - Spills and accidents — Pressure directive
  - Working with or in proximity to hazardous materials (Haz Com)
    - Sludge from reclaimer
    - Feed of amines
    - Laboratory
    - HAZOP, PSM review or equivalent safety and operability hazard review

7.7.2 Operational management

To ensure a proper management of the PCC plant within the CCS value chain, the following operating conditions should be considered:

- CO_2 stream variations and start-up and shutdown (e.g. pressure/temperature level, etc.)
- Settings to be kept in regard to proper quantification and verification of CO_2 gas streams
  - Other than normal operation conditions
    - Power failure (safe operation mode)
    - Failure in DeNOx, ESP or FGD in core power plant

  - Variation in CO_2 quality (failure of absorber/desorber)

7.7.3 Relationship with other areas for CCS standardization

- Transport
  - Flow control (acceptable mass flow variations)
  - Capture plant failure
  - Transport system failure (reaction time, buffering, etc.)
- Storage
  - Flow control (acceptable mass flow variations)
  - Capture plant failure
- Quantification and verification
  - Flow recording (acceptable mass flow variations)
  - CO_2 quality recording
- Cross-cutting issues
  - Risk management
  - Life cycle assessment

7.8 Reference plants

Amine process (A)

- Econamine FG Plus[4] technology; 100 TPD of CO_2 from Kraftwerke Wilhelmshaven Power Plant of E.ON SE
- KM CDR Process technology; 500 TPD of CO_2 from Barry Power Plant of The Southern Company to supply the captured CO_2 in the Citronelle formation as part of the DOE partnership program[21]
- Hitachi Ltd.; a large mobile pilot plant (5 MW_{th}) in Europe
- Toshiba Corporation; Mikawa PCC Pilot Plant of 10 TPD of CO_2 from Sigma Power Ariake Co., Ltd. Mikawa Power Plant
- Shell Cansolv Technology; 50 TPD of CO_2 from a slipstream at RWE npower Aberthaw PC plant in Wales[21]
- A mobile amine pilot facility of Just Catch[5] technology which completed its testing at the National Carbon Capture Center in Wilsonville, Alabama, using coal-derived flue gas[21]
- Shell Cansolv Technology; 1 MTPY of CO_2 from coal-fired power plant, Saskatchewan Power Corporation Boundary Dam (BDPS) integrated CCS project[78]
- The CO_2 Technology Centre Mongstad with an amine plant and a CAP plant from two CO_2 sources: flue gas from Combined Heat and Power (CHP) Plant with an annual capacity of 22 000 tonnes to 25 000 tonnes of CO_2, as well as off gases from a Residue Catalytic Cracker (RCC) from the nearby

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[4] Econamine FG Plus is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

[5] Just Catch is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

Mongstad Petroleum Refinery with an annual capacity of 74 000 to 82 000 tonnes of CO_2, operating since 2012[79][80]

Chilled Ammonia Plants

- 40 TPD CAP plant at We Energies Pleasant Prairie Power Plant on PRB Coal (7 700 operating hours)[74]
- 40 TPD CAP plant at E.ON SE Karlshamn Power Plant on Oil (2 000 operating hours)[48]
- 315 TPD CAP plant at AEP Mountaineer Power Plant on Bituminous Coal (7 800 operating hours)[75]
- 200 TPD CAP plant at Technology Centre Mongstad (TCM) on Residual Cat Cracker Flue Gas (4 500 operating hours)[76][77]
- 50 TPD CAP plant at Technology Centre Mongstad (TCM) on Natural Gas Turbine from Combined Heat and Power Plant (CHP) (1 500 operating hours)[76][77]

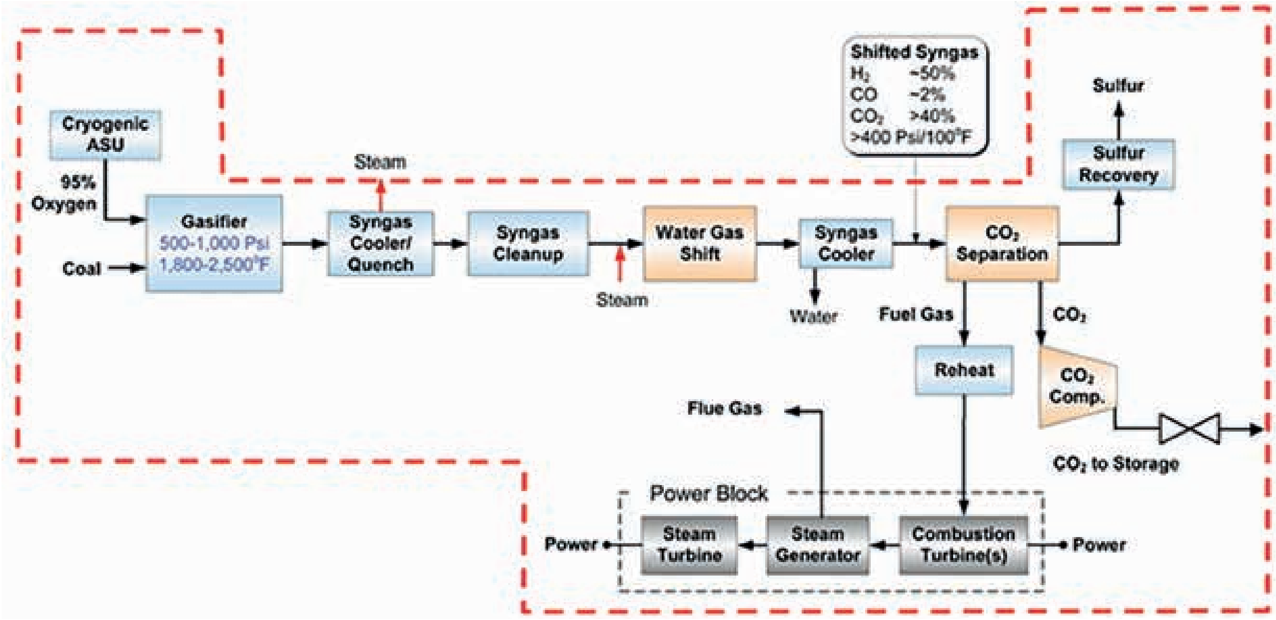
Amino acid salts

In August 2009, Siemens began operation of a 1-MWe equivalent pilot unit at E.ON SE Staudinger 5 PC unit near Hanau, Germany.[21]

8 Pre-combustion capture in power industry

8.1 General

Pre-combustion capture, one of the CO_2 capture methods, is deployed for power generation based on an Integrated Coal Gasification Combined Cycle (IGCC) power system. It is different from the capture system that would be deployed on conventional coal-fired (or fueled by other solid hydrocarbons) power-generating units.[81][82][83][84][85] Figure 16 shows a schematic system diagram.



NOTE See Reference [82].

Figure 16 — Schematic of pre-combustion capture of CO_2 capture in IGCC

In IGCC, a gasifier converts coal, biomass, petroleum coke, or natural gas into a syngas composed mainly of carbon monoxide (CO) and hydrogen (H_2). This system can allow for a blend of power production and production of either chemicals or fuels. IGCC's are typically divided into three different types of gasifiers: fixed bed, fluidized bed, and entrained flow, and their air-blown and oxygen-blown varieties.

[99] Only a small number of gasifier designs have reached the stage where they are viable candidates for large-scale power production and hence candidates for pre-combustion carbon dioxide capture systems.

In an IGCC plant without a CO_2 capture system, once the syngas has been produced, it is then passed through an acid gas removal unit to remove impurities such as sulfur before the clean syngas is sent to gas turbines. CO_2 is generated by the combustion of CO, just as it is in a coal-fired power generation plant.

In contrast, an IGCC plant equipped with a pre-combustion CO_2 capture system creates syngas then converts CO that has been formed into CO_2 and H_2 through a shift reaction. The shift occurs by injecting water vapour (H_2O) into the syngas in the shift reactor. This process essentially allows all the energy in the coal to be transferred to the H_2, while all the carbon in the coal is in the form of CO_2, where it can be removed through a CO_2 capture system. The H_2-rich syngas then is supplied to the gas turbines for combustion.

There are two types of shift reactions: the sour shift reaction, which supplies the syngas to the reactor without removing H_2S or COS, and the sweet shift reaction that removes H_2S before the gas is forwarded to the reactor. In most cases, the sour shift is preferred, because it better utilizes the steam in the syngas. If sulfur is removed prior to the shift, some of that steam will be condensed out. The CO_2 capture method is generally through physical absorption.

Compared to post-combustion, the advantages of the pre-combustion include the following: only a small volume of gas needs to be treated for CO_2 capture because the processing occurs before dilution with combustion air and the high-pressure of target gas reduces its volume flow rate. Hence, compared with post-combustion capture processes used for conventional coal-fired power plants, pre-combustion capture keeps the CO_2 capture system compact.[82] However, the shift reaction reduces the heating value of the syngas, and an IGCC power plant has higher capital costs than a conventional pulverized coal power plant.

8.2 System boundary

The system boundary is drawn around the entire IGCC plant with capture. This is required because adding CCS to an IGCC affects every unit operation in the plant. There are three major sections that need to be added:[83]

a) Shift (typically a sour shift of either two or three reaction stages);

b) Acid gas removal (typically a two-stage unit that removes both CO_2 and H_2S);

c) CO_2 compression and dehydration.

The design considerations that impact the rest of the IGCC power plant include:

- The type of syngas cooler/quench. For no CCS, a radiant quench design is typical. However, with CCS, a direct quench is preferred. The water added in the quench can then be utilized in the shift reactors. This is the most efficient way to generate steam for the shift reaction, but only makes sense if doing a sour shift.
- Turbine design. An IGCC without CCS has a syngas containing CO plus H_2. With CCS, the syngas is primarily H_2. The turbine design for each of these cases is very different in an Oxygen-blown gasifier. For the CCS case, N_2 from the ASU is generally required to mix with the H_2-rich syngas prior to combustion.
- The relative sizing of the ASU, gasifier, and turbine changes by adding CCS. The CCS process produces a lower heating value syngas than the IGCC without CCS. Therefore, either the ASU/gasifier needs to be oversized or the turbine needs to be derated.
- Since the syngas heating value is lower in the CCS case, piping and equipment between the shift reaction and the acid gas removal sections need greater capacity.

8.3 Technologies, equipment and processes

8.3.1 Establishment of CO_2 capture rate

The amount of CO_2 captured from the syngas is largely determined by the extent of carbon monoxide conversion in the shift reactors and the carbon dioxide removal efficiency of the absorber of the AGR.[83] Theoretically, the capture rate could be controlled by modifying the extent of shift reaction, bypassing some of the syngas around the shift reactor, and/or modifying the removal efficiency of the AGR.

It is now expected that the AGR would be operated the same regardless of desired capture rate. A typical two-stage Selexol6) will remove up to 95 % of the carbon dioxide in the syngas although capture greater than 97 % is possible. Bypassing some of the syngas around the shift reactors would likely necessitate a COS hydrolyzer for that bypass stream, and the practicality of this option is not yet determined. This leaves modification of the extent of shift reaction as the primary method of achieving a specific capture rate.

For most gasifier designs, conversion of about 96 % of the carbon monoxide is achieved by using two stages of shift. The installation of only a single stage of shift will result in a moderate conversion, and the resulting carbon dioxide can then be removed in the AGR. Some of the carbons are skimmed off in the gasifier itself, because carbon dioxide is generated in the gasifier prior to the conversion in a shift reactor. This is referred to as “skimming.” The overall CO_2 capture achieved depends on the gasifier, shift specifications, and AGR. Skimming may result in capture up to 25 %, while 50 % to 80 % capture may be achieved with only a single stage shift. While installing discrete numbers of pieces of equipment will achieve distinct capture rates, the capture rate can be further tailored by controlling the extent of the shift reaction through the steam/CO ratio and catalyst type variation.

8.3.2 CO_2 capture process

This subclause will focus on the new process components required for CCS in pre-combustion capture, namely the water-gas shift and the acid gas removal. While CO_2 compression is fairly standard and discussed in Clause 7, there are several unique aspects of CO_2 compression in pre-combustion applications: the CO_2 is generally available at elevated pressure since the syngas stream from which it is removed is at elevated pressure; and the CO_2 is often available at more than one pressure level due to the fact that physical absorption-based solvents are often regenerated through successive flash steps at different pressures.

8.3.2.1 Water-gas shift process

See References [86], [87], [88] and [89].

8.3.2.1.1 Sour shift

The sour shift reaction is a process in which syngas is supplied directly to the reactor to convert CO into CO_2. Figure 17 shows sour shift process. In the reactor, steam is directly added to the syngas containing such components as H_2S and COS, and then the syngas is converted into CO_2 by a sulfurized catalyst using the WGS reaction ($CO + H_2O \Rightarrow CO_2 + H_2$, $COS + H_2O \Rightarrow H_2S + CO_2$).

Sour shift is normally performed within the temperature range of 200 °C to 480 °C. Using a cobalt molybdenum catalyst, sour shift is normally located after the water scrubber. The syngas is saturated with water at a temperature between 230 °C and 260 °C, depending on the gasification conditions and the amount of high-temperature heat recovery. To avoid damage to the shift catalyst by water, the syngas in the scrubber is reheated from the saturation temperature to a higher temperature by 15 °C to 30 °C.

One of the benefits of the sour shift reaction is that it converts COS and other organic sulfur compounds into H_2S, making downstream sulfur removal easier. As a result the WGS-treated syngas does not require a separate COS hydrolysis process and allows for a simplified equipment configuration. In

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6) Selexol is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

addition, sour shift also reduces energy requirement. These factors make sour shift a superior process for an IGCC plant with CO_2 capture.

Past experience in combining sour shift and physical absorption has confirmed that reducing the amount of steam supply has the potential of significantly improving power generation efficiency. But an excessive reduction in steam supply may cause secondary reactions in addition to the CO shift reaction and lead to a decrease in catalyst robustness due to carbon deposits. Thus, it is important to identify optimal operating conditions.

After passing through the sour shift reactor, CO_2-rich gas is sent to the H_2S removal equipment and then to the CO_2 absorber to separate and recover high-purity CO_2.

To remove H_2S and CO_2 by the sour shift process, it is common to use physical absorption (see 8.3.2.2.1), in which the degree of CO_2 saturation is changed using a single type of absorbent to allow for a selective capture of H_2S and CO_2, or the Methyl diethanolamine (MDEA) process.

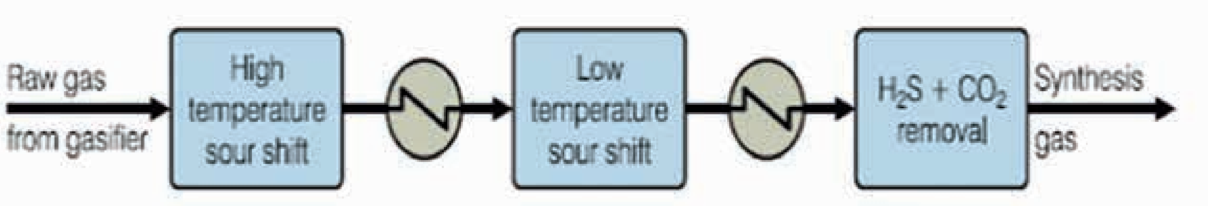

Figure 17 — Schematic of sour shift and acid gas removal

8.3.2.1.2 Sweet shift

In the sweet shift reaction, sulfur compounds such as H_2S and COS are removed from syngas in advance, then the cleaned gas will be supplied to the WGS reactor. Figure 18 shows sweet shift process.

In sweet shift, the shift reaction is performed after the syngas is cooled and sent to the H_2S removal equipment. During this process, all the moisture gained in the water scrubber is condensed. For this reason, all the steam required for the shift reaction in the sweet shift reactor should be injected and heated. In the sour shift process, in contrast, the moisture gained in the water scrubber can be used for the shift reaction, leading to a reduction in steam consumption. From this perspective the sour shift process is considered to be a more favourable process.

In the sweet shift process, the H_2S and CO_2 removal systems are respectively located before and after the shift reactor. Physical absorption and chemical absorption, to be discussed in 8.3.2.2, are commonly used as the removal method.

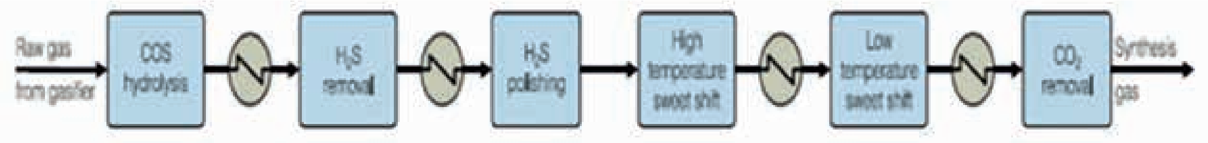

Figure 18 — Schematic of acid gas removal and sweet shift

8.3.2.2 Acid gas removal

8.3.2.2.1 Physical absorption

In physical absorption,[90] CO_2 (and H_2S) are absorbed into an absorbent at high pressure. Desorption is achieved by reducing the pressure (i.e. pressure-swing). Physical absorption is relatively easy to scale, to apply to a large-capacity operation making it suitable for a large-scale processing of high-pressure gas. The energy requirement for physical absorption is much less than that for chemical absorption used in post-combustion capture.

Physical absorption, as its name indicates, physically absorbs CO_2 into an absorbent. According to Henry's Law, at equilibrium and a given temperature, the amount of solute dissolved is directly proportional to its partial pressure in the gas. Since CO_2 has a high partial pressure in the syngas, physical absorption is ideally suited to capture it.

After a sour shift, the physical absorbent process can be arranged in two stages. In the first stage, the H_2S is preferentially removed and in the second stage, the CO_2 is removed. Examples of absorbents used for physical absorption include methanol and Dimethyl ethers of Polyethylene glycol (DEPG). Leading physical absorption processes are listed in Annex C. The Weyburn project, in which CO_2 captured from gasified coal is used for EOR, uses Rectisol®7) process.

8.3.2.2.2 Chemical absorption

In chemical absorption,[91][92] CO_2 is absorbed into a solvent through a chemical reaction and is desorbed by heating the solvent. One of its advantages is that it is easy to scale so as to apply a large-capacity operation. It is also well-suited to the separation of low-concentration gas components and a large-scale treatment of low-pressure and low-concentration gases. Shortcomings include a large amount of energy required and the risk that some of the chemical substances contained in the absorbent may be released into the environment.

Solvents used for the chemical absorption of CO_2 from high pressure syngas streams in pre-combustion capture applications include alkanolamine solvents such as MDEA and hot potassium carbonate solvents. Because chemical reactions are used for chemical absorbents, this method allows a highly selective separation of CO_2 while absorbing less of hydrocarbons such as methane. It also absorbs CO_2 well even under a low partial pressure. Leading chemical absorption processes are described in Annex A.

8.3.2.2.3 Other CO_2 capture technologies

Membrane separation is a technology that takes advantage of the faster permeability rate of CO_2 through a polymeric or another membrane to separate and capture CO_2. In pressure swing adsorption (PSA), CO_2 is adsorbed into an adsorbent under a high pressure and desorbed under a low pressure to capture CO_2 from the process gas. At present, neither technology has a large-scale use in CO_2 capture. However, development for large-scale applications is underway to take advantage of their low energy requirement. Other potential improvements to pre-combustion capture systems are at various stages of technical readiness although none could be considered commercial. A number of alternative concepts involving solvents, sorbents, and advanced membrane-based processes are in the R&D pipeline. Table 7 shows the comparison of Pre-combustion capture commercial technologies.

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7) Rectisol is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

Table 7 — Pre-combustion capture technologies

Technology	Process	Absorbent	Absorption temperature	CO_2 content[a]	Regeneration method
Physical absorption	Rectisol	Methanol	−20 °C to −70 °C	ppm range	flash and/or stripping
	Selexol	Polyethyleneglycol dimethylether	ambient temperature	ppm range	flash and/or stripping
Chemical absorption	MDEA	MDEA +additives	35 °C to 65 °C	100 ppm range	steam
	Benfield[b]	K_2CO_3 +additives	70 °C to 120 °C	ppm range	steam
Chemical and physical combined	Sulfinol[c]	Sulfolane +MDEA	40 °C to 90 °C	50 ppm range	flash and/or steam

[a] Minimum CO_2 concentration in the treated syn gas.

[b] Benfield is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

[c] Sulfinol is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

8.4 Carbon dioxide streams, gas streams and emissions, process and waste products

This subclause will discuss gas streams and other emissions from CO_2 capture systems. It also addresses liquid and solid (physical) wastes including waste/by-product absorbents.

Three primary types of gas streams emitted from CO_2 capture systems are described below (see Figure 19).

a) CO_2 streams — CO_2 captured by the CO_2 capture system. To be transported for storage or other end use.

b) Synthetic gas streams — Synthetic gas after CO_2 has been separated and captured. Mostly used for power generation.

c) Waste — Waste produced by the CO_2 capture system.

The list of potential wastes includes solids, liquids, slurries/sludges, off-gases, excess CO_2, spent absorbents, etc.

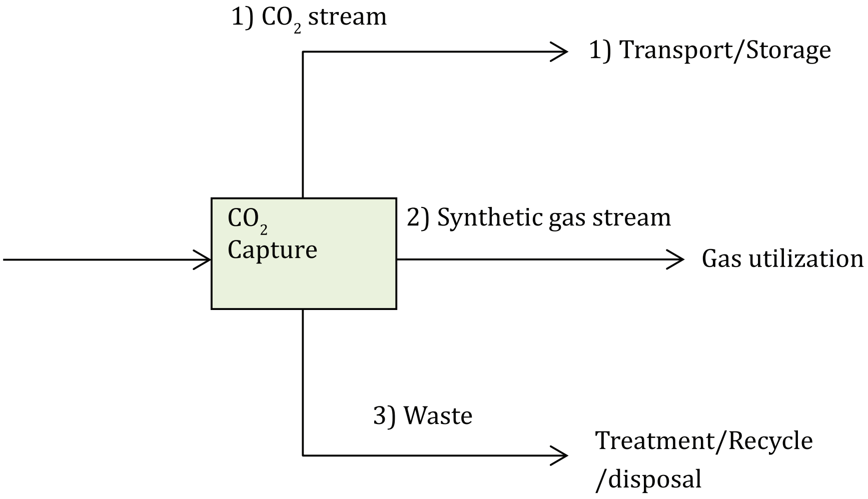


Figure 19 — Schematic of CO_2 stream flows

8.4.1 CO_2 streams

CO_2 streams are defined as gas streams captured by the CO_2 capture process with CO_2 as the main component.

The purity, allowable value of impurities, temperature, and pressure of CO_2 streams are discussed below.

8.4.1.1 Purity of CO_2 streams

The purity of the product CO_2 stream is dependent on the end use: geologic storage, enhanced oil recovery, food-grade applications, feedstock for chemical production, or other; as well as pipeline transportation limitations, if applicable. Generally, high purity CO_2 streams are required. In the case of CO_2 sequestration, this requirement is largely defined by transport (i.e. pipeline) requirements and injection well requirements/standards. When CO_2 capture is performed through chemical absorption using aqueous solutions, CO_2 is selectively absorbed by chemical reaction and dissolves very little of other gases such as nitrogen and CO. In contrast, physical absorption is impacted by the partial pressures of gas components. N_2, H_2 and other components in CO_2 may be absorbed depending on their partial pressures and their affinity to the absorbent. Therefore, stringent regulations and permit requirements on impurity values may impact the design of the CO_2 capture process (such as adding a purification step), increasing the energy required for CO_2 capture.

There are two interrelated issues:

a) the minimum CO_2 purity required to maintain single phase flow at the conditions of interest;

b) the allowable concentration of specific impurities.

Item b) is particularly difficult because the allowable concentrations vary depending on the combination of impurities present. Guidance on purity may be determined by the requirements identified on the transportation or storage side and by permit/regulation. The purity level of CO_2 in the Weyburn project, where CO_2 is used for EOR, is set at 96 mol% or above.[92]

8.4.1.2 Allowable amount of impurities in CO_2 streams

In the context of CCS system and equipment design, the impurity content affects not only the design of CO_2 transportation and storage systems but also the selection and design of CO_2 capture systems. It is expected that, in many countries, the limits on impurities will be set by the requirements in the injection permit.

The presence of impurities affects the materials of construction for equipment, pipelines, and associated fittings as well as the motive power required for the final compression of CO_2. Impurities also change the physical properties of CO_2 for transportation. Allowable values need to be established for toxic gases such as H_2S and CO as well as moisture to prevent safety and corrosion problems, and a system design should conform to such values.

CO_2 from the pre-combustion catalyst cleaning process normally contains 1 % to 2 % of H_2 and CO and a very small amount of H_2S and other sulfur compounds.[93] An IGCC power generation plant with pre-combustion capture can be designed to remove mixtures consisting of CO_2 vapour and sulfur compounds, so as to reduce cost and avoid the production of solid sulfur[93] in the pipeline and/or injection wells.

8.4.1.2.1 Impact of H_2O

Moisture, one of the impurities, dissolves CO_2 and other acid gases and produces the associated acid, causing corrosion on the inner surface of pipes. At a low temperature, water and CO_2 generate hydrate and cause blockages in valves and scaling in pipes. For this reason captured CO_2 normally requires dehydration to prevent the production of free water in pipelines. Water knockout and dehydration during compression is standard. In chemical absorption using aqueous solutions in particular, captured CO_2 contains moisture saturated at the temperature of the stripper outlet and in some cases requires dehydration using glycol during the CO_2 compression process. Other options besides glycol, e.g. molecular sieves are available for dehydration.

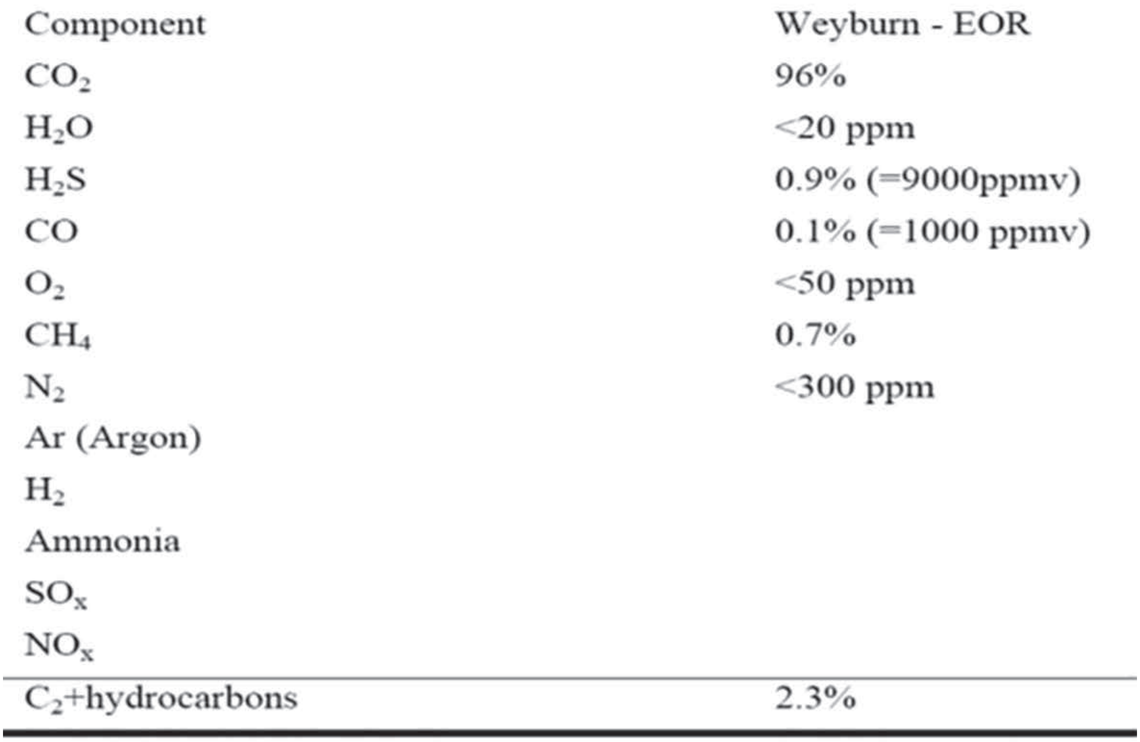
8.4.1.2.2 Impact of toxic gas

The potential range of contaminants in the CO_2 product stream is impacted by the CO_2 source gas and the particular capture technology. In pre-combustion applications, likely gas contaminants include CO, H_2S, NH_3, CH_4, H_2, COS, HCl, Hg, and HCN. The limits for contaminants will be determined by the minimum allowed for transport, end use, and/or permit requirements. The literature is replete with studies that have examined various aspects of the CO_2 capture and sequestration supply train, notably including contaminant limits. The US Department of Energy's National Energy Technology Laboratory compiled a summary of many such studies and published the results in the document "Quality Guidelines for Energy System Studies: CO_2 Impurity Design Parameters." (http://www.netl.doe.gov/File%20Library/Research/Energy%20Analysis/Publications/QGESS_CO2Purity_Rev3_20130927_1.pdf) While providing an insightful summary of impurity considerations, ultimately each application is unique in terms of the combination of contaminants, moisture content, and end use. Thus, actual limits will either be set on a case-by-case basis, or through overarching regulations or permit requirements.

Another factor that can impact impurity limits is potential liability due to accidental release of the CO_2 stream. Risk management practices may dictate limits that are lower than required due to physical process factors such as corrosion. Such limits will be project-specific and project-developer-specific, and as such cannot be addressed at a global level.

Supply of CO_2 to the Weyburn oil fields for enhanced oil recovery is an active project. The typical CO_2 composition for that project is shown in Table 8. This provides an example of a project-specific application, but as noted above, each project is expected to have unique aspects that will impact the allowable impurity levels (see Reference [93]).

Table 8 — Typical composition of the gas of the Weyburn EOR project[93]



Component	Weyburn - EOR
CO_2	96%
H_2O	<20 ppm
H_2S	0.9% (=9000ppmv)
CO	0.1% (=1000 ppmv)
O_2	<50 ppm
CH_4	0.7%
N_2	<300 ppm
Ar (Argon)	
H_2	
Ammonia	
SO_x	
NO_x	
C_2+hydrocarbons	2.3%

8.4.1.3 Temperature and pressure of CO_2 streams

The temperature and pressure of the CO_2 stream are prescribed by the transportation and storage conditions, and generally CO_2 streams are kept under supercritical conditions. The critical point of pure CO_2 is 31,1 °C and 73 Bar (see Figure 20).

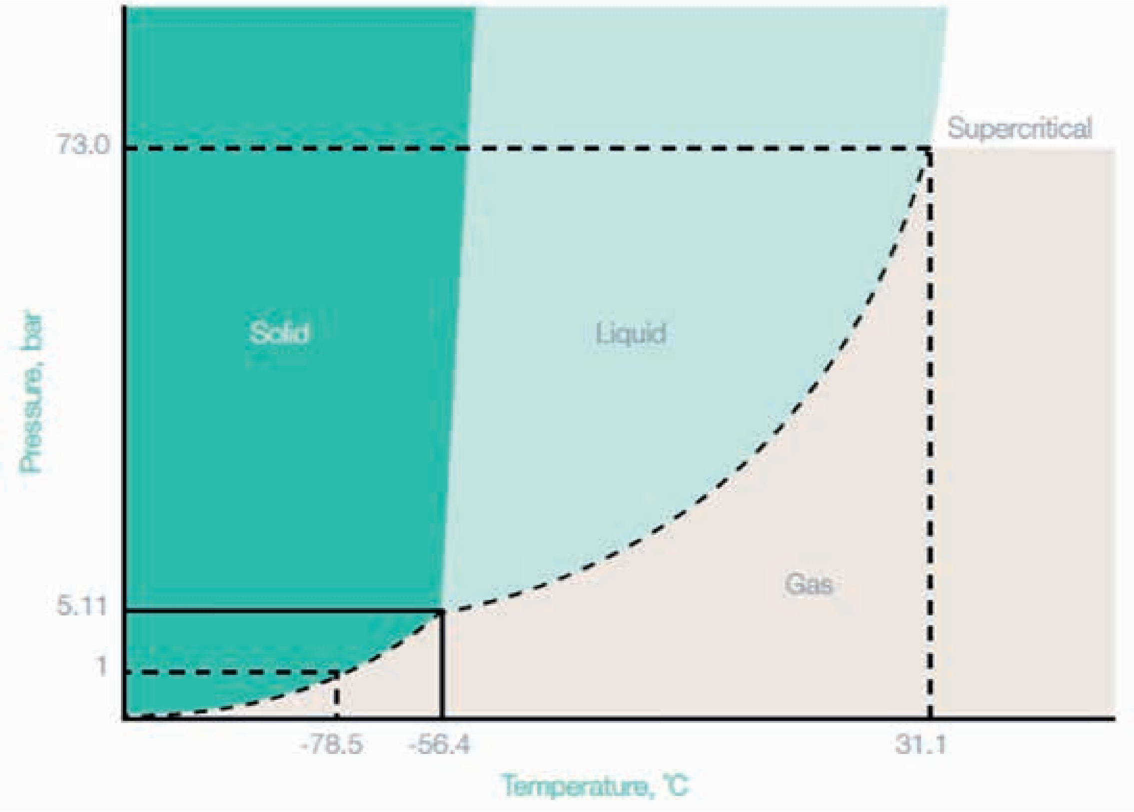


Figure 20 — Phase diagram of CO_2

In a two-component mixture consisting of CO_2 and a contaminant gas, the critical pressure generally increases while the critical temperature decreases as the concentration of the contaminant gas rises, with the exceptions of H_2S,SO_2, and NO_2, whose critical temperature and pressure both rise. It is important to keep in mind that in the CO_2-contaminant mixture, the physical properties of the gas mixture change significantly as the amount of the contaminant increases.

8.4.2 Synthetic gas streams

Synthetic gas considered within this subclause is mainly used for power generation (primarily combined cycle generation). The degree of purity, allowable levels of impurities, temperature, and pressures of synthetic gas streams are set by the facilities where the synthetic gas streams are used. For example, the allowable levels of impurities in a power generation plant are set by the corrosive elements in gas turbines and environmental regulations. In the case of chemical synthesis facilities, the values are similarly set by the presence of catalyst poisoning elements.

The pressure requirement in an IGCC application is set by the combustion turbine specification at the fuel valve. The gasifier should be operated at sufficiently high pressure so that after accounting for the pressure drop through all piping, fittings, and process equipment, including the CO_2 capture process, the fuel valve requirement is met.

There is no fixed synthetic gas temperature requirement. From an efficiency perspective, maximizing the temperature is desirable since that increases the overall efficiency of the combustion turbine. However, conventional mercury removal technology (carbon beds) and many pre-combustion CO_2

capture technologies require low syngas temperatures to be effective. Warm gas clean up processes are being developed, but are not yet commercial.

8.4.3 Waste products

A commercial, solvent-based pre-combustion capture technology like Selexol generally produces both a liquid and solid waste stream for treatment and/or disposal. The purge water stream from the reflux loop in the condenser generally contains dissolved H_2S and CO_2 as well as trace amounts of other contaminants that may have been present in the capture system feed stream. This waste water stream should be treated prior to discharge according to project permit levels. Metal carbonyls, when soluble in the CO_2 capture solvent, are converted to sulfides and removed in the lean solvent filters.

Other technologies, like Rectisol, produce only a liquid waste stream that contains primarily small amounts of the solvent (methanol in the case of Rectisol). Absorbed higher hydrocarbons can be recovered in an extraction stage if necessary. The waste water stream should be treated prior to discharge in compliance with the rules and regulations of each country and/or region (for example, in the US, state-by-state). Additionally, a sour gas stream as output from Selexol/Rectisol should be treated.

Capture technologies like membranes and solid sorbents that are still in the development stage don't have well-defined information on details like waste products. Factors like permeance and selectivity will determine impurities in the CO_2 product gas using membranes, and sorbent attrition properties will impact potential solid waste products from sorbent-based processes.

Related processes like water gas shift utilize a catalyst material that deactivates over time and should periodically be replaced. The spent catalyst should be disposed off according to local guidelines.

8.5 Evaluation procedure for capture performance

8.5.1 Definition of greenhouse gas (GHG) capture rate

Two definitions of GHG capture rate are provided here. The broad definition is based on a power generation system, which is one of the GHG emission source, while the narrow definition is dedicated to indivudual CO_2 capture systems such as Acid Gas Removal (AGR) system.

8.5.1.1 Broad definition

For the purpose of developing measures against global warming, the GHG capture rate should be defined as the amount of GHG captured in moles per the mole flowrate of GHG-generating substances. GHG-generating substances are those substances that turn into CO_2 following (or starting from) a combustion process, such as CO and COS. In other words, the mass of GHG-generating substances can be understood as the mass of carbon in the feed.

From the above, the GHG capture rate in IGCC is defined as the flow rate of GHG (e.g. CO_2, CH_4) captured in moles per the mass flow rate of carbon in the feed gas and the supplementary fuel in moles (see Figure 21).

GHG capture rate (%)

= C: captured GHG(mol)/total carbon(mol) of A: fuel and B: supplement fuel

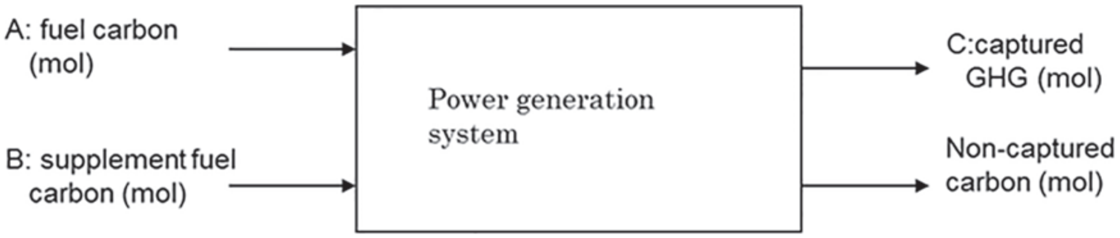


Figure 21 — Schematic of CO_2 capture — Broad definition

8.5.1.2 Narrow definition

The CO_2 capture system receives gas from the upstream, removes CO_2 within and send it to the downstream. The CO_2 capture rate is expressed as follows (see Figure 22).

CO_2 Capture Rate = (CO_2 in Captured CO_2 stream)/(CO_2 in Feed Gas)

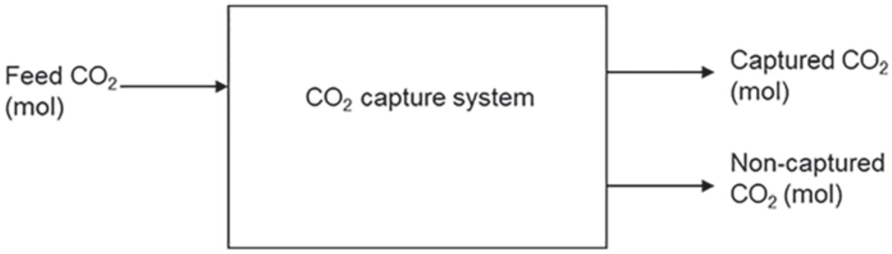


Figure 22 — Schematic of CO_2 capture — Narrow definition

8.5.2 Evaluation procedure for capture performance[96]

The premises of comparison are defined as follows:

- Comparisons of economic performance will not be made since a wide variety of conditions of capture facilities need to be considered;
- The objective of the evaluation is to compare it against others.

8.5.2.1 Broad definition

The GHG capture performance of a power generation system is determined by the amount of GHG captured per unit of power output [t-GHG/MWh] and can be compared based on power station efficiency [LHV%]. Figure 23 shows the evaluation process.

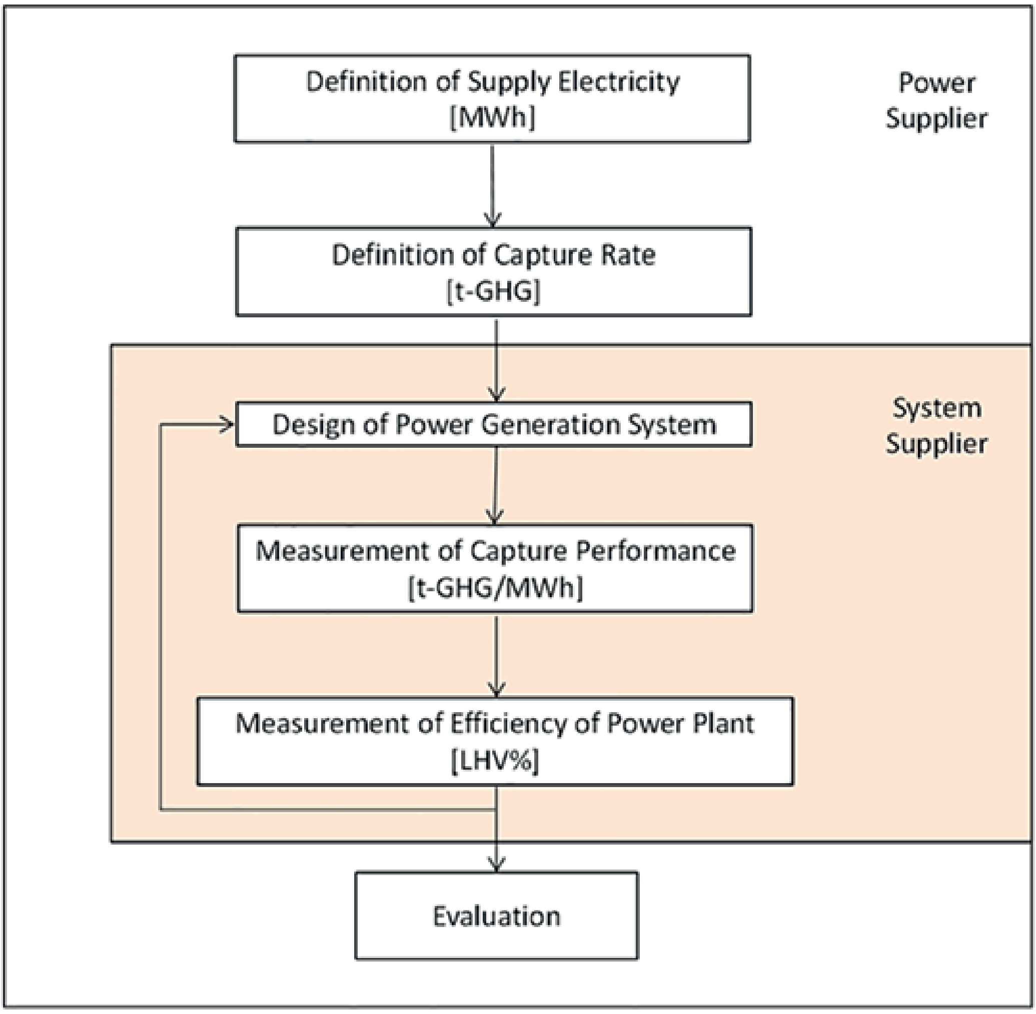


Figure 23 — Flowchart of evaluation process

The measurement of capture performance should include the operation rate and therefore should be evaluated on an annual basis.

8.5.2.2 Narrow definition

The broad definition dealing with global mass balance of GHG is an important part of GHG capture. Nonetheless, the evaluation of the particular CO_2 capture system is a crucial part to understand the performance of the technology, which is the narrow definition. Some metrics focused on process components can be understood and evaluated (e.g. absorbent loss); others may be very difficult to measure in a highly integrated system. Basically, Individual measurements should fit into a broader scheme.

Evaluation procedures for physical absorption, a common process used for pre-combustion capture, will be discussed.

8.5.2.2.1 CO_2 capture rate

See 8.5.1

8.5.2.2.2 Absorbent loss

The vapour pressure of the absorbent is a major factor contributing to absorbent loss.

It is also dependent on operating temperature and pressure. Absorbent loss occurs at the top of the absorber and the desorber. Therefore the amount of absorbent lost with the gas from the top of the towers as airborne droplets will be measured.

In case that the absorbent degradation is likely to take place, contaminated absorbent needs bleed-off and the introduction of make-up absorbent.

8.5.2.2.3 Power consumption and thermal loads[97]

The thermal loads in physical absorption vary largely depending on equipment configuration. In general, the thermal loads in physical absorption are smaller than those in chemical absorption.

Power consumption (MW_{el}) = Σ(Power consumption$_{el\ pump}$) + (Power consumption$_{el\ compressor}$) + (Power consumption$_{el\ other}$)

- The thermal loads of boilers and coolers are expressed as follows:
  - Heating load(MW_{th}) = Σ(Thermal loads$_{th\ boiler}$)
  - Cooling load(MW_{th}) = Σ(Thermal loads$_{th\ cooler}$)
- The ratios of captured CO_2 to the parameters above can be expressed as intensity.
  - Power consumption intensity(MW_{el}h/kg) = (Power consumption MW_{el})/(CO_2 capture rate kg/h)
  - Heating intensity (MW_{th}h/kg) = (Steam consumption MW_{th})/(CO_2 capture rate kg/h)
  - Cooling intensity (MW_{th}h/kg) = (Heat removal by coolant MW_{th})/(CO_2 capture rate kg/h)

Up to this point, the capture and desorption processes of CO_2, the main processes in CO_2 capture, have been discussed. When the scope of assessment is expanded to include sour shift, H_2S removal, and CO_2 pressurization, the entire process flow will be evaluated by considering the amount of steam added and heat generated by reactions, including in the calculations the corresponding power consumption and thermal loads of the additional processes.

The assessment of the characteristics of a CO_2 capture process can be made by focusing on the above-mentioned capture rate, absorbent loss, power consumption and thermal loads. However, since each process has different operating conditions, it is necessary to establish a method to normalize the state of fluids and operating conditions.

In any case, the above-mentioned elements will be used to evaluate the process characteristics of the physical absorption.

The discussion above can be expressed in a table format as shown in Table 9 and Table 10. Other items worth consideration can also be included in this table as causal parameters for the evaluation.[98]

Table 9 — CO_2 Capture Evaluation Sheet (Example)

1. CO_2 conversion process

	Unit	Case-A	Case-B	Case-C
Performance				
Conversion Rate to CO_2 from CO	—			
Input Steam/CO	—			
Steam Amount Charged	t/h			
Condition of Steam Charged	MPaG, °C			
Steam Amount Produced (through shift reaction)	t/h			
Condition of Steam Produced	MPaG, °C			

Table 9 *(continued)*

Operation State				
CO conc. in Feed Gas	mol%			
CO conc. In Treated Gas	mol%			

Table 10 — CO_2 Capture Evaluation Sheet (Example)

2. CO_2 capture process

	Unit	Case A	Case B	Case C
Performance				
CO_2 Capture Rate	t/h			
Absorbent Loss	t/h			
Steam Heat Duty	MW_{th} (@ °C)			
Coolant Cooling Duty	MW_{th} (@ °C)			
Power Requirement	MW_{el}			
Operation State				
CO_2 conc. in Feed Gas	mol%			
CO_2 conc. in Treated Gas	mol%			
CO_2 purity in recovered CO_2 rich gas	mol%			
CO_2 Loading in Rich Absorbent	mol/L			
CO_2 Loading in Lean Absorbent	mol/L			
L/G	L/Nm^3			
Pressure and Temperature in Feed gas	MPaG, °C			
Pressure and Temperature in recovered CO_2-rich gas	MPaG, °C			
Absorbent property				
Vapour Pressure	MPaA			
Viscosity	Pa·s			
CO_2 Solubility	g/L			
Normalization				

8.5.2.3 Operation and maintenance evaluations

Operation and maintenance evaluations are also crucial to minimizing GHG emissions in plant life cycle in addition to the evaluations of facility performance discussed above.

Although there is one example of quantitative indicator that has been derived from an operation availability analysis, there are no standardized quantitative evaluation systems available at present.

8.6 Safety issues

In general, facilities and equipment dedicated for the corresponding capture technology are designed and constructed in compliance with the existing and applicable international, regional and national standards such as ISO and ASME. In addition, compliances with the laws, regulations and requirements in the region or country where the plant is located, provide additional securities for safety. Those are not subject to establishing a new standard for the CO_2 capture processes in CCS.

The following can be considered as remarkable subjects when the corresponding International Standard will be discussed in the future.

8.7 Reliability issues

The necessity of reliability assessment as described in 7.6.1 should be considered for pre-combustion capture technology as well.

8.8 Management system

8.8.1 Management system between capture plant and emission source

For pre-combustion capture, an EHS evaluation may be required. EHS document management is pursuant to ISO 9000 and many of those system components complies with international management system requirement such as ISO 14001 and OHSAS 18001 or regional emission regulations (air pollution prevention, water pollution prevention, waste treatment and so on). Key elements of EHS management system (EHSMS) is the "check" of performance; furthermore, at the same time it is preferred to meet ISO 14000, OHSAS 18000 and the corresponding sustainability specifications/standards. For all the EHS aspects the legal requirements, risks and operational mitigation measures have to be considered. For all EHS aspects, monitoring plans need to be developed. Records also need to be kept.

The following are examples for key elements of EHS management system.

- EHS aspects
- Environmental aspects:
  - Accidents/incidents with environmental impacts
    - For all systems possible accidents to be identified
    - Special focus on compressor system (gas leak)
  - Consumption of energy — primary/secondary energy
    - Inventory of energy consumption to be established (if possible energy management to be applied)
    - Insulation to be optimized
  - Consumption of resources
    - Optimization fuel input (plant efficiency)
    - Use of absorbents to be minimized
    - Optimizing consumables
    - Optimized layout
  - Usage of water (fresh/waste water)
    - Optimizing cooling water demand
  - Use of land
    - Optimization of plant footprint
  - Disposal/waste management
    - Optimization of absorbent usage
  - Emissions to air
    - Amines and resulting reaction products

    - Reduction of pollutants
  - Hazardous waste disposal
    - Sludge from reclaimer, discharged absorbent
  - Noise emissions
    - Noise concept
  - Soil contamination
    - Delivery and storage of chemicals
    - Leaks scenario
    - Spills from accidents (water from firefighting, etc.)
- Health and Safety hazards aspects:
  - Air quality, e.g. dust, air conditioning, inadequate ventilation
    - Absorber/desorber venting
  - Gas leak hazard
    - Detection of gas leaks (i.e. CO_2)
    - Selection of materials and equipment
  - Hazardous substances, e.g. carcinogens
    - Amines exposure in work areas
    - Insulation materials during construction
  - Plant and equipment hazard
    - Spills and accidents — Pressure directive
  - Working with or in proximity to hazardous materials (Haz Com)
    - Sludge from reclaimer
    - Feed of amines
    - Laboratory
    - HAZOP, PHA review or equivalent safety and operability hazard review

8.8.2 Operational management

To ensure a proper management of the pre-combustion capture plant within the CCS value chain, the following operating conditions are to be considered:

CO_2 stream variations and start-up and shutdown (e.g. pressure/temperature level, etc.)

Settings to be kept in regard to proper quantification and verification of CO_2 gas streams

- Other than normal operation conditions
  - Power failure (safe operation mode)
  - Failure in core power plant

  - Variation in CO_2 quality (failure of absorber/desorber)

8.8.3 Relationship with other areas for CCS standardization

- Transport
  - Flow control (acceptable mass flow variations)
  - Capture plant failure
  - Transport system failure (reaction time, buffering, etc.)
- Storage
  - Flow control (acceptable mass flow variations)
  - Capture plant failure
- Quantification and verification
  - Flow recording (acceptable mass flow variations)
  - CO_2 quality recording
- Cross-cutting issues
  - Risk management
  - Life cycle assessment

9 Oxyfuel combustion power plant with CO_2 capture

Oxyfuel combustion is the process of burning the fuel with nearly pure oxygen instead of air. In order to control the flame temperature, some part of the flue gas is recycled back into the furnace/boiler.

While oxyfuel combustion has a variety of applications depending on its users and the fuel used, the scope of this Technical Report is limited to the application of oxyfuel combustion to coal-fired power generation with CO_2 capture.

To capture the CO_2 from a coal-fired power plant, the main purpose of using oxyfuel combustion is to generate a flue gas with very high concentration of CO_2 and water vapour; and then separate the CO_2 from the flue gas by dehydration and low temperature separation processes.

An oxyfuel combustion for coal-fired power plant with CO_2 capture can be broadly classified as Oxy-PC or Oxy-CFB. Figure 24 and Figure 25 present their respective simplified schematic flow diagrams. Oxy-PC is based on the pulverized coal combustion technology, while the Oxy-CFB is based on the circulating fluidized bed combustion technology.

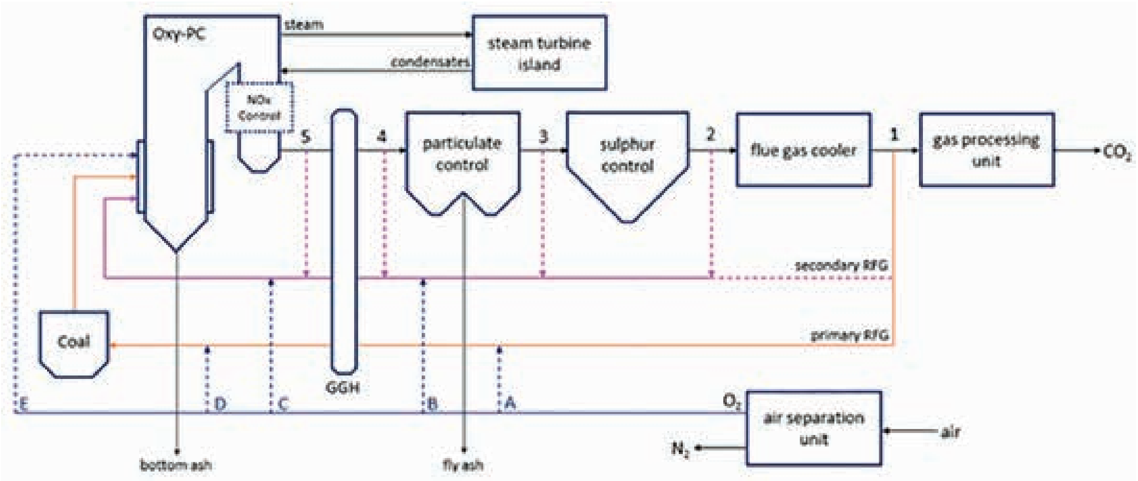


Figure 24 — Simplified schematic flow diagram of Oxy-PC coal-fired power plant with CO_2 capture

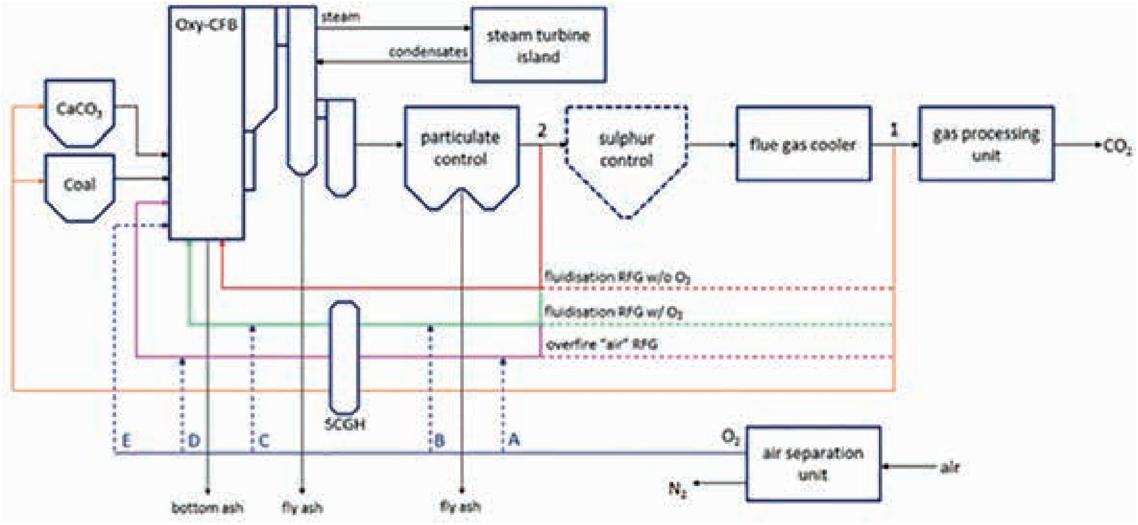


Figure 25 — Simplified schematic flow diagram of Oxy-CFB coal-fired power plant with CO_2 capture

9.1 System boundary

An oxyfuel combustion coal-fired power plant consists of

- steam and power generation unit (BTG or power island):
  - boiler island and auxiliary equipment;
  - steam turbine island and generators;
- air separation unit (ASU),
- flue gas processing units (which could consist of PM, NO_x, SO_x and Hg control, also known as environmental island, flue gas clean-up system, flue gas cleaning; also related to AQCS or GQCS),
- flue gas condenser [also known as flue gas cooler (FGC); also related to direct-contact cooler, LP scrubber, LP quencher, DCC, DCCPS],
- CO_2 processing unit or CPU (also known as CO_2 compression and purification unit or gas processing unit),

— balance of plant.

For the purpose of this Technical Report, the focus of the discussion will only cover the boiler island, air separation unit, relevant areas of the flue gas processing units and CO_2 processing unit. This subclause aims to provide information relevant to the development of future standardization work in the area of oxyfuel combustion. Specifically, information need to understand the energy performance, plant flexibility, product CO_2 composition, vent and emissions, health and safety are considered in the various parts of this subclause.

9.2 Technology, processes and equipment

9.2.1 Boiler island and auxiliary equipment

The boiler island and its auxiliary equipment consist of the furnace, banks of economizer, evaporator, reheater and superheater tubes to generate the steam (HP and RH steam), gas-gas heaters, fans (FD, ID, RFG), flue gas/oxygen mixing nozzles, ash handling, and with an option to include additional flue gas heaters if necessary (i.e. when cold flue gas is recycled). For oxy-PC, this includes the coal preparation and mills; while for oxy-CFB, this includes the limestone and lump coal injection facilities, and steam coil gas heaters. Except for the in-furnace SO_x and dust removal which are intrinsic to the design of the CFB, all equipment relevant to handling of criteria pollutants, such as PM, NO_x and SO_x, are presented in the flue gas processing units.

9.2.1.1 Oxy-PC

Current state of the art PC boilers have maximum capacity of ~1 000 MWe to 1 100 MWe generating ultra-supercritical steam. For the first generation oxy-PC demonstration power plants, it is expected to be in the range of ~100 MWe to 400 MWe[8]. For oxy-PC as compared to conventional air-fired boiler, it is expected that there will be no significant changes to the design of the boiler.

The main parameters to control the combustion are dependent on how the O_2 and the recycled flue gas (RFG) are introduced into the boiler. It could be illustrated from Figure 24 that a number of different configurations are possible depending on where the flue gas is recycled (Figure 24, keys 1 to 5) and where oxygen is injected (Figure 24, keys A to E).

Normally, the oxy-PC is designed and operated to match the heat transfer profile of an air-fired boiler. For this case, around 65 % to 75 % of the flue gas is recycled. Depending on the fuel, the overall oxygen content in the furnace is maintained at around 28 % to 32 % (but typically not higher than 40 %). It should be noted that the volume of RFG and its O_2 content that goes through the burner throat is very specific to the boiler and burner design.

The recycled flue gas (RFG) is typically split between the primary RFG (about 30 % to 35 % of the total RFG) and the secondary RFG (about 65 % to 70 % of the total RFG). Some boiler/burner design could also incorporate tertiary RFG or overfire “air” system. Oxygen from the ASU could be introduced into the boiler by mixing with the RFG or directly injecting into the burner/boiler or both. Oxygen could also be pre-heated or not pre-heated.

Factors such as the sulfur and water contents in the fuel and the water content in the flue gas are the main considerations in determining the configuration on how the O_2 and RFG are introduced into the boiler. Additionally, the amount of SO_2 that is recycled back into boiler will be conservatively limited to a tolerable level to minimize the problems to the boiler tubes (i.e. corrosion issues).

Other factors such as NO_x reduction considerations (i.e. use of stage burners), or improving energy efficiency by using hot/warm RFG or optimising the usage of oxygen without affecting the combustion stability and burner/boiler performance (i.e. without increasing the CO and un-burn carbon in the ash) will also be considered and could influence the manner how O_2 and RFG are introduced into the

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[8] FutureGen2.0 has a capacity of 168 MWe (gross) and ~100 MWe (net); White Rose Project has 426 MWe (gross) and ~340 MWe (net).

burner/boiler. For the latter consideration, by understanding the burner's operating envelope could consequently minimize the level of excess O_2 in the flue gas.

For the primary RFG, this is generally cooled and washed in the FGC to reduce its water content (typically reduced down to ~25 °C to 40 °C dew point, DP) and to remove most of the halides (i.e. HCl, HF, HBr) and SO_3. In some cases, where alkali (i.e. NaOH, $NaCO_3$, $NaHCO_3$, etc.) is also used in the water wash of the FGC, SO_2 will also be removed. The removal of most of the water and acid components in the flue should prevent any problems in the operation of the mill. Also, due to the higher degree of dryness and operating temperature of the primary RFG, the performance of the coal mill could reduce the gas flow rate as compared to when operating with air.[101][102] However, any possible improvement to the mill performance is dependent on the type of coal mill selected.

Conservatively, RFG with low dust loading is preferred. But, the option to use flue gas with high dust loading (i.e. flue gas taken before the particulate control, Figure 24, key 4 or 5) is possible depending on the selection of the type of RFG fan (i.e. radial flow fans could withstand up to ~75 g/m^3 to 80 g/m^3 at STP dust and temperature range of ~250 °C to 300 °C, but radial fan's efficiency are generally lower as compared to axial fan). This will be limited by reliability issue due to corrosion, erosion, etc.

9.2.1.2 Oxy-CFB

Current state of the art CFB boilers have a maximum capacity in the range of 500 MWe to 600 MWe (with supercritical steam). For the first generation oxy-CFB demonstration, it is expected that the capacity should be in the range of 100 MWe to 300 MWe[9].

For oxy-CFB, it is possible to reduce boiler and furnace size by reducing the amount of recycled flue gas.[103][104][105] This is doable due to the additional heat extraction from the recycled solids. Thus, for a boiler with the same size, the oxy-CFB could have ~10 % to 20 % higher gross output as compared to its air-fired counterpart.[103][106]

The limestone injection is a key feature employed by CFB but not used in PC. This is an in-furnace SO_x removal technique. Thus, external FGD may not be necessary (however, in some worst case scenario when it is needed, i.e. burning of very high-sulfur coal or petcoke, the external FGD is added and it is expected to deal with lower level of SO_x as significant part of it has been removed in the furnace). Furthermore, cyclone is also part of the boiler to collect the solids and recycled back to the boiler, therefore this should also reduce the dust loading of the flue gas. As compared to the PC boiler, operating temperature is lower (i.e. 850 °C to 950 °C); therefore the NO_x level could be lower. However, level of N_2O is not negligible and thus, should be factored into the design of the CPU.

How RFG and oxygen are introduced into the boiler are the main parameters that control the combustion. These are very specific to the OEM's boiler design. In general, only a small fraction of the RFG are taken from the point after the FGC for use as transport gas of the coal and limestone, and the rest of the RFG are taken from the point after the particulate control to provide the fluidisation and overfire "air". The oxygen will be mixed with the RFG. This could be split between the RFG for fluidisation and RFG for overfire "air". Also, direct injection of oxygen into the boiler is an option. Figure 25 illustrates one of the basic configurations of an oxy-CFB power plant.

9.2.2 Steam turbine island and generators

As a rule, the steam turbines are isolated from the combustion process, except when low-pressure feed water or condensate is used to recover heat from the flue gas or used as cooling medium for various compressors of the ASUs and CPUs. Therefore, there will be no special modifications to the steam turbine needed if oxyfuel combustion is used to capture CO_2 from coal-fired power plant.

The steam turbines used for oxyfuel combustion power plant, are generally the same steam turbines used in conventional air-fired power plant. It could be designed to operate with subcritical, supercritical (SC), ultra-supercritical (USC) or advance ultra-supercritical (A-USC) steam. The use of A-USC steam would generally result to significant efficiency improvements due to higher pressure and higher temperature steam conditions.

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[9] Compostila Oxy-CFB300 Project has a capacity of 345 MWe (gross) and 238 MWe (net).

However, in some cases where the compressors of the ASU are driven by high pressure steam, the modification to the steam turbine or to the boiler is necessary. The manner on how the steam is extracted and delivered to the ASU is vendor specific. This is coordinated between the suppliers of the steam turbine/boiler and the main air compressors of the ASU. This option is not normally considered in retrofit cases. It should be expected that the impact to the net efficiency of the oxyfuel combustion power plant should be improved due to reduction of the conversion loss between mechanical and electrical energy.

The steam turbine island consists of the following main components:

- high-pressure (HP), medium-/intermediate-pressure (MP or IP), or low-pressure (LP) turbines and their controls;
- water condenser;
- cooling water pumps, cooling tower (if needed);
- condensate and boiler feed water (BFW) pumps;
- supply water heaters, de-aerators.

Generally, the gross output of the power plant with oxyfuel combustion will be comparable to the gross output of the conventional coal-fired power plant. Most of the loss in the power output of the plant is due to the power consumption of the ASUs and CPUs. Thus, it follows that cost estimates for the steam turbines and its uncertainty should be comparable to both types of power plant.

9.2.3 Air separation unit (ASU)

The technologies available for oxygen production are cryogenic separation, pressure swing adsorption (PSA), and membrane separation. When a very large volume of oxygen in the range of 100 000 Nm^3/h to 500 000 Nm^3/h is needed for thermal power plant, the cryogenic separation is the only method that could produce this large volume of oxygen at the lowest possible cost.

For oxyfuel combustion coal-fired power plant with CO_2 capture, the oxygen required is of very large tonnage with low purity (~95 % to 97 %) and low pressure (~1,5 Bara to 2 Bara). Typically, for base load operation, only gaseous oxygen (GOX) is needed and there is no requirement for other co-products.

The ASU consists of the following equipment packages:

- air filter;
- main air compressor (MAC) and booster air compressor (BAC);
- direct-contact after cooler (DCAC);
- front-end purification (including dehydration and removal of CO_2, HC, other air impurities);
- main heat exchangers (BAHX);
- JT valves and turbo expander;
- distillation columns;
- reboiler/condenser;
- liquid subcooler.

If the ASU requires operation flexibility to meet the power plant demand, additional equipment package such as LOX boiler, cold compressor, GOX liquefier, liquid (LOX, LIN or liquid air) storage, etc., could be included depending on the ASU cycle selected.

ASUs are based on a mature technology developed and refined over 100 years. The differences between ASUs used for oxyfuel combustion in coal-fired power plants and those used for the production of industrial oxygen are as follows.

— The quantity of oxygen required could be larger for oxyfuel combustion power plant as compared to other large users (i.e. steel, IGCC, CTL, GTL, etc.). For reference, a 500 MWe (net) oxyfuel coal-fired power plant will require ~10 000 TPD (~295 000 Nm^3/h) O_2. This can only be met by multiple trains of ASUs for every train of oxyfuel combustion boiler.

Currently, the largest operating single train ASU has a capacity of 3 900 TPD (~115 000 Nm^3/h) O_2. However, five trains of ASU are now under construction for very large petcoke gasification complex in India; and each train having a capacity of 5 250 TPD (~155 000 Nm^3/h) O_2. This will be expected to be commissioned between 2015 and 2016. Although it is for gasification application, several key learnings of building these very large trains of ASU could be adapted to the ASUs for oxyfuel combustion application.

— The purity of industrial oxygen is generally very high at 99,5 %, as this is required by the users (mostly driven by the steel industry today). For oxyfuel combustion application, a lower purity between 95 % and 97 % is used to reduce the energy consumption. At this range, consumption of large amount of energy to separate O_2 and Ar is avoided.

Additionally, due to the excess O_2 needed and the air ingress into the boiler and downstream equipment during combustion, it is a necessity to separate the residual O_2, N_2 and Ar from the product CO_2. Thus, there is no perceived benefit of employing higher purity O_2.

— Other large industrial users of oxygen today requires oxygen supplied at a high pressure (i.e. for steel industry — BF and BOF require O_2 at ~5 Bara and ~25 Bara respectively; for GTLs, CTLs, IGCCs require O_2 at >10 Bara and could be as high as 80 Bara). For oxyfuel combustion application, since combustion is at atmospheric conditions, oxygen required is at relatively low pressure (i.e. <2 Bara).

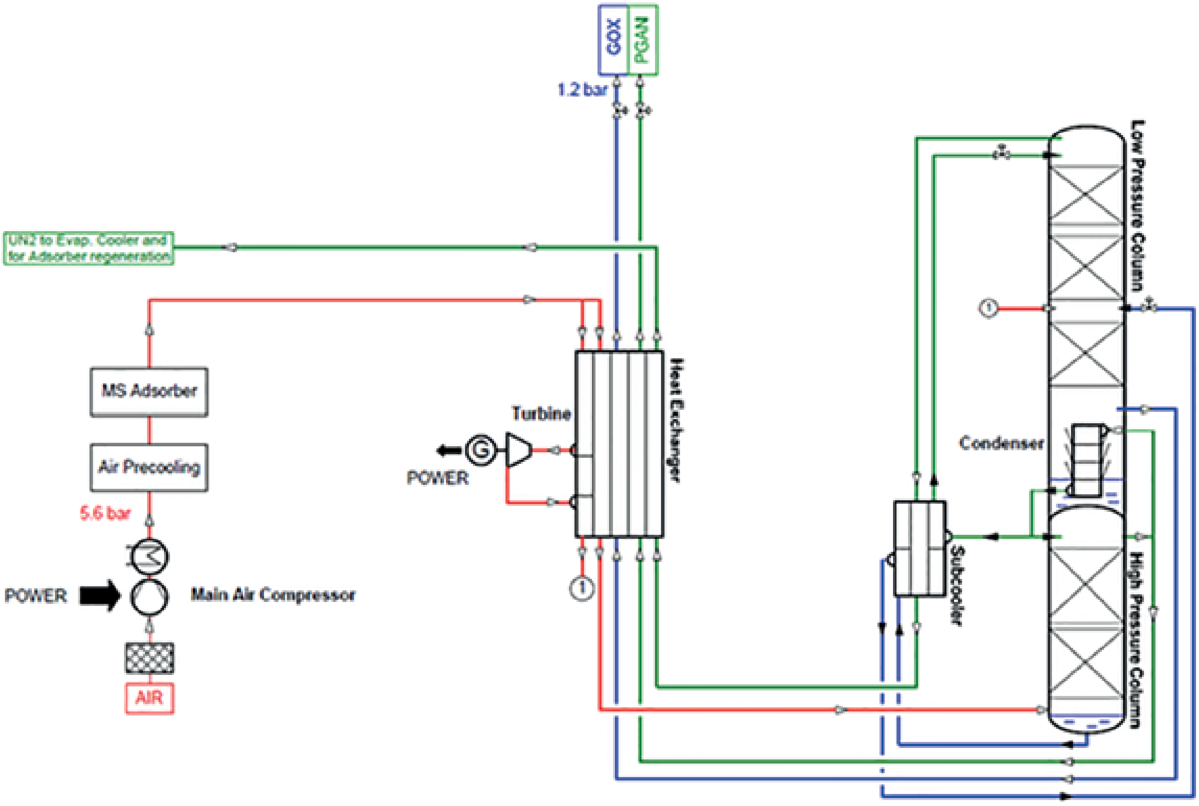
— Other large industrial users of oxygen today also requires other co-products (i.e. the steel industry requires large volume of gaseous Ar for their AOD operation, a liquid steel purification process; IGCC requires large volume of medium to high pressure gaseous N_2, PGAN for their gas turbine). For oxyfuel combustion, only gaseous oxygen (GOX) is required and in some cases, only the liquid oxygen (LOX) as co-product maybe required if plant flexibility is needed.

— The ASUs for power plants should have the capability in order to satisfy the demand of the generation unit and need to have a sufficient output margin for operation, and the fluctuation to the O_2 demand by oxyfuel combustion could be unpredictable. Such requirements are normally not imposed by other large users of oxygen.

Because of these differences, industrial gas companies have developed different ASU cycles to meet the demand for oxyfuel combustion. They have identified key areas where improvement could be made to the performance of the plant and reduce cost. Additionally, integration opportunities between the power plant and the ASU have also been identified.

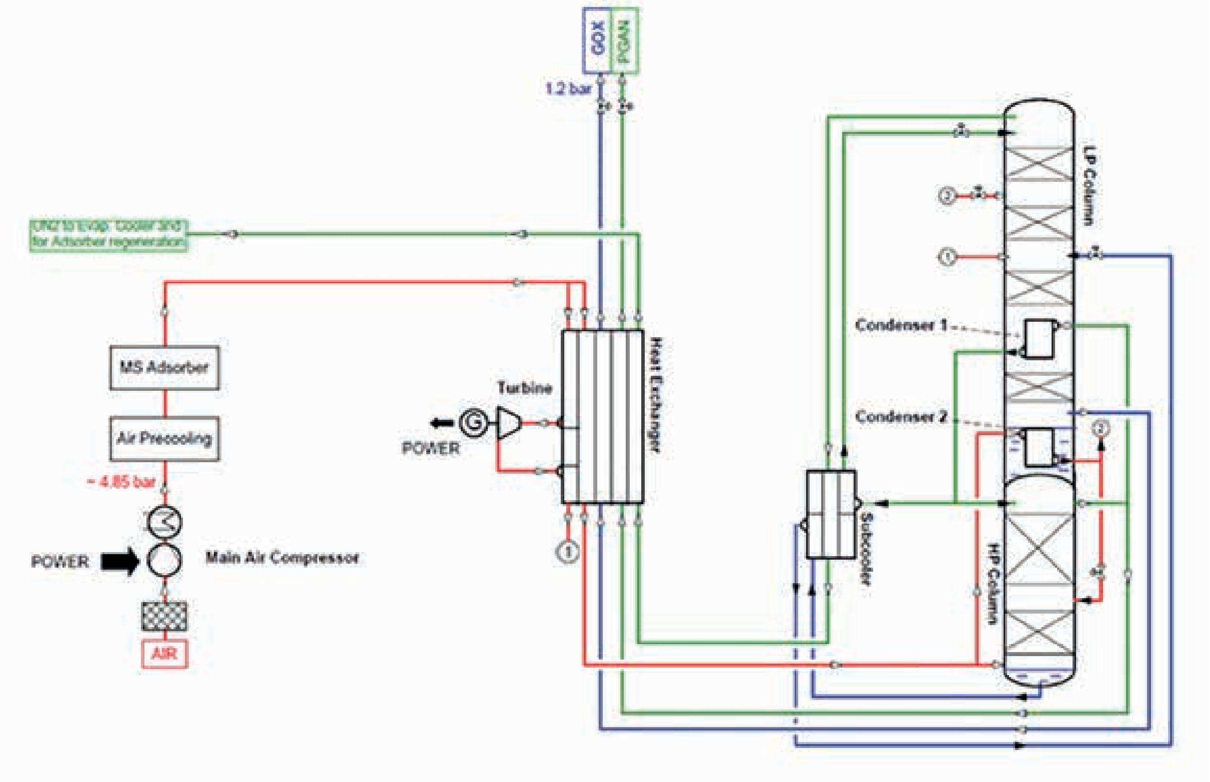
It could be noted that development of the new ASU cycles is totally different to the conventional two columns ASU cycle (as shown in Figure 26). There are several variations reported, but in general, could be grouped either as dual reboiler cycle (as shown in Figure 27) or triple column cycle (as shown in Figure 28). A more detailed discussion on the different ASU cycles developed for oxyfuel combustion is presented in various conference proceedings.[107][108][109][110][111][112][113] Fundamentally, the development of these cycles aimed to minimize the total power input by reducing the feed air pressure, producing oxygen at no more than its specified pressure, and with all of the nitrogen produced vented. This could be illustrated in Figure 26, Figure 27 and Figure 28.

In the classic two-column cycle producing 95 % purity oxygen (as shown in Figure 26), the pressure of the feed is set at ~5,6 Bar. On the other hand, for the single pressure dual reboiler cycle (as shown in Figure 28), the pressure of the feed air could be reduced to ~4,9 Bar. This is due to the improvement gained by reducing the thermodynamic loss of the LP column through the introduction of the second reboiler/condenser. About 4 % improvement in energy performance could be achieved as compared to the two-column cycle. Further improvements could be gained to this cycle by employing MAC and BAC dual pressure arrangements and side condenser for LOX evaporation, which should result to an improvement of about ~10 % to 14 % in the ASU energy performance. By employing a triple columns or dual high pressure columns cycle (as shown in Figure 27), the pressure of the feed air is reduced to 3,1 Bar; and only a part of the feed air is pressurized to 4,8 Bar to provide the necessary refrigeration of the cold box. With this arrangement, it was reported that around 20 % to 25 % improvement could be gained. If integration of the ASU with the boiler is included, additional 5 % to 10 % improvement could be further achieved.[107][108][113][114][115]



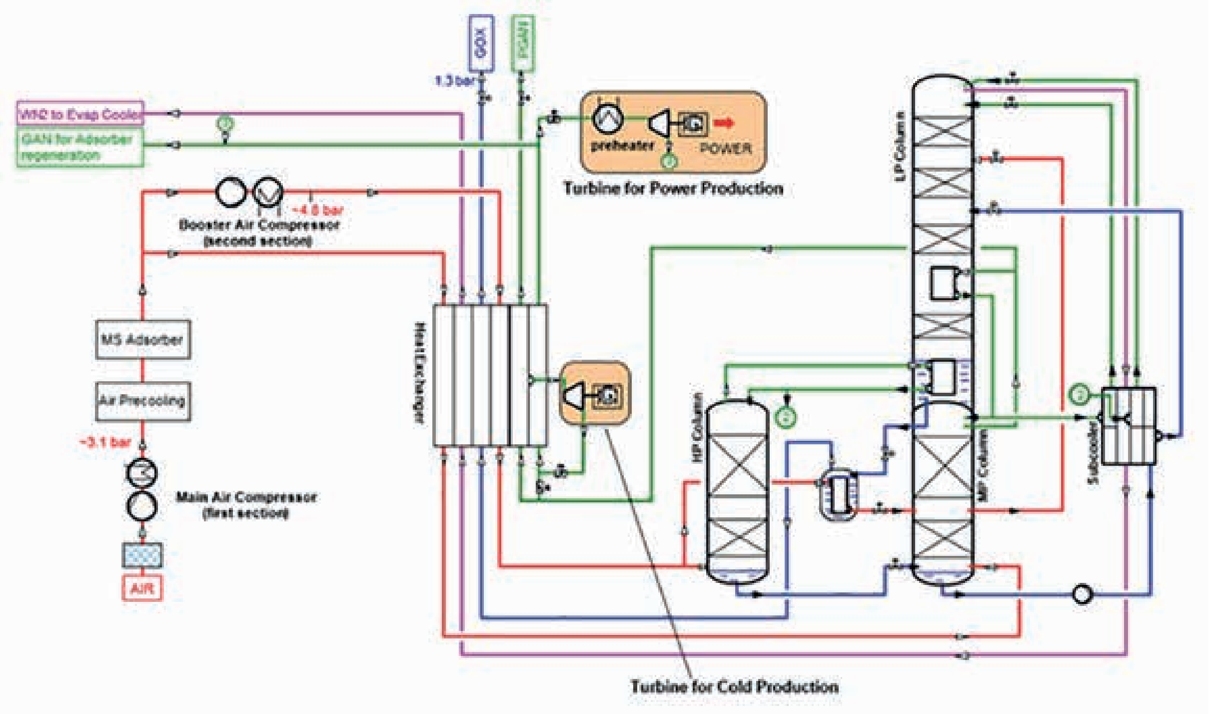
NOTE See Reference [108].

Figure 26 — Schematic PFD of the classic single-pressure, two-column ASU cycle



NOTE See Reference [108].

Figure 27 — Schematic PFD of the single-pressure, dual-reboiler ASU cycle



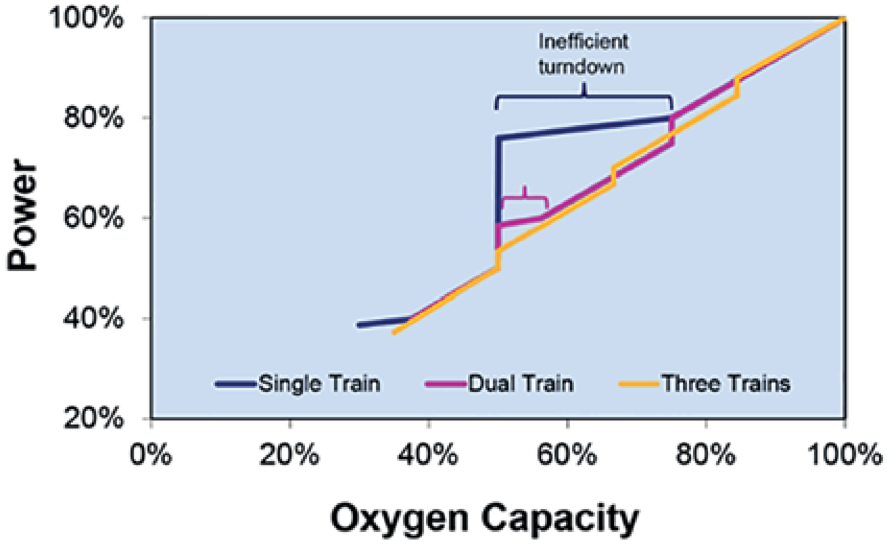
NOTE Adapted from Reference [113].

Figure 28 — Schematic PFD of the dual-pressure, triple-column ASU cycle

Another challenge to the development of the ASU for oxyfuel combustion is the need to meet the demand of the power plant in various operating mode including high level of flexibility. Industrial gas companies have offered several options to meet such demand. These are discussed and reviewed in various literature and proceedings.[107][110][111][113][114]

In this area of development, the following could be summarized.

- The normal operating range of a single train ASU (with single train MAC) without LOX storage is about 80 % to 105 %.
- The ASU could meet changes to the demand of the power plant (i.e. turn down) with a ramp rate of up to 1 %/min to 3 %/min without any need of liquid oxygen, however, at 3 %/min ramp rate, this should be incorporated in the design of the ASU. This is primarily a trade-off between the arrangement of the number of MAC/BAC per train of ASU and the number of trains of ASUs. The energy performance of the single train vs multiple trains ASUs during turn down could be illustrated in Figure 29.

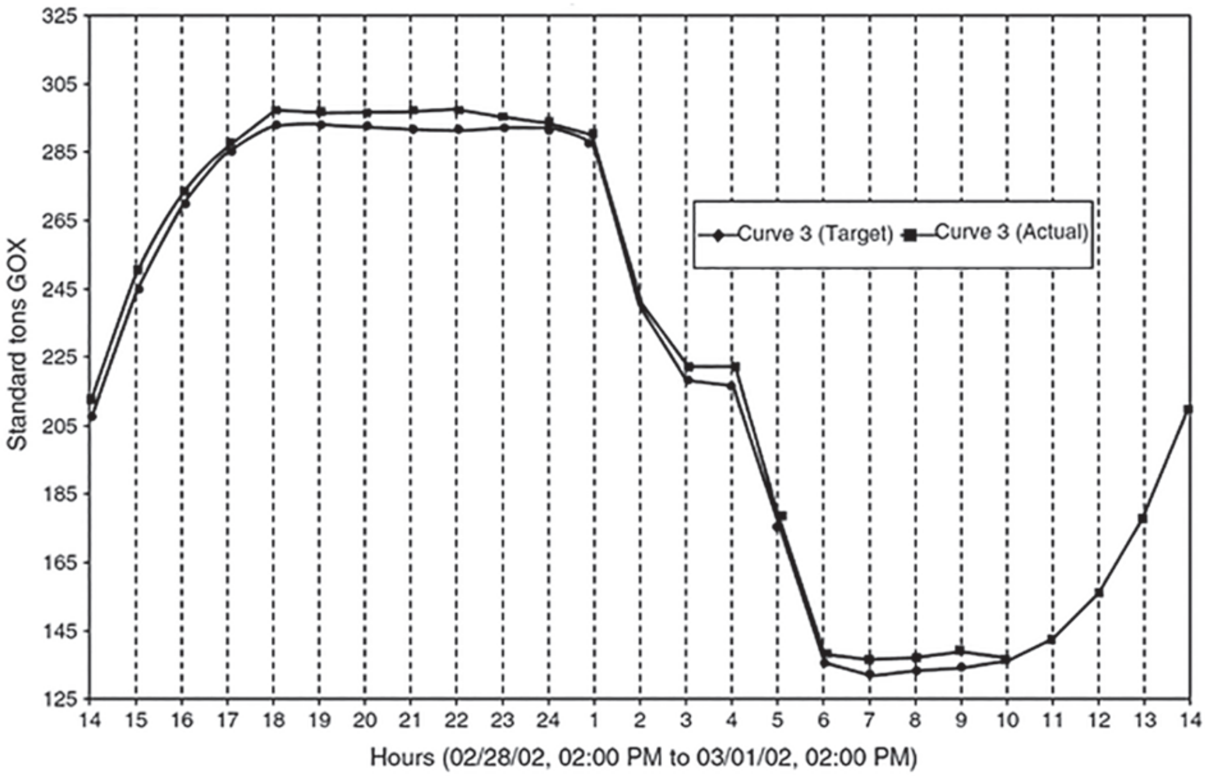


Basis: Each train of ASU includes two parallel main air compressors

NOTE See Reference [111].

Figure 29 — Turn down performance of the ASU for single train vs multiple trains

- For ramp rate greater than 4 %/min, the use of liquid oxygen or other liquid gas could be necessary. As stored LOX is used to smooth out the peak and trough of the oxygen demand of the power plant. Strategies used and experience gained during the number of years operating a variable O_2 demand in the steel industry could be adapted. The capabilities of the ASU to meet the fluctuation in demand could be illustrated in Figure 30.

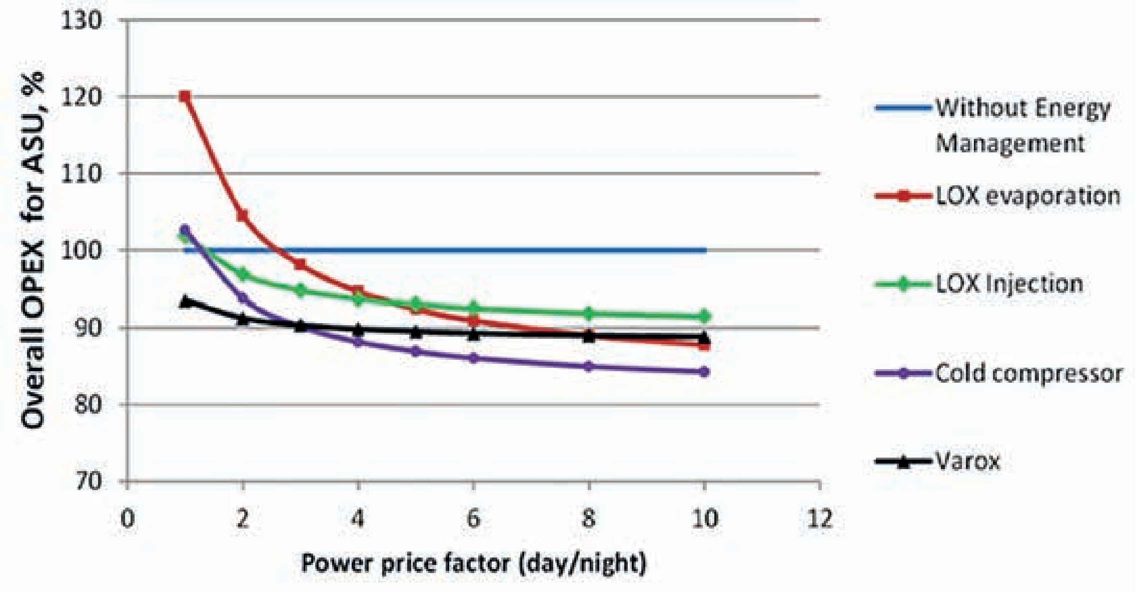


NOTE See Reference [116].

Figure 30 — GOX production meeting the fluctuating demand of the customer

— In scenarios where there is a price differential between day and night operation, the ASU could be managed as an "Energy Storage" facility. This also involved with the use of liquid oxygen and/or other liquid gas products (i.e. LIN or liquid air). Several industrial gas companies have developed different schemes.[110][113][115]

To illustrate what options are available to meet such type of demand profile from the power plant, Goloubev et al.[113] have presented four different options which include simple evaporation of LOX (option 1), evaporation of LOX with integration to the cold box (option 2), use of cold compressor (option 3) and swapping of liquids (option 4). Results of their evaluation are summarized in Figure 31.



NOTE See Reference [113].

Figure 31 — Concepts of energy management between ASU and power plant

There are still several areas where improvements could be gained to the ASUs for oxyfuel combustion. However, further development could not be pursued until the first large-scale demonstration power plant is built, operated and its performance validated.

The different FEED studies[114][115][117][118][119] undertaken in various large-scale demo projects have identified key equipment where improvements could be gained and where possible integration between boiler, ASU and CPU could be developed. Further development is necessary in the following areas:

- development of the main air compressor to provide wider range of turn down;
- development of process control system to allow smooth operation of the ASU meeting the variable O_2 demand of the power plant;
- development of process integration options of the ASU with the power plant and the CPU;
- utilization of waste N_2 from the ASU. (i.e. use of additional Brayton Cycle using N_2 as working fluid).

Without the large-scale demonstration plant, this will still pose some uncertainty that could push up the cost estimates of ASUs. They include scaling-up of equipment to larger sizes than ever experienced (e.g. larger diameter valves, turbo machineries, evaporators with larger diameters and various types of heat exchangers) as well as guaranteeing required purities or motive power to meet the required dynamic performance. Generally speaking, such contingency costs are necessary to the few early mover projects, and will be less needed as the experience in deployment of nth plant have been achieved.

9.2.4 Flue gas processing units (environmental island)

It is expected that flue gas from an oxyfuel combustion boiler has higher concentration of CO_2 and H_2O as compared to flue gas from conventional air-fired boiler. Additionally, the concentration (reported as ppm or mg/Nm^3) of different criteria pollutants such as NO_x and SO_x are generally 2 to 5 times higher as compared to the emissions from air-fired boilers.

To maintain the integrity of the boiler and its auxiliary equipment against the impact of high concentration of acidic gases, various controls to reduce SO_x and particulates are used. Mostly, these equipment are also employed in conventional air-fired boilers. Generally, this could be grouped together as Flue Gas Processing Units or also commonly known as the environmental island.

The flue gas processing units mainly consists of the following equipment package:

- Particulate control — dry ESP, wet ESP or bag/fabric filter (FF);
- SO_X control — wet FGD or dry/semi-dry FGD (including CDS, SDA, DSI, etc.);
- NO_X control — SCR, SNCR;

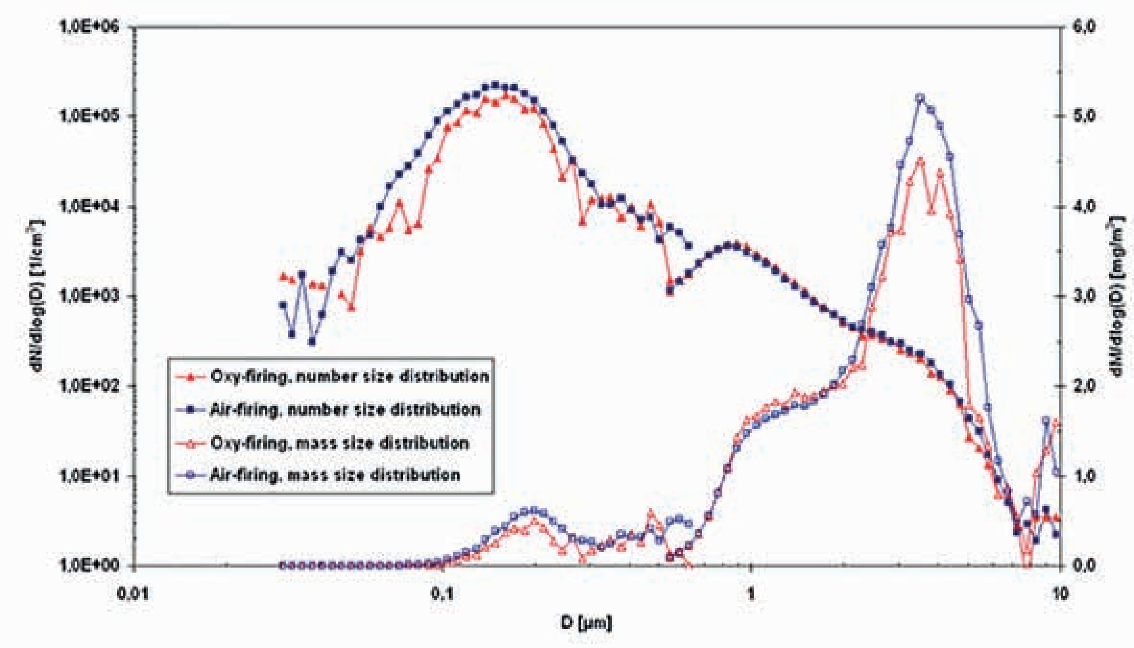
9.2.4.1 Particulate control

For air-fired boiler, particulate control is strictly required to reduce particulate emissions due to regulatory requirements. For oxyfuel combustion, in addition to environmental consideration, removal of particulate is essential to maintain the integrity of the fans (i.e. RFG fans), ducting and other boiler equipment from erosion; and additionally, it is also important to completely remove bulk of these particulate matters to reduce the dust loading going into the flue gas filter and protect other CPU components (such as compressors and heat exchangers) downstream.

For particulate or dust control, both oxy-PC and oxy-CFB has the option to employ either electrostatic precipitator (dry and/or wet ESP) or fabric filter (FF).

Large industrial-scale operation experience from Vattenfall's Schwarze Pumpe Pilot Project[120][121][122] reported that the ESP has performed very well during oxyfuel combustion testing. Similarly, experience from Callide Oxyfuel Project[102] and CIUDEN Technological Development Project[123] using fabric filter have also indicated good performance with the PM measured after the FF reduced by ~50 % as compared to air firing mode.

Figure 32 shows the size distribution profile of the particulate matter measured from the flue gas of Schwarze Pumpe Pilot Plant operating in both air and oxyfuel combustion.[120] The results clearly indicated that particulate emissions are similar in both air and oxyfuel combustion mode, thus, indicating that it is independent from the type of firing mode.



NOTE See Reference [120].

Figure 32 — Particle number size distribution and mass size distribution measured downstream of the ESP for oxyfuel and air firing conditions

9.2.4.2 SO_X control

For air-fired boiler, SO_X is limited by environmental regulations. For oxyfuel combustion, SO_X should be reduced to an acceptable level in the recycled flue gas to maintain the integrity of the boiler, flue gas reheating equipment and associated RFG piping/ducting, etc. Similarly, SO_X emission regulation should be met during plant start up and shut down operation; and if the power plant is designed to operate in dual mode (air-fired or oxyfuel-fired). The control method and process arrangements (i.e. position of the FGD) are dependent on the sulfur content of the coal, the CAPEX and OPEX.

During oxyfuel combustion, the sulfur species (mostly SO_2 and SO_3) in the flue gas could be reduced externally by the flue gas desulfurization (FGD) unit or by in-furnace sorbent injection technique. Additionally, SO_X could also be removed downstream at the FGC and/or at the warm part of the CPU.

For oxy-PC, the FGD could be installed inside the flue gas recycle loop, outside the flue gas recycle loop, or both. There are several options available for flue gas desulfurization, and these include the following:

— wet flue gas desulfurization (FGD) using limestone;

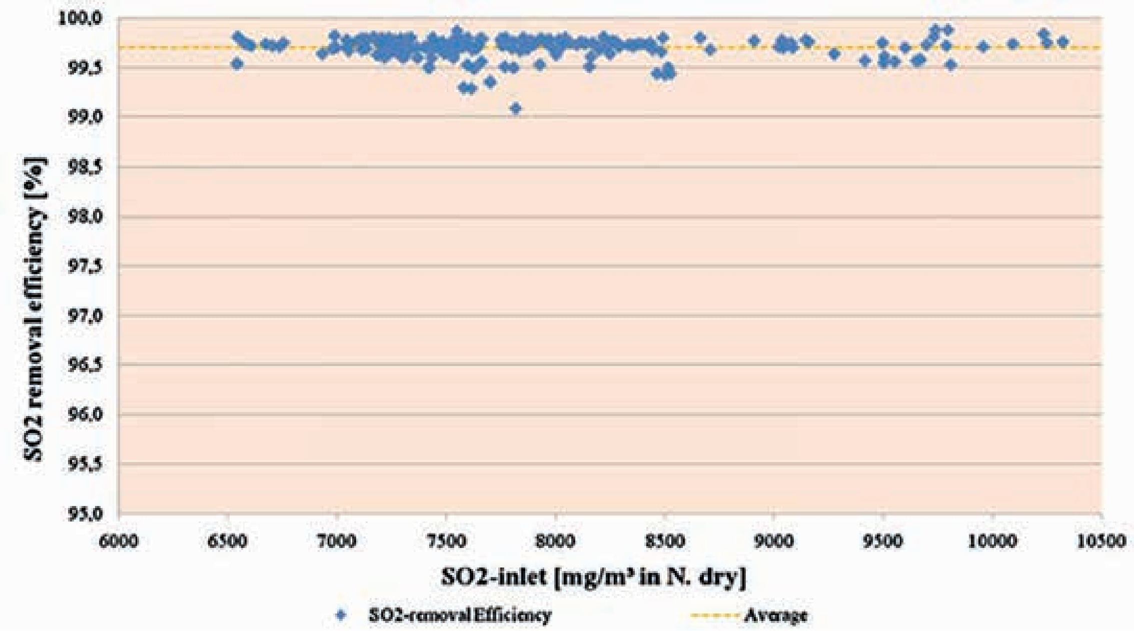
— circulating dry scrubber (CDS) using hydrated lime;

— spray drying absorption (SDA);

— dry sorbent injection (DSI).

Typically, for high-sulfur coal (i.e. greater than 1,5 % to 2 % S), installing the FGD inside the flue gas recycle loop could be necessary to meet the tolerable level of SO_X specified by the boiler manufacturers. On the other hand, for low-sulfur coal (i.e. <0,3 % to 0,5 % S), it is possible to eliminate the use of FGD in the environmental island or at most using only DSI to reduce SO_3. The remaining SO_X in the flue gas could be removed downstream in the FGC or in the warm part of the CPU.[124][125]

Vattenfall Schwarze Pumpe Pilot Plant has demonstrated that wet FGD could remove >99 % SO_X. This is shown in Figure 33. To reduce the air ingress, the sulphite oxidation tank is separated from the main FGD column (which is not typical for conventional FGD used in air-fired boilers). Performance of the FGD has been described in various literature.[121][127][128][129][130]



NOTE See References [127], [128], [129] and [130].

Figure 33 — Performance of the limestone forced oxidation wet FGD during oxyfuel combustion

For oxy-CFB, the limestone injection is the primary measures to control SO_x. This is an in-furnace desulfurization technique as described earlier. Typically, by using Ca/S of about 2,7 to 3,2 and with operating bed temperature of between 850 °C and 950 °C, the sulfur removal efficiency of greater than 95 % could be achieved even for very high sulfur fuel (i.e. up to 5 % S). The experiences gained at the CIUDEN's facility have reported that the performance of the limestone injection in removing SO_x at high bed temperature is more efficient during oxyfuel combustion than in air firing mode; but performance may decline at temperature below calcination.[131][132][133]

It should be expected that any remaining SO_x in the flue gas not recycled to boiler will be removed downstream either at the FGC or at the warm part of the CPU. In some scenario as described earlier where an external FGD may be incorporated (i.e. due to burning very high S fuel) to the oxy-CFB power plant, it is necessary to optimize the SO_x removal between the limestone injection in the furnace and the external FGD. This is determined by the level of SO_x in the recycled flue gas and OPEX considerations.

9.2.4.3 NO_x control

During combustion, NO_x is formed from the conversion of the fuel nitrogen to NO, thermal and prompt NO mechanism. For coal combustion, NO_x from fuel nitrogen is more dominant. NO is the dominant species produced during combustion (~90 % to 95 % of the NO_x). The other NO_x species, NO_2, are formed from the conversion of the NO at lower temperature.

In oxyfuel combustion, the flue gas is recycled back into the burner area of the boiler. Thus, most of the NO_x in the recycled flue gas is decomposed in the reducing environment near the burner region (i.e. reduction through NO_x reburn mechanism), thereby limiting the concentration of NO_x to approximately 1,5 to 2 times the concentration (reported as ppm or mg/Nm^3) of NO_x as compared to the NO_x emissions during air combustion mode.

Due to the effectiveness in reducing NO_x in the boiler during oxyfuel combustion, the external NO_x control equipment such as SCR or SNCR may not be necessary. Remaining NO_x in the flue gas could be removed downstream, mostly at the warm part of the CPU.

However, if the power plant is to be operated in dual combustion mode (i.e. air and oxy firing mode), SCR or SNCR may be necessary to comply with environmental regulations when the power plant is in air firing mode, thus, could increase the capital and operating cost of the power plant.

9.2.5 Flue gas condenser (flue gas cooler)

The flue gas condenser or FGC is a general classification for direct or indirect cooling of the flue gas from the oxyfuel combustion boiler. The use of large-scale flue gas condenser is well-established in various biomass-fired power plant or waste incineration plant producing hot water for district heating.

Direct cooling using water or alkali wash is favourable as compared to indirect cooling due to the co-benefit of removing the water soluble acidic components. On the other hand, problems encountered such as fouling and corrosion issues experienced by the latter option make it less fashionable. Thus, FGC could be synonymous to direct contact cooler, flue gas cooler, flue gas quencher, low pressure quencher, or low pressure scrubber.

FGC is the link between the boiler and the CPU. It plays an important role in the preliminary drying and cooling of the flue gas prior to compression and purification. Some equipment vendors specify the FGC as part of the flue gas processing unit. But some other vendors specify this as part of the CPU.

In this Technical Report, for the purpose of clarity, FGC is classified and described separately from the environmental island and the CPU.

The FGC could consist of the following equipment package:

- FGC using direct cooling:
  - spray tower or any other similar mass transfer equipment (i.e. packed tower scrubber, venture scrubber, etc.);

  - demister (i.e. to reduce the carryover of H_2SO_4);
  - recirculating pumps, waste water pumps, etc.;
  - reagents storage facilities;
- FGC using indirect cooling:
  - shell and tube heat exchanger (could have condensing or non-condensing option);
  - recirculating pumps, waste water pumps, etc.;
  - condensate traps.

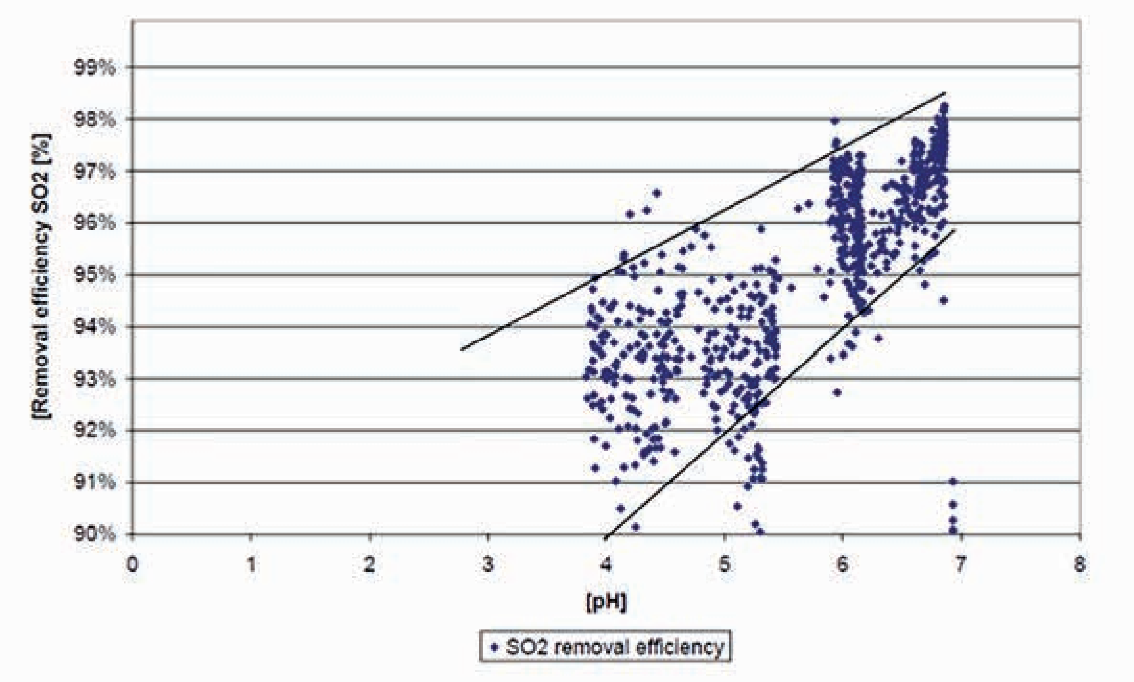
Typically, the flue gas that is fed into the FGC contains about 20 % to 40 % water (depending on moisture content of the fuel). This could also be saturated if wet FGD is used upstream.

The use of water wash generally removes most of the water soluble acidic components such as HCl, HF, HBr, SO_3, NO_2. However, any H_2SO_4 mist may not be captured effectively in this unit. The significant bulk of fine particulates remaining in the flue gas could also be effectively removed.

For oxy-PC, part of the cleaned flue gas (i.e. ~40 % to 50 % of the feed gas into the FGC) is returned to the boiler as primary RFG and the remaining flue gas is delivered to the CPU. While, for oxy-CFB, only a small part (i.e. 10 % to 15 % of the feed into the FGC) is returned as transport gas for coal and limestone.

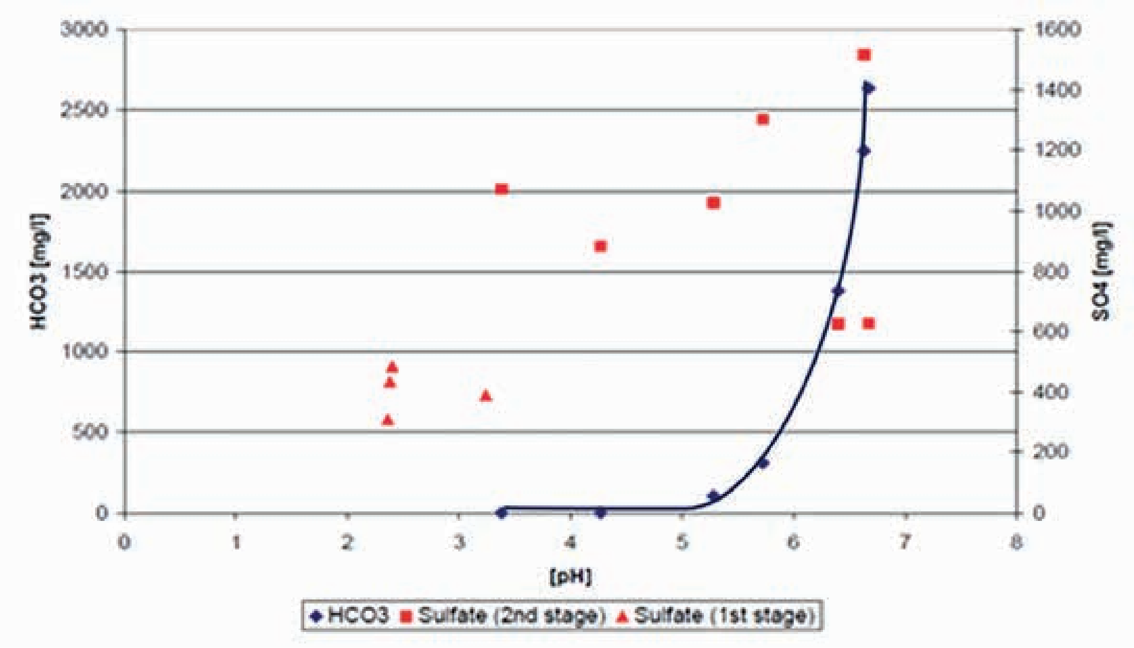
If alkali wash is used, the remaining SO_2 in the flue gas is also removed. The extent of the SO_2 removal is dependent on the inlet SO_2 concentration and operating pH. Based on the experience from Vattenfall's Schwarze Pumpe Pilot Plant (i.e. where FGD is used upstream), the SO_2 concentration is small and the removal efficiency was observed to be between 94 % and 98 % at pH between 6 and 7 (as shown in Figure 34).[124] The downside of using alkali wash is the co-absorption of CO_2 to form HCO_3^- at pH >5,5. This is due to very high concentration of CO_2 and low level of SO_2 remaining in the flue gas. This is shown in Figure 35.[127]

Options of using acid wash are also considered and this is presented by Air Liquide relating to their second-generation technology for the "warm part of the CPU".[134]



NOTE See Reference [127].

Figure 34 — SO_2 removal efficiency of the FGC



NOTE See Reference [127].

Figure 35 — Co-absorption of CO_2 as HCO_3 in the FGC at pH >5,5

9.2.6 CO_2 processing unit (CPU)

The CO_2 processing unit (CPU) is also known as CO_2 purification unit, compression and purification unit, or gas processing unit.

In general, the CPU may consist of the following components:

- warm part of the CPU, which could include:
  - flue gas filter;
  - flue gas compressors (with intercooler or adiabatic);
  - front-end purification units, mainly the NO_x, SO_x removal process;
  - cooling water pumps;
  - water chillers;
  - dehydration unit;
  - mercury removal unit;
  - CO removal unit;
- cold part of the CPU:
  - flash and/or distillation/rectifier columns;
  - main heat exchangers (BAHX);
  - JT valves, turbo expanders;
  - product compressor or pumps;
  - cooling water;
  - vent gas heater.

The general consensus among OEMs is to recommend the use of auto-refrigeration cycle, i.e. the use of impure liquefied CO_2 as refrigerant. However, in cases where refrigeration is provided externally, the refrigeration package should be included in the list.

Furthermore, the additional recovery of the CO_2 from the CPU vent could also be added; thus, allowing greater than 98 % CO_2 capture/recovery rate. If this is in place, any of the following equipment packages could also be included in the list:

- membrane;
- PSA;
- VPSA

It should be noted that the list of equipment could be technology specific to the OEMs and should be considered as indicative only.

Among the different stakeholders of oxyfuel combustion, it could be roughly said that the CPU was considered to have the highest potential risk among the different components of oxyfuel combustion with respect to the power plant cost and future regulations of CCS. This is due to the fact that the design and engineering of the CPU is very dependent to the specification of the product CO_2 (i.e. once this parameter is fixed and the power plant built, it will be costly to modify the CPU if there will be major changes to the required specification of the product CO_2 during the operating life of the power plant).

In one possible scenario, where the transport of the product CO_2 is of short distance and the geological storage allows the co-capture of other non-CO_2 components, the best available technology and the most cost effective way to design the CPU will only require the cooling, dehydration and compression of the flue gas from oxyfuel combustion boiler. Thus, the resulting product CO_2 will have low purity CO_2 in the range of 80 % to 90 %[10]. The water content level of the CO_2 will be limited by the design of the compression and dehydration unit, this could range from minimum allowable water content for safe operation of the pipeline (i.e. ~500 ppm to 600 ppm, with no free water)[11] to a very dry CO_2 product (i.e. <10 ppm) if needed. Normally, there is no crucial need to employ deep dehydration of the flue gas given that this will not be subjected to low temperature processes. The level of NO_x and SO_x in the product CO_2 will depend on the upstream flue gas processing units and the final concentration of acidic gas species will be determined by the process arrangements of the compression and dehydration unit, taking into account the physics and chemistry of the NO_x and SO_x reaction in the presence of O_2 and water during compression.

A practical example to the scenario described above is the experience gained by Total in their Lacq Project. The capture of CO_2 is based on oxyfuel combustion retrofitted to a ~30MW_{th} steam generation plant firing NG. Around 110 TPD of CO_2 is transported in "gaseous" phase at ~40 Bar to a depleted NG reservoir at Rousse, France. The design of the flue gas processing and the CPU is simple and could easily meet the minimum requirements for a converted pipeline (i.e. originally used for NG and re-conditioned for CO_2 transport). The processing of the flue gas from the boiler only includes the direct contact cooler that cools down the flue gas down to 30 °C. The CPU consists of a three stage reciprocating compressor and molecular sieve for gas dehydration. A part of the dry CO_2 is recycled back to the compression unit. The product CO_2 has a purity level in the range of 91 vol% to 93 vol% CO_2 (dry basis). The gas delivered to the pipeline is nearly bone dry (i.e. <10 ppm). Other non-CO_2 components included in the product CO_2 are O_2 (5 vol% to 7 vol%), N_2 (1 vol% to 3 vol%), Ar (0,5 vol% to 1 vol%), CO (<10 ppmv) and NO_x (mostly NO_2 at ppmv level).[135]

In another scenario, where the purity requirements is not stringent (i.e. "relaxed CO_2 purity scenario", where this could be applicable to CO_2 storage in saline aquifer), the engineering and design of the CPU will then be dependent on the economics of the CO_2 transport and storage. Typically, the product CO_2 could have purity in the range of 90 % to 98 %. The moisture content will be very dry (i.e. <10 ppm), as this is required because the flue gas is processed at low temperature conditions (~i.e. could be subjected to as low as −53 °C). The level of NO_x and SO_x in the product CO_2 will be mainly dependent on the selection of the technology used in the upstream flue gas processing unit and the technology used in the warm part of the CPU.

For a scenario where the product CO_2 requires stringent purity (i.e. "high CO_2 purity scenario" that could be possibly applied to EOR operation producing sweet crude as an example), the engineering and design of the CPU will be dependent on the limits imposed on the oxygen content of the product CO_2. Typically, the product will have greater than 99 % to 99,5 % CO_2. In this case, deeper separation of the non-CO_2 components will be required and this could be accomplished by adding distillation column and/or the recycling of some part of the product CO_2 into the feed gas of the cold box.

In summary, it should be underlined that the final design of the CPU is governed by the specification of the CO_2 product as required by the downstream processes (i.e. transport and storage). But there are no existing guidelines to provide such specification. Nonetheless, it should be emphasized that developing such guidelines are still pre-mature until several large-scale demo plant are operational and to learn from their experiences. Currently, it is expected that for the first generation oxyfuel combustion power plant, the specification of the product CO_2 is determined by project and site specific requirements.

To mitigate any uncertainty and risk to the investment of the oxyfuel combustion power plant, it is necessary to develop research programmes that will aid in the understanding the impact of the non-CO_2 components to the whole CCS chain. Particularly, work in the following areas should be pursued.

— To develop research programme aiming to improve and validate the accuracy of the thermodynamic data on vapour-liquid equilibrium (VLE) of binary and multi-components mixture consisting of

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[10] This is applied to coal-fired power plant and dependent on the condition of the boiler and fuel's ultimate analysis. 80 % to 90 % is typical for burning of hard coal in a new build boiler with minimal air ingress.

[11] To achieve 500 ppm to 600 ppm moisture level, only minimal dehydration is needed and this could be achieved by a simple glycol unit. Additionally, at this level, it is assumed that there is no free water in the product CO_2. It is also possible to achieve this level of water content in the CO_2 compression unit where water is removed between stages in the knockout drum. However this will be limited by the temperature of the cooling water available. Chilling the cooling water could help achieve this level.

CO_2, O_2, N_2, Ar, and other minor components such as CO, NO_x, SO_x, N_2O, etc. In the perspective of the CPU development, this is essential in order to improve the dynamic modelling of the CPU processes especially near the freezing temperature of the mixture.

- To evaluate the energy performance of different concepts of CO_2 purification involving partial condensation. This should also include the demonstration of auto-refrigeration cycle at appropriate industrial scale pilot plant that uses the “impure liquid CO_2” as refrigerant. This should provide the necessary engineering data to help develop process controls of the CPU — thus, also addressing the possible impact of fluctuating feed composition from the boiler delivered to the CPU.
- To evaluate the fate of the NO_x and SO_x in the compression and dehydration of the flue gas. The effectiveness of NO_x and SO_x removal during compression should be demonstrated at appropriate industrial scale pilot plant. Additionally, the cost-benefit and risk assessment of adding or removing the different NO_x and SO_x control measures upstream of the CPU vs. NO_x and SO_x removal at the warm part of the CPU should also be evaluated.

9.2.6.1 Flue gas filter

Any remaining particulate matters should be removed in order to maintain the desired performance of the compressors and BAHX downstream. This should prevent any fouling to the compressor. Also, once fine dust enter the BAHX, it is impossible to remove; and if these dust accumulate, then the pressure drop across the BAHX increases thereby increasing the energy consumption of the CPU.

For oxyfuel combustion, it is expected that the FGC using direct contact cooling and scrubbing using either water or alkali wash could remove most of the particulates in the flue gas.[102][134][136] The filter (either a dynamic or static filter) if installed could serve as a polishing step to ensure the removal of the remaining fine particulates down to tolerable level.

9.2.6.2 Flue gas compressor

For the first-generation demo plant, an isothermal or adiabatic compressor could be selected. For isothermal compressor, intercooler is required. For adiabatic compressor, there is no intercooler; thus, higher temperature is expected at the discharge where heat could be recovered at the aftercooler unit. This heat can be used to preheat the condensate or boiler feed water as part of the integration between CPU and the boiler island or the vent gas of the CPU cold box if required.[124][137][138][139]

The selection of the flue gas compressor should take into consideration that the machinery will be subjected to a very acidic condition. Thus, materials selection is crucial to the reliability and safe operation of the flue gas compressor.

9.2.6.3 Options for NO_x and SO_x removal

Recognizing the reaction between NO_x and SO_x in the presence of H_2O and O_2 under pressure is an important finding that has been crucial in the advancement of the different approach made by various OEMs to develop the warm part of the CPU.[137]

White and Allam[140][141] noted that in the presence of water and oxygen, SO_2 will be converted to H_2SO_4 and NO will be converted to HNO_3 at higher pressure due to the following reactions:

$NO + 1/2\ O_2 \leftrightarrow NO_2$ (1) Slow

$2\ NO_2 \leftrightarrow N_2O_4$ (2) Fast

$2\ NO_2 + H_2O \leftrightarrow HNO_2 + HNO_3$ (3) Slow

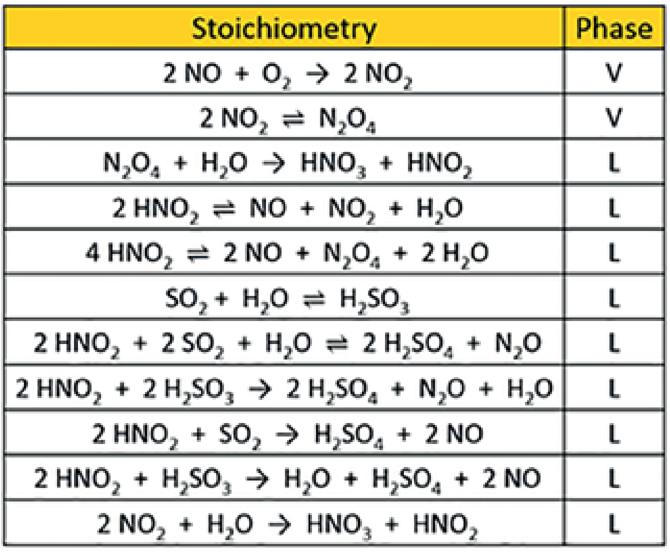
$3\ HNO_2 \leftrightarrow HNO_3 + 2\ NO + H_2O$ (4) Fast

$NO_2 + SO_2 \leftrightarrow NO + SO_3$ (5) Fast

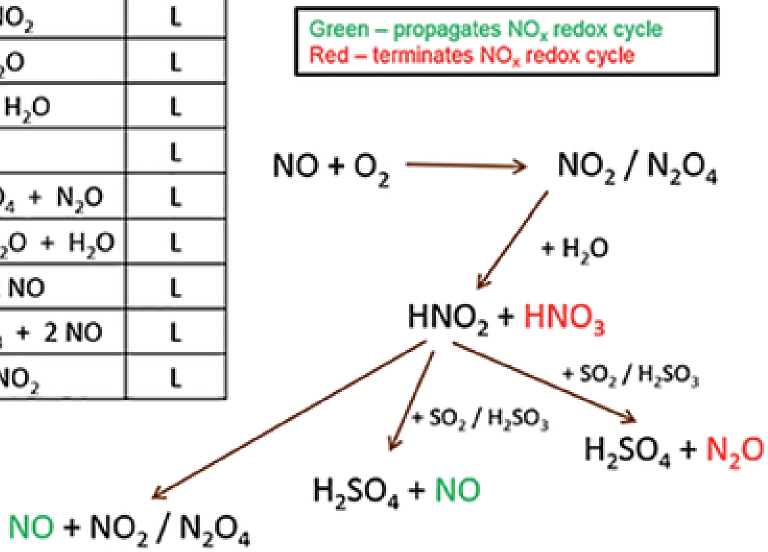
$SO_3 + H_2O \leftrightarrow H_2SO_4$ (6) Fast

This overall reaction will be limited by the first reaction which is favourable at higher pressure (i.e. greater than 10 Bar). The presence of NO_2 will initiate the catalytic conversion of SO_2 to SO_3 with NO_2 serving as the catalyst. In the presence of water, SO_3 will be absorbed and converted to H_2SO_4. It was hypothesized that NO will not be converted to HNO_3 until all the SO_2 are converted.

A more detailed kinetic evaluation of this reaction led to better understanding of the fate of NO and SO_2 during compression. It could be noted that it is predominantly a liquid phase reaction. This could be illustrated in the network of reactions shown in Figure 36.



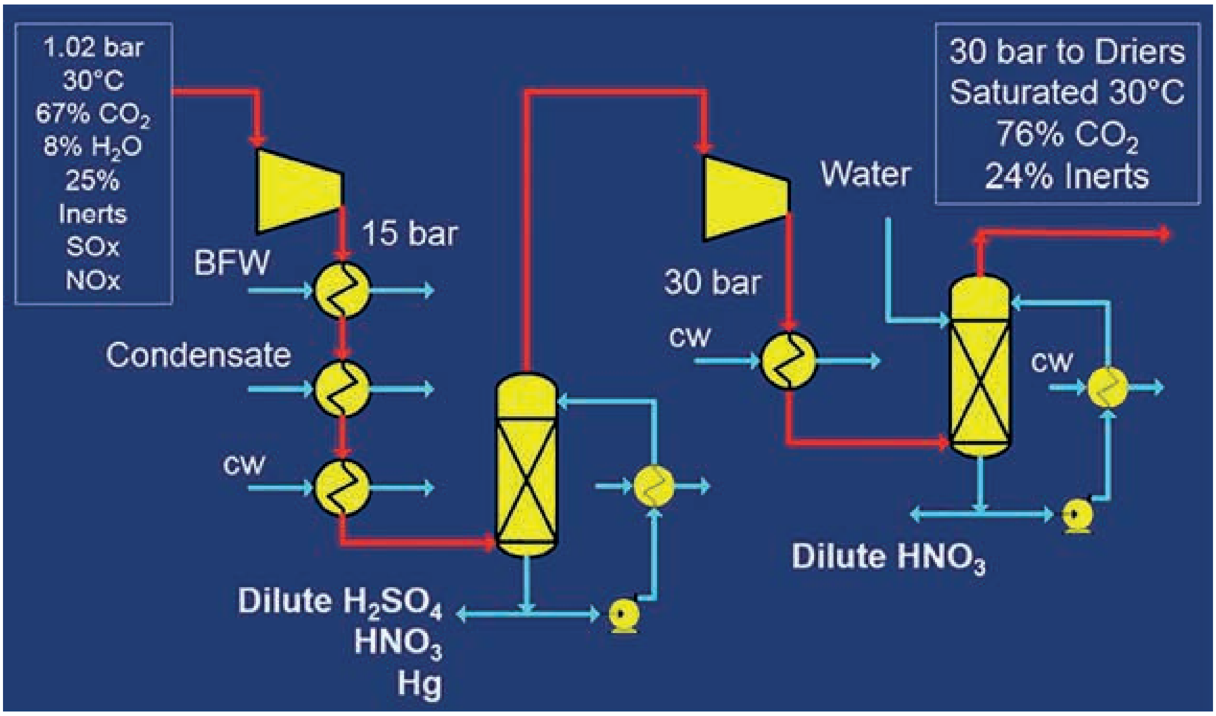
Stoichiometry	Phase
$2\ NO + O_2 \rightarrow 2\ NO_2$	V
$2\ NO_2 \rightleftharpoons N_2O_4$	V
$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$	L
$2\ HNO_2 \rightleftharpoons NO + NO_2 + H_2O$	L
$4\ HNO_2 \rightleftharpoons 2\ NO + N_2O_4 + 2\ H_2O$	L
$SO_2 + H_2O \rightleftharpoons H_2SO_3$	L
$2\ HNO_2 + 2\ SO_2 + H_2O \rightleftharpoons 2\ H_2SO_4 + N_2O$	L
$2\ HNO_2 + 2\ H_2SO_3 \rightarrow 2\ H_2SO_4 + N_2O + H_2O$	L
$2\ HNO_2 + SO_2 \rightarrow H_2SO_4 + 2\ NO$	L
$2\ HNO_2 + H_2SO_3 \rightarrow H_2O + H_2SO_4 + 2\ NO$	L
$2\ NO_2 + H_2O \rightarrow HNO_3 + HNO_2$	L



NOTE See References [142], [143] and [144].

Figure 36 — Updated SO_x and NO_x reaction during compression

Taking into account these reactions, Air Products proposed the Sour Compression Scheme to remove both NO_x and SO_x during the flue gas compression as shown in Figure 37. For this option, the design of the HP scrubbers is crucial in the removal efficiency of both SO_2 and NO_x. The SO_2 loading in the flue gas coming from the FGC, operating pressure and residence time are some of the important parameters considered. It has been reported that ~99 % of SO_x and at least 95 % of NO_x are removed as mixture of acids of H_2SO_4, HNO_3 and HNO_2 at ~15 Bar.[140][141][144][145][146]



NOTE See Reference [140].

Figure 37 — Updated SO_x and NO_x reaction during compression

The Linde Group[138][139][147][148][149] proposes the use of LICONOX[12) process to remove the NO_x. The origin of the LICONOX reaction is based on using ozone to oxidize NO to NO_2. However, during the compression of the flue gas, the ozone is not needed; the conversion of NO to NO_2 is favourable to proceed at higher pressure (as described earlier). It is expected to remove >99 % of the SO_x at the FGD and/or FGC upstream. Thus, the SO_2 loading in the flue gas entering the LICONOX process will be minimal (i.e typically in the range of <5 ppm to 10 ppm depending on SO_x removal efficiency upstream). The cleaned gas is compressed to 12 Bara to 15 Bara; thus, converting all NO to NO_2; and then NO_2 is removed by using alkali wash (using NH_3 water or NaOH). This process has been evaluated at Vattenfall's Schwarze Pumpe pilot facility.

A removal efficiency of at least 95 % of NO_x input was reported. If ammonia water is used, the by-product produced from the reaction consists of spent salt of ammonium nitrite and nitrate. With this option, the salt loading could be further reduced by preheating the salt solution to 60 °C therefore reducing the salt of nitrite to N_2 and H_2O. This is illustrated in Figure 38. A more detailed description of their process is presented in various publications.[147][148][149]

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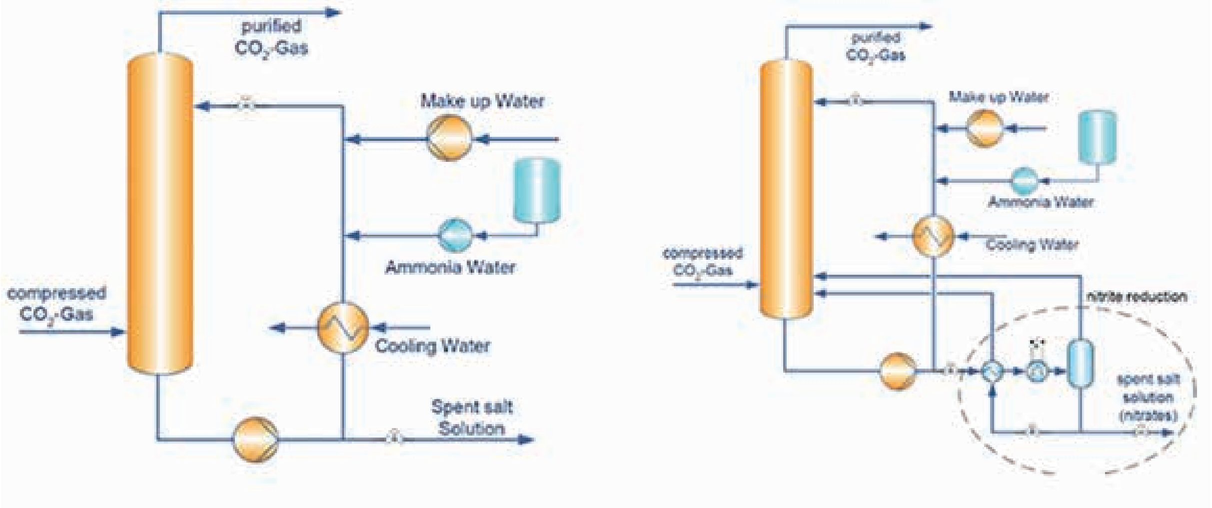
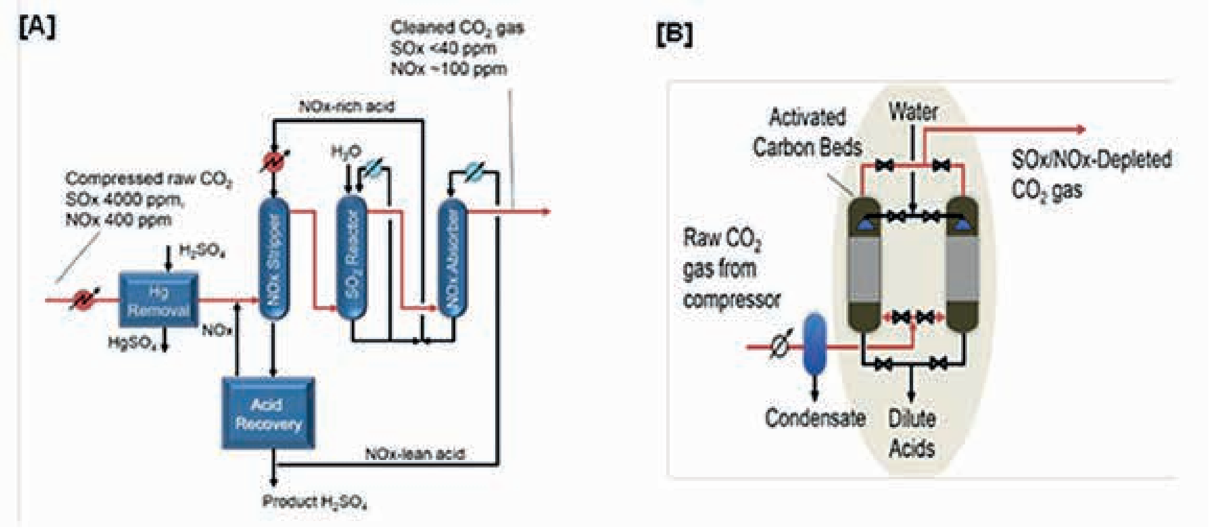
12) LICONOX is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.



NOTE See Reference [139].

Figure 38 — LICONOX (Cold DeNOx) process with and without nitrite reduction

Praxair Inc.[150][151][152] presented two possible options to remove the NO_x and SO_x in the flue gas coming from the FGC. The first option uses sulfuric acid wash to recover nitric acid as shown in Figure 39 a). This would result in a clean gas containing <50 ppm SO_x and ~100 ppm NO_x. The second option uses activated carbon to adsorb any SO_x and NO_x resulting in dilute acid during regeneration as shown in Figure 39 b). It was claimed that nearly 99 % of the SO_x and 98 % of the NO_x could be removed.

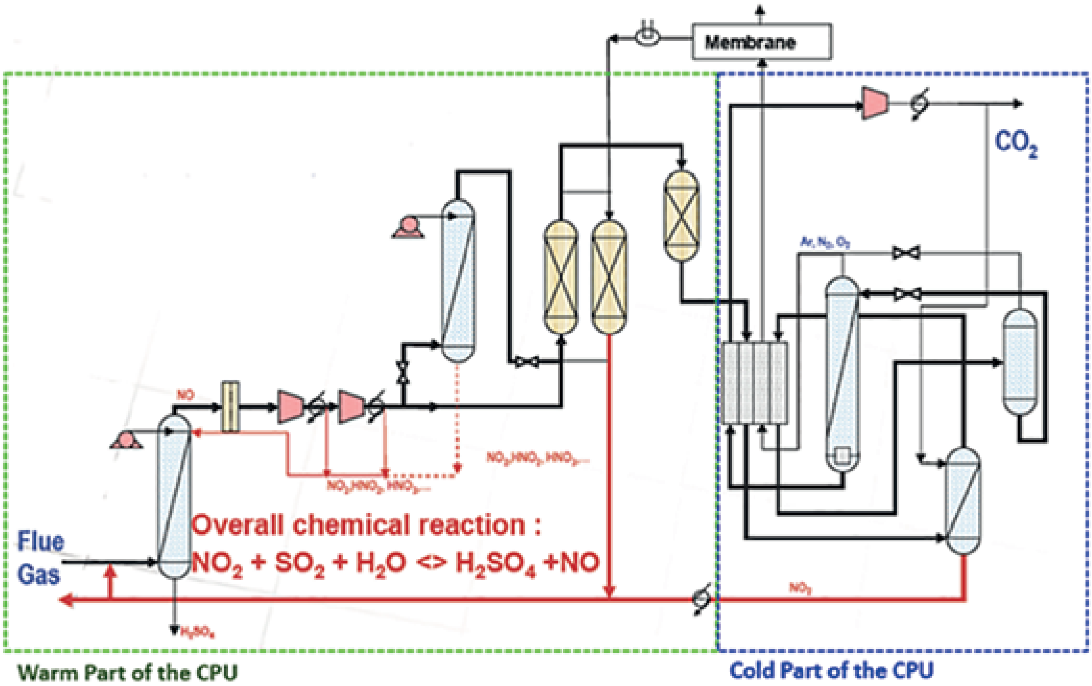


a) by sulfuric acid wash b) by activated carbon bed

NOTE See References [150] and [151].

Figure 39 — NO_x and SO_x removal

Air Liquide [134][136][153][154][155] proposes the use of $NaCO_3$ or NaOH in the FGC as salt of sulfates and sulphites. This should reduce the SO_x down to <10 ppm and expecting that most of the remaining SO_x entering the flue gas compressor to be as H_2SO_4. Similarly, the majority of the NO_x is expected to be removed during the compression due to the conversion of NO to NO_2, and then collected in the knockout drums of the compressor and/or at the HP scrubbers as HNO_3 or HNO_2. It was reported that <0,1 ppm of SO_2 and <10 ppm of NO_2 is achievable after compression. However, for their second-generation CPU, the remaining SO_x in the flue gas is removed as sulfuric acid by recycling the NO_2, HNO_2 and HNO_3 as reagent in the LP scrubber as shown in Figure 40. To reduce further the NO_x down to <1 ppm, it was proposed that a distillation column can be added to separate NO_2 at low temperature conditions.



NOTE See Reference [134].

Figure 40 — Simplified schematic flow diagram of Air Liquide (second-generation) CPU

Alstom is also developing their own CPU design and called it as gas processing unit or "GPU"[156]. However, information about their warm part of their GPU process is not yet available in the open literature, thus, should be revisited in the future.

9.2.6.4 Dehydration unit (water removal)

The cold part of the CPU is operated at low temperature conditions (i.e. down to ~-55 °C), thus, it is essential to remove water to <10 ppm to 20 ppm to prevent any ice formation in the cold box.

It should be noted that plant downtime for defrosting is expensive. Thus, the selection of dehydration process is based on operation reliability rather than economics.

For the CPU of oxyfuel combustion power plant, it is expected that TSA using molecular sieve will be employed and water content of <1 ppm is achievable but typically <10 ppm to 20 ppm is guaranteed. [102][116][136][137][138][157]

Additionally, any remaining SO_2 in the flue gas could be permanently adsorbed by the TSA/molecular sieve. Thus, this should contribute to the long term performance degradation of the molecular sieve and should be factored into the design and maintenance regime of the dehydration unit.[144]

Any remaining NO_x in the flue gas that are adsorbed in the TSA/molecular sieve are regenerated, and should have no impact to the long term operation of the dehydration unit.[102][137][144][159]

Mercury in the gas could also be captured in the TSA.[116] However, the possible re-emission of the mercury captured in the molecular sieve during operation is not yet well understood and should be evaluated.

9.2.6.5 Mercury removal unit

Mercury is known to corrode any aluminium-based equipment downstream such as the BAHX, turbo expanders, etc.[160] In the natural gas industry, it was established that mercury at <1 µg/Nm^3 could significantly reduce the risk to any aluminium equipment. For oxyfuel combustion power plant, this limit could be achievable. However, regulations should be reviewed in the context of clarifying uncertainty about measuring Hg during oxyfuel combustion.

The damage caused by mercury to any aluminium-based equipment is commonly due to accumulation, thus, any mercury contamination in the BAHX or any other aluminium-based equipment could be very sudden and unpredictable.

For oxyfuel combustion, the fate of mercury species in the flue gas have been evaluated extensively and enough understanding has been gained.[160][161][162][163][164][165] It has been established that oxidation of Hg could be similar or higher during oxyfuel combustion.[161][162][163][164]

Most of the oxidized mercury will be captured in the different flue gas processing units such as FF/ESP, FGD, FGC and/or flue gas filters.

For the elemental mercury, the presence of HNO_3 acid during the compression of the flue gas could also promote and effectively remove the mercury (as any form of mercury is highly reactive to the NO_2, N_2O_4 and/or HNO_3).[165]

Additionally, as mentioned earlier, mercury could also be trapped in the TSA/molecular sieve dryer. However, understanding its re-emissions during operation is important.[116]

Given the ample opportunities where mercury could be removed, OEMs will remain conservative to their approach due to some uncertainties that yet to be clarified. The addition of the mercury removal unit using activated carbon bed impregnated with sulfur will be installed. This is a well-established technique in reducing potential contamination. This could be positioned before or after the TSA/molecular sieve dryer.

Furthermore, the use of mercury resistant design BAHX could also be an additional precaution. Option to capture the mercury in the "cold compartment" is also possible (i.e. at temperature between −30 °C and −40 °C, mercury is solid, thus, should drop out easily from the gas).[166]

9.2.6.6 CO removal unit

CO has very similar low temperature properties to the N_2. Thus, bulk of the CO remaining in the flue gas will remain in the gaseous phase and will go through the cold box. Most of it will end at the CPU vent. Given that the volume of the CPU vent is small, the concentration of the CO (reported as ppm or mg/Nm^3) may exceed the regulatory limit. Additionally, a small fraction of the CO could be co-captured in the CO_2 product.

There are two possible options to deal with CO.

- Dilute the vent gas using waste nitrogen of the ASU and do nothing.
- Use catalytic combustion to oxidize the CO to CO_2. It is expected that the effectiveness of such process could reduce CO in the vent gas down to <10 ppm.[150][151][152][166]

9.2.6.7 Cold part of the CPU

The main considerations in the design and engineering of the cold part of the CPU include the following:

- specification of the CO_2 products;
- minimum CO_2 recovery rate (also known as capture rate);
- energy consumption;

— CAPEX and OPEX.

Operating parameters, such as pressure, temperature and CO_2 composition in the feed gas, define the product CO_2 composition and recovery rate, while the vent gas of the CPU is dependent on the VLE of gas mixture at a given operating temperature and pressure.

In the open literature and various conference proceedings,[137][167] around 40 different concepts have been reported. Primary considerations include the basic arrangements of the flash and/or distillation column; and this could have several options, for example:

— single flash, single column;

— dual flash, flash-column, dual columns;

— triple flash, 2 flash + 1 column, 1 flash + 2 columns, triple columns.

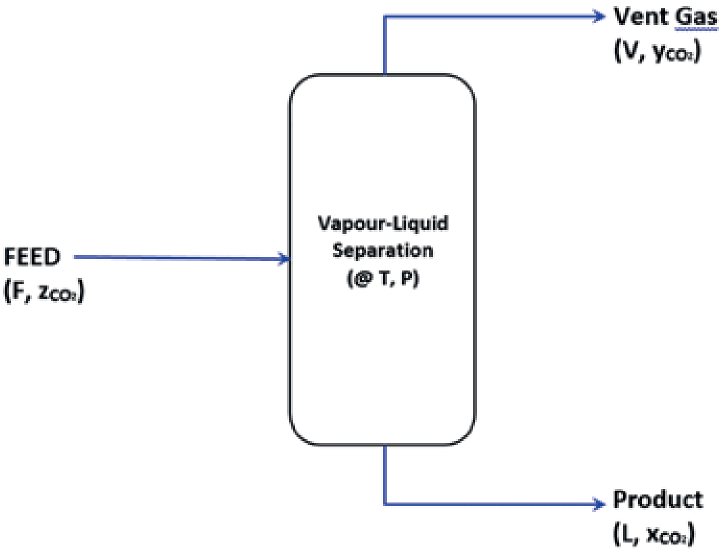
Other variations to the design of the cold box and associated equipment include the following:

— selection of the refrigeration package (this could have a choice between external refrigeration vs. auto-refrigeration cycle or combination of both);

— processing of the vent gas (i.e. manner on how energy are recovered from the vent);

— option to include additional process to recover the CO_2 and/or O_2 from the vent (to be discussed in 9.2.6.9).

To illustrate how product composition is affected by the pressure, temperature and feed composition; the performance of the single stage flash separation (as shown Figure 41) is presented.

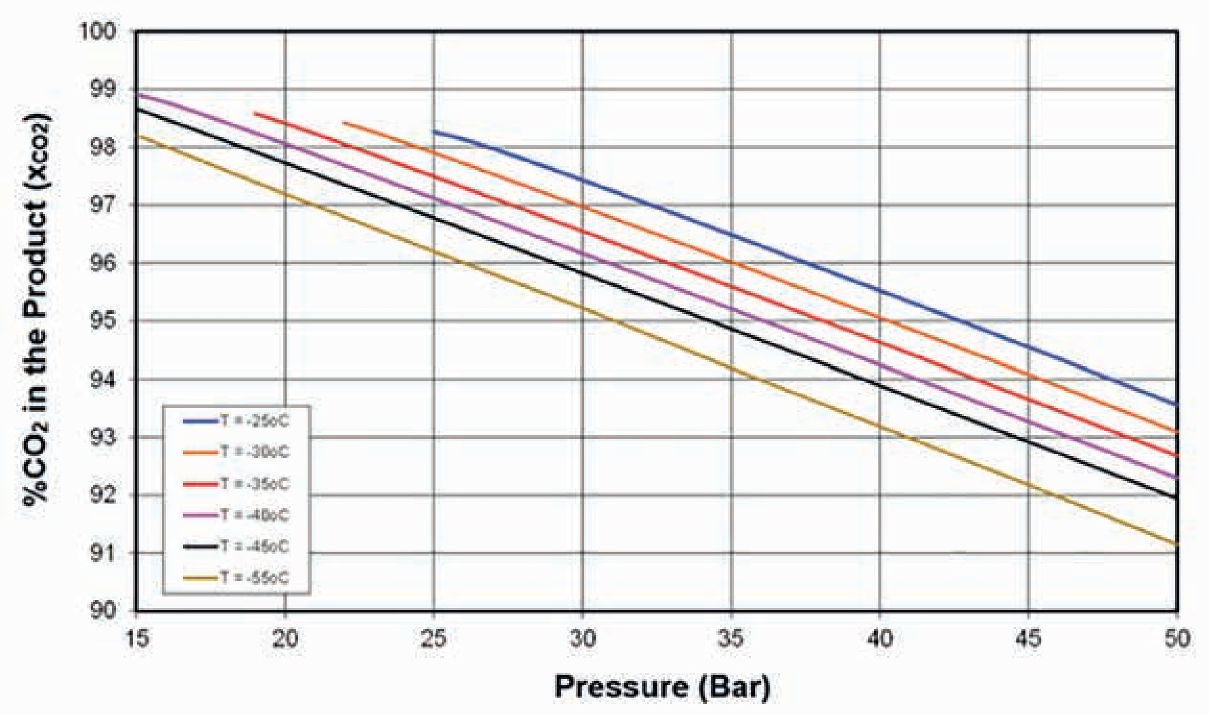


NOTE See Reference [141].

Figure 41 — Single stage flash separation

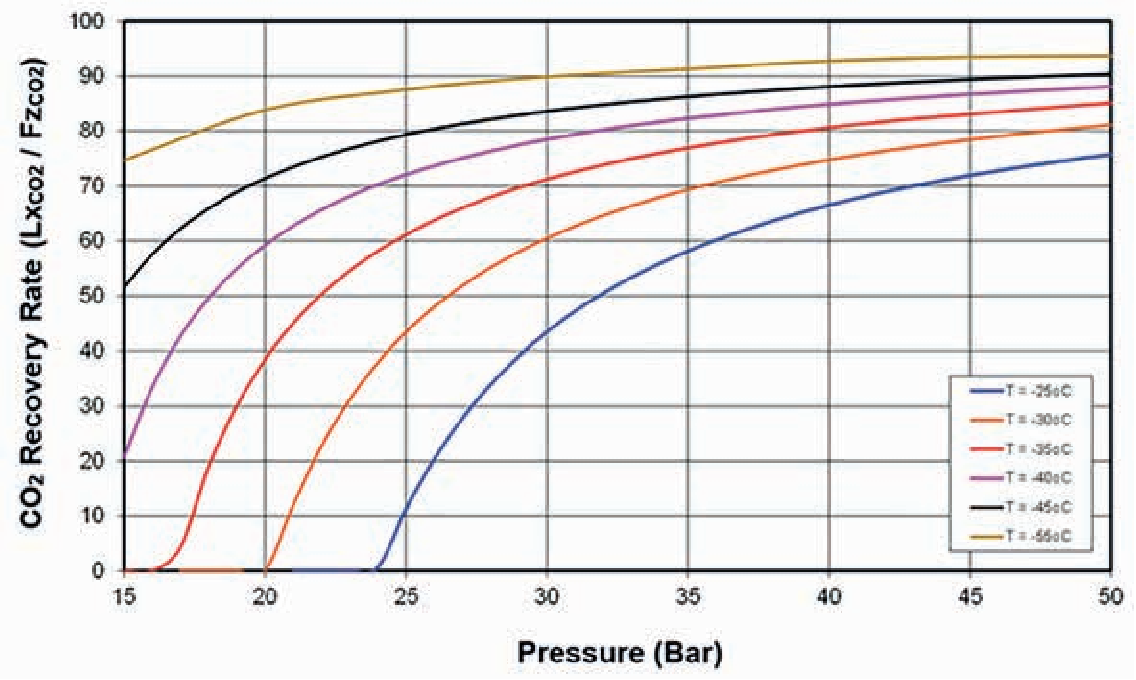
The operating pressure of the vapour-liquid separation column (flash column) could impact the product CO_2 composition and recovery rate. At higher pressure, the CO_2 purity decreases but the CO_2 recovery rate increases. For example, when the flash column is operating at 15 Bar and −45 °C, the product CO_2 is ~98,6 % pure, but the recovery rate is only ~51 %. By doubling the operating pressure of the flash column to 30 Bar and keeping the temperature the same at −45 °C, the product CO_2 purity reduces to ~95,8 % and the recovery rate increases significantly to ~84 %. These basic principles are illustrated in Figure 42 and Figure 43.

The feed composition could influence the recovery rate. Higher recovery rate could be achieved when %CO_2 in the feed gas is higher. For example, at 30 Bar and −52,5 °C, ~95 % of the CO_2 is recoverable, if the feed composition is ~90 % CO_2; on the other hand, this reduces to ~82 % CO_2 recovery if the feed composition is at ~65 % CO_2. This is shown in Figure 44.



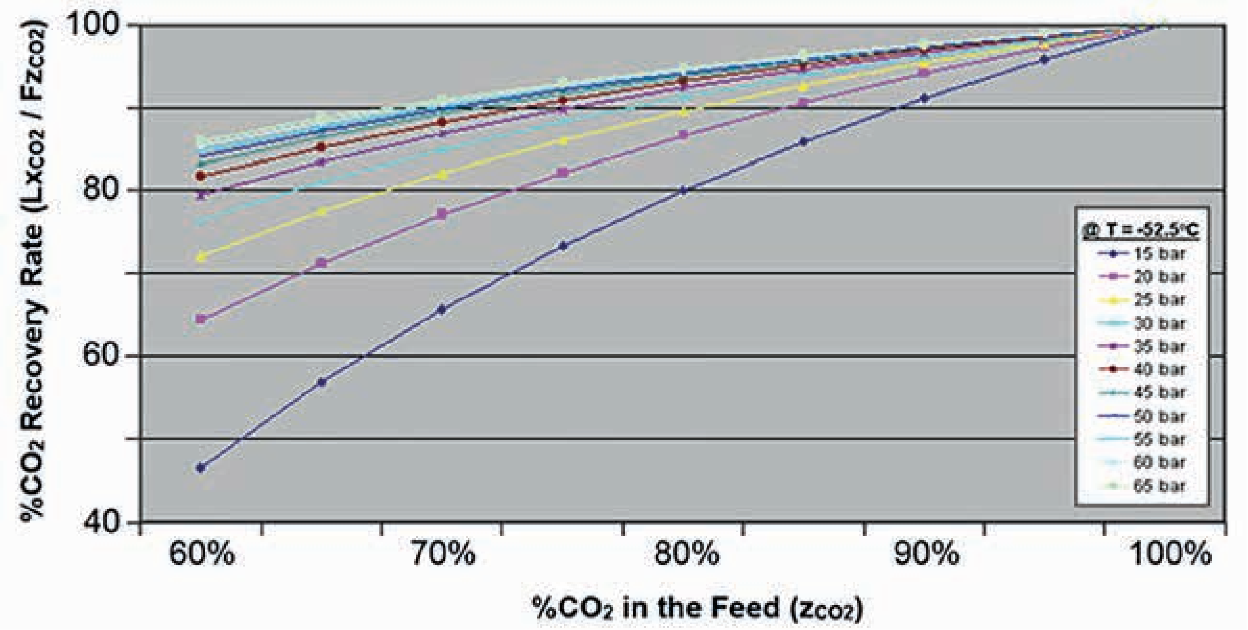
NOTE Source: References [137] and [141].

Figure 42 — Pressure vs CO_2 product purity (with %CO_2 in the Feed at ~75 %)



NOTE Source: References [137] and [141].

Figure 43 — Pressure vs CO_2 recovery rate (with %CO_2 in the Feed at ~75 %)

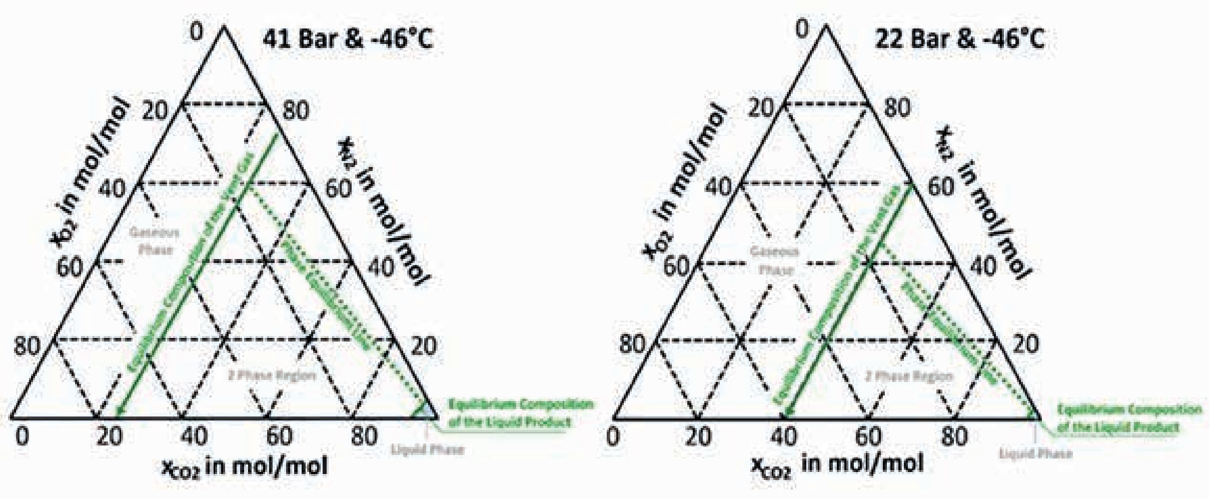


NOTE See Reference [134].

Figure 44 — Feed composition vs. CO_2 recovery rate

Furthermore, due to the VLE of the gas mixture, i.e. at a given feed composition, there will be zero recovery of the CO_2 at temperature and pressure where it is not possible to have any CO_2 condensation. For example, for feed composition with 75 %CO_2, it is expected that there will be zero recovery at temperature of −25 °C and pressure below 23 Bar. Similarly (with 75 %CO_2 in the feed), there is no recovery at −30 °C and pressure below 20 Bar.

On the other hand, the vent gas composition is controlled by the VLE of the gas mixture (as illustrated in Figure 45); and given a specific temperature and pressure, it is not affected by the feed composition (as illustrated in Figure 46). For example, at 41 Bar and −46 °C, the vent composition should have ~23 % CO_2. However, at lower pressure of 22 Bar and −46 °C, the vent gas should have ~40 %CO_2.

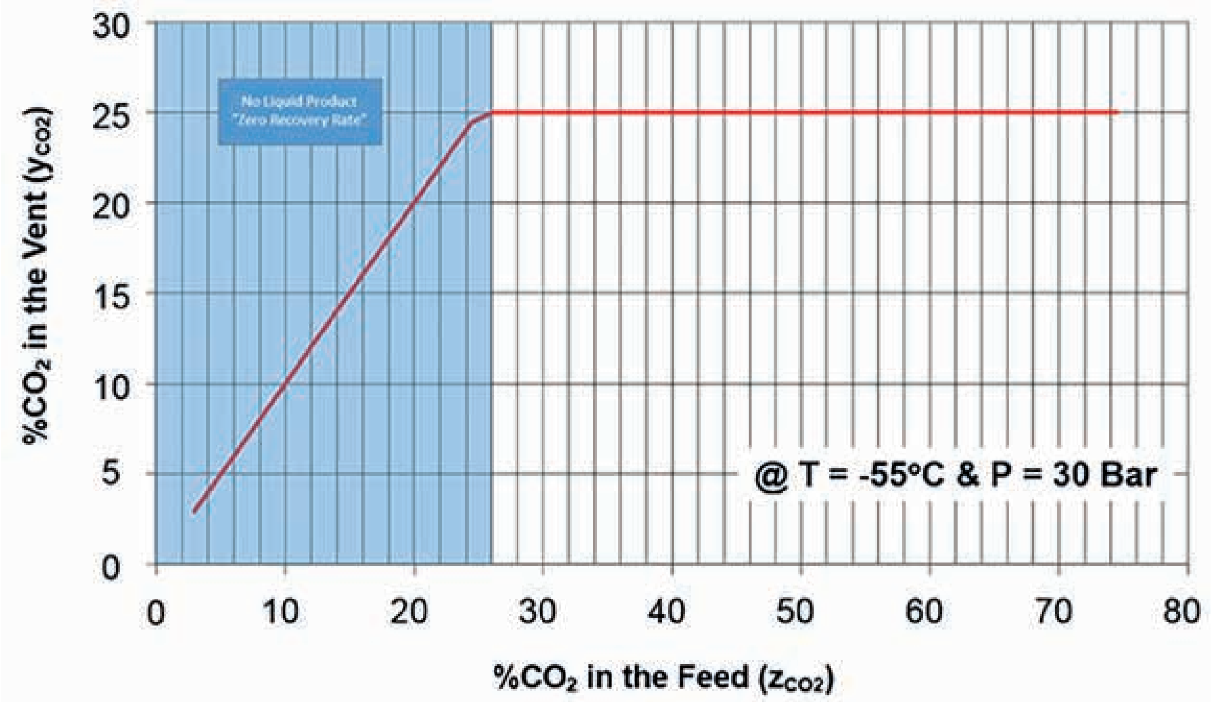


a) subjected to 41 Bar

b) subjected to 22 Bar

NOTE Source: Reference [168].

Figure 45 — Vapour-liquid equilibrium (VLE) of CO_2, N_2 and O_2 at −46 °C



NOTE See Reference [137].

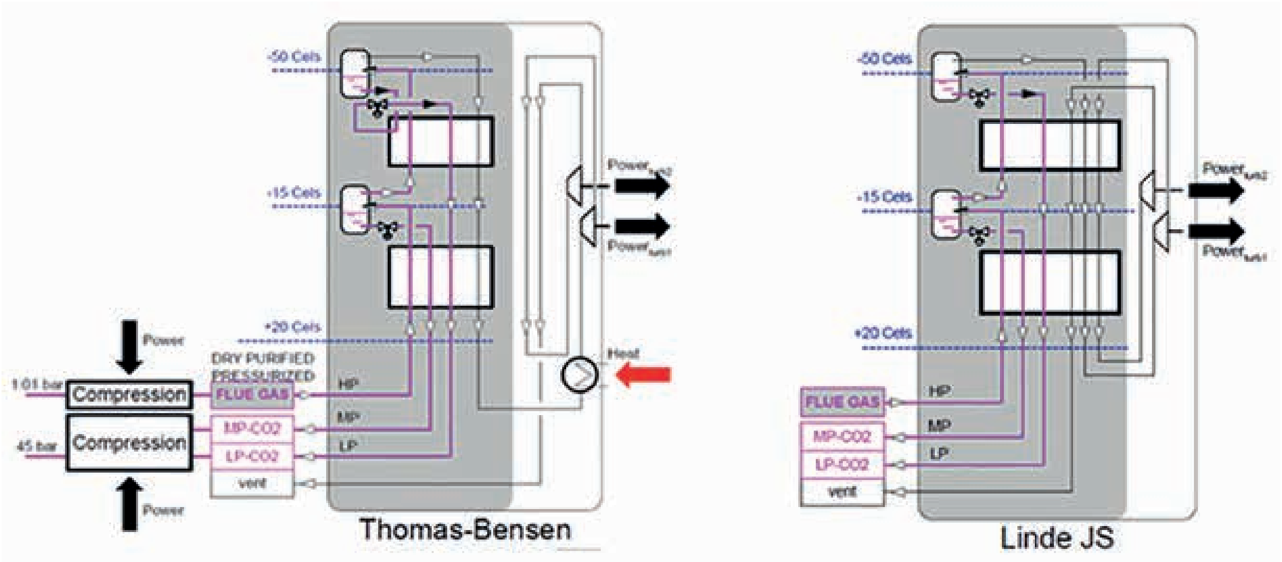
Figure 46 — Composition of the vent gas at 30 Bar and −55 °C

It is not possible to discuss all CPU concepts reported in the open literature or conference proceedings. However, broadly the most common concepts for the cold box of the CPU presented are based on flash-flash and flash-distillation arrangements. For the purpose of illustrating the expected performance of the cold box relative to recovery rate and CO_2 product purity, four different concepts are reviewed.

Figure 47 (Thomas Bensen) and Figure 47 (Linde JS) present the simplified schematic PFD of two different CPU concepts employing flash-flash arrangement respectively.[167]

The flue gas entering both CPU process schemes are generally compressed to the set operating pressure of the flash columns (typically in the range of 30 Bar to 40 Bar, HP). The CO_2 products delivered to the product compression unit are at two levels of pressure typically in the range of 15 Bar to 20 Bar (for the MP product CO_2) and 6 Bar to 10 Bar (for the LP product CO_2). In general, the operating temperature could be in the range of −15 °C to −25 °C for the first stage flash and could not be colder than the freezing temperature of the gas mixture entering the second-stage flash (about −53 °C to −55 °C).

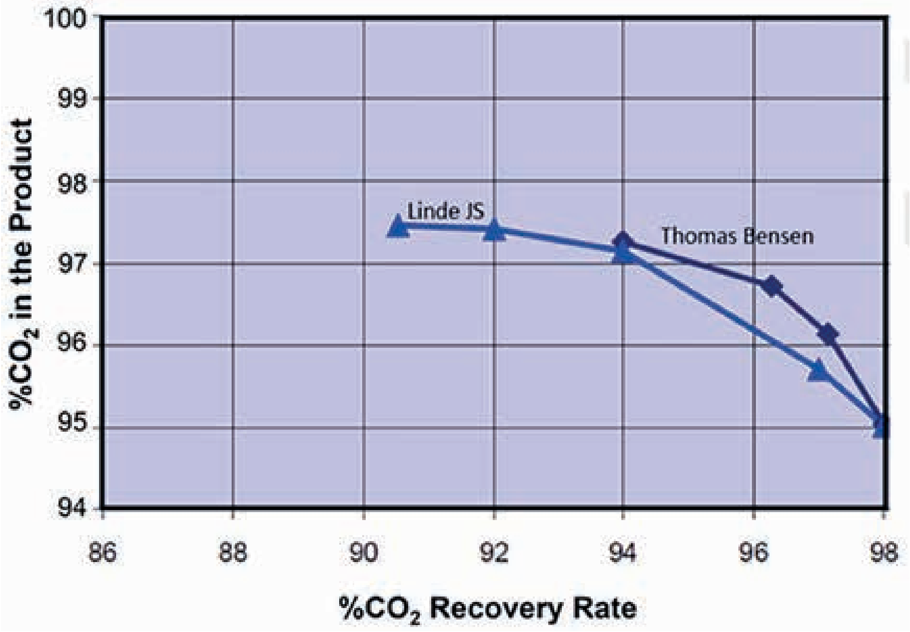
For the Thomas Bensen process, the expansion of the vent is done outside the cold box. Additionally, the liquid CO_2 taken from the second flash is preheated before being throttled in the JT valve. The CPU vent is heated (to ~300 °C) and then expanded in the turbo expanders to generate electricity. The heating of the vent is required to prevent any frosting to the turbo expander. On the other hand, for the Linde JS process, the vent is expanded without preheating and recycled back into the cold box. Thus, in addition to generating electricity, the expansion of the vent also provided refrigeration to the CPU cycle.



NOTE See Reference [167].

Figure 47 — Simplified PFD of two CPUs based on flash-flash arrangements

Figure 48 presents the product CO_2 purity and recovery rate of both processes. At 95 % recovery, both processes deliver the product CO_2 at 95 % purity. Between 94 % and 97 % recovery rate, the Thomas Bensen produces slightly higher purity due to the lower operating pressure and/or colder operating temperature as compared to the Linde JS process.

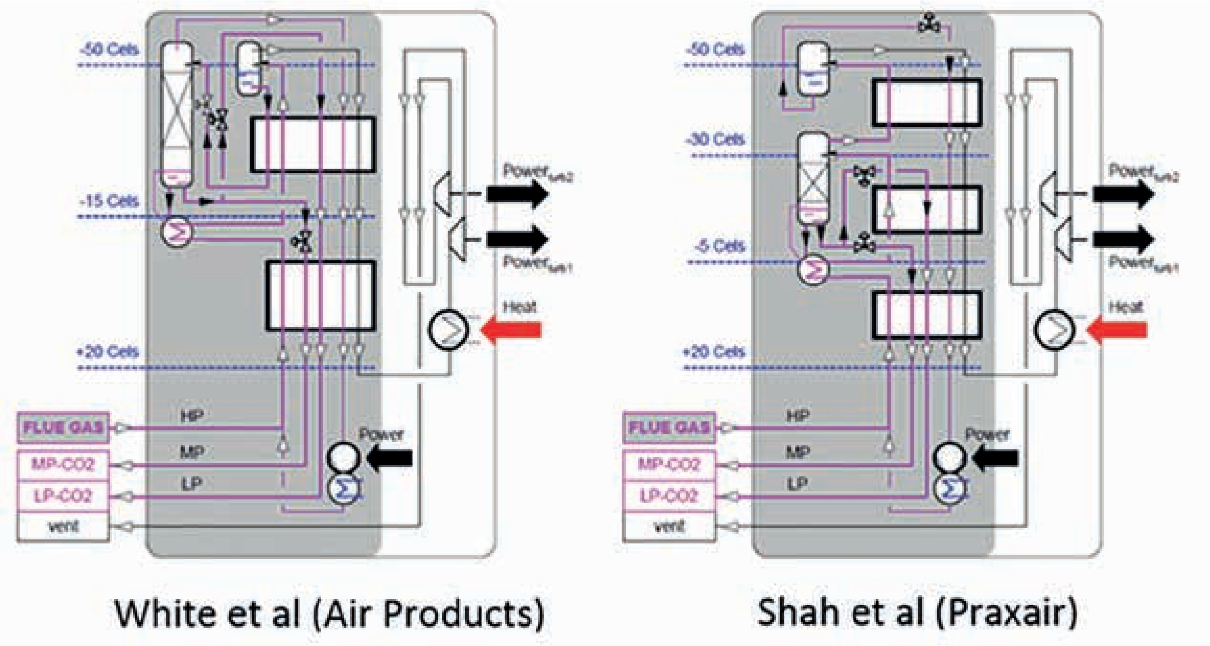


NOTE Source: Reference [167].

Figure 48 — Product purity vs recovery rate of the CPU based on Thomas Bensen and Linde JS concepts

To increase the purity of the CO_2 product, a distillation column could be employed. Additionally, part of the liquid CO_2 is recycled back and mixed with the flue gas. Thus, increasing the %CO_2 in the feed results to an increase in both purity and recovery rate.

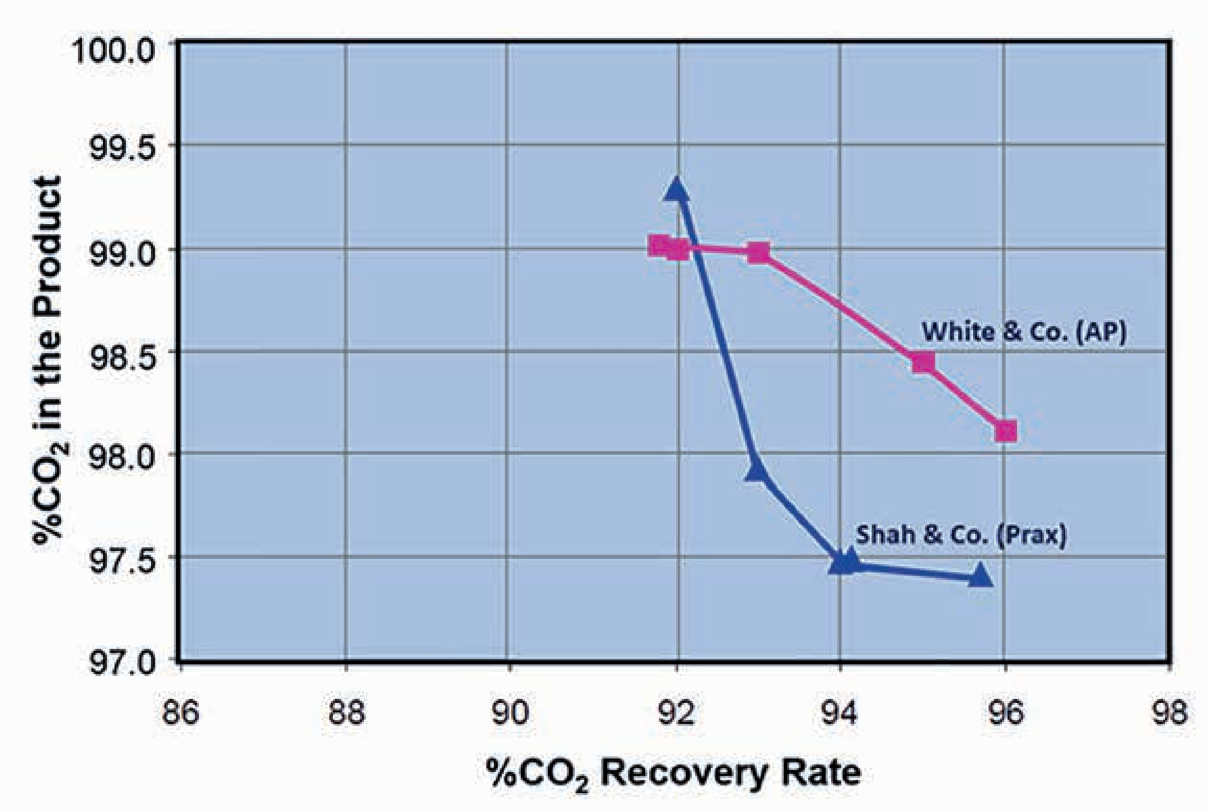
Figure 49 (White and Co) and Figure 49 (Shah and Co) present two different CPU schemes with flash-distillation column combination. The scheme proposed by White and Co has a flash-distillation column arrangement; while the scheme proposed by Shah and Co has distillation column-flash arrangement. Both concepts employ the recycling of the CO_2 products collected from the second-stage separation unit to the pressurized feed gas. This should consequently increase the %CO_2 in the feed gas entering the first stage separation unit and should also improve the recovery rate of the flash (White and Co) or the distillation column (Shah and Co), i.e. first stage separation. One of the differences between the two concepts presented is the operating temperatures. The concept of Shah and Co presented a scheme with three levels of temperature and a "warmer" distillation column; thus, leading to lower product purity. Figure 50 presents the product purity and recovery rate of both schemes.



White et al (Air Products) Shah et al (Praxair)

NOTE See Reference [167].

Figure 49 — PFD of two CPU schemes based on flash-column arrangements



NOTE Source: Reference [167].

Figure 50 — Product purity vs recovery rate of the CPU based on flash-column arrangement

By increasing the requirements to the product purity, it could be observed that complexity of the process increases. To require the product purity greater than 99,5 %, several strategies maybe employed and these could include but not limited to

- installing additional flash or distillation column,
- increasing operating pressure of the distillation process; thus, may require additional external refrigeration, and
- employing additional recovery of the CO_2 from the vent and recycling back the recovered CO_2 rich gas mixture to the CPU cold box.

9.2.6.8 Product CO_2 compressors and pumps

The product CO_2 coming from the cold box of the CPU is generally available in two pressure levels at MP (~10 Bar to 20 Bar) and LP (6 Bar to 10 Bar) or single pressure level at MP. The temperature is dependent on the design point at the exit of the BAHX. The product is nearly bone dry (moisture content of <10 ppmv to 20 ppmv).

The selection of compressor or pumps is dependent on final pressure required. This is a design point of the power plant.

It should be noted that using liquid CO_2 pumps has better energy efficiency than compressors.

9.2.6.9 Additional CO_2 recovery from the CPU vent

The vent from the CPU cold box typically consists of the inert and the residual CO_2. Normally, at operating pressure of 30 Bar and with the coldest point of the CPU at −50 °C to −55 °C, the vent gas consists of ~25 % CO_2 and available at pressure. At lower operating pressure, the vent gas is expected to have higher CO_2 content.

The quality of the CPU vent gas, i.e. available at high CO_2 concentration and moderately high pressure, provided an opportunity to recover additional CO_2 and achieve greater than 98 % recovery rate at reasonable additional energy requirement. Additionally, it could also minimize the impact of the air ingress in the boiler system.

In general, the development of this technology is based on two possible objectives: a) to recover the CO_2 from the vent; thus, providing high CO_2 recovery rate; and also b) to recover the oxygen, reducing the oxygen required from the ASU.

Some of the processes presented by the different OEM vendors are described below.

- Air Products[141][145][146] proposed the use of membrane [Prism[13]] where the permeate mainly consists of CO_2 and O_2, is recycled back to the boiler. It is claimed that with this process installed, the O_2 requirement from the ASU could be reduced by 3 % to 5 %. The simplified process flow diagram is presented in Figure 51. (It should be noted that the CPU cycle of the cold box presented in Figure 51 is the Thomas Bensen scheme as described earlier. The only modification to that scheme is the addition of Prism membrane to the vent of the CPU process).
- The Linde Group[138][139][169] proposed the use of PSA to further recover CO_2 from the vent gas of the CPU. The CO_2 rich gas recovered is recycled back to the dehydration unit and to the flue gas compression unit of the CPU; while the remaining gas could be fed into the front end purification unit of the ASU. It is claimed that energy consumption of the CPU will increase by 6 % as compared to the CPU without PSA installed. However, Linde have not reported the possible savings that could be gained in the ASU. The overall process flow diagram is presented in Figure 52.
- Praxair Inc. proposed the use of VPSA to recover CO_2 from the vent of the CPU. The CO_2 rich gas recovered is recycled back to the flue gas compressor just after the FGC. Praxair Inc. has not yet reported the energy performance of this process.[150][151][152] The overall process flow diagram is presented in Figure 53.
- Air Liquide[134][166] proposed the use of membranes to recover CO_2 from the vent of the CPU and the permeate is recycled back to the flue gas compressor situated at the warm part of the CPU. An overview of the membrane process is shown in Figure 54.

Details of these processes are described in several literature and conference proceedings.[137] Advantages of recycling the captured O_2 from the CPU vent and its impact to the ASU have also been examined.[170][171]

Although the membranes and PSA/VPSA are well established technology that are commercially available and used in other industries, the application of these processes in oxyfuel combustion has yet to be demonstrated in a large-scale power plant. Issues of scaling up may need to be addressed. Only the deployment of large-scale demo project will allow these options to be validated.

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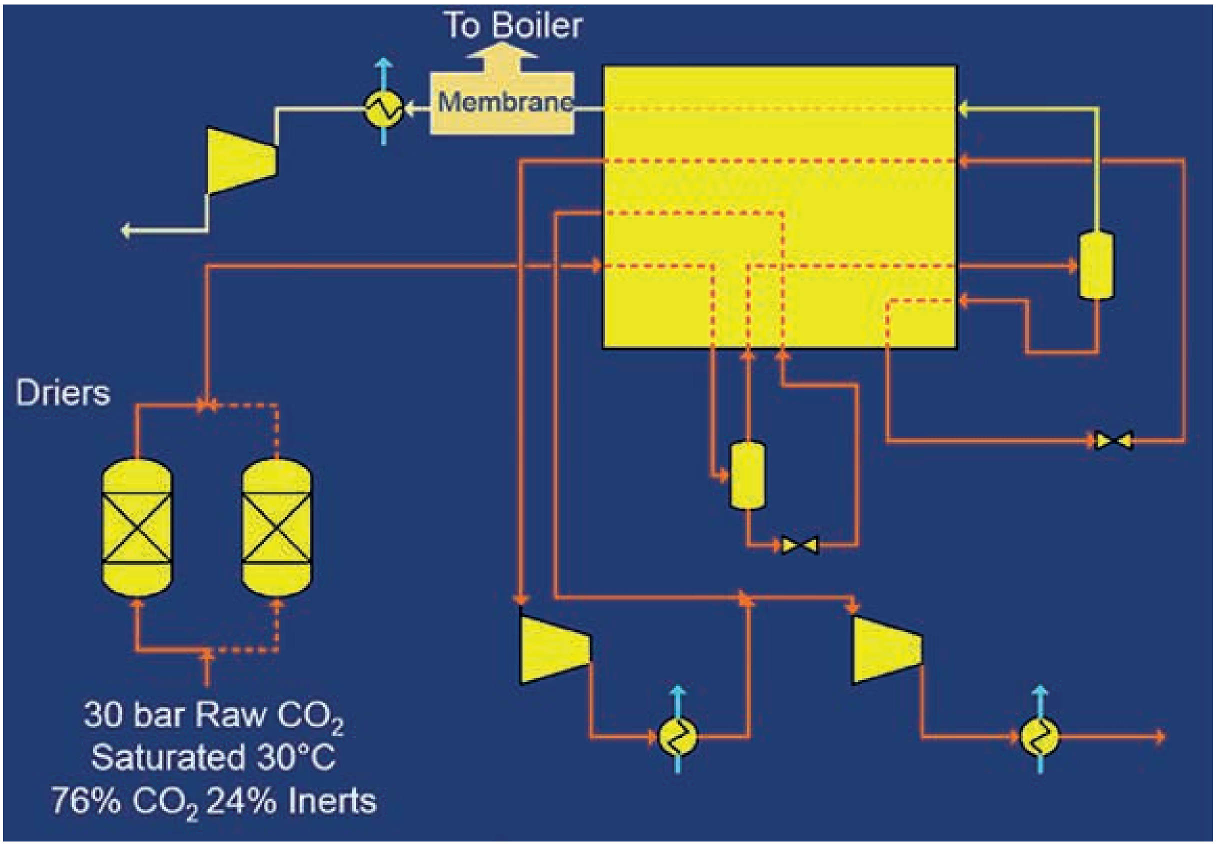
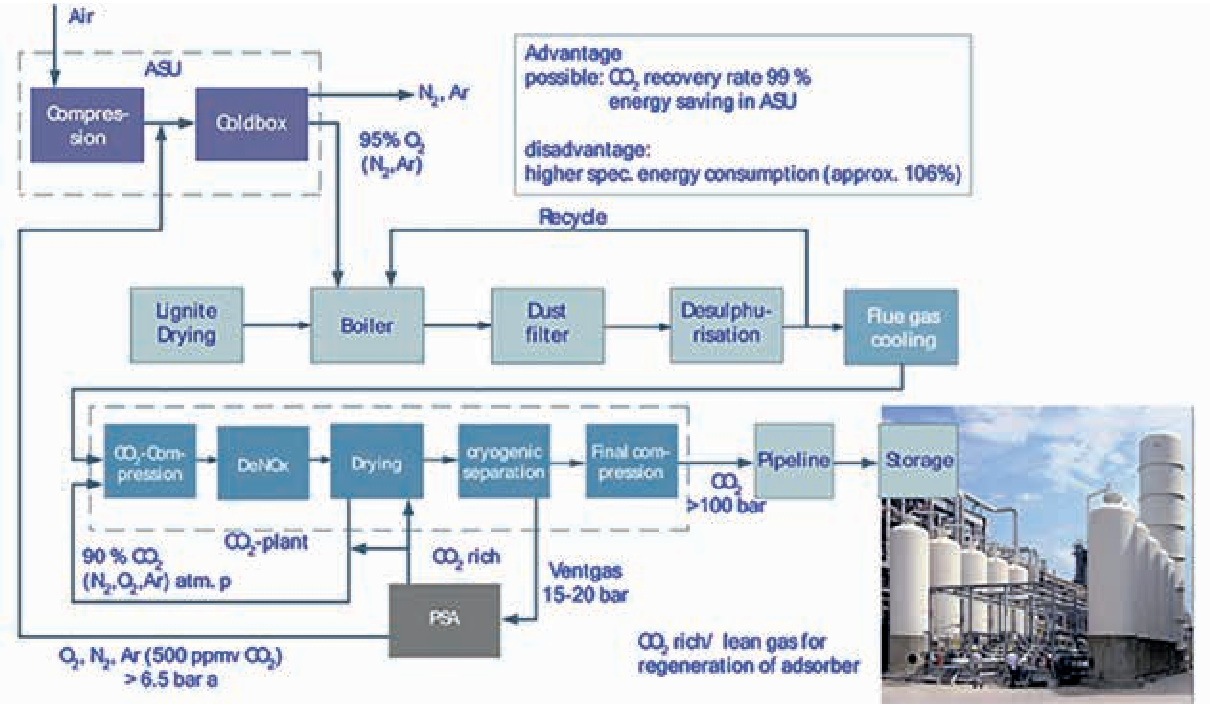
13) Prism is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.



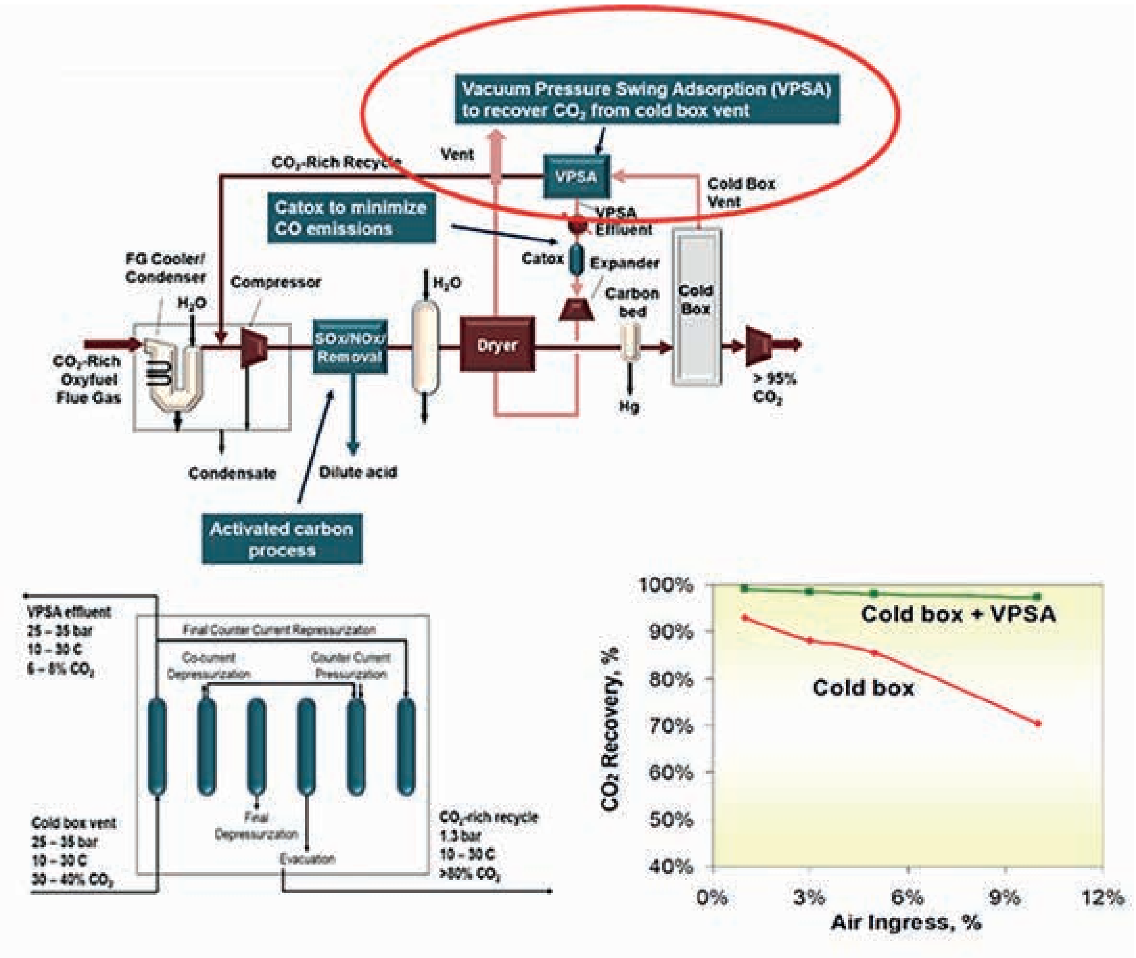
NOTE See Reference [141].

Figure 51 — Simplified PFD of the CPU with additional recovery of CO_2 by using a prism membrane



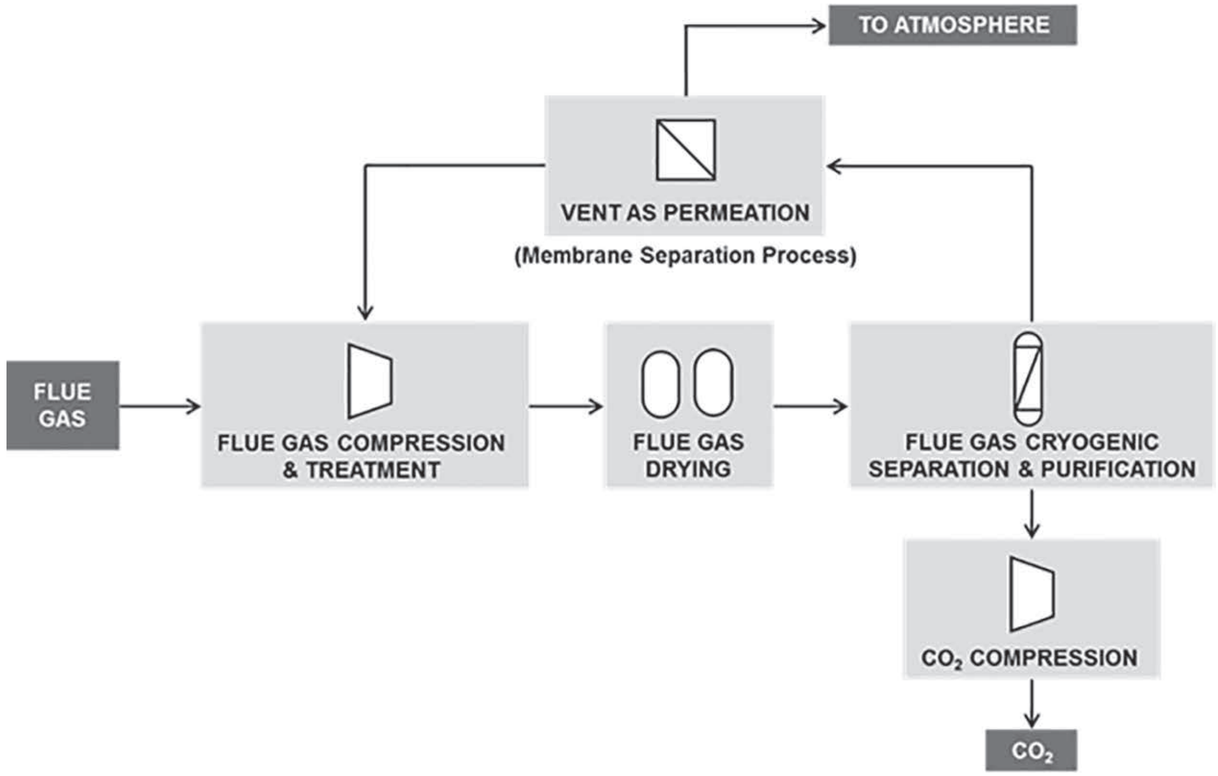
NOTE See Reference [138].

Figure 52 — Additional recovery of CO_2 and O_2 using PSA



NOTE See References [150], [151] and [152].

Figure 53 — Additional recovery from the vent using VPSA



NOTE 1 See Reference [166].

NOTE 2 A more detailed PFD is also shown in Figure 40. See also Reference [134].

Figure 54 — Recovery of CO_2 from the CPU vent using membrane

9.2.7 Balance of plant

The balance of plant (BOP) could include the following components:

- transformer, switchgear;
- in-plant utility switchgear;
- coal yard/coal handling facility;
- ash treatment equipment/ash disposal area;
- water supply/water treatment facilities;
- waste water treatment facility/waste water facility.

Except for the waste water treatment facility, which will be expected to be enlarged to accommodate additional waste water collected from the FGC and CPU, other components will not be affected by the deployment of the oxyfuel combustion.

In some scenario especially in the area where water supply is limited, waste water collected from the combustion of the fuel that is condensed in the FGC could be processed and can be sold as commodity.

9.3 Product CO_2, other major gas streams, emissions and waste products

9.3.1 Product CO_2

The composition of the product CO_2 varies from plant to plant. This is dependent on the design, engineering and operation of the boiler (including impact of the air ingress and purity of O_2 used), flue gas processing unit, FGC and CPU.

As described in 9.2, the product CO_2 coming from the CPU could range from

- low-purity CO_2 (i.e. ~80 % to 90 %),14)
- intermediate-purity CO_2 (~94 % to 98 %),15)
- high-purity CO_2 (~98 % to 99,5 %),16)
- very high-purity CO_2 (99,5 % to 99,9 %),
- ultra high-purity CO_2 (>99,9+ %).

The purity of the product CO_2 is delivered based on the design of the CPU and to meet the minimum requirements of the downstream processes (i.e. transport and storage).

Other non-CO_2 components expected could include:

- oxygen (O_2);
- nitrogen (N_2);
- argon (Ar);
- nitrogen oxide (NO_x);
- sulfur dioxide (SO_2);
- carbon monoxide (CO);
- other trace elements.

The list of other trace elements that could possibly be included in the product CO_2 is described in the Compressed Gas Association Handbook.[172] It should be noted that these are specific to the operation of the whole power plant and the fuel used.

Table 11 presents the CO_2 product purity of the different pilot plants and the indicative design specification for different large-scale demonstration project.

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14) This range is achieved by minimal processing of the flue gas, i.e. only cooling, dehydration and compression. Product CO_2 purity will be dependent on fuel specification (i.e. carbon content), operation of the boiler (i.e. level of air ingress) and oxygen purity used.

15) This is a typical range of product CO_2 purity achievable by the CPU with dual flash scheme. A CPU with triple flash scheme could reach 98 % to 99 %.

16) This is a typical range of product CO_2 purity achievable by the CPU with flash-distillation scheme.

Table 11 — Reported composition of the product CO_2 from various pilot plant project and FEED studies for large demonstration projects (both active and inactive)

Product Composition	Actual Operating Results				Engineering Design Specification / Predicted Values			
	Large Scale Pilot Facility			Mini-Demonstration Project	Large Scale Demo Project (Inactive)			Large Scale Demo Project (Active)
	Vattenfall Schwarze Pumpe Pilot Plant	CIUDEN Oxy-CFB Pilot Plant	TOTAL Lacq Project	COSPL Callide Oxyfuel Project	Vattenfall Janschwalde Project	OxyCFB300 (Compostilla Project)	KEPRI Yeong Dong Project	FutureGen 2.0
	Lignite ~30MWt	Anthracite / Petcoke ~30MWt	NG ~30MWt	Coal ~90MWt	Lignite ~250MWe	Anthracite / Petcoke ~300MWe	Coal ~125MWe	Coal 168MWe
CO_2	> 99,9%v	> 99,9%v	91-93%v	> 99,95%v	> 95%v	98%v	95%v	> 99,8%w
O_2	< 0,001%v	< 10ppm	1-3%v	< 30 ppm	< 0,8%v	<2%v	<4%v	~110 ppmw
N_2	< 0,01%v	< 0.01%v	5-7%v	trace	< 4,2%v			< 0,04%w
Ar			0,5-1%v					
NOx (as NO_2)	< 5ppm	< 10 ppm	< 0,01%v	< 15 ppm	< 50 ppm	< 10 ppm	N.R.	< 1600 ppmw
NOx (as NO)	< 5ppm			< 2,5 ppm			N.R.	
SOx (as SO_2)	<1ppm	< 0,01 ppm	N.A.	< 0,01 ppm	< 25 ppm	< 10 ppm	N.R.	< 1 ppmw
SOx (as SO_3)	< 0,3 ppm	-	N.A.	< 0,01 ppm	< 10 ppm		N.R.	
CO	< 2 ppm	N.R.	< 10 ppm	< 10 ppm	N.R.	N.R.	N.R.	N.R.
H_2O	< 5 ppm	< 1 ppm	< 10 ppm	< 20 ppm	< 25 ppm	< 10 ppm	N.R.	< 1 ppmw
Pressure	-	-	-	-	125 Bar	150 Bar	N.R.	~146 Bar
Temperature	-	-	-	-	< 50 °C	38 °C	N.R.	22 °C

NOTE Data are from various sources.

The bulk of the non-CO_2 components in the product consists of N_2, Ar and O_2. These gases are mainly derived from

a) contained N_2 and Ar in the O_2 delivered by the ASU (dependent on O_2 purity used by the boiler),

b) excess O_2 (residual O_2 after combustion), and

c) air ingress (also known as air infiltration or air in-leakage) into the system.

Items a) and b) are part of the operation of the oxyfuel combustion power plant.

But, air ingress into the system is an issue that needs to be addressed during the lifetime of the oxyfuel combustion power plant. This contributes to the energy penalty of the power plant as it affects the performance of the CPU.

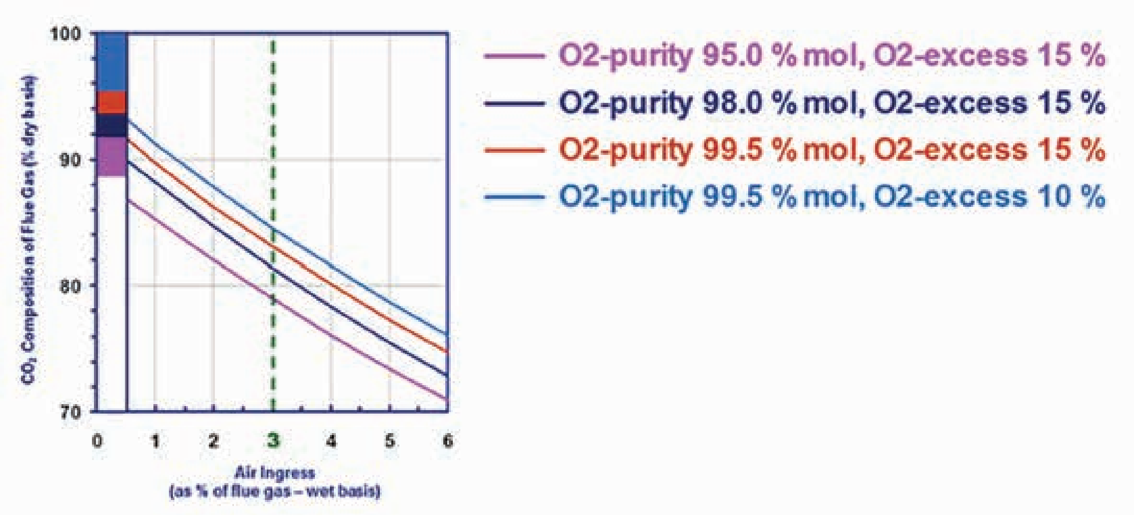
9.3.1.1 Air ingress and its management

In a conventional coal-fired boiler, the system downstream of the furnace is typically operated at a negative pressure, air may leak into the system through cracks in the equipment or areas that are opened during operation. This air ingress could be as high as 10 % to 15 % over the lifetime of the boiler. However, the impact of the air ingress in a conventional air-fired coal power plant is generally negligible.

The primary objective of oxyfuel combustion is to maximize the concentration of CO_2 by burning the fuel with O_2. This should benefit the whole power plant, as higher %CO_2 in the feed gas of the CPU could help achieve better CO_2 recovery.

Thus, for oxyfuel combustion, air ingress into the boiler is not desirable, but cannot be completely avoided. This increases the flue gas flow to the downstream processes. Thus, could increase cost and power consumption.

Figure 55 illustrates an indication on how CO_2 composition (% dry basis) of the flue gas from the oxy-PC boiler could be affected by the purity of the oxygen, level of excess O_2 and level of air ingress.



NOTE Source: Kather, 2007.

Figure 55 — CO_2 composition of dry flue gas (impact of O_2 purity, excess O_2 and air ingress)

The graph is calculated based on combustion of hard coal. It should be emphasized that the numbers presented in the graph are specific to the coal properties (i.e. ultimate analysis), and operating parameters such as composition of the recycled flue gas and measures taken to reduce criteria pollutants (i.e. NO_x and SO_x).

For a new build boiler, the air ingress is about 3 % at most. As the boiler ages, air ingress is expected to increase. Thus, considerations to avoid air ingress should be made in the design and the maintenance regime of the boiler and downstream equipment.

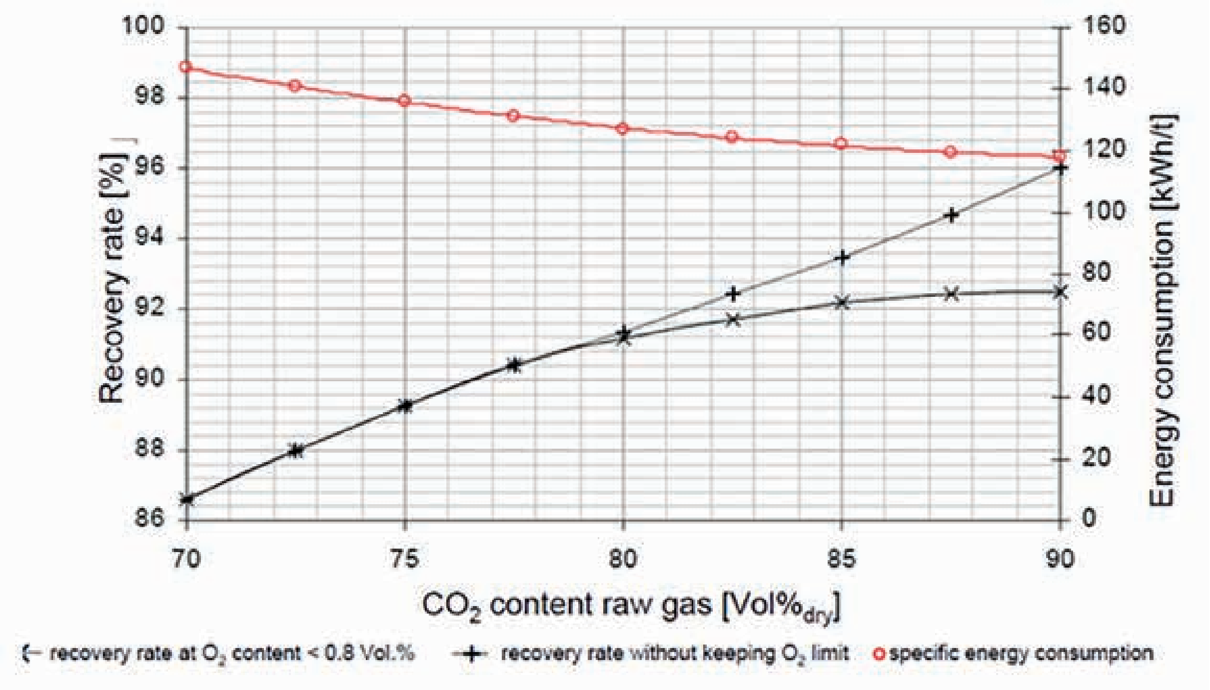
To minimize the air-ingress into the boiler, the point of the zero pressure or balance pressure is expected to be lowered from the top of the furnace (typical for balanced drought furnace) down to the lower level (i.e. inlet of the secondary RFG or exit of the FG from the boiler). This should create slight positive pressure relative to atmosphere. Due to this adjustment, safety considerations are important with regard to the ventilation of the boiler house.

Additionally, the use of CO_2 for gas sealing could also be deployed; thus, reducing air ingress into the boiler.

If the air ingress has increased above the design point considered as it ages, it could be noticed in the performance of the ID fans, various flue gas processing units and CPU. An increase in air ingress could generally lead to an increase in energy consumption of the CPU due to an increase in the flow of the CPU vent and reduced recovery rate. Additionally, this could also be manifested in the reduced demand of oxygen from the ASU (since oxygen in the air ingress could increase oxygen content of the RFG).

9.3.1.2 Oxygen content in the product CO_2

Oxygen content in the product CO_2 strongly influences process performance. To illustrate such influence, Figure 56 presents the impact of controlling and not controlling the level of oxygen in the product CO_2 on the recovery rate. Required residual oxygen in the product CO_2 is significant in the consideration to the design of the cold box of the CPU.



NOTE 1 See References [118] and [119].

NOTE 2 Data are from Vattenfall Janschwalde Project — FEED Study.

Figure 56 — Recovery rate and energy consumption of the CPU

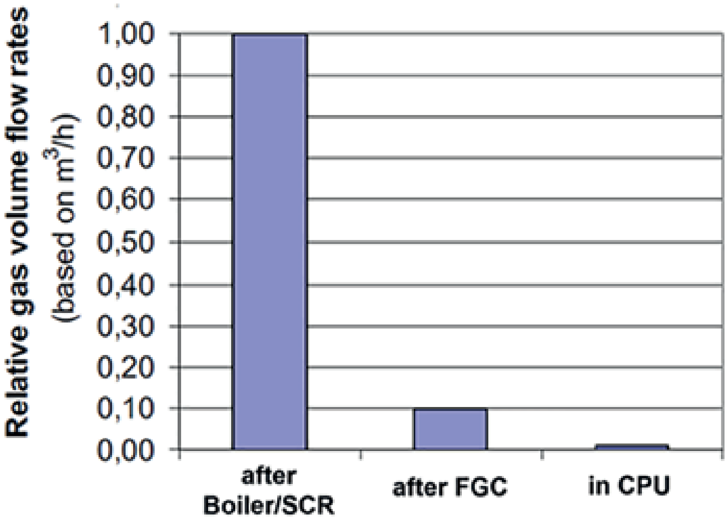
9.3.2 Other gas streams

Other major gas streams of oxyfuel combustion are

- ASU vent,
- flue gas from the boiler,
- primary recycled flue gas,
- secondary/tertiary recycled flue gas, and
- CPU vent.

9.3.2.1 Flue gas from the boiler

The relative volume of the flue gas of the oxyfuel combustion power plant entering the CPU is shown in Figure 57.

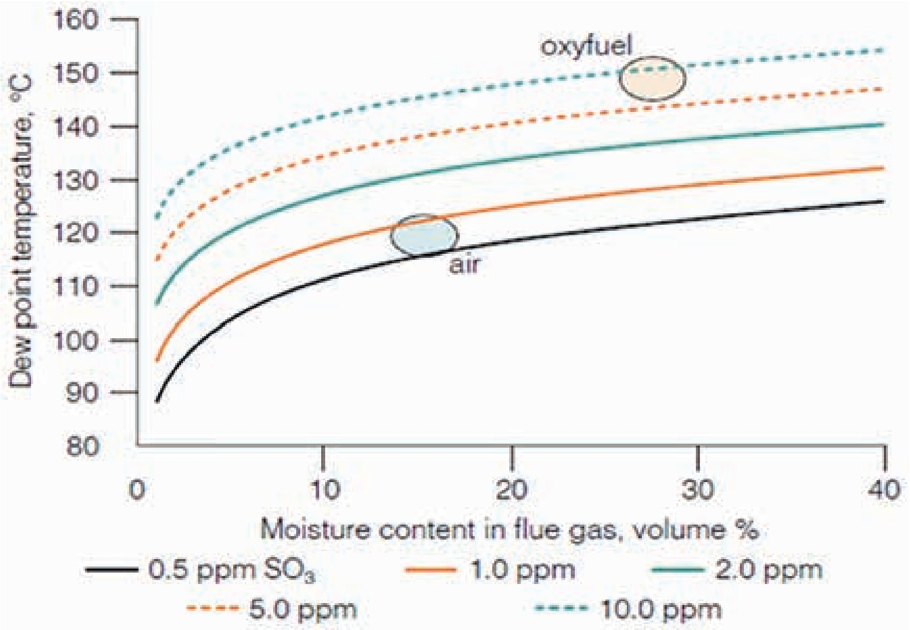


NOTE Source: References [127] and [158].

Figure 57 — Relative flue gas volume of oxyfuel combustion power plant firing lignite

To match the heat transfer profile of an air-fired boiler, the flue gas in the boiler of an oxyfuel combustion is only about 65 % to 75 % relative to the volume of the flue gas of an air-fired boiler. As the volume of the flue gas decreases, the concentration of all the criteria pollutants such as NO_x, SO_x, PM, and trace metals become higher by a factor of 2 to 5. Also, the water content increases. As a consequence to these changes, the SO_2/SO_3 species in particular could have some negative impact on the operation of the boiler, auxiliary equipment, associated flue gas ducting and different flue gas processing units.

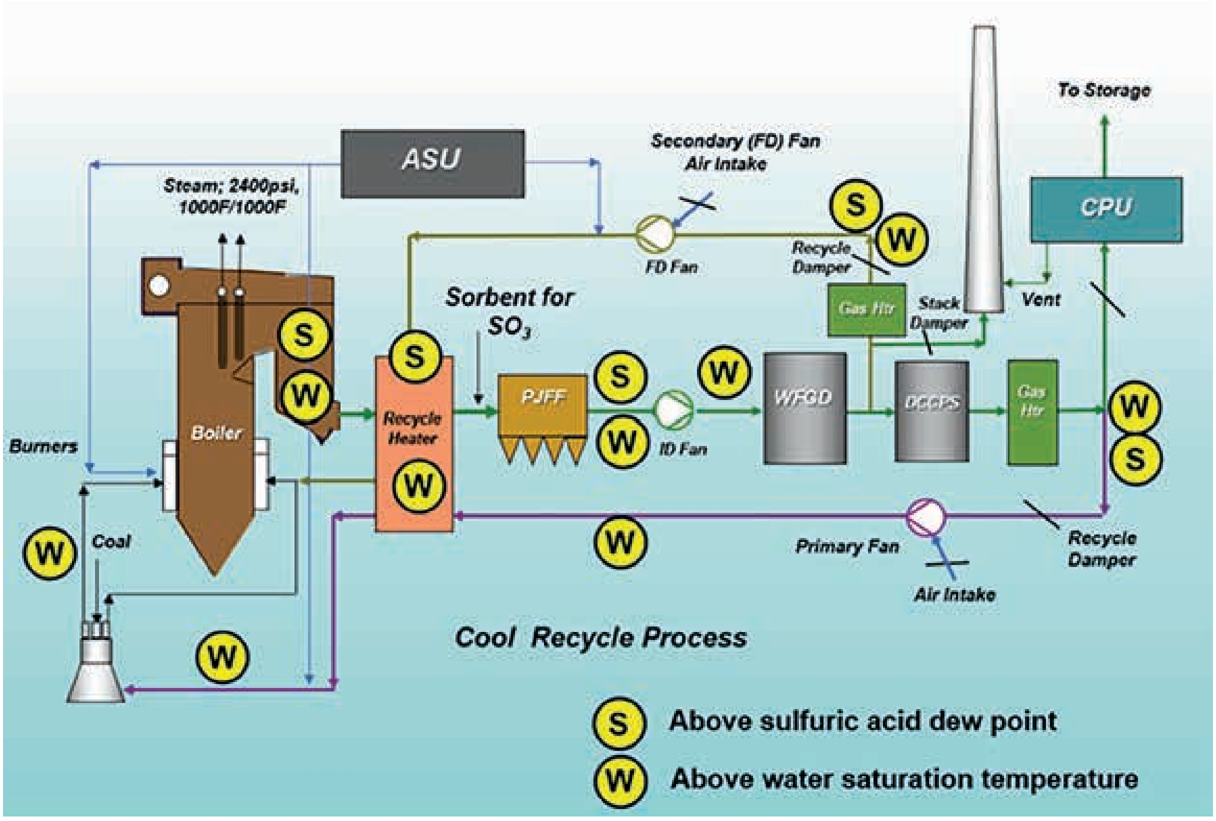
Figure 58 shows the relationship between the moisture content in the flue gas and the dew point temperature. The dew point temperature in oxyfuel combustion is higher by 20 °C to 30 °C than in air combustion.



NOTE See Reference [100].

Figure 58 — Relationship between the moisture content in the flue gas and the dew point (comparison between air combustion and oxyfuel combustion)

Therefore, it is essential to assess where areas of the plant have a risk of any low temperature corrosion to occur and it is necessary to consider mitigation measures against the risks in the engineering and design of the plant. Figure 59 illustrates an example of such assessment.

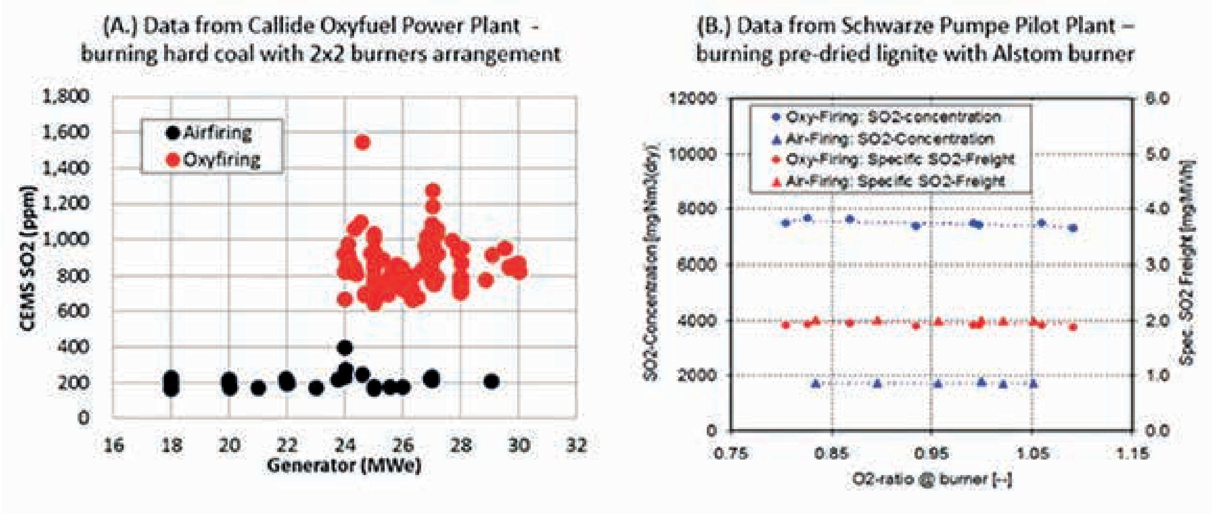


NOTE See Reference [126].

Figure 59 — Plant wide assessment of conditions of the flue gases of the oxyfuel combustion power plant

9.3.2.2 Fate of SO_x in the flue gas

Figure 60 presents the SO_2 concentration measured at the exit of the boiler at varying load[173] and at varying burner throat stoichiometry.[174]



NOTE 1 Data taken after the ID fan of the boiler, i.e. after the PM control, a) at varying load[173] and b) at varying burner stoichiometry.[174]

NOTE 2 Data taken from Callide Oxyfuel Power Plant using 2×2 burners firing hard coal [xx] and Vattenfall Schwarze Pumpe Pilot using a single-cell downfire Alstom burner firing pre-dried lignite [xx] for (A) and (B), respectively.

Figure 60 — SO_2 concentration in the flue gas for air-fired and oxyfuel combustion

The level of SO_2 from the boiler is dependent on fuel S content and the manner how the flue gas are cleaned and recycled (i.e. desulfurized or not). Bulk of the SO_x in the form of SO_2 are removed upstream of the CPU (i.e. primarily in the FGD and/or FGC, as discussed in 9.2).

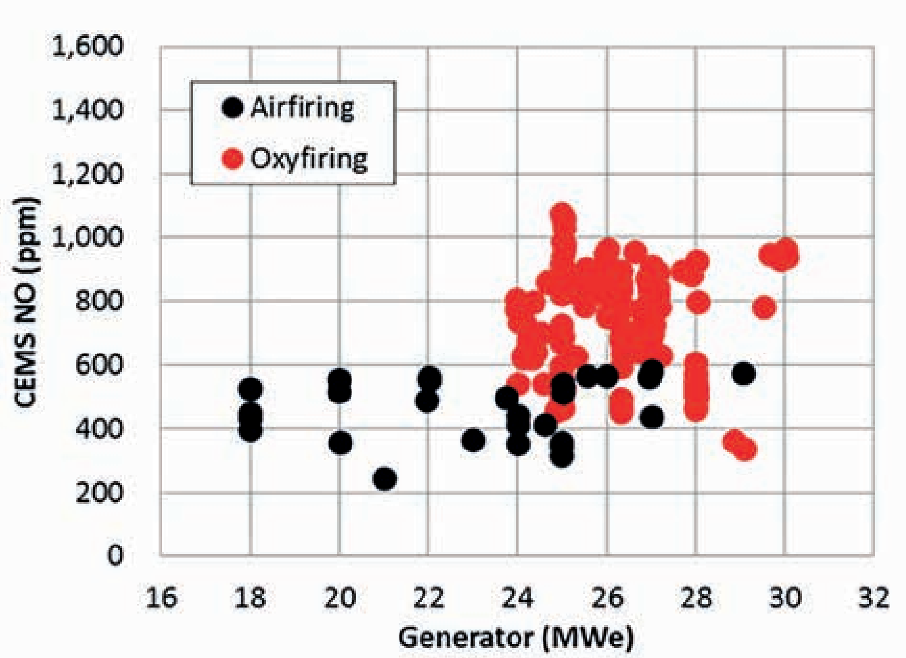
It is generally aimed to reduce SO_x to ensure that level of SO_2 and SO_3 are tolerable and would not cause any damage to the boiler and flue gas ducting. The SO_x removal efficiency of the different FGD and FGC installed are technology dependent and also dependent on the process arrangements.

As a rule, the SO_x in the recycled flue gas used in mills and transporting of coal should have very low SO_3 (i.e. <10 ppm). On the other hand, SO_x in the recycled flue gas used as secondary/tertiary RFG is recommended to be ~2 000 ppm to 3 000 ppm. In the furnace, SO_x is recommended not to exceed ~5 000 ppm to 7 000 ppm.

Nearly all of the remaining SO_x that enters the CPU is expected to be removed as H_2SO_4 in the HP water wash or as salt of sulfate/sulphite if alkali wash is used. Any residual SO_x that is not removed and enters the cold box of the CPU is most likely to remain in the product CO_2. Nonetheless, it should be noted that residual SO_x entering the cold box is typically <1 ppm.

9.3.2.3 Fate of NO_x in the flue gas

NO is the predominant NO_x species in the flue gas coming from the boiler. Figure 61 presents the NO concentration measured at the exit of the boiler at varying load.[173]



NOTE 1 See Reference [173].

NOTE 2 Taken after the ID fan of the boiler at varying loads.

Figure 61 — NO concentration in the flue gas for air-fired and oxyfuel combustion

It is expected that NO will not be removed in the environmental island or FGC unless an SCR/SNCR has been installed. Nonetheless, when the flue gas is compressed, >90 % to 95 % of the NO will be converted to NO_2 at pressure >10 Bar to 15 Bar. Most of the NO_2 will be absorbed in the knockout drums and different water wash installed after compression (i.e. in the warm part of the CPU); thus, ending up as HNO_2 or HNO_3. If Alkali wash is used, the NO_x is converted to salt of nitrite or nitrate. The remaining NO that goes into the cold box is expected to most likely end up in the vent gas; while the remaining NO_2 that enters the cold box is most likely to remain with the product CO_2. Other NO_x species such as N_2O_4, N_2O, etc., will normally be adsorbed in the molecular sieve dryer.

9.3.2.4 CPU vent

The CPU vent is the main release point of all the other gases not captured in the product CO_2. This primarily consists of CO_2, N_2, O_2 and Ar. Some other gas species such as CO could also be included. The composition of the vent gas is dependent on the equilibrium composition of the feed gas entering the cold box (at given operating temperature and pressure) as described earlier.

In some cases, part of this CPU vent is also used to regenerate the TSA/molecular sieve. Thus, any re-emission of the NO_x captured in the molecular sieve during its regeneration should therefore end up in the CPU vent stream. This becomes the source of NO_x emissions of the oxyfuel combustion power plant. Nonetheless, the NO_x released through the CPU vent should be minimal (i.e. <20 ppm to 30 ppm).

In case where additional recovery of the CO_2 in the vent gas has been employed, the vent gas composition will change and this will be dependent on the technology and process scheme selected.

9.3.3 Emissions and waste products from oxyfuel combustion power plant

For an air-fired coal combustion power plant, the criteria pollutants such as NO_x, SO_x, CO, trace metals (such as Hg) and PM are released in the flue gas through the stack. These pollutants are also generated during oxyfuel combustion. The reaction mechanism involving the formation and destruction of these substances should be no different than air combustion.

However, due to extensive flue gas cleaning in oxyfuel combustion, it is expected that near zero emissions could be achieved.

Most of the criteria pollutants such as NO_x, SO_x, PM and trace metals will be removed in various points of the power plant (i.e. FF/ESP, FGD, SCR), flue gas condenser, and/or CO_2 processing unit. Majority of these substances is expected to end up in the condensates or waste water collected from the FGC and from the knock out drums of the flue gas compressors. Some of these will also be adsorbed in adsorbents (i.e. molecular sieve and/or activated carbon bed). Thus, these substances are managed in the waste water treatment plant.

The by-products of the oxyfuel combustion should have the same by-products of the air-fired combustion. These include fly ash, bottom ash and gypsum (if limestone FGD is installed). Additionally, other by-products such as salt of nitrate/nitrite and sulfate/sulphite will also be generated if alkali wash is used.

9.4 Evaluation procedure for CO_2 capture performance

The capture of CO_2 using oxyfuel combustion is a case of revamping the power plant, and as such the energy performance should be best evaluated like any other power plant.

In oxyfuel combustion, the capture of CO_2 is an integrated system. Performance of individual units (i.e. evaluating and reporting the performance of the boiler, ASU or CPU separately) will not reflect the overall performance of the whole power plant (and could be subjected to misinterpretation).

Typically, the ASU and CPU together is responsible for nearly 95% of the energy penalty of oxyfuel combustion power plant as compared to a conventional power plant.

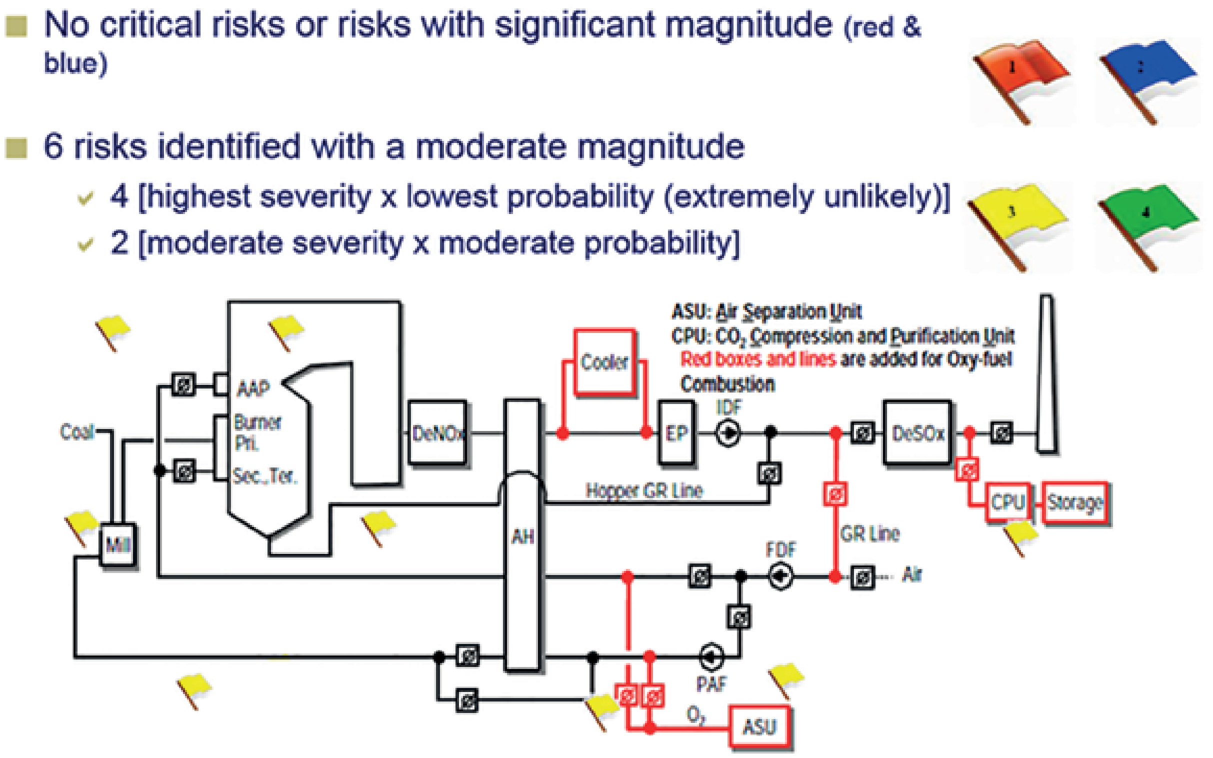
To evaluate the performance of an oxyfuel combustion power plant, the use of levelized cost of electricity (LCOE) is a suitable indicator of the performance.

To standardize the evaluation performance of an oxyfuel combustion power plant, standard parameters (such as cooling water, elevation, environmental conditions, load shift, etc.), properties of captured CO_2 (e.g. CO_2 purity, concentrations of all the non-CO_2 components, temperature, pressure), target CO_2 recovery rate, and operation conditions of air combustion should be well defined.

9.5 Safety issues

It should be emphasized that discussion of risk and safety issues relevant to the design, engineering and operation of oxyfuel combustion coal-fired power plant will require a comprehensive review of the whole plant. This has been done in various activities (i.e. operation of large-scale pilot plants, FEED projects, etc.) and some the results are reported in the open literature and in various proceedings. Figure 62 presents an example of this assessment.

Thus, the discussion of this subclause will only present some of the important aspects that will need considerations during the design, engineering and operation of the power plant. Therefore, discussion will be limited and should be treated as indicative only and can’t be considered comprehensive.



- No critical risks or risks with significant magnitude (red & blue)
- 6 risks identified with a moderate magnitude
  - ✓ 4 [highest severity x lowest probability (extremely unlikely)]
  - ✓ 2 [moderate severity x moderate probability]

ASU: Air Separation Unit
CPU: CO_2 Compression and Purification Unit
Red boxes and lines are added for Oxy-fuel Combustion

NOTE The safety assessment exercise was conducted by Fortum Corp., Air Liquide and Mitsubishi Hitachi Power Systems Ltd. (formerly Babcock-Hitachi K.K.). See Reference [175].

Figure 62 — Results of the risk and safety assessment of the Meri-Pori Oxyfuel Combustion Retrofit Demo Project (inactive)

In consideration for the safe operation of an oxyfuel combustion power plant, the following areas may require important considerations.

9.5.1 Safe operation of the ASU and handling of oxygen on site

The safe operation of the ASU and the handling of oxygen on site should follow existing international, regional and national regulations and standards. This should not be different to any operating ASU worldwide.

Standards for materials compatibility with oxygen, covering flammability and materials properties are of importance considerations. For example, the use of stainless steel in oxygen piping and oxygen delivery equipment are necessary as a general rule to prevent any rapid oxidation incidents with normally non-combustible materials (important when handling of pure or gas mixtures with greater than 80 % O_2).

Likewise, when handling high purity O_2, it is important that pipeline is clean, i.e. without any external objects or contaminants that may become the source of ignition or fire.

Important considerations should also be given to the design of the reboiler/condenser of the ASU. This should follow the international guidelines provided in the harmonized document of EIGA, AIGA, CGA, ASTM, ANSI, ASME, and other industrial gas associations. For example, prevention of HC ingress and its accumulation in the reboiler/condenser, which may cause explosion in the cold box.

Specific to oxyfuel combustion, a review to identify possible source of explosions due to localized enriched oxygen is essential. This includes safety net during flame blowout, mill fires, etc. For example, burner's oxygen mixing and/or injection should have additional trips to ensure that oxygen supply is automatically shut down during flame blow out. This should prevent any accumulation of oxygen in the furnace.

9.5.2 Prevention procedure of known risks to fire and/or explosion in the boiler or mills should be revisited for oxyfuel combustion operation

Boiler and mill explosion or fires could occur in both conventional and oxyfuel combustion power plant. The same principles of preventing any such incidents will also be practiced. However, in addition to standard practice, the prevention should strongly involve the coordination with the operation of the ASU and handling of oxygen on site.

Some examples of safety considerations include:

- Flame blowout is generally the main source of explosion in the boiler. Immediate shut down of the oxygen supply is important to prevent any explosion.
- Rapid temperature rise in coal mills is an indication of mill fires. Temperature sensors should be installed at strategic points to ensure detection of any rapid temperature increase. Response should include redundancy in the control of fuel, recycled flue gas and oxygen.

9.5.3 Accidental release of CO_2, flue gases, or other inert gases including liquid gas products

Accidental CO_2 release is a known risk inherent to CCS and not specific to oxyfuel combustion power plant. This may lead to hypoxia incident. Important precaution includes the installation of sensors and alarms at the lowest point of the site. It is expected that CO_2 has a tendency to accumulate at the lowest point of the site due to CO_2 being heavier than air.

Accidental release of flue gases or other inert gases (i.e. from CPU or ASU vent) including accidental release of any liquid gases (i.e. from ASU) are inherent risks to oxyfuel combustion power plant. It is essential that procedures and controls are in place to redirect any gases to the stack in cases where there are accidental release incidents. The location of the ASU and CPU vents and areas where possible accidental discharge of liquid gases that may cause O_2 deficient environment should be identified. Sensors and alarms should be in place to prevent any incidents of hypoxia.

Additionally, in case where there is an accidental release of flue gas from the recycle loop, it is important that interlock mechanisms should be in place between oxygen, fuel and recycled flue gas to prevent any oxygen enrichment and explosion in the boiler or flue gas ducting.

9.5.4 Prevention of any low temperature corrosion that could compromise the structural integrity of equipment

As discussed earlier, the main concern of oxyfuel combustion flue gas is their inherent high SO_2/SO_3 and high moisture content. This increases the dew point temperature; and it is essential to review where possible condensation can occur.

Prevention of sulfuric acid condensation is necessary not only during steady-state operation but also during shut down of the power plant.

During shut down (planned or unplanned) of the power plant, procedure should be in place to ensure no condensation can occur. This could be done by purging the line with nitrogen.

It is also expected that there will be a trade-off between materials selection and good practices to ensure condensation of the sulfuric acid (that will lead to low temperature corrosion) will have no impact to the equipment and ducting.

10 Capture from cement production processes[176][177]

The cement manufacturing industry is a large CO_2 emissions source, reaching approximately 1,8 gigatonnes worldwide in 2005. Due to improved energy efficiency and fuel conversions, the unit emissions of CO_2 per 1 tonne of cement output have been decreasing. The industry, on the other hand, is a growth industry in developing countries, and total global CO_2 emissions are on the rise.

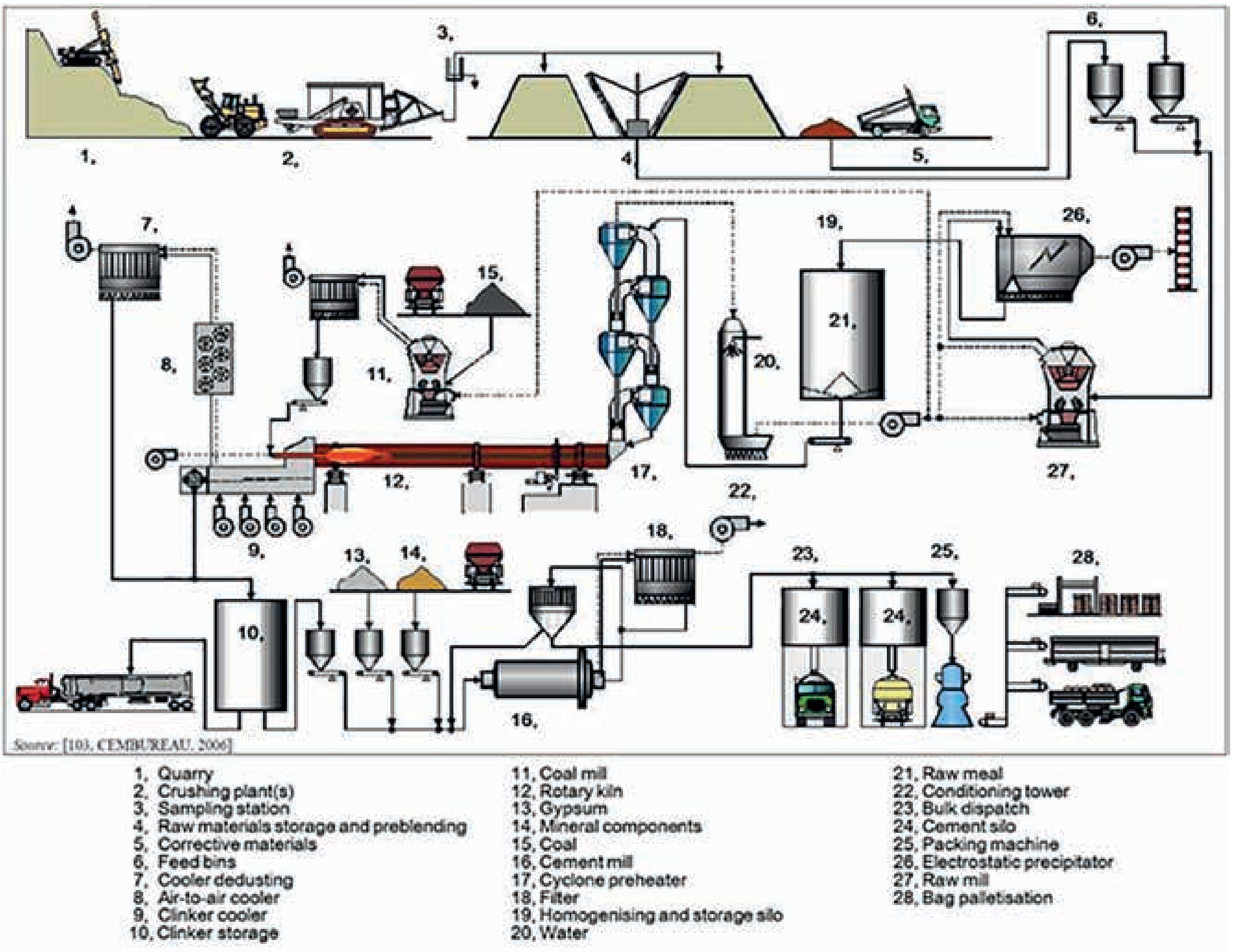
The difference between a cement plant and a thermal power plant from the perspective of CO_2 capture is that the former produces CO_2 not only in the combustion process (of fossil fuel) but also by decarboxylation reactions in the calcination process (of raw cement materials).

The industry has been advancing fuel conversion as a strategy for reducing fossil energy consumption and CO_2 emissions, and as a result it uses waste products, by-products, biomass, and others as additional fuels. In addition, other approaches for alternative CO_2 capture and disposal systems have been proposed (and some are building their first, large-scale units or large pilot plants).[182][183][184]

10.1 System boundary

Figure 63 shows a typical production flow of modern cement manufacturing (see Reference [178], Figure 2.6).

A solution for CO_2 capture in the cement manufacturing is to remove CO_2 mainly from flue gases of the kiln and the preheater.



Source: [10], CEMBUREAU, 2006]

Figure 63 — Production of cement by the dry process

Although Figure 63 is not an ideal representation, it presents a conceptual image of a real cement plant. Figure 64 is a more complete flow diagram (see Reference [181], Figure 1), because of the applicability of CO_2 emission boundary.

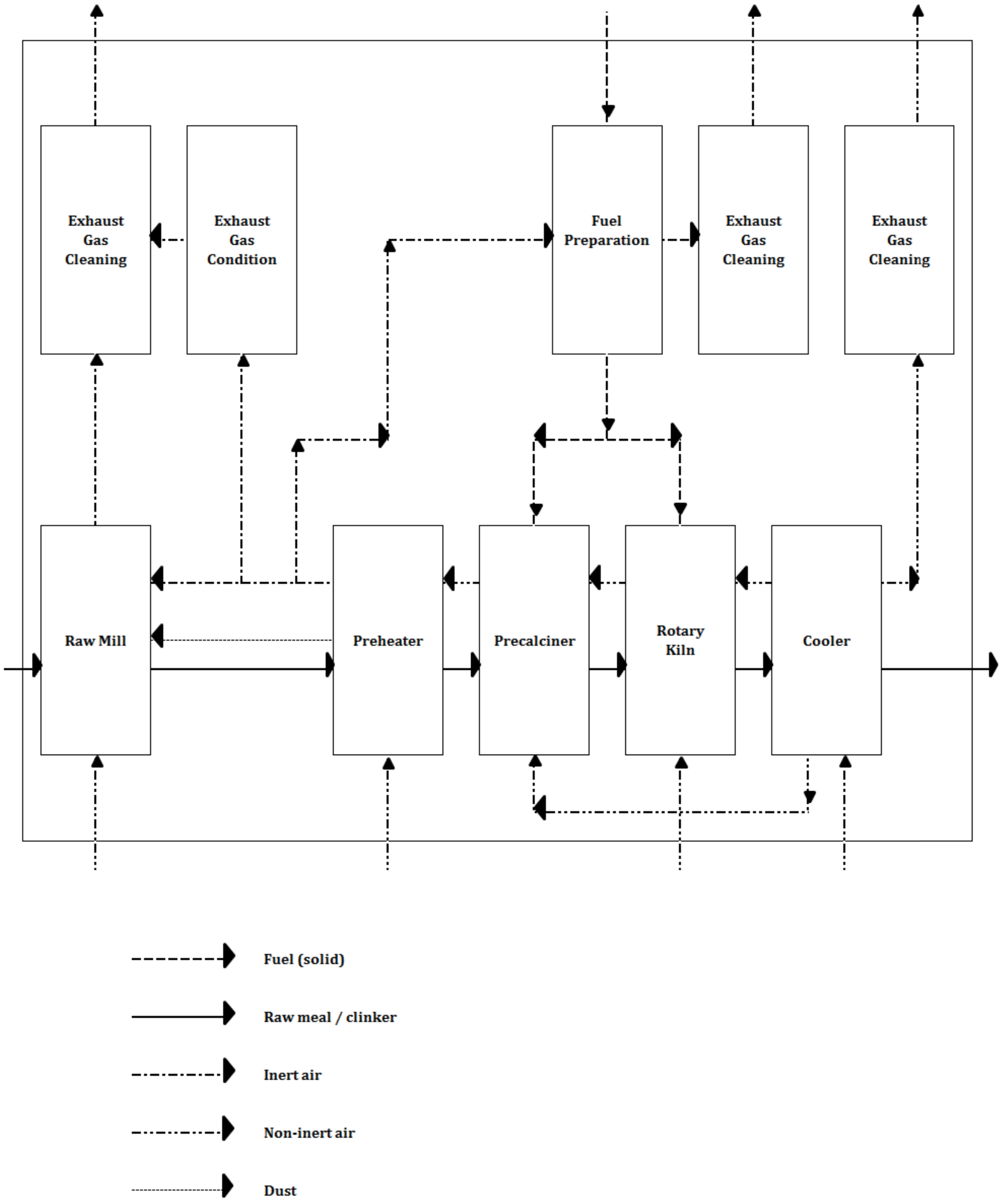


Figure 64 — Cement plant without CO_2 capture

10.2 Technologies, equipment and processes

As shown in Figure 65, cement production (see Reference [178], Figure 2.2) involves

a) raw material preparation and pulverization,

b) clinker calcination, and

c) finishing of the pulverization processes.

The total solid input including additives per 1,0 tonne of clinker is 1,5 tonnes to 1,6 tonnes.

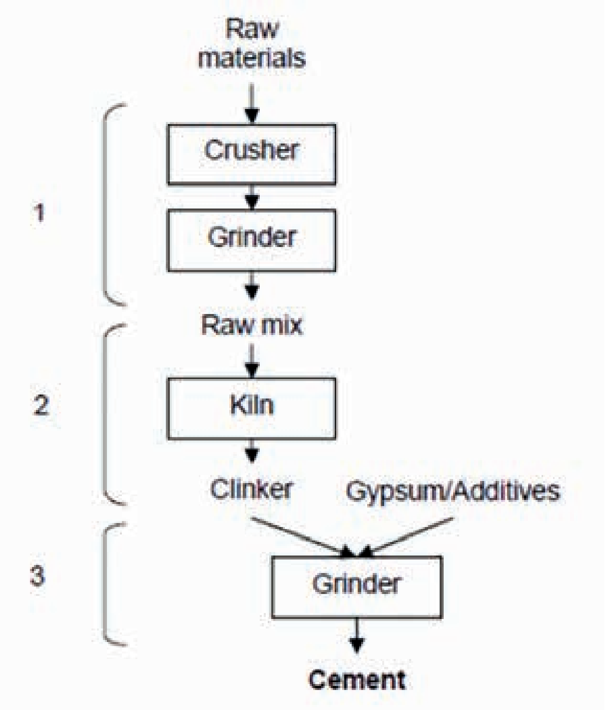


Figure 65 — Simplified cement making process schematic

There are four stages in the raw material heating process (Table 12). The calcination process, where CO_2 is released from the raw material, is performed at 850 °C to 950 °C (see Reference [178], Figure 2-3).

Table 12 — Kiln Chemical Reaction

Kiln temperature(°C)	Chemical reaction
20–900	Drying and Preheating: the release of free and chemically bound water
850–950	Calcination: the release of CO_2 from calcium carbonate (limestone) and initial reactions with formation of clinker minerals and intermediate phases
1 250–1 450	Sintering or clinkerization: the formation of calcium silicates and partial melting
1 350–1 200	Kiln internal cooling: crystallization of calcium aluminate and calcium ferrite from the partial melt

Some of the possible reduction measures of CO_2 emissions from cement plants are listed below. Among these, the introduction of fuels from waste products and the reduction of clinker content are considered unique to the cement industry.

- Improved system energy efficiency.
- Switching to clinker production processes of higher energy efficiency (e.g. wet process to dry process).
- Fuel change (to a fuel with a lower carbon content).

- Introduction of fuels extracted from waste products or biomass fuel.
- Reduction of clinker content in the product cement.
- Removal of CO_2 from flue gases (CO_2 capture).

All of these measures can reduce CO_2 emissions more or less and has partly been taken into use. CCS is, however, the only method to significantly reduce CO_2 emissions industry wide by 85 % or more (European goal set for year 2050).

CO_2 capturing methods employed by cement plants are described below.

10.2.1 Post-combustion method (PCC)

In the PCC method (see Figure 66), CO_2 is separated from the flue gas after a fuel such as coal, combustible gas, or biomass is burnt in the air (see Reference [178], Figure 3-4). Biomass (wood wastes, waste paper), waste tires, and waste plastics is used as supplemental fulel. Municipal waste gasifier syngas (including hydrogen, carbon monoxide) and other hydrocarbons have also been considered. By placing CO_2 capture at the end of the process flow, no fundamental changes are required in the cement manufacturing process. See Clause 7 for details.

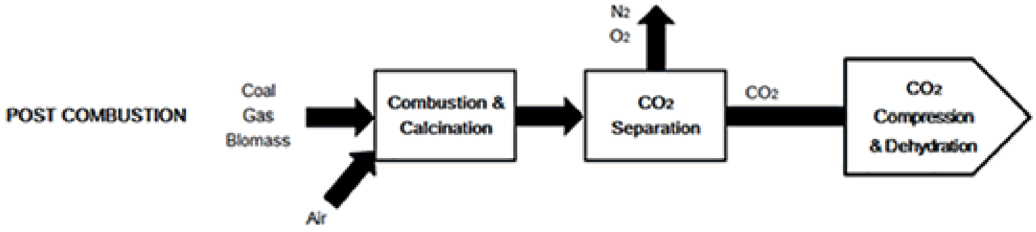


Figure 66 — PCC process for cement manufacture

There is an ongoing project lead by NORCEM and ECRA evaluating at least different four post-combustion capture technologies tested in Breivik, Norway.

10.2.2 Oxy-combustion method

In the oxy-combustion method (see Figure 67), a fuel such as coal, combustible gas, or biomass is burnt in the mixture of high-purity oxygen and captured CO_2 (see Reference [178], Figure 3-3).

The flue gas from the kiln and pre-calciner is expected to contain some amount of non-CO_2 components due to the excess air needed during the combustion, air ingress, the purity of the O_2 used, and amount of criteria pollutants such as NO_x and SO_x. The CO_2 from this flue gas is captured through low temperature or cryogenic process in the CO_2 processing unit (CPU). This unit could be designed based on the required CO_2 specifications. Typical purity should have 95 % and more.

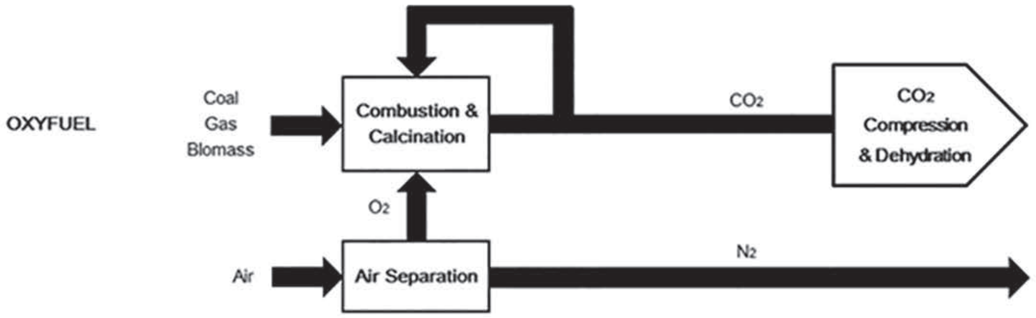


Figure 67 — Oxyfuel-combustion CO_2 capture process for cement manufacture

10.3 Carbon dioxide streams, gas streams and emissions, process and waste products

There are two sources of CO_2 emissions in a cement plant as shown in Table 13: the combustion of heat sources and the thermal breakdown of raw materials (see Reference [178], Figure 2-5). Ignoring motive-power related CO_2, the ratio of these streams is almost between 1:1 and 2:3. That is why the CO_2 concentration in the flue gas is relatively high at around 20 %. The basic unit of CO_2 per product varies significantly based on the type of fuel for heating and the clinker ratio of the product cement.

Table 13 — Dry and wet-process CO_2 emissions

Process emissions		Process and fuel-related emissions (in kg/kg of cement produced)[a]							
		Dry process				Wet Process			
Clinker/ cement ratio	*Clinker*	*Coal*	*Fuel oil*	*Natural gas*	*Waste*[b]	*Coal*	*Fuel oil*	*Natural gas*	*Waste*
55 %	0,28	0,55	0,50	0,47	0,36	0,67	0,59	0,53	0,36
75 %	0,38	0,72	0,66	0,61	0,47	0,88	0,77	0,69	0,47
95 %	0,49	0,89	0,81	0,75	0,57	1,09	0,95	0,90	0,57

[a] Emissions from electricity consumption are included.

[b] Assumed to be zero emission fuel.

The volume of CO_2 generated at a cement plant can be calculated using the protocol described by the Cement Sustainability Initiative (CSI).[180]

In addition to CO_2, major emissions of cement plants include nitric oxides (NO_x) and sulfuric oxides (SO_x). Table 14 shows the emission components that were identified in a 1997 survey conducted at cement kilns in Europe (see Reference [178], Figure 2-6).

Table 14 — Data of emissions from European cement kilns

	Reported emissions from European cement kilns[a]		
Emissions	**mg/Nm^3**	**kg/tonne clinker**	**tonnes/year**
NO_x (as NO_2)	145 – 2 040	0,33 – 4,67	334 – 4 670
SO_2	Up to 4 837	Up to 11,12	Up to 11 125
Dust	0,27 – 227	0,000 62 – 0,522 1	0,62 – 522
CO	200 – 2 000	0,46 – 4,6	460 – 11 500
CO_2	—	Approx. 672 g/t cement	1,545 million
TOC/VOC	1 – 60	0,002 3 – 0,138	2,17 – 267
HF	0,009 – 1,0	0,021 – 2,3 g/t	0,21 – 23,0
HCI	0,02 – 20,0	0,046 – 46 g/t	0,046 – 46
PCDD/F	0,000 012–0,27 ngI–TEQ/Nm^3	0,027 6 – 627 ng/t	0 000 027 6 – 0,627 g/year
Metals			
Hg	0 – 0,03	0 – 69 mg/t	0 – 1 311 kg/year
Σ(Cd,Tl)	0 – 0,68	0 – 1 564 mg/t	0 – 1 564 kg/year
Σ(As,Sb,Pb,Cr, Co,Cu,Mn,Ni,V)	0 – 4,0	0 – 9 200 mg/t	0 – 9 200 kg/year

[a] Mass figures are based on 2 300 m^3/tonne clinker and one million tonnes of clinker per year.Emission ranges are yearly averages and are indicative values based on various measurement techniques. The reference O_2 content is normally 10 %.

Cement kilns have an exhaust emission control system installed in its flue gas line. Table 15 shows, as an example, the result of a study on the performances and costs of dust removal, denitrification, and desulfurization systems (see Reference [178], Figure 2-7).

Table 15 — Common flue gas clean-up methods

Technique	Kiln system applicability	Reduction efficiency	Reported emissions		Reported costs (10^6€/tonne of clinker)[c]	
		(%)	mg/m^3[a]	kg/tonne[b]	Investment	Operating
Dust						
Electrostatic precipitators	All	—	5–50	0,01–0,1	2,1–4,6	0,1–0,2
Fabric filters	All	—	5–50	0,01–0,1	2,1–4,6	0,15–0,35
NO$_x$						
SNCR	Preheater and precalciner	10–85	200–800	0,4–1,6	0,5–1,5	0,3–0,5
SCR	Possibly all	65–95[f]	100–500	0,2–0.4	ca. 2,5[d] 3,5–4,5[e]	0,2–0,4[d] uncertain[e]
SO$_x$						
Absorbent addition	All	60–80	400	0,8	0,2–0,3	0,1–0,4
Dry scrubber	Dry	Up to 90	<400	<0,8	11	1,4–1,6
Wet scrubber	All	>90	<200	<0,4	6–10	0,5–0,1
Activated carbon	Dry	Up to 95	<50	<0,1	15[g]	uncertain

[a] Kg/tonne clinker: based on 2 000 m^3/tonne clinker.

[b] Investment costs 10^6 Euros and operating cost in Euros/tonne of clinker. Dust: to reduce emissions to 10 mg/m^3 to 50 mg/m^3 from initial emissions.

[c] Of up to 500 g dust/m^3, NO$_x$: to reduce emissions from initial levels of up to 2 000 mg NO$_x$/m^3.

[d] Costs estimated by Okopol for a full scale installation (kiln capacities from 1 000 tonne to 5 000 tonne clinker/day and initial emissions from 1 300 mg NO$_x$/m^3 to 2 000 mg NO$_x$/m^3), operating costs ca. 25 % lower than for SNCR..

[e] Costs estimated by CEMBUREAU.

[f] There has been a limited study of the application of SCR to the cement manufacturing process and the literature that exists provides conflicting data on SCR performance. The wide efficiency range shown reflects this uncertainty.

[g] This cost also includes an SNCR process, referring to a kiln capacity of 2 000 tonnes of clinker/day and initial emissions of 50 mg SO$_2$/m^3 to 600 mg SO$_2$/m^3.

Table 16, Table 17, and Table 18 shows examples of regulatory requirements for dust, SO$_2$ and NO$_x$ for cement plants (see References [178] and [179], Figures 2-8 and 2-9).

Table 16 — UK emission limits for dust for the production of cement

Plant	Unit	Kiln Stack	Clinker cooling	Cement grinding	Other point sources
New/modified	mg/Nm^3	40[a]	50[a]	40[a]	50[a]
Existing[b]	mg/Nm^3	—	—	—	—

NOTE IPC Guidance Note S2.3.01.

[a] Benchmark releases.

[b] Benchmark releases are, in particular, not applicable to existing plant but are a factor in considering appropriate limits.

Table 17 — UK emission limits for SO_2 and NO_x for the production of cement

Plant	Unit	SO_2 Normal situation	SO_2 S-rich raw materials	NO_x
New/modified	mg/Nm^3	200[a]		900[a]
Existing[b]	mg/Nm^3	Note[b]	600–2 500[d]	500–1 200[b,d]

NOTE IPC Guidance Note S2.3.01.

[a] Benchmark releases.

[b] Benchmark releases are, in particular, not applicable to existing plant but are factors in considering appropriate limits.

[c] Limit values reflect the actual levels of releases. Daily averages and reference condition of dry gas and actual O_2 content.

[d] Actual releases, daily averages, not all plants currently have limits.

Table 18 — BAT emission levels

Emission	Best Available Techniques (BAT)	Emission Level
NO_x	flame cooling, low-NO_x burners, mid-kiln firing, staged combustion, selective non-catalytic reduction(SNCR) and selective catalytic reduction(SCR)	<200 mg/Nm^3 – 450 mg/Nm^3 for preheater kilns 400 mg/Nm^3 – 800 mg/Nm^3 for Lepol and long rotary kilns NH_3 slip : <30 mg/Nm^3 – 50 mg/Nm^3 (in case of using SNCR)
SO_x (as SO_2)	absorbent addition and wet scrubber	<50 mg/Nm^3 – 400 mg/Nm^3 (daily average value)
Dust	fabric filters or new or upgraded electrostatic precipitators	<10 mg/Nm^3 – 20 mg/Nm^3 by kiln firing, cooling and milling processes <10 mg/Nm^3 by dusty operations (other than the above)

Discussed below are the properties of NO_x, SO_x, dust, and HCl, typical emissions from cement plants, and the impacts of the application of chemical absorption using amine.

10.3.1 NO_x

NO_x emissions include thermal NO_x and fuel NO_x, but rotary kilns mostly generate thermal NO_x. NO_x includes NO and NO_2, and NO_2 reacts with amine absorbent to produce thermally stable salts. The content of NO_2 in the flue gas from cement plants is reportedly at 10 % or less.[181]

10.3.2 SO_x

SO_x is generated by sulfuric compounds from two sources: raw materials and fuel. Such compounds are desulfurized by strong alkali in the kiln and the preheater and are incorporated in the clinker, resulting in a low SO_x concentration in the flue gas. When absorbent is applied, SO_x reacts as an acid compound with amine to produce salts. In other words, SO_x reduces the level of amine in the absorbent. The lower the level of SO_x is, the better; Reference [178] recommends that the SO_x level be kept at 10 ppmv [at 6 % O_2] or less.

10.3.3 Dust

The flue gas emitted by cement plants contains around 3,000 mg/m^3 of dust, most of which is collected by electrostatic precipitators (ESPs) or bag filters to be recycled back as a raw material. In the case of amine absorption, dust is trapped and slowly accumulated in the absorbent, causing efficiency loss. Dust concentration should therefore be kept at a minimum.

10.3.4 HCl (Hydrogen chloride)

When cement plants use waste materials as fuel, hydrogen chloride (HCl) may be emitted since waste products contain chlorine. HCl, however, can be reduced in quantity by selective catalytic reduction (SCR) or flue gas desulfurization (FGD). In amine absorption, HCl is taken into the absorbent to produce hydrochloride salts by reacting with amine. As a result, efficiency will decrease. That is why a low concentration of HCl is desirable.

10.4 Evaluation procedure for capture performance

Refer to Clause 7.

Energy consumption varies; for instance, waste heat may be utilized by installing a waste heat power generator. Cement plants have waste heat available for relatively easy utilization, which is advantageous for CO_2 capture equipment.

10.5 Safety issues

In general, facilities and equipment dedicated for the corresponding capture technology are designed and constructed in compliance with the existing and applicable international, regional and national standards such as ISO and ASME. In addition, compliances with the laws, regulations and requirements in the region or country where the plant is located provide additional securities for safety. Those are not subject to establish a new standard for the CO_2 capture processes in CCS.

The following can be considered as remarkable subjects when the corresponding international standard will be discussed in the future.

Given that post-combustion capture appears to be the capture technology that applies to almost all extant cement plants, issues dealing with safety, reliability, and management systems are described in 7.5, 7.6 and 7.7. It is important to conduct a risk assessment early in the design stage. In addition, there are possible safety concerns connected with transport and storage of the captured CO_2 which need to be considered when considering safe operations of a capture system upstream of these other processes. Table 19 shows the preliminary design risk assessment for a cement plant with post-combustion CO_2 capture (see Reference [178], Figure 4-6).

Table 19 — Preliminary design risk assessment for post-combustion CO_2 capture cement plant

Hazard Ref	Hazard	Stage of work	Risk control measures	Owner	Comment
1	Risk of operator suffocation, as CO_2 is an asphyxiant	Operation	1) Standards, codes of practice, etc., to be adopted during design. 2) Appropriate material selection during design. 3) HAZOP study to be undertaken.	Contractor	Hazards associated with handling CO_2 are well understood by other industries.
2	Risk of dust explosion in fuel milling and drying stages.	Operation	1) Standards, codes of practice, etc., to be adopted during design. 2) HAZOP study to be undertaken. 3) ATEX assessment to be performed.	Contractor	Hazards associated with explosive dusts are well understood within the cement industry.
3	Risk of corrosion damage due to presence of acidic components (e.g. SO_2, SO_3 and HCI) in gas streams.	Operation	1) Standards, codes of practice, etc., to be adopted during design. 2) Appropriate material selection during design.	Contractor	Hazards associated with acidic components in gas steams are well understood by other industries.
4	Risk of injury to operator due to handling of ammonia solution.	Operation	1) Standards, codes of practice, etc., to be adopted during design. 2) Appropriate material selection during design. 3) HAZOP study to be undertaken.	Contractor	Hazards associated with handling of ammonia are well understood by other industries.
5	Risk of operator suffocation, as N_2 is an asphyxiant.	Operation	1) Standards, codes of practice, etc., to be adopted during design.	Contractor	Hazards associated with handling N_2 are well understood by other industries.
6	Risk of operator injury, as MEA is a corrosive material.	Operation	1) Standards, codes of practice, etc., to be adopted during design. 2) Appropriate material selection during design. 3) HAZOP study to be undertaken.	Contractor	Hazards associated with handling MEA are well understood by other industries.
7	Risk of damage caused by release of high pressure, as high pressures are present in CO_2 compression units.	Operation	1) Standards, codes of practice, etc., to be adopted during design. 2) HAZOP study to be undertaken.	Contractor	Hazards associated with handling high pressures are well understood by other industries.

10.6 Reliability issues

Given that post-combustion capture appears to be the capture technology that applies to almost all extant cement plants, issues dealing with safety, reliability, and management systems are described in 7.5, 7.6 and 7.7.

10.7 Management system

Given that post-combustion capture appears to be the capture technology that applies to almost all extant cement plants, issues dealing with safety, reliability, and management systems are described in 7.5, 7.6 and 7.7.

11 CO_2 Capture in the iron and steel industry

11.1 Overview — Global steel production

Steel is the most globally traded metal. In 2013, around 1,65 billion tonnes of crude steel were produced worldwide; of which ~51 % was from China. Other leading steel producing regions or countries include the EU28 (10 %), NAFTA17) (7 %), CIS18) (5 %), Japan (7 %), and India (4 %).[185] The iron and steel industry is one of the largest industrial sources of CO_2. Globally, it accounts for approximately 7 % of anthropogenic CO_2 emissions (approx. 2,5 to 2,6 Gt CO_2/year).[186]

In principle, steel is produced either from virgin ore or from steel scrap. Currently, there are three leading groups of technologies that produce steel from virgin ore. These include:

a) Blast Furnace — Basic Oxygen Furnace (BF-BOF) route;

b) Smelting Reduction — Basic Oxygen Furnace (SR-BOF) route;

c) Direct Reduction — Electric Arc Furnace (DRI-EAF) route.

The electric arc furnace (EAF) is the leading technology that produces crude steel from scrap; and the use of the induction furnace to produce crude steel is unique to the Indian steel industry. In 2013, around 72 % of crude steel was produced from BOF route and 27,5 % was produced from EAF route19).[185]

Figure 68 illustrates the different routes on how crude steel is produced.

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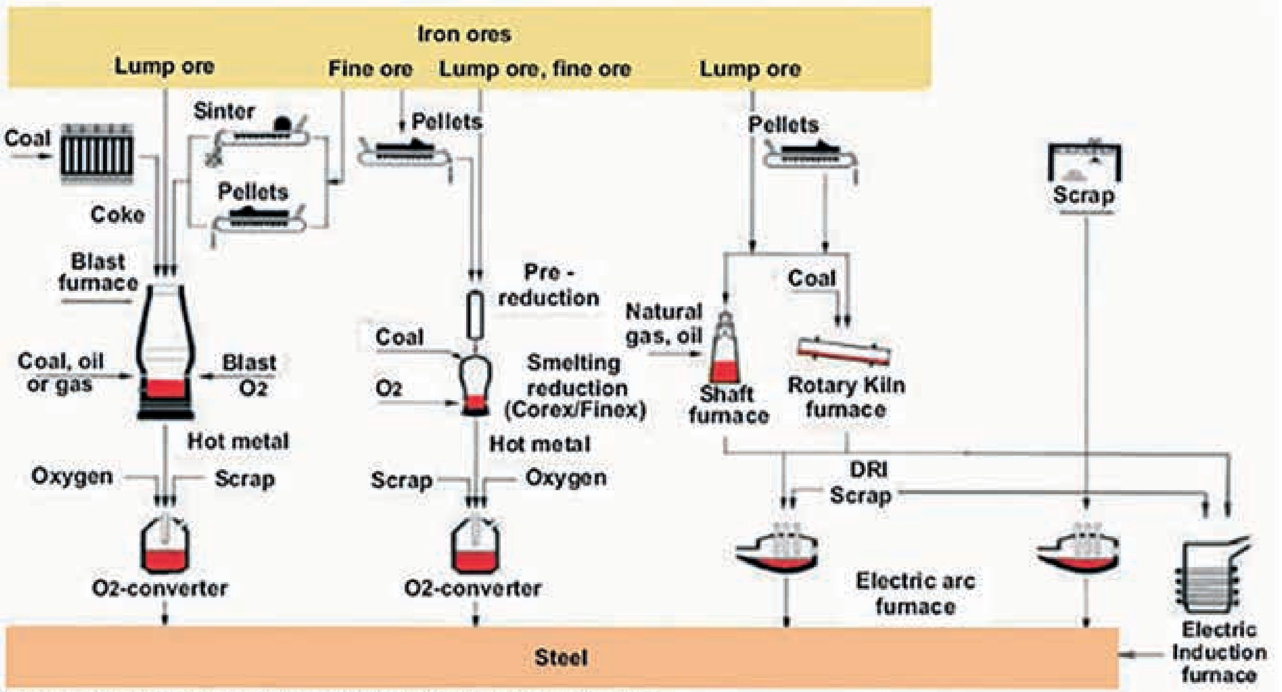
17) NAFTA is the North American Free Trade Agreement which comprises: USA, Canada and Mexico.

18) CIS is the Commonwealth of Independent States, which is a regional organization whose participating countries are former Soviet Republics, formed during the breakup of the Soviet Union. This includes Russia, Ukraine and other CIS.

19) A small fraction of crude steel produced is based on open hearth furnace which is an obsolete technology.



Note: Use of Electric Induction Furnace to produce crude steel is unique to Indian steel industry

NOTE Source: Steel Institute VDEh, WSA and EU BAT document. See References [185] and [208].

Figure 68 — Simplified schematic of the different crude steel production routes

11.2 Point sources of CO_2 emissions within the iron and steel production

11.2.1 Calculation of CO_2 emissions from the steel mill

The ISO 14404 series[189][190] was established to support steel producers in standardizing the calculation and reporting of the CO_2 emissions attributable to a site.

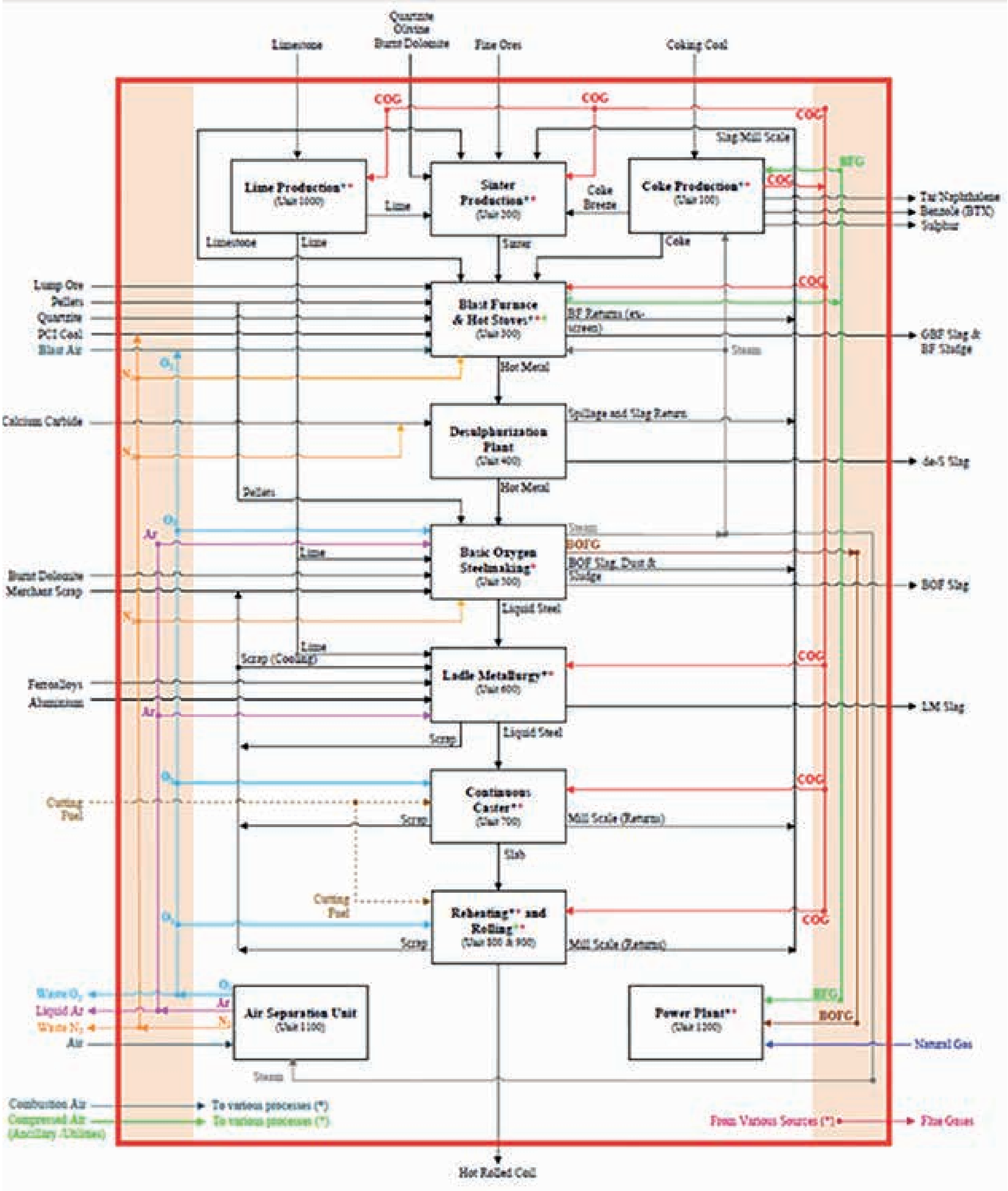
This includes boundary definition, material and energy flow definition and emission factor of CO_2. Besides the direct CO_2 emissions reported within the boundary, a CO_2 audit using the upstream and credit concept is also applied to exhibit the plant CO_2 intensity.

11.2.2 Direct CO_2 emissions in an integrated mill producing steel through the BF-BOF route

Generally, the production of steel through the BF-BOF route includes the following processes:

- raw materials preparation (ore agglomeration, coke and lime production);
- hot metal production (blast furnace and hot metal desulfurization);
- steelmaking process (primary, i.e. BOF, secondary steelmaking);
- casting;
- finishing mills.

Figure 69 illustrates a more detailed block flow diagram presenting the different processes involved in the production of steel (i.e. hot rolled coil) through the BF-BOF route.



NOTE See Reference [187].

Figure 69 — Schematic process flow diagram of production of steel through the BF-BOF route

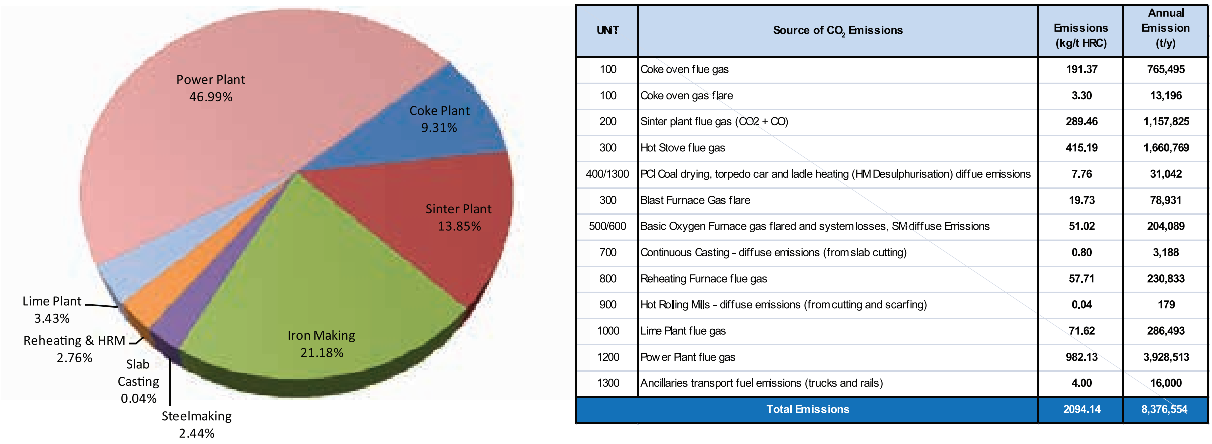
It should be noted that CO_2 emissions in an integrated mill comes from multiple point sources.

For the steel production through the BF-BOF route, the hot metal production (i.e. ironmaking process/blast furnaces) is the most carbon intensive process.[187][188] This is responsible for up to 80 % to 90 % of the CO_2 emitted by the whole steel mill. However, the direct CO_2 emissions allocated to this process is only ~20 % to 25 % of the total emissions (i.e. predominantly the CO_2 emitted from the flue gases of the hot stoves). Others are emitted in other processes when burning of the blast furnace gas (BFG) as fuel.

Within the whole site of the integrated mill, the direct CO_2 emissions comes from the different flue gases as a consequence of using the different process gases (also known as off-gases) coming from the coke ovens, blast furnaces and basic oxygen furnaces; and in some cases, to include the use of other fuels imported into the steel mill.

The allocation of the direct CO_2 emissions among the different facilities within the integrated mill is very site specific and is dependent on the manner how the process gases are used. An example is shown in Figure 70. This example is based on the calculation using the composition of the different process gases as presented in Table 20, and how these process gases are used within the steel mill.

Table 21 presents the typical composition of the different flue gases of the integrated steel mill presented in Figure 69 and Figure 70.



UNIT	Source of CO_2 Emissions	Emissions (kg/t HRC)	Annual Emission (t/y)
100	Coke oven flue gas	191.37	765,495
100	Coke oven gas flare	3.30	13,196
200	Sinter plant flue gas (CO2 + CO)	289.46	1,157,825
300	Hot Stove flue gas	415.19	1,660,769
400/1300	PCI Coal drying, torpedo car and ladle heating (HM Desulphurisation) diffue emissions	7.76	31,042
300	Blast Furnace Gas flare	19.73	78,931
500/600	Basic Oxygen Furnace gas flared and system losses, SM diffuse Emissions	51.02	204,089
700	Continuous Casting - diffuse emissions (from slab cutting)	0.80	3,188
800	Reheating Furnace flue gas	57.71	230,833
900	Hot Rolling Mills - diffuse emissions (from cutting and scarfing)	0.04	179
1000	Lime Plant flue gas	71.62	286,493
1200	Power Plant flue gas	982.13	3,928,513
1300	Ancillaries transport fuel emissions (trucks and rails)	4.00	16,000
Total Emissions		2094.14	8,376,554

NOTE See Reference [187].

Figure 70 — Example of the distribution of the CO_2 emissions within the site of an integrated mill producing 4 million tonnes of steel (HRC) annually through the BF-BOF route

Table 20 — Example of the composition of the process gases used in estimating the CO_2 emissions of an integrated mill producing 4 MTPY of steel as presented in Figure 69 and Figure 70

Wet basis (%vol)	**Coke Oven Gas (COG)**	**Blast Furnace Gas (BFG)**	**Basic Oxygen Furnace Gas (BOFG)**
CH_4	23,2	NA	NA
H_2	60,1	3,6	2,6
CO	3,9	22,1	56,9
CO_2	1,0	22,3	14,4
N_2	5,8	48,3	13,8
O_2	0,2	NA	NA
H_2O	3,2	3,2	12,2
Other HC	2,7	NA	NA
NOTE See References [187].			

Table 20 *(continued)*

Wet basis (%vol)	Coke Oven Gas (COG)	Blast Furnace Gas (BFG)	Basic Oxygen Furnace Gas (BOFG)
LHV (MJ/Nm^3) — wet basis	17,5	3,2	7,5
Users of the Process Gases (An Example)	Hot Stoves, Coke Ovens, Lime Kilns, Reheating Furnaces and others	Hot Stoves, Power Plant	Power Plant
NOTE See References [187].			

Table 21 — An example of the composition of the different flue gases[a] of an integrated mill producing 4 MTPY of steel as presented in Figure 69 and Figure 70

Flue gas	Unit (wet basis)	Coke oven	Sinter plant	Lime plant	Hot stoves	Reheating furnaces	Power plant
CO_2	% (v/v)	14,8	4,8	19,7	27,3	4,6	26,4
CO	% (v/v)	—	0,7	—	—	—	—
O_2	% (v/v)	5,0	14,9	7,6	0,8	7,2	0,7
N_2	% (v/v)	69,5	72,7	60,0	65,5	71,9	65,9
H_2O	% (v/v)	10,8	6,9	12,7	6,4	16,3	7,0
NO_x	mg/Nm^3	~280	~200	~29	~60	~500	~60
SO_x	mg/Nm^3	~10	~300	~10	~10	~10	~10
Dust	mg/Nm^3	<5	<5	<5	<5	<5	<5
Fuel used (an example)		COG and BFG	Coke breeze and COG	COG	COG and BFG	COG	BFG, BOFG and NG

[a] These flue gases represent ~95 % of the overall direct CO_2 emissions of the integrated steel mill as illustrated in Figure 69 and Figure 70.

NOTE See References [187].

11.2.3 Overview of CO_2 emissions from alternative steel making processes

Other alternative ironmaking processes involve the direct reduction or the smelting reduction processes. In 2013, the direct reduction and the smelting reduction processes are responsible for ~6 % and ~0,5 % of the total iron production worldwide respectively.

For direct reduction processes, the main products produced are cold/hot DRI or HBI. The dominant commercial processes are the Midrex[20)] and Energiron (HYL)[21)] plants. These are gas-based DRI processes. On the other hand, coal-based DRI processes are dominant in some part of the world (i.e. India). The rotary kiln is most dominant technologies for coal-based DRI. There are also other emerging technologies. An example of which is the use of Rotary Hearth Furnace which produces iron nugget.

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20) Midrex is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

21) Energiron (HYL) is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

For smelting reduction processes, the main products produced are liquid hot metal. There are several variants to these technologies. Currently, only the COREX[22) and the FINEX[23) plants are operated commercially. Other technologies are in various stages of development.

A more detailed description of these processes are described in several literature.[188][191][192][193][194] Some of these technologies involve the separation of CO_2 from their process gases (i.e. ENERGIRON and FINEX). Others would require modifications to their processes to allow the separation of CO_2 from their process gases. These are briefly described in 11.9

Table 22 and Figure 71 present an overview and a summary of the CO_2 emission intensity of the different alternative ironmaking processes that are commercially in operation today.

Table 22 — Range of CO_2 emissions from alternative ironmaking processes[a]

Steel production routes	**Type of iron products**	**Maximum iron production capacity per module (MTPY)[b]**	**Specific CO_2 emission estimates (kg CO_2/tcs)**	**Annual CO_2 emissions per module (MTPY of O_2)[c]**
Blast Furnace through BOF	Hot metal	5,30	1 650 ~ 1 00	8,8 ~ 10,1
COREX through BOF	Hot metal	1,50	2 200 ~ 3 000	3,3 ~ 4,5
FINEX through BOF	Hot metal	2,00	2 200 ~ 3 000	4,4 ~ 6,0
Rotary kiln/Hearth through EAF	DRI/HBI	0,50	2 200 ~ 3 000	1,1 ~ 1,5
Midrex through EAF	DRI/HBI	2,00	1 000 ~ 1 350	2,0 ~ 2,7
Energiron (HYL) through EAF	DRI/HBI	2,50	1 000 ~ 1 350	1,6 ~ 3,4

[a] Estimated specific CO_2 per tonne of crude steel. Emissions account for Scope 1 and 2.

[b] These data are based on the largest operating module worldwide in 2015. These also include plants that are under construction.

[c] Calculation is based on the largest capacity module.

NOTE See Reference [188].

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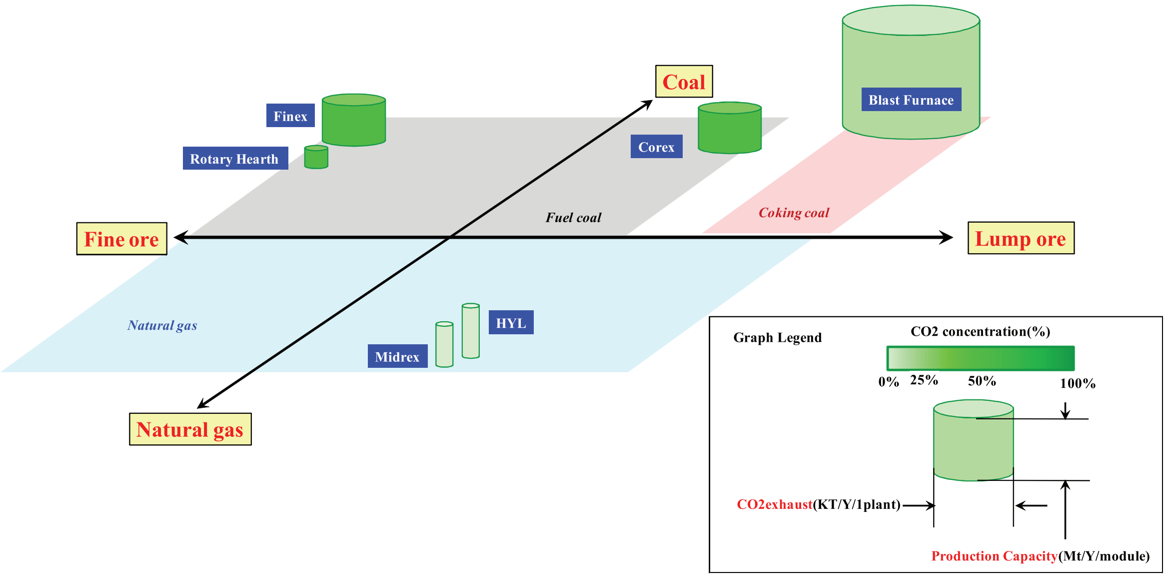
22) COREX is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

23) FINEX is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.



Based on the technology map of Prof.Ariyama Bulletin of the iron and steel institute of Japan,18(2013),645

NOTE Source: Technology Roadmap presented by Prof. T. Ariyama to the Japanese Iron and Steel Institute. See Reference [195].

Figure 71 — Schematic illustration of relative CO_2 emission intensity per module from different ironmaking processes

11.3 CO_2 reduction and CCS deployment strategy in the steel industry

To reduce the CO_2 emissions (i.e. maintaining 450 ppm CO_2 in the atmosphere by 2050) as recommended by IEA in their recent ETP report,[186] deployment of CCS technologies in the energy intensive industries are required. The steel industry recognizes the importance of reducing their CO_2 intensity from their production processes. All possible pathways to reduce CO_2 emissions are explored. Several of these pathways involve measures to improve energy efficiency (i.e. reduce energy intensity). Some involves new innovative processes. However, for very deep reduction of CO_2 emissions, deployment of CCS in the steel industry is essential.

Currently, the primary focus of various CCS R&D Programmes[195][196][197][198][199][200][201][202][203] aims to develop technologies to capture of CO_2 from the blast furnace (i.e. ironmaking process) — as this process is the most carbon intensive and it is responsible for nearly 80 % to 90 % of the carbon input to the steel production from iron ore. The major research programmes worldwide are described briefly in 11.4.

The capture of CO_2 from the different flue gases derived from the combustion of the process gases (i.e. post-combustion CO_2 capture) are technically possible. However, several studies have concluded that capturing CO_2 from these flue gases are considered relatively more expensive and with limited potential to deeply reduce the energy consumption of the CO_2 capture process.

Therefore, this Technical Report mainly covers the review of the different CO_2 capture process applicable to the ironmaking process.

Figure 72 illustrates the different CO_2 emission reduction and CCS activities considered by the industry. The interaction between energy efficiency improvement and CCS are clearly manifested in various CO_2 breakthrough programmes (as described in 11.4).

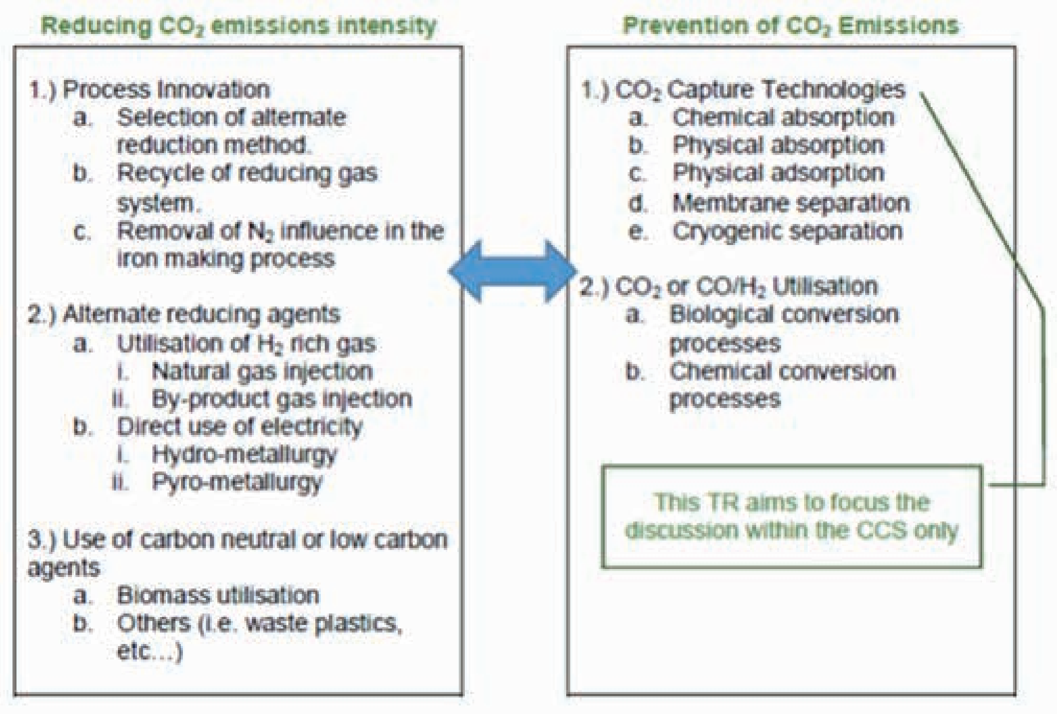


Figure 72 — Some of the possible radical CO_2 emissions reduction activities considered by the steel industry

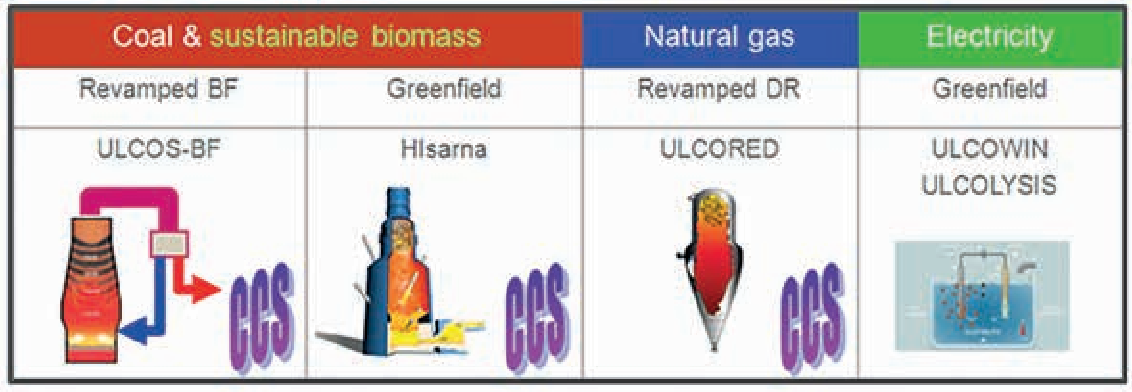
The extent of the deployments of CO_2 capture technologies in the steel industry could be complex. These are generally dependent on various factors; and some of these are

- price of coke,
- price of electricity,
- price of CO_2,
- price and availability of scrap and other alternative iron burden inputs, and
- price of other possible steel mill by-products (i.e. chemicals, etc.).

11.4 Review of major CO_2 breakthrough programmes worldwide

11.4.1 ULCOS programme

The ULCOS programme[195][196][197] is a consortium of European steel and allied industry with an objective to evaluate options for at least 50 % reduction of GHG emissions from steel production. Figure 73 presents the different options pursued for further development under ULCOS. These include the ULCOS BF[24)](TGR BF), HISARNA[25)], ULCORED[26)] and ULCOWIN[27)]/ULCOLYSIS[28)]. The first three of the processes would require CCS and the later process would require carbon free electricity.

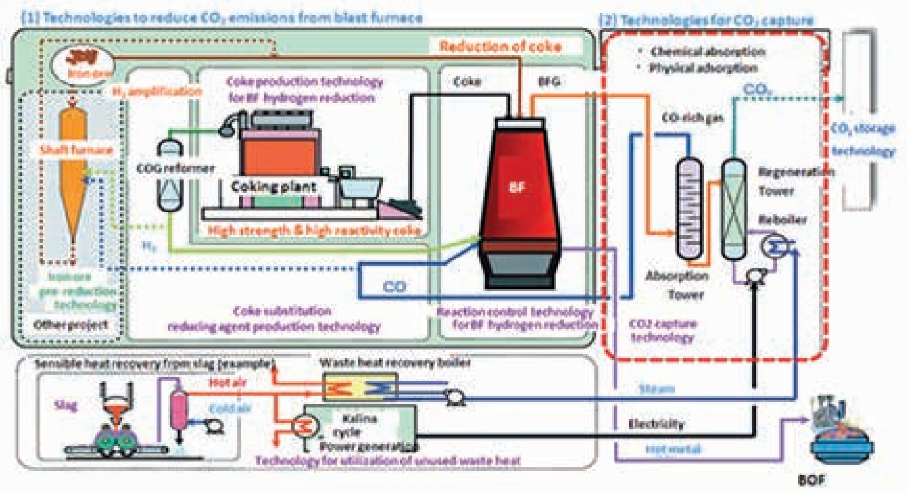


NOTE See References [195] to [197].

Figure 73 — ULCOS CO_2 breakthrough programme

11.4.2 COURSE50 programme

The COURSE50 programme[198][199][200] is a consortium of Japanese steel and allied industry funded by NEDO with an objective to evaluate options to reduce CO_2 emissions from steel production.



NOTE See References [198] to [200].

Figure 74 — Overview of the COURSE50 programme

[24)] ULCOS BF is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

[25)] HISARNA is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

[26)] ULCORED is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

[27)] ULCOWIN is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

[28)] ULCOLYSIS is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

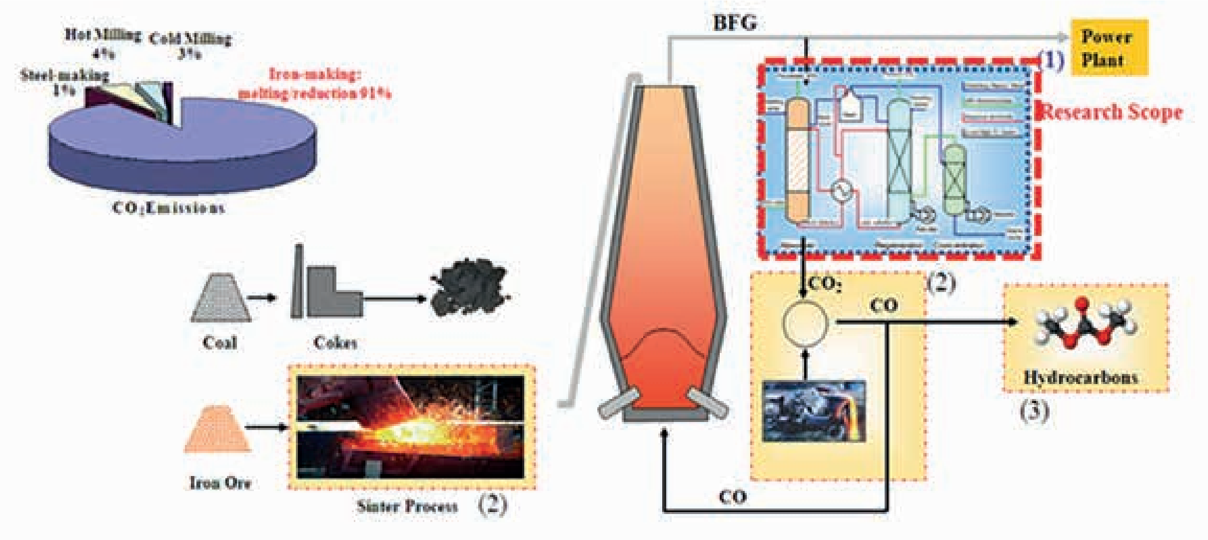
Figure 74 presents the different technology options evaluated under COURSE50 which include the following:

- technologies that reduces CO_2 emissions from the blast furnace (i.e. technologies that reduces coke consumption of the BF);
- technologies for CO_2 capture and storage (i.e. CO_2 capture technologies from the BFG);
- technologies that support COURSE50 technologies.

Relevant to this Technical Report is the development of CO_2 capture technologies based on chemical absorption and physical adsorption principles. These are described in 11.6.1 and 11.6.3.

11.4.3 POSCO/RIST programme

Development of CCS technology for non-power sector in South Korea is currently led by the consortium of POSCO and RIST.[201][202][203] This involves the evaluation of CO_2 capture technologies specific to the steel industry applications. The pilot scale demonstration of CO_2 capture technology is funded by the Korean Ministry of Knowledge with some contribution from the private sector. Figure 75 presents the main research areas and ideas undertaken by the consortium.



NOTE See References [201] to [203].

Figure 75 — Overview of the Posco/RIST programme

The main scope of work includes:

- capture of CO_2 from the BFG;
- recovery and utilization of waste heat within the steelworks;
- utilization of CO_2 and CO for other industrial users.

Relevant to this Technical Report is the development of CO_2 capture technologies using warm ammonia process. These are described in 11.6.2.

11.5 System boundary

Given that the coverage of this Technical Report is limited to the operation of the CO_2 capture facilities developed by the steel industry; therefore, it has been agreed that the system boundary will be limited to the process gas conditioning unit and the CO_2 capture and compression facility as illustrated in Figure 76.

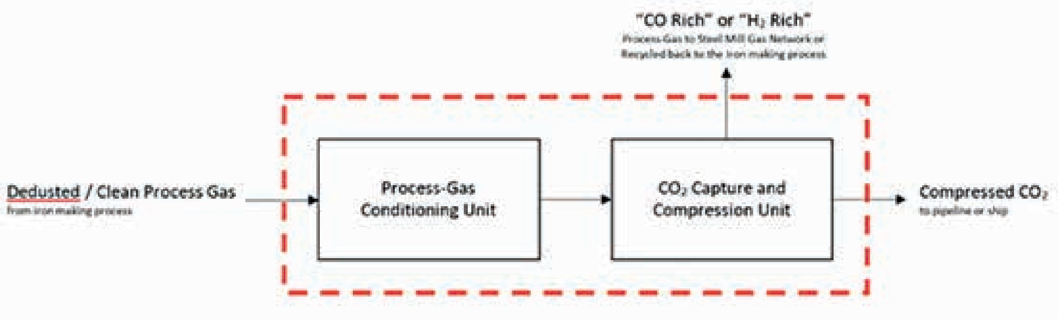


Figure 76 — Simplified schematic diagram of the system boundary

Relative to the steel mill or to the ironmaking process, the system boundary described are enclosed in a red box as shown in the various process flow diagrams. Brief description of the technology, process and equipment are presented in this review.

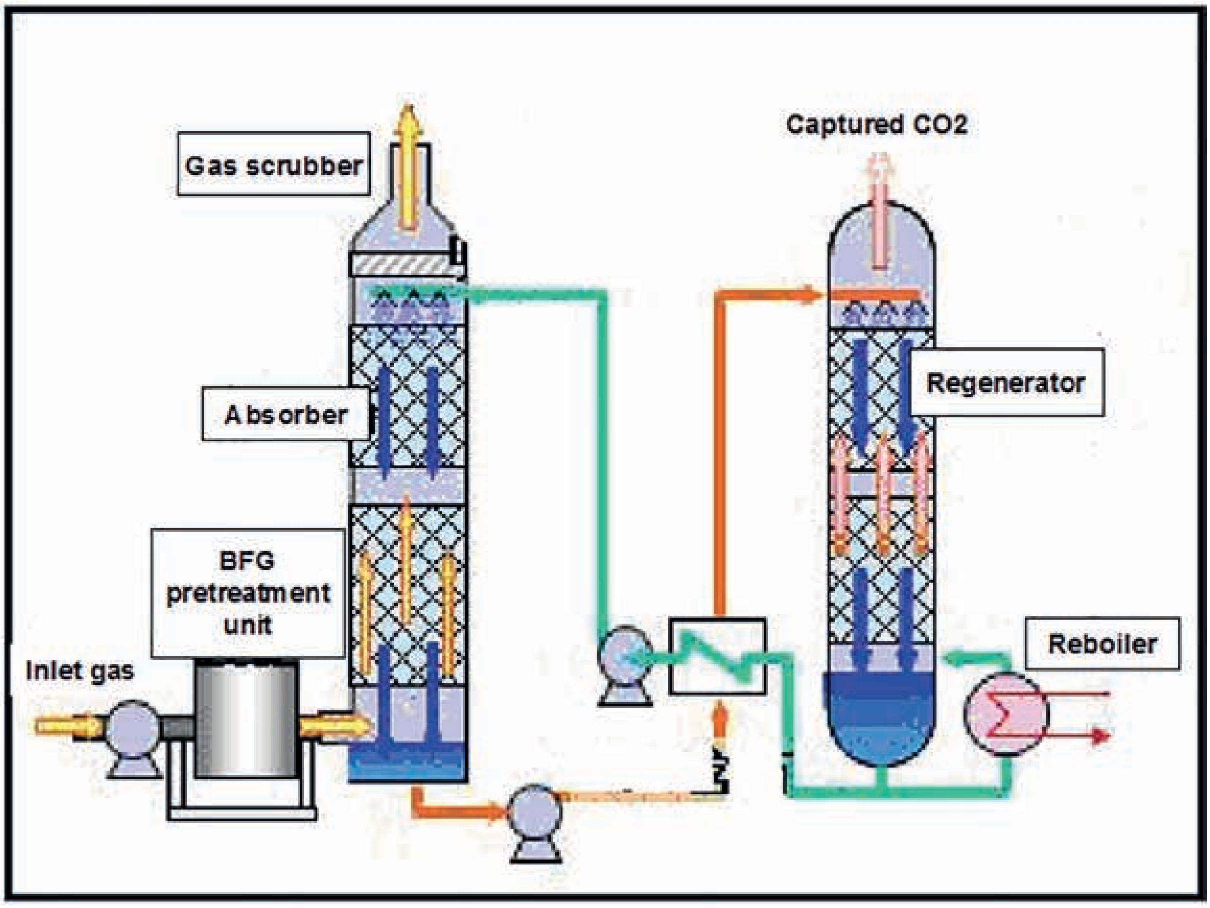
11.6 Capture of CO_2 from blast furnace gas

Typically, the blast furnace gas consists of CO_2, CO, H_2 and N_2. The capture of CO_2 from BFG would produce a process gas from the capture plant that could serve as additional reductant/fuel to the blast furnace or as gaseous fuel that could be used in other part of the steel mill.

The capture of CO_2 from the BFG could result to full decarbonization (i.e. removal of both CO_2 and CO) or partial decarbonization (i.e. only the removal of the CO_2). Depending on the level of decarbonization, the resulting process gas could be “CO rich” or “H_2 rich” gas. Additionally, the resulting process gas from the capture plant could be a suitable feedstock for production of other chemicals.

11.6.1 Development of chemical absorption technology under the COURSE50 programme

One of the technologies developed under the COURSE50 Programme evaluates the use of amines to remove the CO_2 from the BFG. The system boundary of the CO_2 capture facility relative to the Blast Furnace is enclosed in the red box shown in Figure 74. The simplified schematic flow diagram of the chemical absorption plant is presented in Figure 77.



NOTE See References [199], [200] and [201].

Figure 77 — Simplified PFD of the chemical absorption technology developed under COURSE50 programme

The CO_2 capture facility consists of the following major equipment:

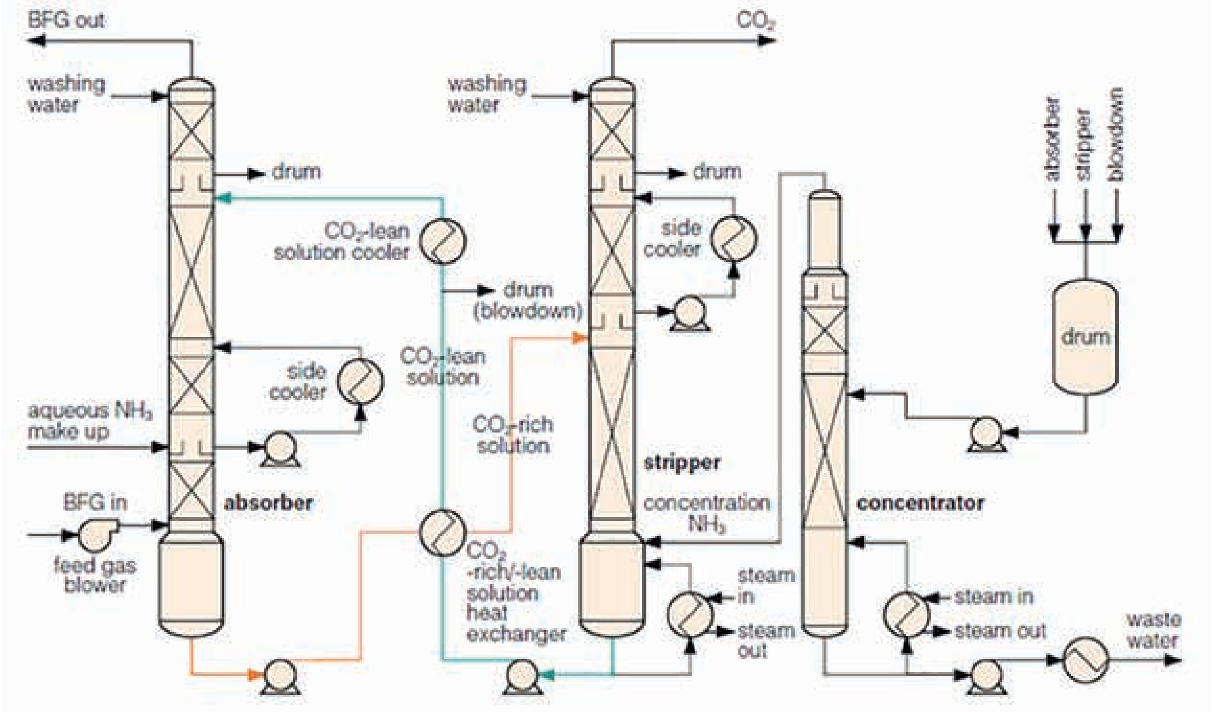
- BFG (inlet gas) FD fan/blower;
- BFG pre-treatment unit (typically consists of wet scrubber and dust removal system);
- absorber column;
- washing water pumps (situated at the top of the absorber column; not shown in Figure 77);
- rich and lean solvent heat exchangers;
- rich and lean solvent pumps;
- stripper (regenerator) column;
- reboiler;

  NOTE This will use steam generated from waste heat recovery from slag.
- condenser (not shown in Figure 77);
- amine make-up pump;
- CO_2 compression and dehydration unit (not shown in Figure 77).

The resulting process gas that comes out of the absorber column is a CO rich gas with <2 % CO_2. The process gas could be recycled back to the blast furnace or used as fuel within the steel works. The product CO_2 from the regenerator (stripper) has a composition of greater than 98 % to 99 % (v/v wet basis) CO_2 and saturated with water.

11.6.2 Development of chemical absorption technology under the POSCO/RIST programme

POSCO/RIST Programme has evaluated the use of aqueous ammonia process to remove the CO_2 from the BFG. The system boundary of the CO_2 capture facility relative to the Blast Furnace is enclosed in the red box shown in Figure 75. The schematic flow diagram of the chemical absorption plant is presented in Figure 78.



NOTE See References [192], [202] and [204].

Figure 78 — Simplified PFD of the chemical absorption technology developed under POSCO/RIST programme

The CO_2 capture facility consists of the following major equipment:

- BFG (inlet gas) FD fan/blower;
- BFG pre-treatment unit (not shown in Figure 78);
- absorber column;
- stripper column;
- concentrator column;
- washing water pumps;
- rich and lean solvent heat exchangers;
- other heat exchangers (lean solvent coolers, side column coolers);
- rich and lean solvent pumps;

- reboilers (situated in both stripper and concentrator columns);
- waste water pump;
- solvent drum;
- CO_2 compression and dehydration unit (not shown in Figure 78).

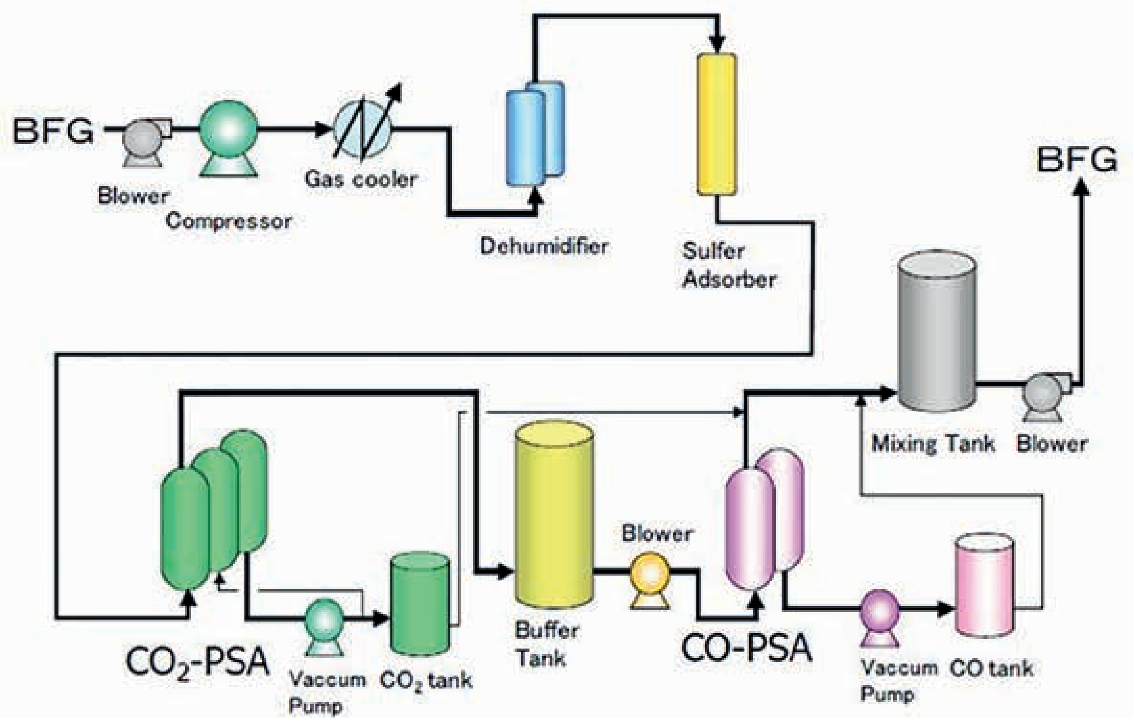
The resulting process gas coming from the absorber column is also a CO rich gas that could be recycled back into the blast furnace and/or used as fuel in other part of the steel mill. Additionally, this could also be considered as feedstock to other chemical production. The concentration of the CO_2 produced from the stripper is generally around 97 % to 98 % (v/v — wet basis).

11.6.3 Development of physical adsorption technology under COURSE50 programme

Another CO_2 capture technology developed under the COURSE50 Programme is the use of adsorbent to remove the CO_2 from the BFG. The ASCOA-3 Project [199][204] has developed a 2 stage multi-steps VPSA process using Zeolite-type adsorbent.

The raw BFG is compressed to ~3 Bar (abs), dehydrated and desulfurized. The CO_2 is separated from the blast furnace gas in the first stage adsorption process then followed by the separation of CO and H_2 from the N_2 in the second stage. CO_2 are recovered during desorption process under vacuum pressure of ~0,07 Bar (abs).

Figure 79 presents the simplified schematic flow diagram of the pilot plant producing ~3 tonnes CO_2/d from raw BFG. Relative to the blast furnace, the system boundary is enclosed in the red box as shown in Figure 74.



NOTE See References [199] and [205].

Figure 79 — Simplified PFD of the physical adsorption technology developed under the COURSE50 programme

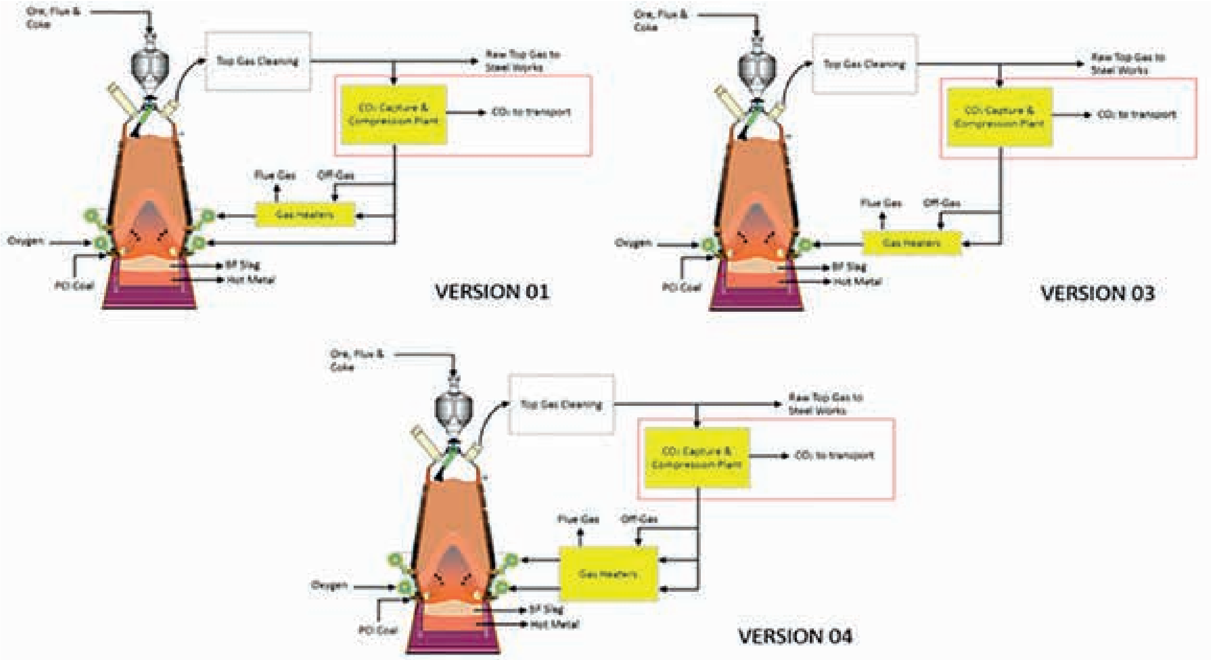
The CO_2 capture facility consists of the following major equipment:

- BFG (inlet gas) FD fan/blower;

- BFG compressor with intercooler;
- BFG dehydration unit;
- BFG desulfurization unit;
- CO_2 adsorbent towers (horizontal configuration);
- CO and H_2 adsorbent towers (horizontal configuration);
- vacuum pumps;
- gas holder;
- CO_2 compression and dehydration unit (not shown in Figure 79).

11.6.4 ULCOS BF — Oxygen-blown BF with top gas recycle

The ULCOS BF is also known as the “Top Gas Recycle Blast Furnace” (TGR–BF) or “Nitrogen Free Blast Furnace” (NFBF). The ULCOS programme has evaluated three different versions of this BF. They have also evaluated different CO_2 removal process from the raw top gas. Figure 80 presents the different versions of TGR-BF evaluated by ULCOS Programme.



NOTE See References [188], [197] and [207].

Figure 80 — Different versions of TGR-BF evaluated by ULCOS

The system boundary for the CO_2 capture plant is enclosed in the red box (as shown in Figure 80). ULCOS Programme has evaluated the following CO_2 separation processes:

- PSA;
- VPSA;
- chemical absorption;
- VPSA combined with cryogenic flash separation;
- PSA combined with cryogenic distillation.

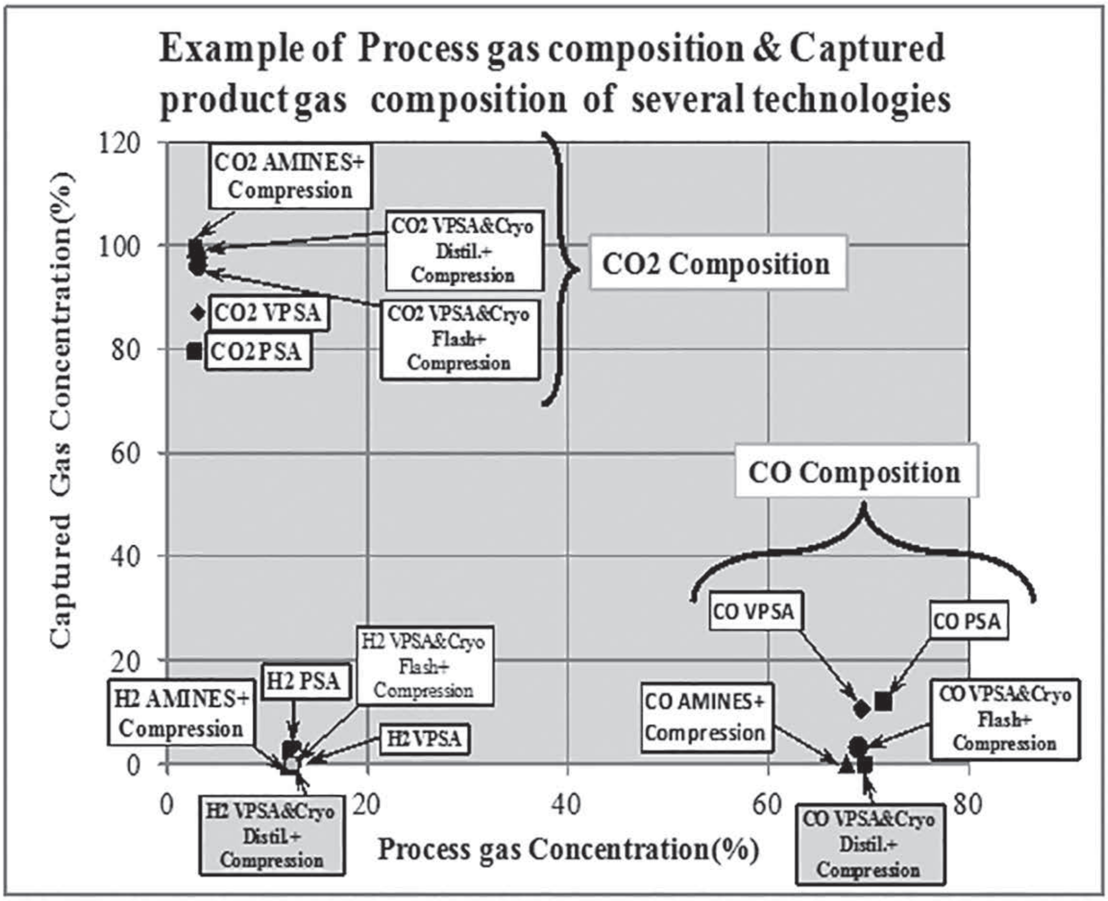
The TGR-BF involves the recycling of the "CO_2 lean" top gas to the blast furnace and the use of nearly pure oxygen (instead of the hot blast or air). This should results to a blast furnace gas with a very low N_2 content and higher CO_2, CO and H_2 content as compared to conventional blast furnace gas (as shown in Table 26).

Depending on the CO_2 removal process used, the product CO_2 could have a purity ranging between 80 % to >99 %. The processed process gas (i.e. recycled top gas) should be <3 % CO_2. Table 23 and Figure 81 present some of the results reported by ULCOS illustrating the typical range of the composition of the "CO rich" process gas and product CO_2 obtained from the different CO_2 capture processes evaluated.

It should be noted that CO_2 removal from a process gas using PSA, VPSA and chemical absorption processes are commercially demonstrated in other alternative ironmaking processes (i.e. FINEX, COREX, Energiron/HYL). These are briefly described in 11.9. On the other hand, applicable to the CO_2 removal from top gas of an ULCOS BF, the demonstration using PSA in combination with cryogenic separation process to separate CO_2 from syngas of an SMR is now under construction at Port Jerome SMR facility of Air Liquide. Likewise, PSA in combination with VPSA to separate the CO_2 from syngas of an SMR is operational at Port Arthur facility of Air Products producing ~1,2 MTPY of CO_2 for EOR application (having achieved CO_2 purity of ~97 % purity).[206]

Table 23 — Comparison of CO_2 capture technologies for an integrated steel mill (BF-BOF route)

		PSA	VPSA	VPSA and Cryo Flash + Compression	Amines + Compression	PSA and Cryo Distil. + Compression
Recycled Top Gas (Process Gas)						
CO yield	%	88,0	90,4	97,3	99,9	100,0
Process Gas Composition (wet basis)						
CO_2	%v/v	2,7	3,0	3,0	2,9	2,7
CO	%v/v	71,4	69,2	68,9	67,8	69,5
H_2	%v/v	12,4	13,0	12,6	12,1	12,4
N_2	%v/v	13,5	15,7	15,6	15,1	15,4
H_2O	%v/v	0,0	0,0	0,0	2,1	0,0
Captured Product CO_2 (dry basis)						
CO_2	%v	79,7	87,2	96,3	>99,9	>99,9
CO	%v	12,1	10,7	3,3	0,0	0,0
H_2	%v	2,5	0,6	0,1	0,0	0,0
N_2	%v	5,6	1,6	0,3	0,0	0,0



NOTE See Reference [206].

Figure 81 — Rearranged comparison of CO_2 capture technologies for an integrated steel mill (BF-BOF route) from the ULCOS project evaluation results

Figure 81 shows data relationship of H_2, CO and CO_2 concentration between process gas composition (wet basis) and captured product CO_2 (dry basis) on each capture technology. The horizontal axis means H_2, CO and CO_2 concentration in process gas, the vertical axis means H_2, CO and CO_2 concentration in captured product CO_2 respectively. For instance, plot “CO VPSA” means CO concentration in process gas and captured product CO_2 on VPSA.

11.6.5 Other commercial development

The potential of using shift reactor to achieve full decarbonization of the BFG have been reported in various literature.[192] This involves two catalytic reactors to react the CO with steam to produce H_2 and CO_2. Typical conversion of CO to CO_2 and H_2 is ~90 % depending on the performance of the catalyst and the steam to CO ratio. Figure 82 illustrates a simplified schematic diagram of the water gas shift reactor.

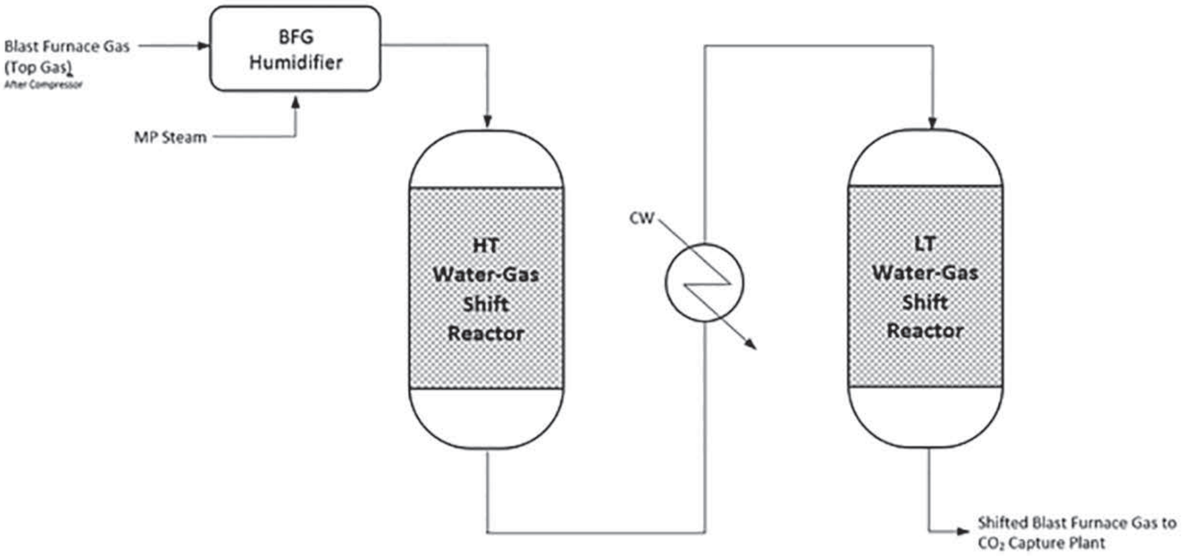


Figure 82 — Simplified PFD of the water-gas shift reactor

An example of this development is the BF Plus[29) technology as proposed by Air Products and Danieli Corus.[207] This is illustrated in Figure 83. According to their patent, the CO_2 capture plant involves the use of physical solvent (i.e. Selexol). To achieve a full decarbonization if required, shift reactors will be used. It should also be noted that the overall efficiency to the steel work is also improved by high level of oxygen enrichment of the hot blast (which should increase the calorific value of the BFG or top gas); and the deployment of combine cycle power plant to produce electricity for the steelwork or for export. For the purpose of this Technical Report, the system boundary of the CO_2 capture plant is indicated by the red dotted line (as shown in Figure 83).

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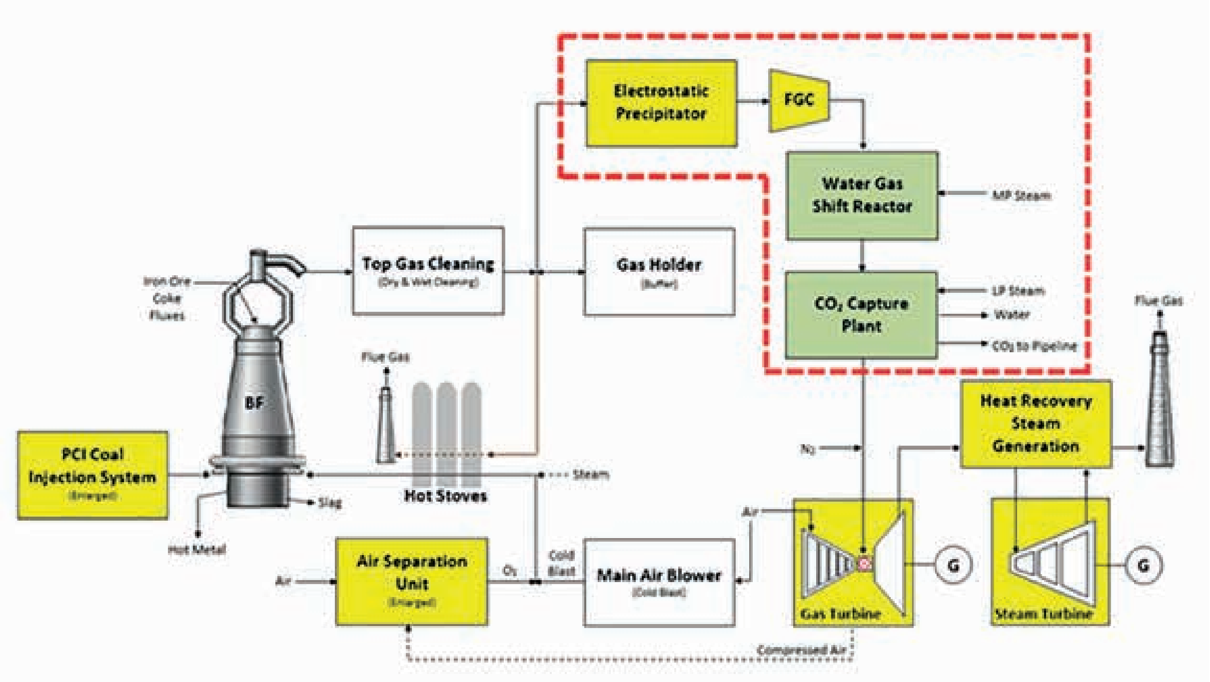
29) BF Plus is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.



NOTE See Reference [208].

Figure 83 — Simplified PFD of air product's BF plus scheme with full decarbonization of BFG

11.7 Specific energy consumption of CO_2 captured

Specific Energy Consumptions of the CO_2 captured are estimated in various projects[201][204][206] and Table 24 summarizes the reported energy consumption of different CO_2 removal processes.

Table 24 — Reported values of energy consumptions from various R&D activities

		Specific energy consumption (GJ/t CO_2)	Reagents	CO_2 capture capacity (TPD)	Remarks	Data source
COURSE50 Programme Results	Chemical Absorption	2,70 primary energy base	RN1[a]	1	Experimental Results (Only regeneration energy)	[201]
	Chemical Absorption	2,50 primary energy base	RN1	30	Experimental Results (Only regeneration energy)	[201]
	Chemical Absorption	2,40 primary energy base	RN1	3 000	Extrapolated	[201]
	Chemical Absorption	2,50 primary energy base	RN3[b]	1	Experimental Results (Only regeneration energy)	[201]
	Chemical Absorption	2,35 primary energy base	RN3	30	Experimental Results (Only regeneration energy)	[201]
	Chemical Absorption	2,25 primary energy base	RN3	3 000	Extrapolated	[201]

[a] RN1 is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of this product.

[b] RN3 is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of this product.

Table 24 *(continued)*

		Specific energy consumption (GJ/t CO_2)	Reagents	CO_2 capture capacity (TPD)	Remarks	Data source
ULCOS Programme Results	Chemical Absorption + Compression	3,81 primary energy base	Amine (MEA)	NR	Reported value includes compression energy	[206]
	PSA	0,36 Secondary energy base		NR		[206]
	VPSA	0,38 Secondary energy base		NR		[206]
	VPSA and Cryo Flash + Compression	1,05 Secondary energy base		NR	Reported value includes compression energy	[206]
	PSA and Cryo Distillation + Compression	1,12 Secondary energy base		NR	Reported value includes compression energy	[206]
POSCO-RIST Programme Results	Chemical Absorption	3,10 primary energy base	Warm Aq. Ammonia	10	Reported value are simulated value of regeneration energy only	[204]

[a] RN1 is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of this product.

[b] RN3 is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of this product.

Generally, with utilization of energy, energy quality should be considered as well as energy quantity. This means that in the case of defining the “Specific Energy Consumption of the CO_2 Captured”, the energy could be classified according to primary energy or secondary energy, given that the quality and quantity of both energies are quite different in the physical point of view. Unfortunately, in this Technical Report, the manner on how the energy consumptions are calculated could not be presented consistently as discussed below.

From Table 24, it could be noted that the reported values are wide ranging. It should be emphasized that comparing the reported values from the COURSE50 programme,[201] ULCOS programme[206] and POSCO-RIST Programme[204] are not possible and could be misleading because of the different assumptions used in defining and calculating the specific energy consumption.

The calculation of the specific energy consumption is based on very site specific assumptions. Some results are directly obtained from pilot plants (i.e. COURSE50 results); while others are obtained from process simulation and validated against pilot plant results (i.e. ULCOS and POSCO-RIST Programme).

Additionally, it is not clear whether how the reported results considered both the primary and secondary energy sources in the calculation. For example, the COURSE50 results only considered the primary energy consumption based on the CO_2 capture plant as the boundary limit, where it only accounts for the regeneration energy (i.e. steam consumption) plus the auxiliary energy needed (i.e. including electricity for the circulation pumps, etc.). On the other hand, ULCOS calculated the results based on the whole steel mill as the boundary limit. The calculation is based on additional total energy required by the capture plant which also accounts for the savings obtained from the coke reduction due to TGR operation and the electricity import from the grid.

Furthermore, the composition of the feed gas going into the CO_2 capture plant reported by ULCOS and COURSE50 are different which could lead to differences to energy performance reported for the CO_2 capture plant. It should be noted that ULCOS' BFG are delivered at pressure with CO and CO_2 content of ~32 % to 35 % (enriched by the Top Gas Recycle) vs. COURSE50s BFG being delivered at atmospheric pressure and with CO and CO_2 composition ranging from 20 % to 24 %.

In summary, the calculation of the specific energy consumptions of the CO_2 capture plant applied to the iron and steel industry should be interpreted with care and should clearly account for the different operational aspects which include, but not limited to

- boundary limit,
- classification of the primary and secondary energy sources,
- feed gas composition,
- feed gas pressure and temperature,
- delivery pressure of the CO_2 product, and
- composition of the CO_2 product.

11.8 Gas streams

11.8.1 Conventional blast furnace gas (BFG)

Blast furnace gas is the by-product gas of the blast furnace during the reduction of iron ore using reductant such as coke. Typical range of composition of the BFG (composition of the gas just after the two stages of de-dusting and scrubbing) is presented in Table 25.

Table 25 — Range of composition of dedusted and cleaned BFG

Treated BFG (Components)	Units	Composition (%)
CO_2	%(v/v) — dry	20 – 25
CO	%(v/v) — dry	20 – 26
H_2	%(v/v) — dry	4 – 9[a]
N_2/Ar	%(v/v) — dry	44 – 52 (balance)

[a] High H_2 content of more than 5 % is due to the use of NG injection.

Typically, BFG that could be fed into the CO_2 capture facilities is delivered from a gas holder and is available at pressure between 2,0 Bara to 3,0 Bara.

The concentration of CO and H_2 in the BFG is typically affected by several factors and these include the properties of the injected fuel (i.e. pulverized coal, natural gas, tar, fuel oil, etc.) into the tuyeres and the level of oxygen enrichment.

If wet scrubbers are used for the final dedusting and gas treatment, the BFG is expected to be nearly saturated with water. Temperature of the gas after this stage is about 30 °C to 40 °C.

11.8.2 BFG from an oxygen-blown BF with top gas recycle (ULCOS BF)

The ULCOS programme has evaluated three different versions of capturing CO_2 from an oxygen blown blast furnace with top gas recycle. These are described in 11.6.4.

Typical composition of the raw top gas that goes into the CO_2 capture plant is presented in Table 26.

Table 26 — Typical range of composition of cleaned raw top gas from ULCOS BF

Raw top gas (components)	Units	Composition
CO_2	%(v/v) — dry	34 – 38
CO	%(v/v) — dry	45 – 50
H_2	%(v/v) — dry	8 – 10
N_2/Ar	%(v/v) — dry	5 – 10 (balance)
NOTE See References [178], [206], [207].		

The variability in the composition (i.e. concentration of CO and H_2) of the raw top gas from the ULCOS BF will also be dependent on various factors including the level and the manner on how the processed top gas are recycled back into the blast furnace. It is expected that similar gas treatment used in conventional BF will be deployed. If wet scrubber is used, the raw top gas is expected to be saturated and temperature is reduced down to 30 °C to 40 °C after this stage.

11.9 CO_2 capture from alternative ironmaking process

11.9.1 Direct reduction ironmaking process

In 2013, around 78 million tonnes of DRI and HBI are produced worldwide. Gas-based DRI production is the most dominant route. This is led by Midrex (60 %) then followed by HYL/Energiron (15 %). Coal-based DRI are predominant in India. The majority of the coal-based DRI production is using Rotary Kiln with Rotary Cooler technologies. Typically, these kilns have a production capacity ranging from between 0,10 to 0,15 MTPY.

This Technical Report only describes the two leading gas-based DRI technologies that have potential for CO_2 capture. Also included in this subclause is the ULCORED technology, a revamped DRI process developed by the ULCOS programme. It should be noted that this Technical Report does not include the options available for coal-based MIDREX, ENERGIRON or ULCORED plants.

11.9.1.1 ENERGIRON (HYL I, HYL III, HYL ZR)

Figure 84 presents the simplified schematic process flow diagrams of Energiron/HYL process which consists of a version with an external SMR [HYL-I30) and HYL-III31)] or a reformerless version [HYL-ZR32)].

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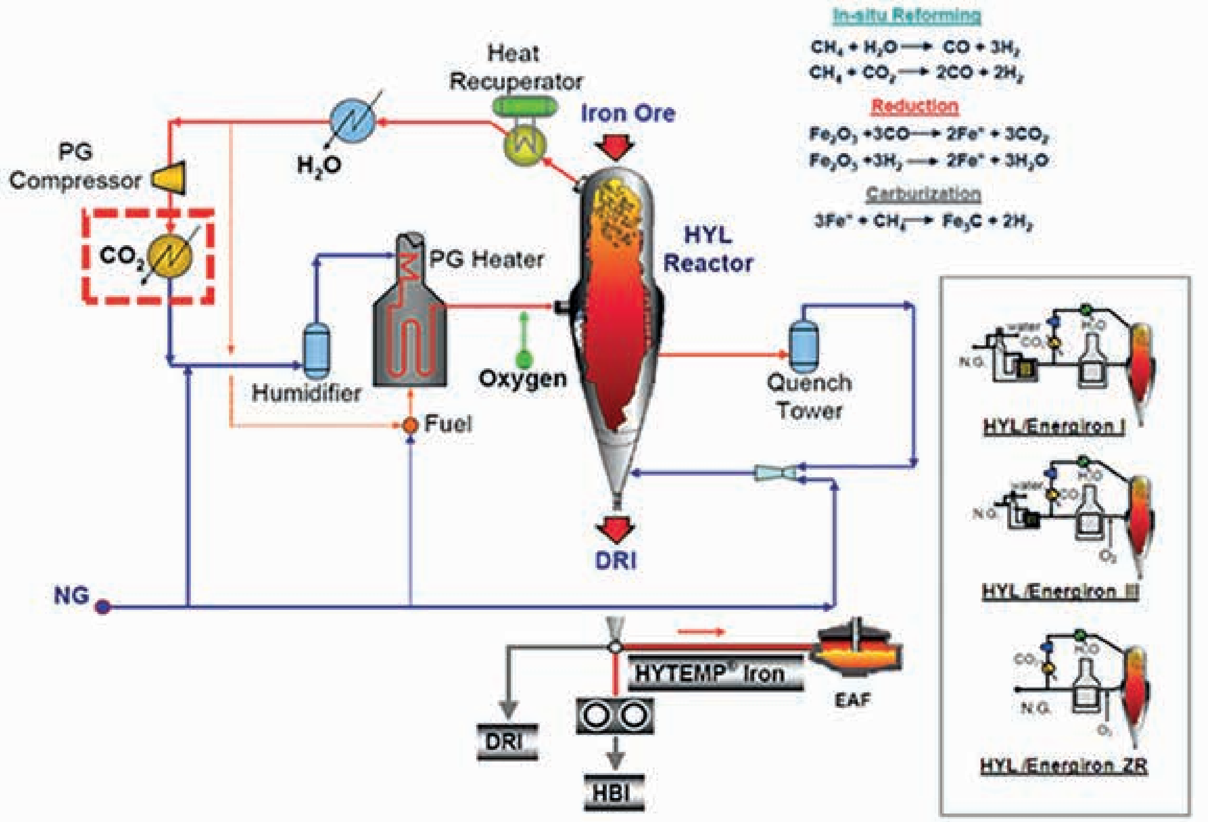
30) HYL-I is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

31) HYL-III is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

32) HYL-ZR is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.



NOTE See References [188], [210] and [212].

Figure 84 — Simplified PFD of HYL/Energiron DRI production process

One of the important features of this process is the inherent removal of the by-products of the ore reduction process (i.e. removal of H_2O and CO_2). This, therefore, provides opportunity for selective removal and capture of CO_2 for reuse (i.e. as food grade CO_2 or EOR operation).

The process of gas leaving the shaft reactor consists mainly CO_2, CO, H_2 and H_2O with temperature in the region of 400 °C. This gas is cooled and water is removed by using a wet scrubber system. Majority of the process gas is compressed to around 7 Bar (abs) to 8 Bar (abs); while part of the process gas is used as supplementary fuel to the process gas heater. The compressed process gas is passed through a CO_2 removal system. This is either a PSA/VPSA or amine/potassium carbonate-based separation technology. The reducing gas from the CO_2 removal unit should typically range between 2 % to 8 % CO_2.

For the purpose of this Technical Report, the system boundary for the CO_2 capture facility is enclosed in the red box shown in Figure 84.

An example illustrating the typical composition of the reducing gas that enters the shaft reactor and the process gas of the ENERGIRON/HYL process is shown in Table 27.

Table 27 — Example of composition of the reducing gas feeding into the shaft reactor

Gas composition (%v/v – wet)	**ENERGIRON with SMR (before humidifier)**	**ENERGIRON Zero Reformer (before humidifier)**	**Process gas (after H_2O removal)**
CO_2	2,2	1,5	35 – 40
CO	13,7	9,6	10 – 15
H_2	76,0	45,0	30 – 35
NOTE See Reference [218].			

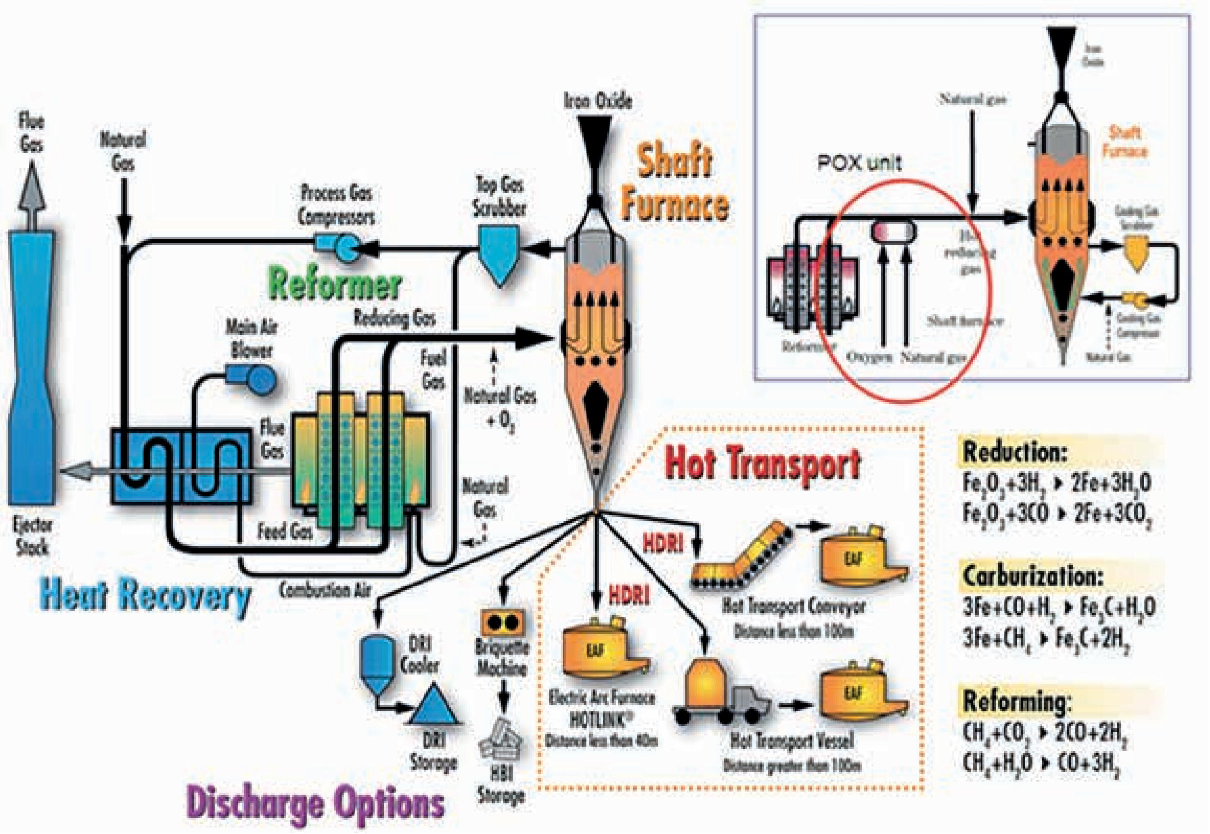
Table 27 *(continued)*

Gas composition (%v/v – wet)	**ENERGIRON with SMR (before humidifier)**	**ENERGIRON Zero Reformer (before humidifier)**	**Process gas (after H_2O removal)**
CH_4	6,0	35,0	10 – 15
H_2O	1,5	8,3	1 – 5
N_2/Ar	0,6	0,6	1 – 2
NOTE See Reference [218].			

Currently, there are five modules of Energiron/HYL operating plants producing food grade CO_2 using amine base CO_2 removal units. These include plants located in Mexico (four modules) and India (one module). Two modules situated in Middle East are being upgraded to include CO_2 removal units with the CO_2 to be used for EOR operation.[213]

11.9.1.2 MIDREX

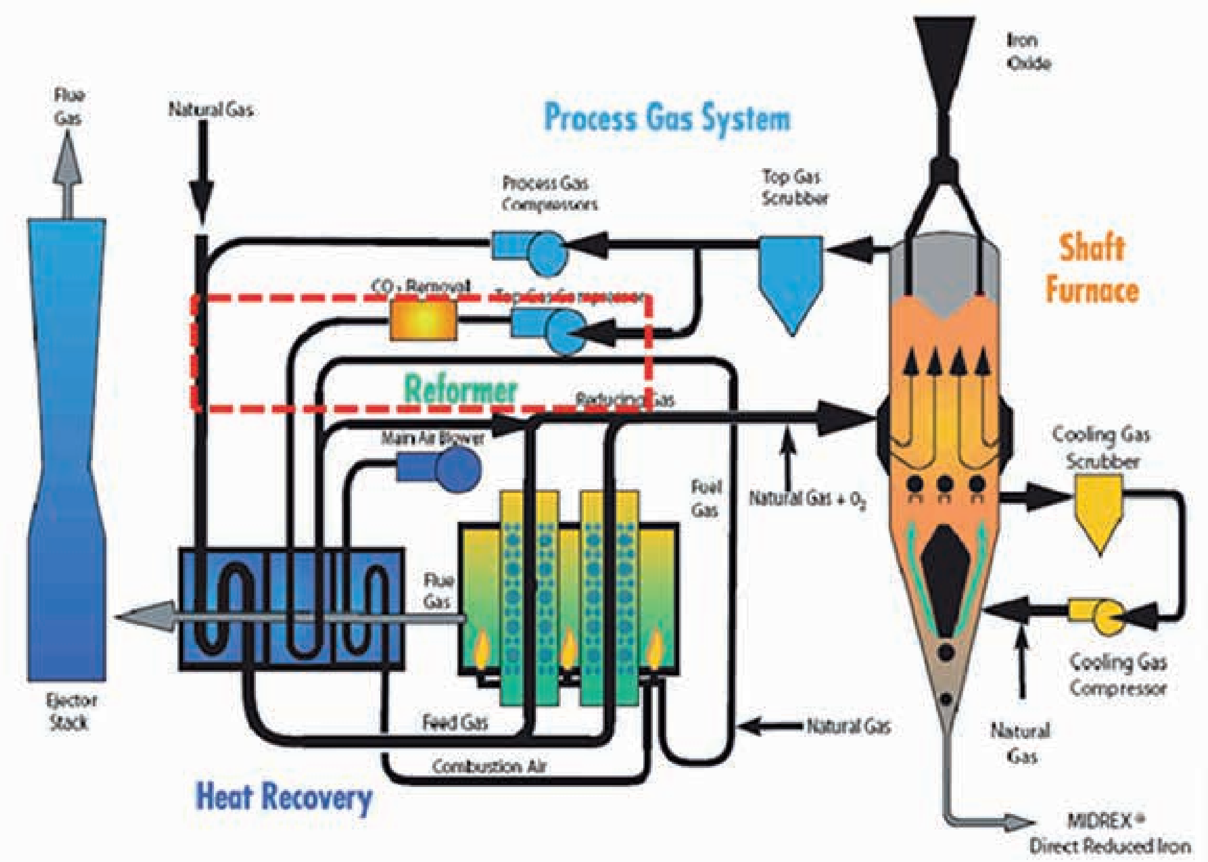
Figure 85 presents the simplified schematic process flow diagrams of a conventional MIDREX process without CO_2 removal.



NOTE See References [214] and [215].

Figure 85 — Simplified PFD of MIDREX DRI production process

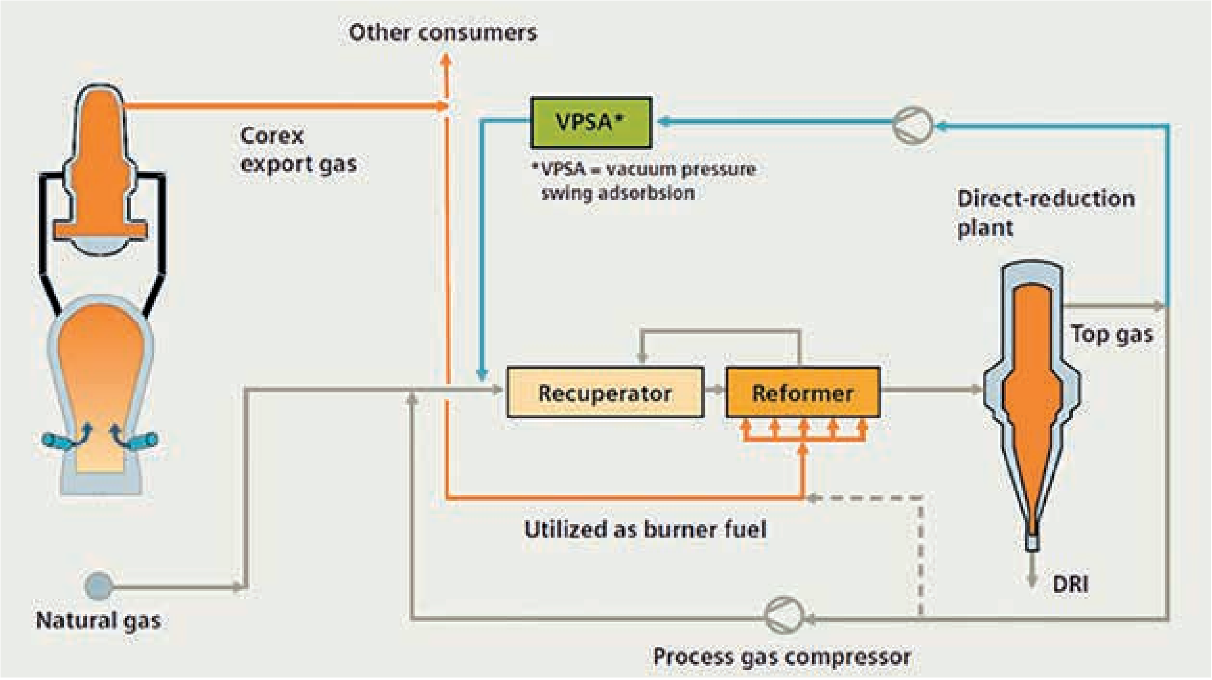
Midrex has suggested a process scheme that would allow the capture of CO_2 from their DRI production plant. This includes the removal of CO_2 from the slips stream of the top gas using PSA or amine-based separation technology. This involves changes to the heat recovery equipment to include the pre-heating of the CO_2-lean top gas (as shown in Figure 86). For the purpose of this Technical Report, the system boundary for the CO_2 capture plant is enclosed in the red box.



NOTE See Reference [215].

Figure 86 — Simplified PFD of MIDREX DRI production with low CO_2 configuration

Currently, there is no standalone MIDREX plant that removes the CO_2 from the top gas. However, there are two MIDREX modules in operation today situated at Essar's Hazira Steel Mill that employs VPSA unit to remove part of the CO_2 from their MIDREX top gas to compliment the natural gas feedstock. The steelwork schematic flow diagram is shown in Figure 87.

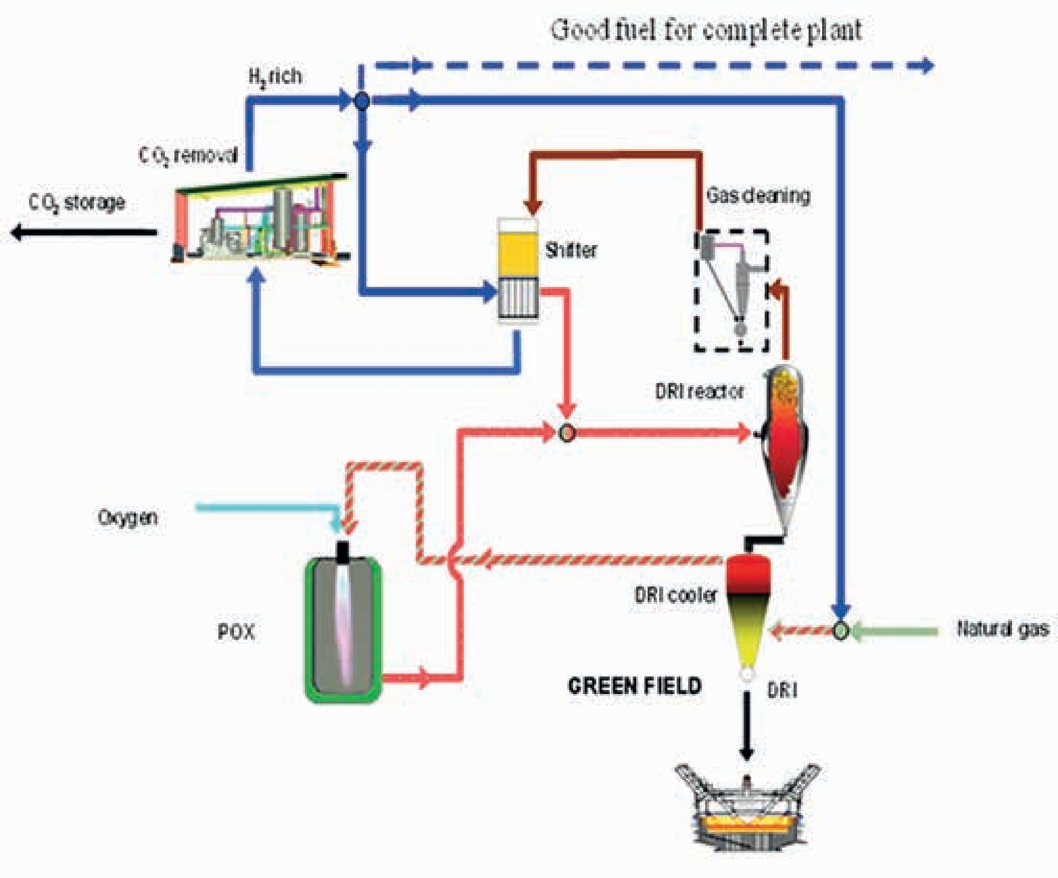


NOTE See Reference [216].

Figure 87 — Simplified PFD of the MIDREX DRI production with partial CO_2 removal

11.9.1.3 ULCORED (ULCOS Programme)

Figure 88 presents the schematic flow diagram of the gas-based ULCORED process. This is a revamped version of gas-based DRI production to maximize the CO_2 removal as compared to ENERGIRON and MIDREX plants.



NOTE See References [217] and [218].

Figure 88 — Simplified PFD of the ULCORED gas-based DRI production with CO_2 removal

Primarily, the production of DRI is based on the use of partial oxidation reactor (POX) to produce the syngas as the primary reducing gas. Additionally, the process involves the use of a shift reactor to convert at least 90 % of the CO in the cleaned process gas from the shaft reactor to produce H_2 and CO_2. The CO_2 is then separated using VPSA or PSA (as shown in Figure 88). Most of the top gas from the PSA/VPSA is used as cooling medium of the DRI. This is generally mixed with natural gas to make up the fuel demand of the POX reactor. Some part of the top gas will be preheated in the shift reactor and mixed with the syngas produced by the POX. Finally, a minor part of the gas could be exported to the steelworks as by-product fuel to bleed out the nitrogen content.

Typical composition the reducing gas entering the shaft reactor and the process gas entering the water gas shift reactor of the ULCORED process is summarized in Table 28.

Table 28 — Example of the composition of the reducing gas feeding into the shaft reactor

Gas composition (%v/v – wet)	**ULCORED reducing gas (before the shaft reactor)**	**Process gas from ULCORED (after dedusting)**
CO_2	0,6	3,3
CO	12,6	8,3
H_2	79,5	51,3
NOTE See Reference [218].		

Table 28 *(continued)*

Gas composition (%v/v – wet)	ULCORED reducing gas (before the shaft reactor)	Process gas from ULCORED (after dedusting)
CH_4	0	0
H_2O	5,7	35,5
N_2/Ar	1,6	1,6
NOTE See Reference [218].		

Currently, there are plans by the ULCOS consortium to build a pilot plant producing 1 tonne DRI/h to demonstrate the ULCORED process.

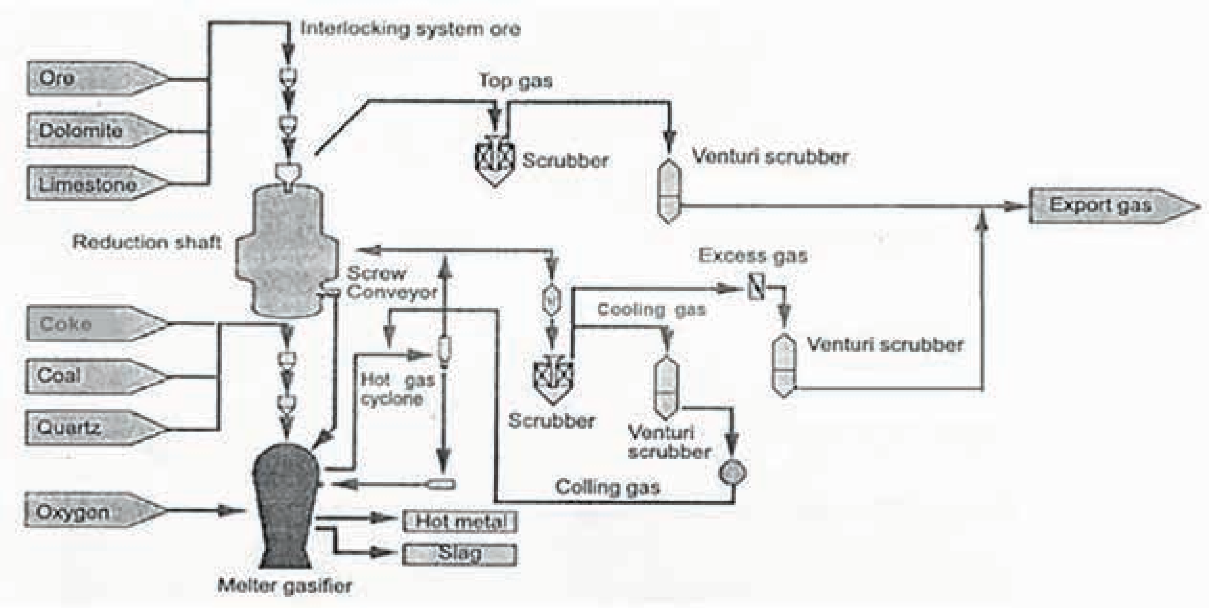
11.9.2 Smelting reduction ironmaking process

Currently, COREX and FINEX are the only smelting reduction technologies that are commercially operated. HISMELT[33) technology was demonstrated but discontinued due to economic reason. Nonetheless, the smelting part of HISMELT has been adapted into the development of HISARNA.

For the purpose of this Technical Report, options for CO_2 capture from smelting reduction will be described. This will be limited to the CO_2 capture options available to COREX, FINEX and HISARNA.

11.9.2.1 COREX

Figure 89 presents the process flow diagram of a COREX plant.



NOTE See References [188] and [192].

Figure 89 — Schematic PFD of a COREX plant

The COREX export gas is a medium calorific value gas that is generally used as fuel for the power plant or as fuel for other part of the steel mill. In some cases, this gas is also used as reducing gas for the DRI plant.

Typical composition of the export gas is presented in Table 29. The gas is normally available at pressure between 1,2 Bar (abs) to 2,0 Bar (abs). The quality of the COREX export gas depends on how the COREX

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33) HISMELT is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

plant are operated. This could have a range with a high energy value (~1,4 MWe/thm) to low energy value (~0,9 MWe/thm).

Table 29 — Range of composition of dedusted and cleaned COREX export gas

Treated BFG (components)	Units	Composition
CO_2	%(v/v) — dry	29 – 32
CO	%(v/v) — dry	42 – 47
H_2	%(v/v) — dry	19 – 22
CH_4	%(v/v) — dry	1,5 – 2,5
N_2/Ar	%(v/v) — dry	1 – 2 (Balance)
H_2S	mg/Nm^3	Not available
Particulate Matter	mg/Nm^3	1 – 10
NOTE See References [219], [220].		

For the purpose of this Technical Report, the system boundary for the CO_2 capture facility could be schematically shown in Figure 90 (as enclosed in the red box).

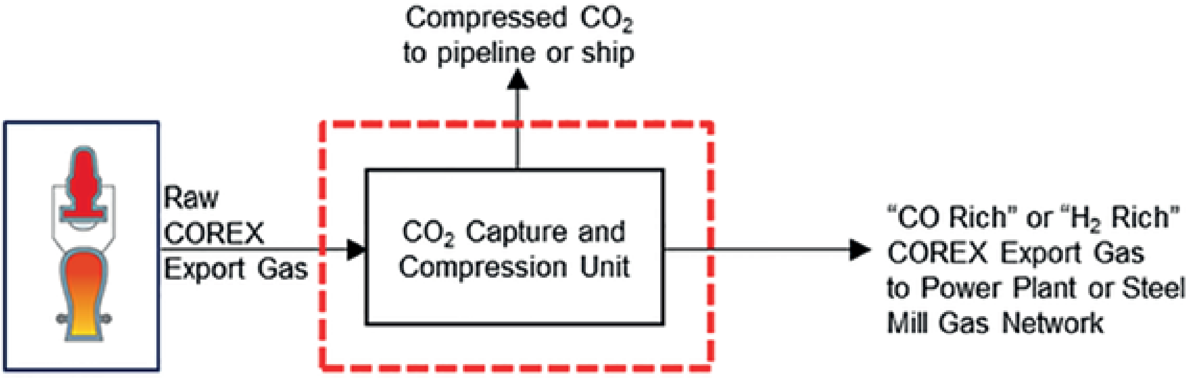


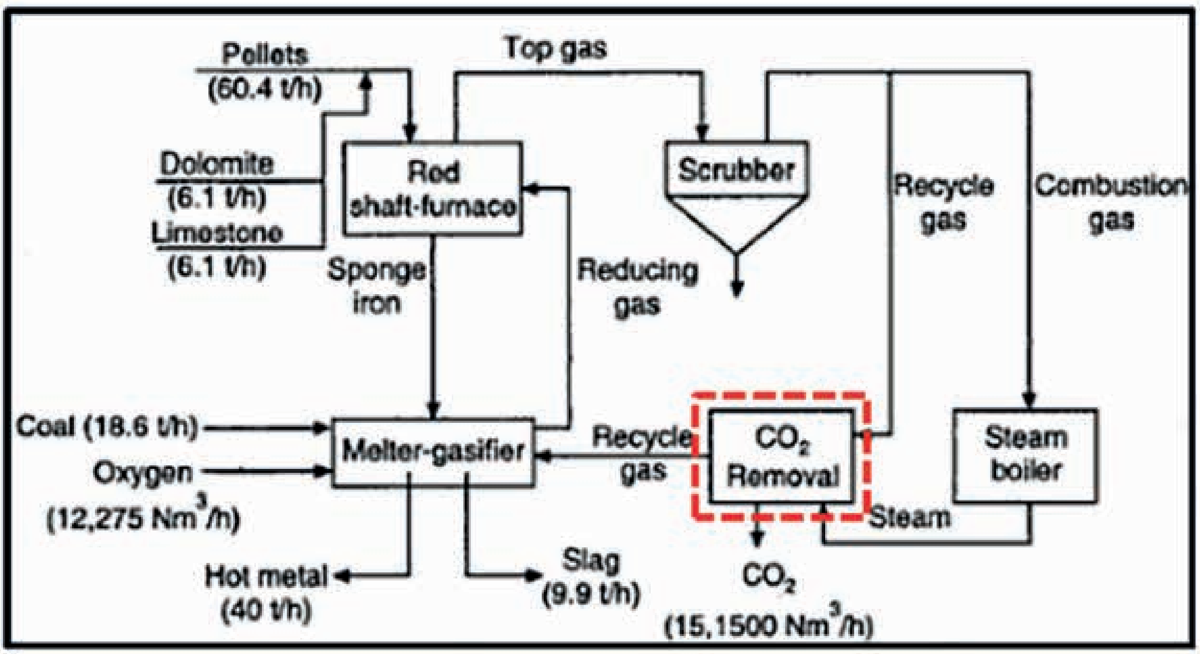
Figure 90 — System boundary of the CO_2 capture plant for the COREX plant

The removal of the CO_2 from COREX export gas is pretty much an "end of pipe" treatment. The decarbonization of the COREX export gas could be achieved partially by removing the CO_2 only; thus, producing a mixture of CO/H_2 rich process gas; or could be fully decarbonized by means of CO shift and CO_2 capture, producing H_2 rich process gas. It should be noted that the resulting process gas from the capture plant are also suitable as feedstock for other chemical production.

There are several options for the CO_2 capture plant that could produce a product CO_2 suitable for transport and storage. All the technology options developed for capturing CO_2 from blast furnace gas (as described in the previous clause) are also applicable to the capture of CO_2 from the COREX export gas. These options could include but not limited to technologies such as

- chemical absorption,
- physical absorption,
- physical adsorption,
- membrane, and
- combination of physical adsorption and cryogenic separation.

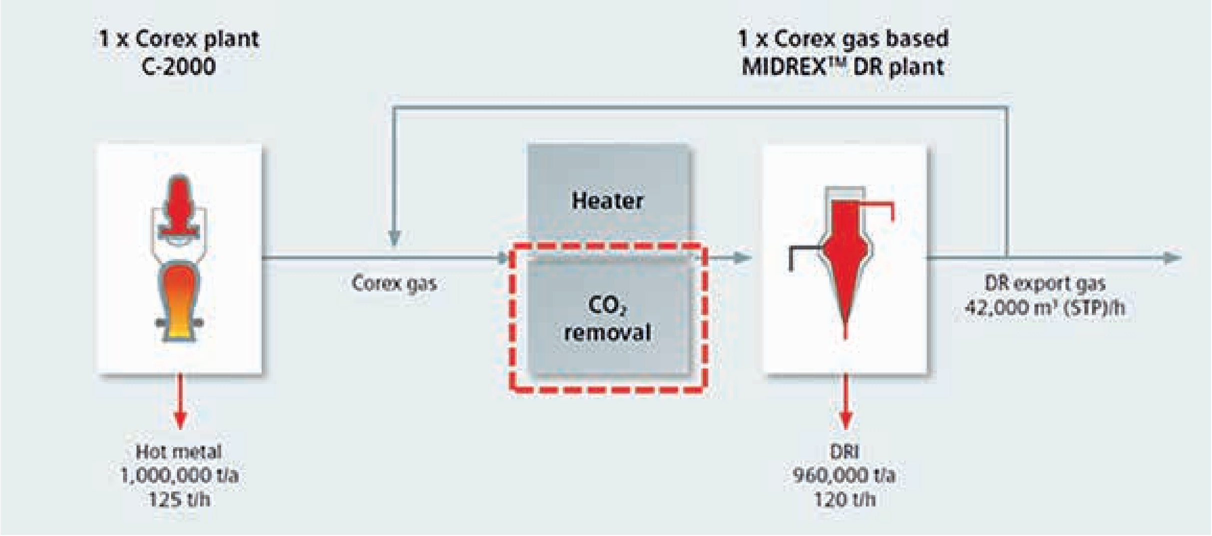
It should be noted that in the early development of the COREX plant, it has been established that by recycling or re-utilizing the COREX gas to the melter/gasifier could result to lower coal and oxygen demand of the COREX plant. This will involve CO_2 removal to produce a process gas with less than ~3 %CO_2. An example of this scheme is illustrated in Figure 91. For the purpose of CO_2 capture and storage, the CO_2 removal system may need additional CO_2 purification steps to meet the required specification of the CO_2.



NOTE See Reference [220].

Figure 91 — Example of a COREX plant with the removal of CO_2 by chemical absorption and re-utilization of COREX gas by the melter/gasifier

Currently, there are no standalone COREX plant that removes the CO_2 from their export gas. However, there are three COREX modules in operation today that remove the CO_2 from their export gas by using VPSA (i.e. one module at AM Saldanha Steelworks, South Africa, commissioned in 2000 and another two modules at JSW Vijayanagar Steelworks, India, commissioned in 2013). The simplified schematic diagram of the COREX-MIDREX configuration is shown in Figure 92.



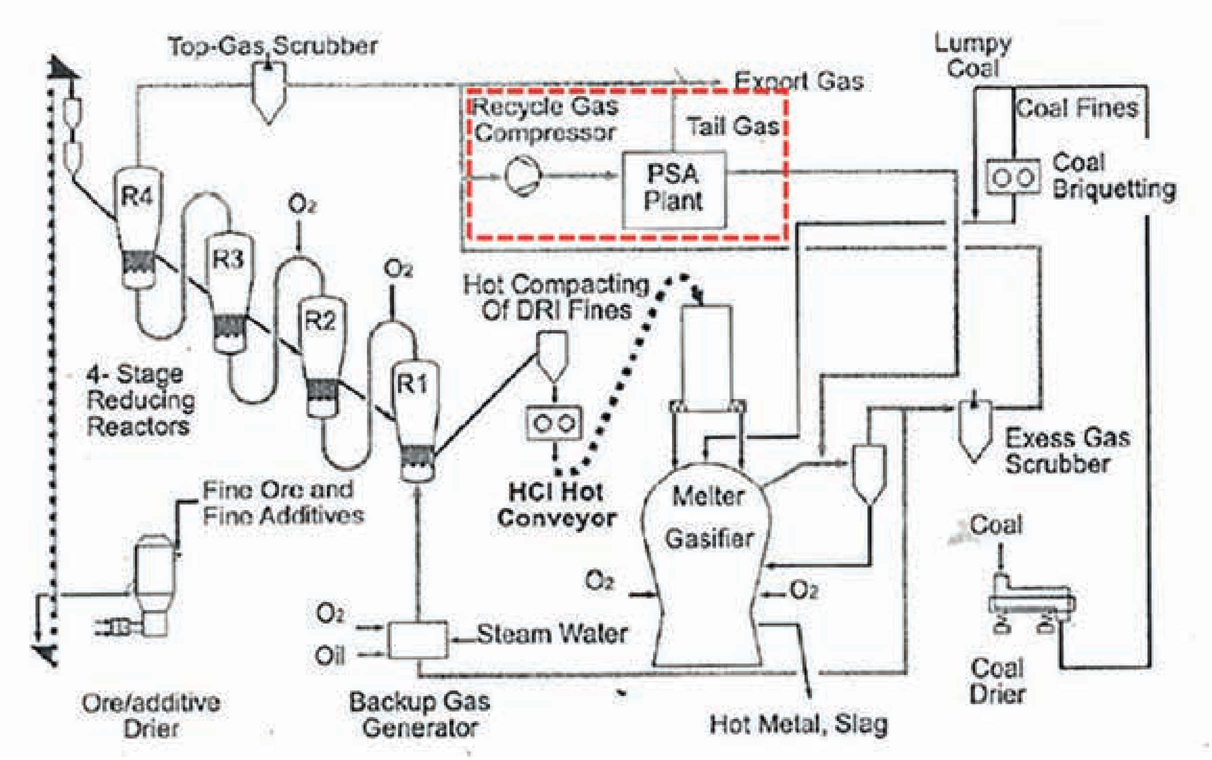
NOTE See Reference [221].

Figure 92 — Simplified schematics for COREX-MIDREX configuration

The raw COREX export gas is generally mixed with the top gas of the Midrex Plant prior to CO_2 removal. The CO_2 lean process gas from the VPSA (i.e. with CO_2 composition ranging between 2 % to 6 %) is then pre-heated and partially oxidized in a process gas heater. This is used as reducing gas to the MIDREX DRI plant. The CO_2 rich gas (i.e. typically consists of 60 % to 80 % CO_2 and 5 % to 15 % CO) obtained from the tail gas of the VPSA unit are currently used as low grade fuel for heating within the steel mill or flared and vented to the atmosphere. To make the CO_2 rich gas suitable for CO_2 transport and storage, CO_2 purification steps could be necessary to achieve at least 95 % CO_2 purity.

11.9.2.2 FINEX

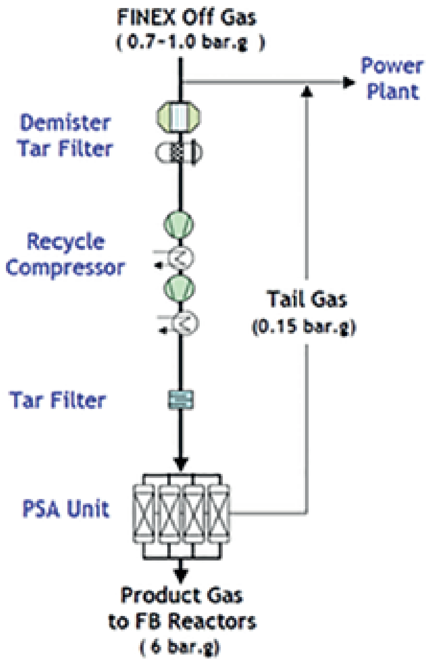
Figure 93 presents the schematic flow diagram of the FINEX plant. For the purpose of this Technical Report, the system boundary considered for the CO_2 capture plant is enclosed in the red box.



NOTE See References [188] and [192].

Figure 93 — Schematics PFD of the FINEX plant

Typically, 30 % of the FINEX process gas is recycled back to the pre-reduction reactor (R1). This gas is processed to remove the CO_2. Figure 94 presents a more detailed schematic flow diagram of the CO_2 removal system of the current FINEX plant. Typical gas composition of the FINEX process gas, PSA tail gas and the Product Gas are also shown.

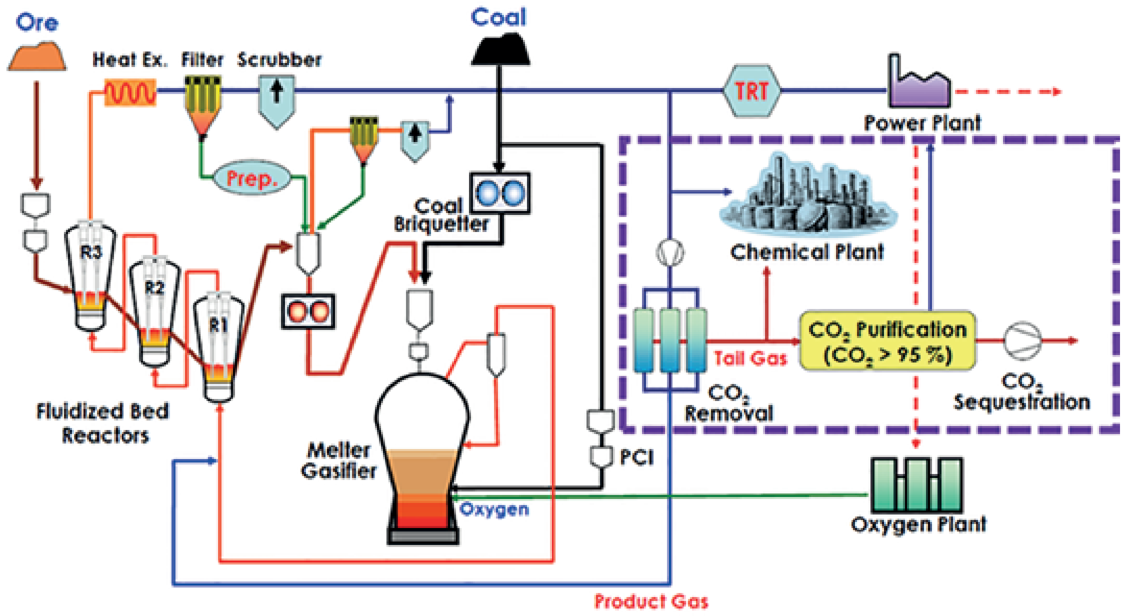


Gas	Composition (%)			
	CO	CO_2	H_2	N_2
Off-Gas	36	33	15	11
Product Gas	53	3	25	18
Tail Gas	17	66	4	3

NOTE See Reference [222].

Figure 94 — Schematics PFD of the CO_2 removal system of the FINEX plant

CO_2 could be potentially captured from the export gas and the tail gas of the FINEX plant by using different capture technology options developed for capturing CO_2 from BFG. Despite this potential, POSCO reported only the development of CO_2 purification steps to capture CO_2 from the tail gas of the PSA. Part of the CO_2 captured will be used as feedstock to the chemical plant. This area of work is illustrated in Figure 95.



NOTE See References [222] and [223].

Figure 95 — Schematics PFD of the FINEX plant with CCUS

There are several options available for the CO_2 purification step of the tail gas from PSA. These options could include, but not limited to the use of

- oxy-fired tail gas incinerator in combination with dehydration and cryogenic separation,
- second-stage VPSA (similar to the scheme developed by Air Products at Port Arthur SMR, USA),
- cryogenic separation (similar to the scheme developed by Air Liquide at Port Jerome SMR, France),
- chemical absorption, and
- physical absorption (i.e. Selexol, Rectisol, etc.).

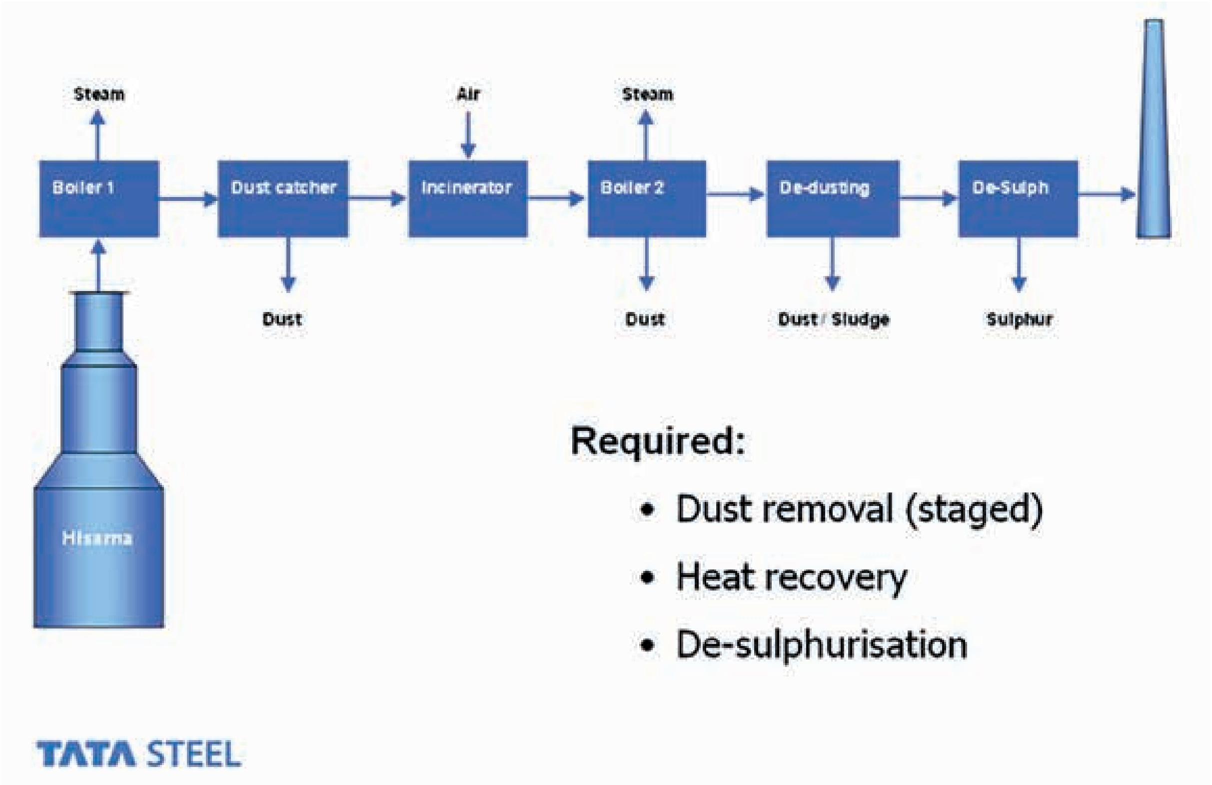
11.9.2.3 HISARNA (ULCOS Programme)

HISARNA process[223][224] is a smelting reduction technology developed under the ULCOS programme. This is a combination of the Cyclone Converter Furnace (CCF) technology for the pre-reduction of the ore and HISMELT for the melter/gasifier.

Figure 96 and Figure 97 present the schematic flow diagram of the HISARNA without and with CO_2 capture.

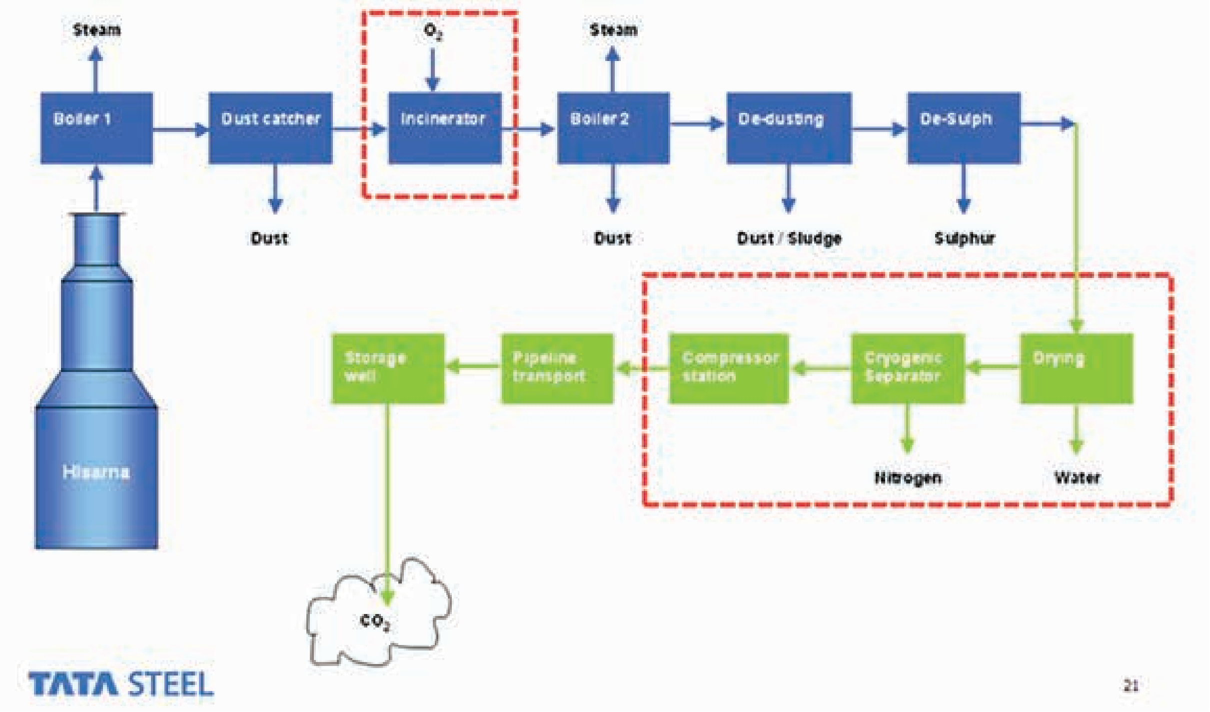
The capture of CO_2 in HISARNA process involves a series of gas cleaning steps which include the dry dust catcher to remove particulates, an incinerator to burn the remaining CO and carried over unburned carbon particulates, a waste heat recovery steam boiler, a scrubber for de-dusting, desulfurization unit, and gas dehydration unit. The resulting dry clean gas should consist at least 90 % to 95 % v/v CO_2 (dry basis). The CO_2 rich gas is processed in the CO_2 processing unit where CO_2 is separated through cryogenic separation and compressed prior to its delivery to the pipeline.

For the purpose of this Technical Report, the system boundary to be considered is enclosed in the red box shown in Figure 97.



NOTE See Reference [223].

Figure 96 — Simplified schematic of the gas cleaning of HISARNA without CO_2 capture



NOTE See Reference [224].

Figure 97 — Simplified schematic of the gas cleaning of HISARNA without CO_2 capture

11.10 Evaluation procedures for capture processes

In several reports specific energy consumption of captured CO_2 are expressed without clear definition. Not only specific consumption but also any other terms related to evaluation of capture are not yet defined in the steel making industry.

11.11 Reliability issues

The following issues will be considered in the future standardization:

- stability or durability for use of absorbents for chemical absorption technology or adsorbents for physical adsorption technology;
- equipment (it is necessary to comply with related national or regional regulations if they exist.).

11.12 Safety issues

Currently, there are very few or no existing law, regulations or standards governing the construction and operation of the CO_2 capture facilities applied to the steel industry. However, there are well established national or regional regulations applied to the construction and operation of iron-making plants and other allied chemical plants. Some of these law, regulations or standards are relevant and adaptable to the building of CO_2 capture facilities.

An example of which is shown in the Figure 98. This illustrates regulation on how to specify the internal maximum pressure of the vessels under the Japanese Industrial Safety and Health Law. For a chemical absorption plant that could be used in the iron and steel industry, the building of the chemical absorption vessels are classified under class-1 and if to be built should be made compliant under this laws.

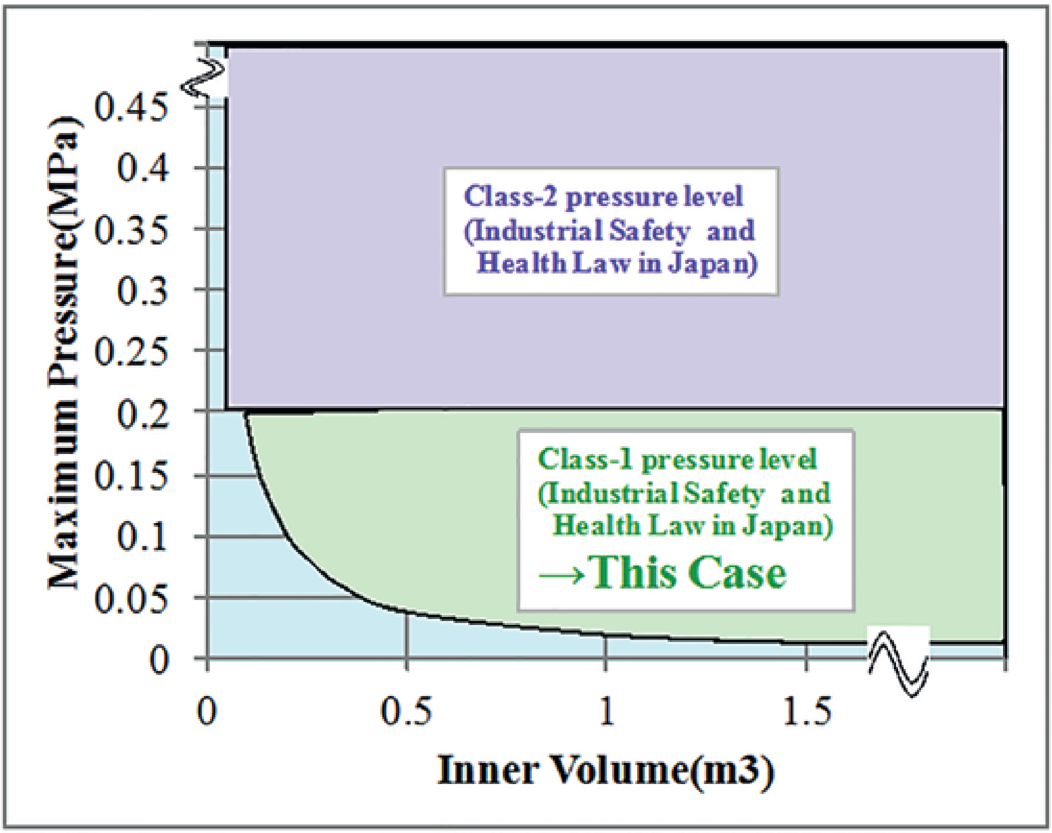


Figure 98 — Categorization of pressure vessel in Japan

It is expected that other existing national and regional laws could be adapted in regulating the different operating aspect of the CO_2 capture facility. For example, the chemicals used and the waste products produced in a Chemical Absorption plant should be regulated under the chemical substances control law and industrial safety and health laws of individual contries or region.

12 Capture from industrial gas production processes

This Clause will discuss large stationary CO_2 sources other than those described in Clause 7 to Clause 11. Among the CO_2 sources, natural-gas sweetening, refineries, and petrochemical industry are subject to this Clause. Most CO_2 emissions from refineries and the petrochemical plants are, however, associated with the combustion of fossil fuel and these emission sources fall within the scopes of the technologies described in Clause 7. As such, this Clause covers natural-gas sweetening, the ammonia production process, and the hydrogen production process.

These industrial processes are used to produce such products as pipeline gas, LNG, ammonia, and hydrogen, and include purification processes as part of the production. The purpose of the purification processes is to remove impurities undesirable for the products or the production processes, and CO_2 is removed as part of such purification processes. Commonly used technologies for CO_2 removal or capture include absorption, adsorption, and membrane separation processes. The CO_2 capture processes described in this Clause are well-established technologies with a record of numerous commercial applications worldwide, due to the fact that CO_2 capture is an essential part of the process in the production of final products.

In these industrial processes, the cost of CO_2 separation is generally included in the prices of the respective products, making their CO_2 very competitive against recovered CO_2 in other sectors. In addition, the industrial processes feature capture of CO_2 conducted at a high partial pressure, resulting in a lower initial cost for the capture facility than those employed in other sectors and a higher purity of CO_2 when recovered.

In order to utilize CO_2 recovered from industrial gas production processes for CCS, a CO_2 compression or liquefaction unit is required. Compared with the power industry where CO_2 capture facilities dedicated to CCS are needed, both technical and economic difficulties for the deployment of CCS are low in the gas production industry. That is why these industrial processes are called “Early Opportunity” and “Low Hanging Fruit” and are expected to be applied to CCS to reduce CO_2 in the amount of approximately 1,10 gigatonnes per year by 2030 and 3,83 gigatonnes per year by 2050 as part of the 2DS scenario of IEA Energy Technology Perspectives 2012.[227]

In fact, according to the GCCSI report of 2013,[228] in Norway and Algeria, natural gas treatment plants with large commercial CCS facilities are operating at around 1 MTPY. In Australia, a CCS plant with a capacity of 3 MTPY is currently under construction. In North America, CO_2 recovered from a chemical plant in the US is used in Canada for enhanced oil recovery (EOR).

As mentioned above, a CO_2 capture process is an essential component of industrial gas production regardless of whether or not CCS is implemented, and CCS itself is not the objective. The process of compressing and liquefying captured CO_2 for underground storage is, however, considered a functionality targeting CCS. In other words, the performance and specifications pertaining to CO_2 capture processes from industrial gas production processes are not covered by the international standardization efforts of TC 265; only the definitions of parameters and/or the methods for evaluation used for evaluating and comparing their performance as CO_2 capture processes from industrial gas production processes are the subject of TC 265. The scope also includes the compression or liquefaction processes for the underground storage of CO_2.

12.1 System boundary

12.1.1 Natural gas sweetening process

At present, natural gas produced from wells in gas fields contains CO_2 ranging from little to more than 10 % in its composition in most cases. In some gas fields in Southeast Asia and Central America, the ratio goes up to as high as a few dozen per cent. CO_2 should be removed for the production of pipeline gas and LNG. Generally, CO_2 is released into the atmosphere after it is captured through the CO_2 capture process.

Figure 99 is a block flow diagram of natural gas treating processes with the boundaries indicating the scope of this international standard. Raw gas from wells undergoes gas-liquid separation if accompanied by crude oil and then CO_2 is removed in the acid gas removal process. The resultant product gas is shipped as pipeline gas or as LNG after dehydration and liquefaction. In case chemical absorption processes are applied as acid gas removal processes, the separated CO_2 stream, which may contain some amount of H_2S, is dehydrated and compressed to raise its pressure for storage. On the other hand, the separated CO_2 stream from physical absorption processes or membrane separation processes usually contains hydrocarbons and other impurities at low concentrations.

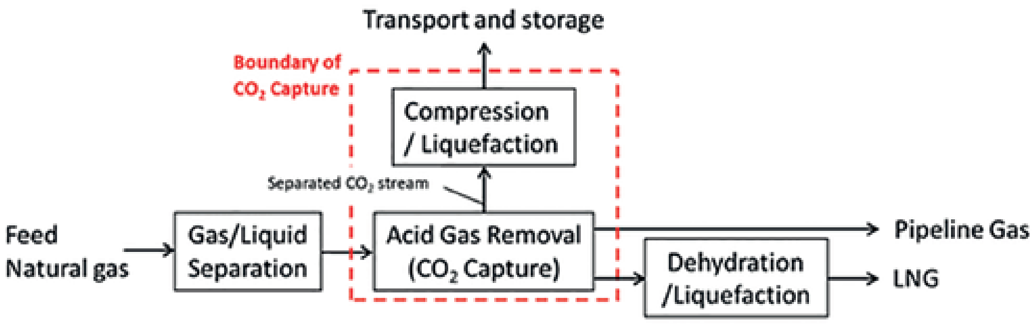


Figure 99 — Block flow diagram of natural gas treating processes and the scope for international standardization

12.1.2 Ammonia production process

Eighty-five per cent of ammonia is produced from natural gas. The scope of this standardization work is defined below for the ammonia production process using natural gas.

Figure 100 shows a block flow diagram of the ammonia production processes and the scope of this international standardization.

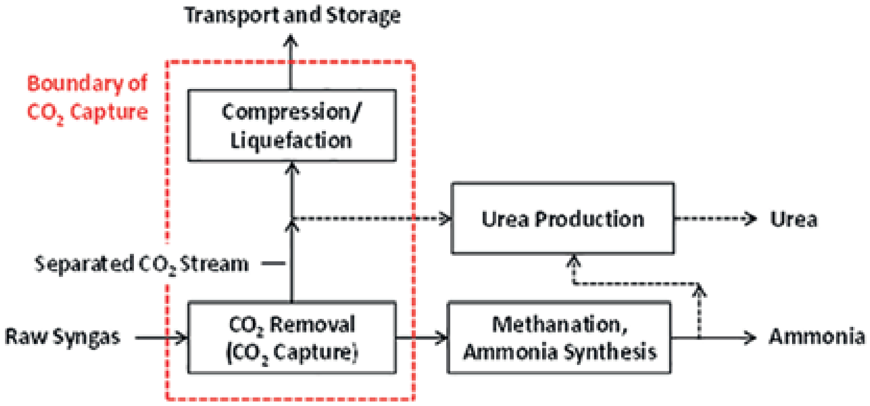


Figure 100 — Block flow diagram of ammonia production process with the boundary for international standardization

Feed natural gas is converted to raw syngas composed of H_2, N_2, CO, CH_4 and CO_2 by the reaction processes of steam reforming, secondary reforming and CO shift conversion. CO and CO_2 are poisonous to ammonia synthesis catalysts because they contain oxygen atoms, and they are therefore removed by a CO_2 removal process and a methanation process before the ammonia synthesis process. The raw syngas is supplied to the CO_2 removal process at a pressure of approximately 3 MPa with a content of roughly 20 % of CO_2; the partial pressure of CO_2 is therefore high, at around 0,6 MPa. The CO_2 concentration in the process gas is reduced to 0,1 % or less by this CO_2 removal step.

It is noteworthy that 50 % or more of the CO_2 generated by ammonia plants is utilized as a raw material for urea production. Small quantity of CO_2 from ammonia production processes is also used for EOR in the United States. According to the statistical data published by IFA,[229] 163 million tonnes of ammonia and 155 million tonnes of urea were produced in 2011.

CO_2 extracted from a CO_2 removal process is high in purity; it can be routed directly to a compressor for eventual storage.

The scope of this international standardization work is defined as CO_2 removal and CO_2 compression/liquefaction processes as shown in Figure 100. As is the case for natural gas treatment processes, the performance and specifications for CO_2 removal processes are not covered by the standardization efforts of TC 265. Only the definitions of parameters and/or the methods for evaluation used for evaluating and comparing the performance of these technologies as a CO_2 capture process are the subject of this international standardization.

12.1.3 Hydrogen production process

The second largest usage of hydrogen after ammonia production is for reaction processes at oil refineries and petrochemical plants. As mentioned before, approximately 125 million Nm^3 per year is consumed for this purpose [226] with estimated CO_2 emissions of approximately 60 MTPY.

Hydrogen generation plants typically employ an absorption process or PSA process for CO_2 capture. The absorption processes have been used for a long time and discharge high purity CO_2. But PSA, which is capable of producing high purity hydrogen of 99,9 % purity or higher, has become the mainstream method in recent years.

In the PSA method, the off-gas contains CO_2 with a concentration level of approximately 50 % after H_2 is recovered. It also contains many combustible gases such as H_2, CH_4, and CO. At present off-gas is recycled as part of the fuel gas for steam reformers. All the CO_2 in PSA off gas ends up in the flue gas after combustion.

Thus, only those hydrogen generation facilities that separate CO_2 by an absorption process are covered by the scope of this subclause, and the system boundary is defined as such.

It is possible to recover CO_2 from the off-gas of PSA hydrogen processing by combination with CO_2 capture processes.[230] For examples, chemical adsorption prosess to capture CO_2 from PSA off gas is adopted in the Tomakomai Project in Japan and Quest Project in Canada. Cycogeic separation process is applied in the Port Jerome Project in France.

Figure 101 shows a block diagram and the scope for the international standardization of hydrogen generation processes. Feed hydrocarbons such as natural gas are converted into raw gas consisting of H_2, CO, CH_4 and CO_2 by the reaction processes of steam reforming and CO shift conversion. From the raw gas CO_2 is then removed by an absorption process to produce pure H_2 of approximately 98 % concentration. The CO_2 removed is typically high in concentration at around 98 % and is ready to be sent to a compressor for compression and storage.

Hydrogen generation plants need to increase the CH_4 conversion at the steam reformer in order to obtain higher purity of H_2 because unconverted CH_4 becomes an impurity in the H_2 product. That is why a higher temperature and a lower pressure are chosen in hydrogen generation than in ammonia production. Thus, the pressure of the raw gas supplied to the CO_2 removal process is around 1,5 MPa to 2 MPa, and the gas contains approximately 20 % of CO_2 at 0,3 MPa to 0,4 MPa in partial pressure. After the CO_2 removal, the concentration of CO_2 in the process gas falls to 0,1 % or less.

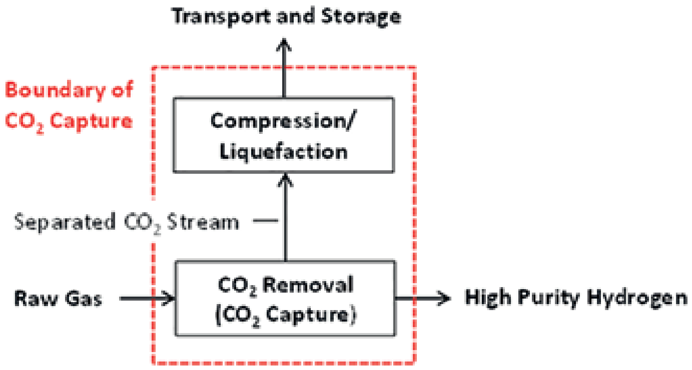


Figure 101 — Block flow diagram and the scope for international standardization of hydrogen production with absorption process

Among the above processes, the scope of CO_2 capture for this international standardization includes the CO_2 removal processes and CO_2 compression/liquefaction processes. As is the case with the preceding two processes, the performance and specifications for CO_2 removal processes are not covered by the standardization efforts of TC 265. Only the definitions of parameters and/or the methods for evaluation used for comparing and evaluating performance of these with other technologies from the perspective of CO_2 capture processes are the subject of this international standardization.

In the case of methanol production, the third largest usage of hydrogen, CO_2 is a part of the feedstock; in principle, no CO_2 emissions are made from methanol production plants other than those contained in the flue gas air. Therefore it is out of the scope of this subclause.

12.2 Technologies, equipment and processes

The CO_2 capture technologies employed in commercial plants are roughly categorized into the following:

- chemical absorption;
- physical absorption;
- membrane separation;
- pressure swing adsorption (PSA).

As each CO_2 capture technology is described in the beginning of Clause 6, it is omitted here and only subjects relating to this subclause are described.

Amine processes, typical technology of the chemical absorption process, have such a long history and have been used so extensively that they can be considered virtually a mature technology in the natural gas treating fields. In Salah and Snohvit, natural gas plants which are operated with CCS, use the chemical absorption process for CO_2 capture. Well-known licensed processes are: OASE34), UCARSOL35), and ADIP36) and so on.

A CO_2 capture technology called HiPACT37) recovers CO_2 at a higher pressure than the conventional chemical absorption method. The new technology reduces both the energy and cost pertaining to the compression in the last stage, thereby contributing to an improved economic performance of CCS.

Natural gas treatment plants need to be large and their design tends to be simple in order to minimize the capital cost.

In ammonia production plants, chemical absorption is mainly employed using the amine process, and thermal potassium carbonate process. Because there is a push for reduced natural gas consumption required for ammonia production, there have been many energy-saving process schemes proposed and commercialized by different licensors(References [232] and [233], for instance).

Physical absorption has failed to gain prevalence in the natural gas treating fields because it absorbs and removes an alarming level of hydrocarbons, which are part of the natural gas products.

Physical absorption is also a mature technology with a long history. However, in the natural gas industry, physical absorption is not commonly used as it involves larger equipment than that used for the chemical absorption and is considered to be more costly. However, when the target gas contains 20 % or more CO_2, physical absorption is considered to be more cost competitive. In particular, the technology has a track record in North America where it has been used for a CO_2-EOR project to separate and captures CO_2 from gas wells with a high CO_2 content.

The membrane separation process suffers from the disadvantage of losing a large amount of product gas, to the CO_2 side because of low CO_2 selectivity. It is, however, used for natural gas treatment for pipeline gases, where a few per cent of CO_2 concentration is permitted in the final product. In addition, when the allowable CO_2 value in the gas product is low (for example, in an LNG plant, the allowable value is kept at approximately 50 ppm to 100 ppm to prevent CO_2 from solidifying), a larger membrane is needed. This not only raises equipment costs but also increases the volume of CH_4 loss in proportion to the increase in the membrane size. In this case, a combined process of membrane separation, where

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34) OASE is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

35) UCARSOL is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

36) ADIP is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

37) HiPACT is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

the bulk of the CO_2 is removed, and chemical absorption, located downstream to remove CO_2 until a low concentration level is achieved, can be typically applied.

The membrane separation process has been used widely in natural gas treatment where the feed gas contains a high concentration (20 %) of CO_2.

Pressure swing adsorption (PSA) is a technology in which CO_2 is physically adsorbed into the pores of a solid adsorbent at high pressure, and the pressure is lowered to desorb and capture CO_2. Because an increase in the amount of target CO_2 demands a corresponding increase in the size of the equipment required, the technology is not used for large-scale plants such as those for natural gas treatment, but is more commonly used in syngas-based hydrogen production processes. However, as stated in 12.1.3, because CO_2-rich off-gas emitted from PSA systems is used as a fuel in the production facilities, CO_2 is released as flue gas. For CO_2 capture, it is necessary to apply the post-combustion capture process or perform a secondary treatment of CO_2-rich off-gas.

Thus, in natural gas treatment, generally speaking, the chemical absorption process generates low CH_4 losses and is suitable for a large plant, while membrane separation, which requires lower energy consumption or a combination of the membrane separation process and the chemical absorption process is commonly used when the feed gas contains a high concentration of CO_2. In syngas purification, the chemical absorption process, which is capable of reducing the level of impurities to the order of 0,1 %, or the PSA process is used. However, as mentioned above, it is not possible to obtain storage-ready CO_2 from PSA facilities. As indicated above, PSA will not be described further in this subclause because PSA facilities are not used specifically in industrial gas production fields.

12.3 Carbon dioxide streams, gas streams and emissions, process and waste products

This subclause will define the following for each of the four technologies (chemical absorption, physical absorption, membrane separation, and PSA) introduced in the preceding subclause, and describe their main gas composition.

- Captured CO_2
- Treated gas
- By-products and waste products

12.3.1 Chemical absorption

12.3.1.1 Captured CO_2

To be recovered from the top of the regenerator.

In natural gas treating processes, the recovered CO_2 has a concentration greater than 98 % (dry) when the only acid gas contained in the feed gas is CO_2, and is saturated with water. When the feed gas contains acid gases such as hydrogen sulfide, the acid gases are also captured.

In ammonia production processes, the captured CO_2 has a purity level of a minimum of 95 %, normally 98 % to 99 % (dry), and contains the impurities H_2 and N_2. In the case of the hydrogen production process, the captured CO_2 has a purity level of 98 % to 99 % (dry) and contains the contaminant H_2. In both cases, sulfur compounds such as H_2S are removed upstream of the absorber since they are poisonous for steam reforming catalysts and CO shift catalysts, and are not contained in captured CO_2.

12.3.1.2 Treated gas

To be obtained at the top of the absorber.

In natural gas treating processes, the concentration of CO_2 is determined by product specifications. In the case of utility gas, the concentration is 2 % to 3 %, while that of LNG is about 50 ppm. The remainder consists of light hydrocarbons, with methane being the primary component. In ammonia and hydrogen production processes, the CO_2 concentration is normally reduced to the 0,1 % level.

12.3.1.3 By-products and waste products

When a high-pressure flash drum is placed between the absorber and the regenerator, flash gas is recycled into the absorber inlet in order to increase the product gas yield. Thus, flash gas does not end up being a by-product. In addition, when a reclaimer is installed for intermittent removal of HSS, indecomposable salts and solids are produced as waste products. These waste products generated in capture facilities are processed on the industrial gas production facility side in an appropriate manner.

A future review is needed for waste products derived from CCS facilities as a result of compression and liquefaction.

12.3.2 Physical absorption process

12.3.2.1 Captured CO_2

As with the chemical absorption process, CO_2 is obtained from the top end of the regenerator. Because the solvent absorbs light hydrocarbons, the main component of feed gas, the recovered CO_2 contains a small amount of hydrocarbon material.

12.3.2.2 Treated gas

As with the chemical absorption process, the treated gas is obtained from the top of the absorber. The gas composition is determined by product specifications.

12.3.2.3 By-products and waste products

When flash gas is not recycled from the flash drum, CO_2 with a relatively high concentration is generated as a by-product.

12.3.3 Membrane separation

12.3.3.1 Captured CO_2

CO_2 streams are obtained on the permeate gas side of the membrane. The concentration of CO_2 varies according to the operating conditions and membrane properties. Taking a natural gas refinery as an example, in the case of single-stage processes, CO_2 may contain a few to over 10 % of hydrocarbon.

12.3.3.2 Treated gas

Product gas is obtained on the non-permeate side of the membrane. While a membrane separation facility is designed according to the specifications of the product gas. For example, in natural gas treatment, it is difficult to fulfill the requirements solely with membrane separation. Thus, a facility for CO_2 separation using the chemical absorption process is often set up downstream.

12.3.3.3 By-products and waste products

Nothing specific.

12.3.4 Evaluation procedure for capture performance

Three parameters, capture rate, energy consumption, and emission, are defined for the purpose of evaluating capture performance. The definitions and evaluation methods are provided below. The parameters are used as indicators for evaluating the performance of a CO_2 capture process. As mentioned at the beginning of Clause 12, the recommended ranges for these performance parameters are not recommended as the subject of this Technical Report.

12.3.4.1 Capture rate

Formula (11) shows the ratio of the amount of CO_2 separated and compressed for CCS to the amount of CO_2 contained in the target gases (such as feed natural gas and raw syngas) within the system boundary defined in 12.1:

$$\text{Capture rate} = CO_2 \text{ in Captured } CO_2 \text{ stream}/CO_2 \text{ in Feed Gas} \tag{11}$$

In the natural gas treating process, the CO_2 concentration is determined by the composition of the gas extracted from underground sources. In addition, the CO_2 concentration in treated natural gas depends largely on the uses of the treated gas (e.g. pipeline gas, LNG). Thus, the capture rate achieved in the natural gas treating process varies from one plant to another depending on the feed gas composition, process configuration, and purposes. It follows then that only evaluation methods, and not the recommended ranges for CCS, are recommended as the subject of this international standardization work.

In ammonia and hydrogen production processes, the CO_2 concentration in the feed gas supplied to the CO_2 capture process is normally around 20 %, although it varies to some extent according to the composition of feed natural gas. The CO_2 concentration in the treated gas is normally about 0,1 %, while it is determined by the overall efficiency of the ammonia production process. Given the above, only the evaluation methods of the capture rate are recommended as the subject of international standardization for the ammonia and hydrogen production processes, and not the recommended ranges.

12.3.4.2 Energy consumption

In the system boundary defined in 12.1, it is desirable to define energy consumption as energy (e.g. steam, electricity) consumed within the system boundary per unit of captured CO_2.

In industrial gas production processes, CO_2 capture is an essential part of the production process, and is not nesessarily performed for the purpose of storage.

In addition to the CO_2 concentration of treated gas and capture rate, the parameters governing the level of energy consumption in CO_2 removal/capture includes the trade-offs between energy cost and equipment cost, which vary from project to project. In general, these parameters are optimized based on the plant cost and treatment cost.

Energy consumption varies according to plant design and operating conditions and also the pressure of the treated gas and feed gas of CO_2 capture and the CO_2 concentration should be identified when presenting the value of energy consumption. Comparing such values in cases where these conditions are different is not valid. That is, it is not possible to evaluate it based on a uniform standard established from the perspective of CCS only. Thus, only evaluation methods are recommended as the subject of international standardization for energy consumption as well, and not the recommended ranges.

12.3.4.3 Emissions

In industrial gas production processes, treated gases are shipped as products or used as intermediates and do not become emissions. In addition, the acid gas is removed as part of the gas production process, and thus, performing CCS does not produce new gas streams that can be an emission source.

However, in some processes, some of the gas streams, including the captured CO_2, are used as fuels, or are released into the atmosphere following appropriate treatment. In such cases, plants are designed and operated in such a manner that their emissions comply with the local environmental regulations.

As such, emissions are out of the scope of international standardization for the CO_2 capture technologies in industrial gas production processes.

12.4 Safety issues

In general, facilities and equipment dedicated to the corresponding capture technology are designed and constructed in compliance with the existing and applicable international, regional and national standards such as ISO and ASME. In addition, compliance with the laws, regulations and requirements in the region or country where the plant is located provides additional securities for safety. Safety issues are not a subject to be considered in the establishment of a new standard for the CO_2 capture processes in CCS.

The emission of toxic substance to the air is not the discussion item because these substances are not released to the air but are contained in the product in the industrial process.

The chemical absorption process, the leading CO_2 capture technology in industrial gas production processes, has been successfully used in commercial applications since the 1950s and has a good track record in terms of safety.

12.5 Reliability issues

As described in the previous subclause, the chemical absorption method, which is the main CO_2 capture technology used in industrial gas production processes, has a track record of many years of commercial application. While some issues have been reported during this time, including the corrosion of equipment and materials, as well as degradation and losses of absorbents and their foaming, there has been a significant progress in the reliability of the process thanks to improvements in the quality of absorbents and processes, as well as the advancement of operation technologies.

12.6 Management system

12.6.1 Management system between capture plant and emission source

For each capture from industrial gas production processes, there is a need to perform an EHS aspect identification and evaluation. EHS document management is pursuant to ISO 9000 and many of those system components comply with international management system requirements such as ISO 14001 and OSHAS 18001 or regional emission regulations (air pollution prevention, water pollution prevention, waste treatment and so on). Key elements of the EHS management system (EHSMS) are the “check” of performance. Furthermore, at the same time it is preferred to meet ISO 14000, OHSAS 18000 and the corresponding sustainability specifications/standards. For all the EHS aspects the legal requirements, risks and operational mitigation measures have to be considered. For all EHS aspects, monitoring plans need to be developed. Records also need to be kept.

The followings are examples for key elements of the EHS management system, especially for chemical and physical absorption CO_2 capture technologies.

- EHS aspects
- Environmental aspects:
  - Accidents/incidents with environmental impacts
    - Possible accidents to be identified for all systems
    - Special focus on compressor system (gas leak)
  - Consumption of energy — primary/secondary energy
    - Inventory of energy consumption to be established (if possible energy management to be applied)
    - Insulation to be optimized
  - Consumption of resources
    - Optimization of fuel input (plant efficiency)
    - Use of absorbents to be minimized

    - Optimizing consumables
    - Optimized layout
  - Usage of water (fresh/waste water)
    - Optimizing cooling water demand
  - Use of land
    - Optimization of plant footprint
  - Disposal/Waste Management
    - Optimization of absorbent usage
  - Hazardous waste disposal
    - Discharged absorbent
  - Noise emissions
    - Noise concept
  - Soil contamination
    - Delivery and storage of chemicals
    - Leaks scenario
    - Spills from accidents (water from firefighting, etc.)
- Health and Safety hazards aspects:
  - Air quality, e.g. dust, air conditioning, inadequate ventilation
    - Absorber/stripper venting
  - Gas leak hazard
    - Detection of gas leaks (i.e. CO_2)
    - election of materials and equipment
  - Hazardous substances, e.g. carcinogens
    - Amines exposure in work areas
    - Insulation materials during construction
    - Plant and equipment hazards
    - Spills and accidents — Pressure equipment directive
  - Working with or in proximity to hazardous materials (Haz Com)
    - Feed of amines
    - Laboratory

12.6.2 Operational management

To ensure the proper management of each capture plant within the industrial gas production process, the following operating conditions should be considered:

- CO_2 stream variations and start-up and shutdown (e.g. pressure/temperature level, etc.);
- settings to be kept in regard to proper quantification and verification of CO_2 gas streams:
  - other than normal operation conditions;
  - power failure (safe operation mode);
  - variations in CO_2 quality (failure of absorber/desorber).

12.6.3 Relationship with other areas for CCS standardization

- Transport
  - Flow control (acceptable mass flow variations)
  - Capture plant failure
  - Transport system failure (reaction time, buffering, etc.)
- Storage
  - Flow control (acceptable mass flow variations)
  - Capture plant failure
- Quantification and verification
  - Flow recording (acceptable mass flow variations)
  - CO_2 quality recording
- Cross-cutting issues
  - Risk management
  - Life cycle assessment

13 Discussion on possible future direction

13.1 General

In the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) Working Group III on April 14, 2014, much more acceleration of the measure toward greenhouse gas reduction is strongly recommended. As one of the measures for carbon dioxide reduction, energy-supply with CCS derived from economical fossil fuel is recommended and the necessity for the measure toward wide-spread expansion of CCS is pointed out.

The purpose of CCS international standardization is to just aim at the spreading and promotion in proper and worldwide of a CCS enterprise, and it can position it as one of the contributions to the measure against a climate change. Therefore, CCS is to be applicable to thermal power generation, cement, steel and industrial gas production such as natural gas sweetening, hydrogen production and so forth, and the future direction on capture in international standardization of CCS is to be discussed based on this Technical Report about applicable capture technologies and industrial sectors for various CO_2 emission sources.

13.2 Possible area of standardization

Standardization of capture in CCS is to develop about capture system based on various industrial sectors and applicable technologies described in this Technical Report. However, simultaneous development of all sectors and technologies already applied to CCS with the same level is not in a realistic way as one task.

In specific national circumstance, it is imperative to have a priority in consideration of the present states on sectors and technologies described in this Technical Report and to develop necessary standard stepwise when developing standardization.

In addition, the following three points are considered as requirements for examining a priority:

a) technical maturity;

b) potential of CO_2 emission amount across the world;

c) regulation trend of CO_2 emission amount.

Maturity of capture technology is preceded in the industrial gas sector such as natural gas sweetening, ammonia or hydrogen production, and there are many track records in a commercial scale, and followed by a combustion-type thermal power generation sector which employs capture technology of Post-combustion capture, Pre-combustion capture, or Oxyfuel combustion capture. These demonstrations are actively conducted for commercialization. Some of them are going into practical stages in North America.

On the other hand, from the viewpoint of the potential of CO_2 emission amount, the emission scale of a combustion-type thermal power generation sector is pretty large as compared with other sectors and fundamentally there is no geological dependence. Therefore, it is under view for a combustion-type thermal power generation sector to regulate specific CO_2 emission amount in specific production of electricity or to require the future installation of CCS (CCS Ready).

Among combustion-type thermal power generations, in particular, coal-fired power generation is expected to expand in many parts of the world including developing countries as comparatively economical energy supply way. Since coal-fired power generation causes high CO_2 emission amount with high CO_2 concentration, this is considered as a sector which practical use of CCS is most in need from now on.

13.3 Discussion

While working on the development of this Technical Report since 2013, we have been discussing the direction of the international standardization efforts in the area of CO_2 capture in CCS.

Firstly, as described in 13.2, combustion-type thermal power generation is considered promising for the early adoption of CO_2 capture, as evidenced by the fact that some work has started to regulate the CO_2 emissions of the industry on the assumption that CCS will be deployed in the future, making it a candidate for international standardization.

The combustion-type thermal power generation is also the most common power source, and it is found worldwide as a source of CO_2 emissions. The industry involves a large number of stakeholders, requiring their consensus and public acceptance for the implementation of CCS. Therefore, this sector is deemed appropriate as the first choice to start international standardization.

Out of all the technologies available for CO_2 capture, the post-combustion capture technology offers the largest stock of public information and has reached the level of readiness to be used as the CO_2 capture process in CCS. Its system boundary is simple and demonstrates the ability to accommodate various CO_2-containing gases. Once a standard is established for post-combustion capture, it is expected to be widely applicable to other industries in the future.

Secondly, we had extensive discussions on the performance evaluation methods of CO_2 capture processes as one of the important items to be standardized.

Specifically for the area of combustion-type thermal power generation, our international standardization efforts should not hinder further development of technologies but rather facilitate their future deployment. Based on this philosophy, the following is a list of items and parameters that the industry and public likely require to evaluate for CO_2 capture technologies.

— Basic performance, which is demonstrated while meeting environmental standards

— Evaluations of energy penalty and utility consumption to help the economic evaluation

— Operability and reliability

— Safety and risk management

These items are at different stages of technical and regulatory developments, and as indicated in 13.2, their priorities are to be determined based on the maturity of the technology and the potential of CO_2 emission across the world, as well as regulatory directions in order to proceed accordingly. The performance evaluation of energy consumption in the CO_2 capture process has a particularly high priority to be worked out before the other items.

While the releases of substances unique to the CO_2 capture process are very important, such emissions should be incorporated into the document gradually after their researches and discussions become mature, taking into account the fact that the regulation of releases require further development.

Specifically speaking, while CCS achieves the important purpose of capturing emitted CO_2 and thereby reducing its release to atmosphere, this process presents the issue of additional energy consumption for the CO_2 capture. The energy penalty for a capture process is significant, making it critical to evaluate such energy penalty appropriately.

There have been many reports on many CO_2 capture processes so far. The criteria for the energy consumption calculations are, however, not clear and inconsistent, making it difficult to properly assess energy penalty.

It is therefore important to establish an appropriate performance evaluation system for CO_2 capture processes by identifying basic information required for characterization and the parameters that can be used for various CO_2 capture processes for performance evaluation such as energy consumption by a uniform performance standard or methodology.

It is also necessary for international standardization to proceed from a long-term perspective assuming the future expansion and penetration of CCS. For CCS to grow in the market and become a part of our economic activities, such characteristics as required for an industrial process, including reliability, safety, and operability, should be studied in order to include them as subjects of our international standardization efforts.

In order to do so, existing international standards and regulations related to industrial processes and technologies should be reviewed to identify other items to be included in the document than those specific to the CO_2 capture in CCS. Such comprehensive approach with a long-term vision to the standard writing is beneficial for all stakeholders including the residents in the communities where CCS is to be carried out. The resulting document can certainly contribute to the wide deployment of CCS.

In summary, CCS is expected to become a major player in our fight against climate change and required to be used around the world in the future. The standardization of CO_2 capture should include a broad range of technologies for a broad range of applications.

We need to keep in mind that international standardization has a set of guidelines for the development steps and associated time limits, and we should determine the content of a given standard appropriately. As outlined in Clauses 7 to 12, there are boundaries and technical elements in the CO_2 capture process unique to different industries, presenting a long list of items that could be included in the document. That is why it is very difficult to cover all industrial sectors and technologies concurrently.

Therefore, it is necessary to set priorities based on the feasibility, impact and other factors, and it is considered most appropriate to start with the evaluation methods of post-combustion capture, which is a typical technology for combustion-type thermal power generation where the commercialization is likely to occur. The continuing development of the standard will be given enough thought to the feasibility to the commercial size of operation.

Annex A
(informative)

Chemical absorption processes

A.1 Amine process

The types of alkanolamines used in the chemical absorption process include MDEA, DEA, and MEA. One molecule of alkanolamine contains one or more molecules of amino and hydroxyl groups each. A hydroxyl group provides aqueous solubility to the absorbent, while an amino group provides high absorption by reacting with acid gases such as CO_2.

In the basic process using alkanolamine, acid gases such as CO_2 are absorbed at a low temperature, and are heated for regeneration. Gas mixtures are supplied to the bottom of an absorber to meet with the absorbent flowing down from the top, which removes acid gases such as CO_2 upon contact. The absorbent loaded with acid gases is discharged from the bottom of the absorber and sent to the top of the regenerator. The loaded absorbent is heated in the regenerator to release the acid gases. The lean solution resulting from the acid gas removal is discharged from the bottom of the regenerator and returned to the absorber. The regenerator releases separated CO_2 and steam. The latter is cooled and condensed to return to the regenerator, leaving the acid gases such as CO_2 (CO_2 concentration >99 %). The loaded solution from the bottom of the absorber and the lean solution from the regenerator pass through a heat exchanger on the way to the other towers. The characteristics of individual chemical absorbents based on alkanolamines are described below.

The MDEA process is a typical chemical absorption process in pre-combustion. MDEA is known as a sweetening solvent for acid gas removal and selective removal of H_2S. It is widely used as the most economical absorbent thanks to its low foaming rate. In order to achieve compact packaging of a gas treatment unit in pre-combustion, it is important to maximize the selectivity of H_2S and CO_2 while satisfying the treatment specification for the composition of the feed gas. It is believed that doing so will lead to a reduction in the capital and operating expenses.

For H_2S absorption, the following steps are involved, but they are not related to the amine series numbers.

— $H_2S(g) \Leftrightarrow H_2S(soln)$

— $H_2S(soln) + R_3N(soln) \Leftrightarrow R_3N \cdot H_2S(soln)$

In CO_2 absorption, primary and secondary amines such as MEA and DEA produce zwitterionic intermediates by directly reacting with CO_2.

— $CO_2(g) \Leftrightarrow CO_2(soln)$

— $CO_2(soln) + R_2NH(soln) \Leftrightarrow R_2N + HCO_2 - (soln)$

The intermediates then form carbamic acid by further reacting with amine.

— $R_2N + HCO_2 - (soln) + R_2NH(soln) \Leftrightarrow R_2NCO_2 - (sol) + R_2NH_2 + (soln)$

This reaction occurs instantaneously, and it is therefore considered non-selective.

The dissolution of CO_2 into MDEA proceeds as follows:

— $CO_2(g) \Leftrightarrow CO_2(soln)$

— $CO_2(soln) + H_2O \Leftrightarrow H_2CO_3(soln)$

— H_2CO_3(soln) + $R_3N \Leftrightarrow R_3NH$(soln) + HCO_3^-(soln)

In this process, the step where CO_2 forms carbonic acid by hydration is the rate-determining step. In this regard MDEA is considered to present the highest selectivity as a solvent. MDEA is also seen as the most stable solvent thermally and chemically because it produces neither stable carbamic acid salts by reacting with CO_2 nor degradable compounds by reacting with COS or CS_2.

The temperature and the partial pressure of acid gas at the gas inlet are additional factors that determine selectivity. When the inlet temperature is 110 F, and the gas partial pressure is 10 psi or less the gas treatment tends to be difficult. It has been reported, however, that this issue can be resolved by changing the formulation of the MDEA solvent. The absorber pressure and the CO_2/H_2S ratio have impacts on the selectivity ratio; the lower the pressure and the higher the CO_2/H_2S ratio of the feed gas, the higher the selectivity ratio.

The equipment configuration for the MDEA process appears to be little different from that of the general amine process configuration described earlier. Filtration is essential for securing the consistency in the quality of MDEA absorbent, which would prevent foaming and corrosion. A combination of a particulate filter made of inert polymer fibre in the first stage and an active carbon filter to remove organic substances in the second stage is believed to be effective. Installing appropriate filters would prevent foaming and corrosion, reducing solvent loss and extending the equipment service life.

While MEA is an inexpensive and the most extensively used solvent, it has high vapour pressure and reportedly presents a higher loss rate.

MEA also reacts with COS and CS_2 to produce compounds (thermally stable salts), making it necessary to remove COS and CS_2 in advance.

It has also been reported that MEA reacts with CO_2 to produce hydroxyethyl ethylenediamine, a corrosive substance, which should be removed by installing a reclaimer. One of the measures available for this issue is to provide corrosion resistance by adding an anti-corrosion agent to turn the inner surface of the absorber into a passive state. This action will allow the concentration of MEA to increase by at least double the conventional level, thereby raising the separation and capture efficiency.

DEA absorbs and separates acid gases such as CO_2, COS, and CS_2. It has a smaller quantity requirement with smaller circulation volume when compared with MEA. MDEA is capable of absorbing and separating CO_2 and H_2S, with a possibility of achieving greater performance by adding an absorption enhancer.

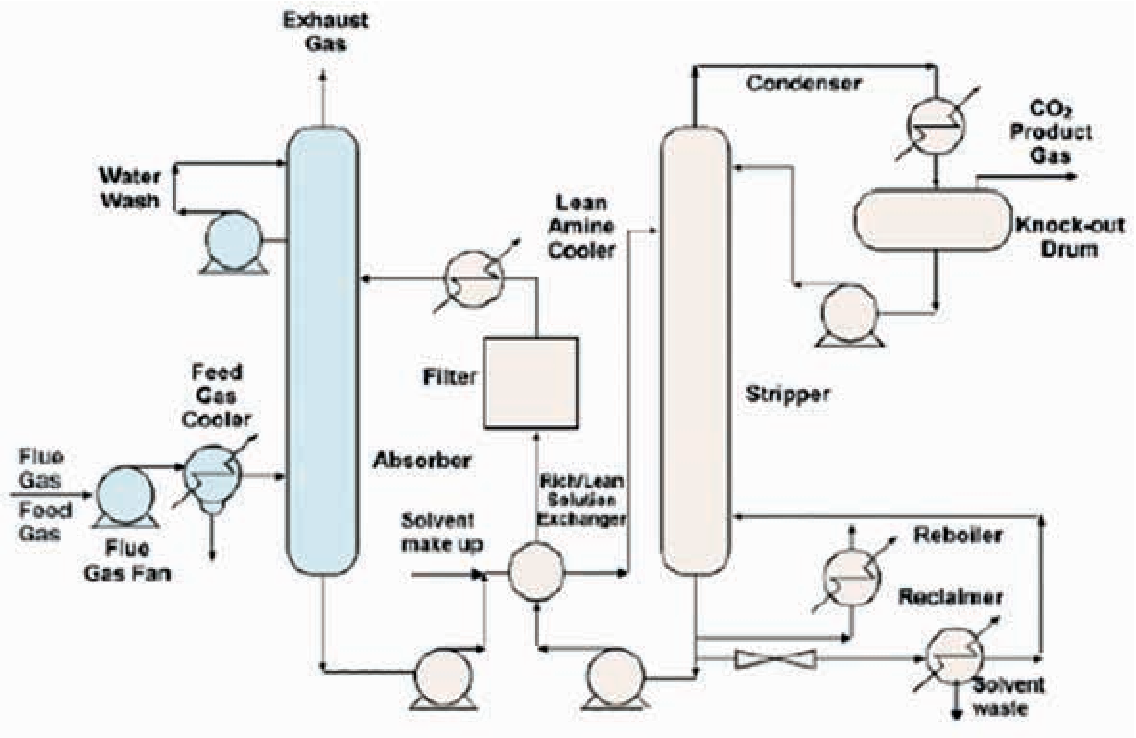

Figure A.1 — Schematic of amine process

A.2 Benfield process

The Benfield process using hot potassium carbonate performs absorption and separation of CO_2 or H_2S under a few atm to a higher pressure of a few dozen atm at around 120 °C as shown below. It is common practice to keep the concentration of the potassium carbonate solution at 40 % to 45 % in order to prevent the precipitation of bicarbonate.

$$K_2CO_3 + CO_2 + H_2O \Rightarrow 2KHCO_3 \tag{A.1}$$

In the Benfield process, the absorber is operated at higher pressure (>10 atm). This pressure forces CO_2 in the absorber to move from the gaseous phase to the liquid phase. The operating temperature is high (>100 °C), and CO_2 is absorbed at virtually the same temperature as in the separation process. That is why neither the pre-cleaning before the entry to the absorber nor the heat exchange between the loaded solution after CO_2 absorption and the lean solution after regeneration is required. When the loaded solution is introduced into the regenerator, dissolved CO_2 and some steam are separated after flashing. Steam is supplied to the loaded solution in order to provide latent heat. The requirement for latent heat is smaller in the Benfield than in the amine process. In addition, the heat generated by the CO_2 and potassium carbonate reaction is significantly smaller than that of the MEA process. Therefore the Benfield process is generally said to have a small heat load.

By adding DEA to the Benfield process, absorption is enhanced. The addition of vanadium pentoxide can prevent corrosion. It is also reported that this process is capable of absorbing and separating CO_2, H_2S, and COS under low pressure and high temperature by adding alkanolamine potassium borate and vanadium pentoxide to the potassium carbonate solution.

Potassium carbonate can limit the solution loss relating to gas exhaustion to a minimum because it is not a volatile compound. Potassium carbonate is also said to have no losses due to degradation, in contrast to MEA.

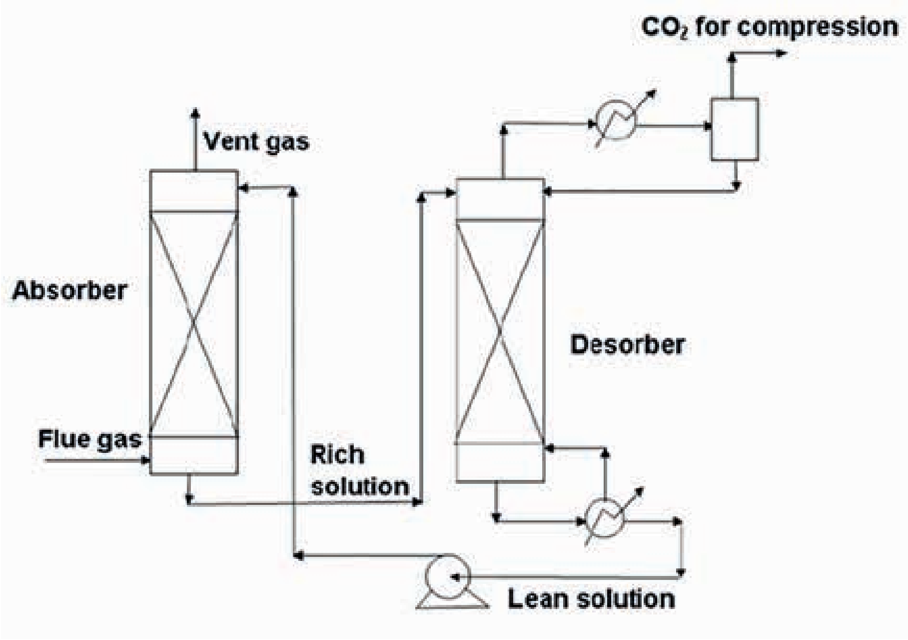

Figure A.2 — Schematic of Benfield process

A.3 Sulfinol process

In the Sulfinol process, H_2S, CO_2, COS and mercaptan are removed from the process gas. This process is capable of reducing the concentrations of sulfur compounds in the treated gas to a ppm level or less. It is applied to large-scale gas treatment such as natural gas procesing. The process presents behaviours of both chemical and physical absorption processes because it uses a mixed solution of sulfolane, DIPA or MDEA, and water.

Compared to purely chemical solutions, the mixed solution for this process has a higher loading level of acid gas, requiring less energy for regeneration. In addition, co-absorption of hydrocarbons is relatively small. The Sulfinol-M[38] process is used when CO_2 is partially absorbed while selectively absorbing H_2S, COS and mercaptan.

The process gas is supplied to the absorber, where it is contacted counter-currently with Sulfinol absorbent. The absorbent is introduced from the top of the absorber. The rich solution after taking in sulfur compounds passes through a heat exchanger with the regenerated lean solution. When it is returned to the regenerator, the loaded solution is heated by steam and releases acid gas. The acid gas separated from the loaded solution is cooled down by air or water, condensing most of water vapour. Any acid condensates are sent back to the system as reflux. The acid gas is sent to the sulfur recovery plant (Claus facility) for capturing elemental sulfur.

This process allows for an extensive range of operating conditions for pressure and impurity concentrations. Organic sulfur compounds are removed by recirculating the solution while monitoring its H_2S and CO_2 concentrations as benchmarks.

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[38] Sulfinol-M is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

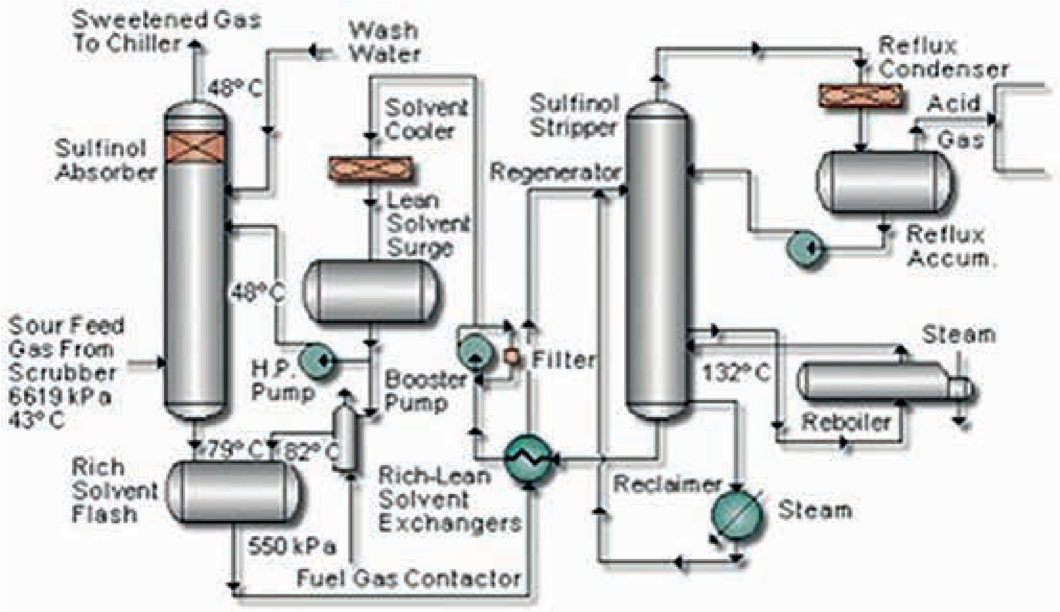


Figure A.3 — Schematic of Sulfinol process from NETL homepage

Annex B
(informative)

Examples of flue gas compositions

B.1 SINTEF, Emission Compound Toxicity Protocol, Annex B, p.152

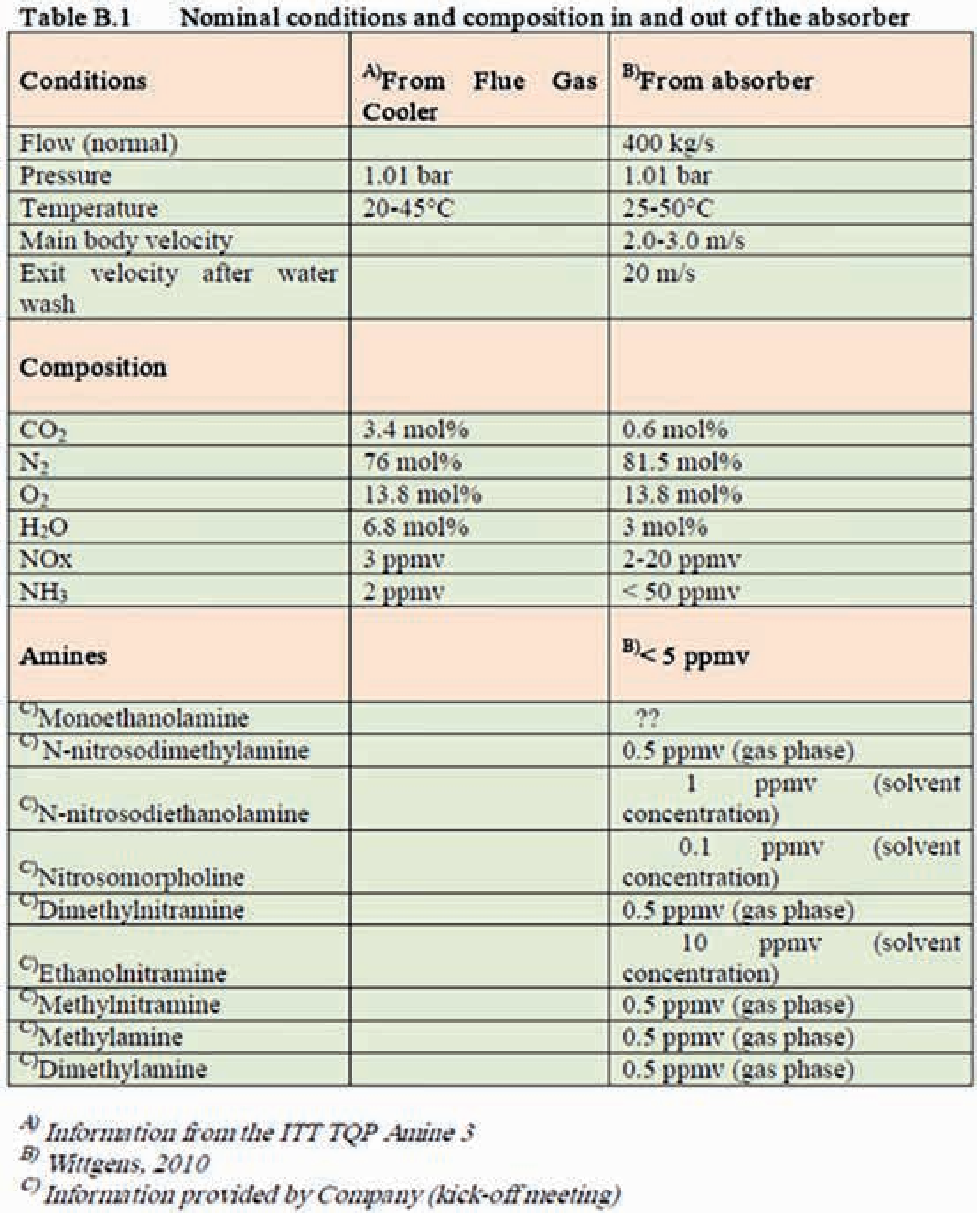


Table B.1 Nominal conditions and composition in and out of the absorber

Conditions	**A)From Flue Gas Cooler**	**B)From absorber**
Flow (normal)		400 kg/s
Pressure	1.01 bar	1.01 bar
Temperature	20-45°C	25-50°C
Main body velocity		2.0-3.0 m/s
Exit velocity after water wash		20 m/s
Composition		
CO_2	3.4 mol%	0.6 mol%
N_2	76 mol%	81.5 mol%
O_2	13.8 mol%	13.8 mol%
H_2O	6.8 mol%	3 mol%
NOx	3 ppmv	2-20 ppmv
NH_3	2 ppmv	< 50 ppmv
Amines		**B)< 5 ppmv**
C)Monoethanolamine		??
C) N-nitrosodimethylamine		0.5 ppmv (gas phase)
C)N-nitrosodiethanolamine		1 ppmv (solvent concentration)
C)Nitrosomorpholine		0.1 ppmv (solvent concentration)
C)Dimethylnitramine		0.5 ppmv (gas phase)
C)Ethanolnitramine		10 ppmv (solvent concentration)
C)Methylnitramine		0.5 ppmv (gas phase)
C)Methylamine		0.5 ppmv (gas phase)
C)Dimethylamine		0.5 ppmv (gas phase)

A) Information from the ITT TQP Amine 3
B) Wittgens, 2010
C) Information provided by Company (kick-off meeting)

Cited document; “TQPAmine3, Protocol for Evaluation of Solvents — Emission Compound Toxicity, Call Off No01”, OG Brakstad, A Booth, AG Melbye, T Nordtug, BH Hansen, SH Vang, K Zahlsen, B Wittgens, T Syversen, P Kaur, M Dusinska, LB Fjellsbo, S Ravnum, SINTEF REORT, F17318 (2010).

B.2 CSIRO, process modelling for amine-based post combustion capture plant, p.91

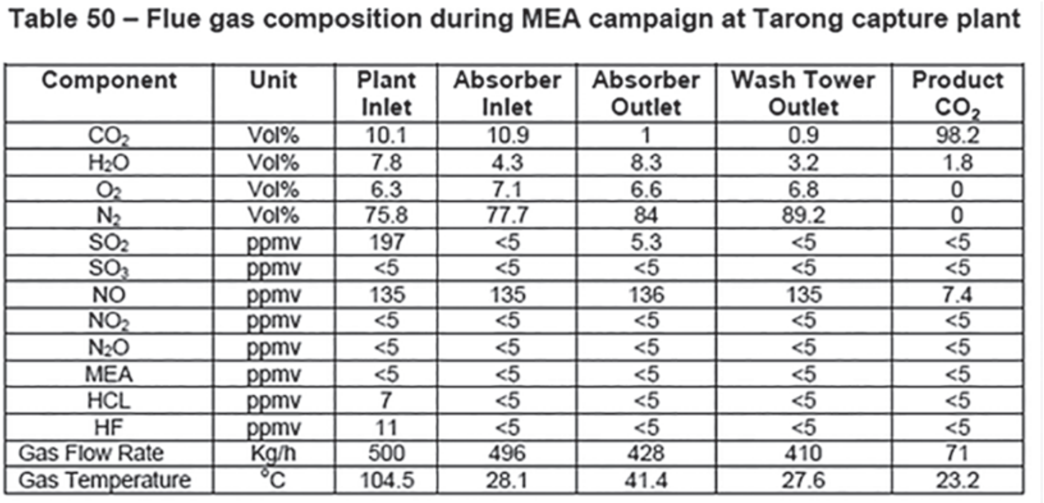


Table 50 – Flue gas composition during MEA campaign at Tarong capture plant

Component	Unit	Plant Inlet	Absorber Inlet	Absorber Outlet	Wash Tower Outlet	Product CO_2
CO_2	Vol%	10.1	10.9	1	0.9	98.2
H_2O	Vol%	7.8	4.3	8.3	3.2	1.8
O_2	Vol%	6.3	7.1	6.6	6.8	0
N_2	Vol%	75.8	77.7	84	89.2	0
SO_2	ppmv	197	<5	5.3	<5	<5
SO_3	ppmv	<5	<5	<5	<5	<5
NO	ppmv	135	135	136	135	7.4
NO_2	ppmv	<5	<5	<5	<5	<5
N_2O	ppmv	<5	<5	<5	<5	<5
MEA	ppmv	<5	<5	<5	<5	<5
HCL	ppmv	7	<5	<5	<5	<5
HF	ppmv	11	<5	<5	<5	<5
Gas Flow Rate	Kg/h	500	496	428	410	71
Gas Temperature	°C	104.5	28.1	41.4	27.6	23.2

Cited document; “Environmental Impacts of Amine-based CO_2 Post Combustion Capture (PCC) Process — Activity 3: Process Modelling for Amine-based Post-Combustion Capture Plant, Do Thong, Narendra Dave, Paul Feron, Merched Azzi, CSIRO Report to ANLEC R&D June 2012 (available from ANLECRD.com.au)”

B.3 GHGT-11, Project Status and Research Plans of 500 TPD CO_2 capture and Sequestration Demonstration at Alabama Power’s Plant Barry, p.6344

According to Table 3 of the cited document, major components of product CO_2 analysis are shown as follows:

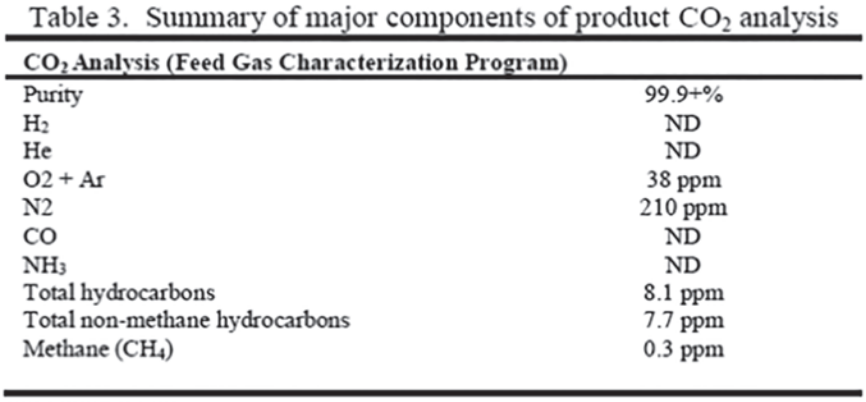


Table 3. Summary of major components of product CO_2 analysis

CO_2 Analysis (Feed Gas Characterization Program)	
Purity	99.9+%
H_2	ND
He	ND
O2 + Ar	38 ppm
N2	210 ppm
CO	ND
NH_3	ND
Total hydrocarbons	8.1 ppm
Total non-methane hydrocarbons	7.7 ppm
Methane (CH_4)	0.3 ppm

Cited document: “Project Status and Research Plans of 500 TPD CO_2 Capture and Sequestration Demonstration”, Michael A. Ivie II, Ph.D., Nick Irvin, P.E., Takuya Hirata, Hiromitsu Nagayasu, Takashi Kamijo, Yasuo Kubota, Tatsuya Tsujiuchi, Takahito Yonekawa, Paul Wood, Energy Procedia 37 (2013) 6335 — 6347

B.4 GCCSI, ROAD CSS Non Confidential Feed Report, p.34

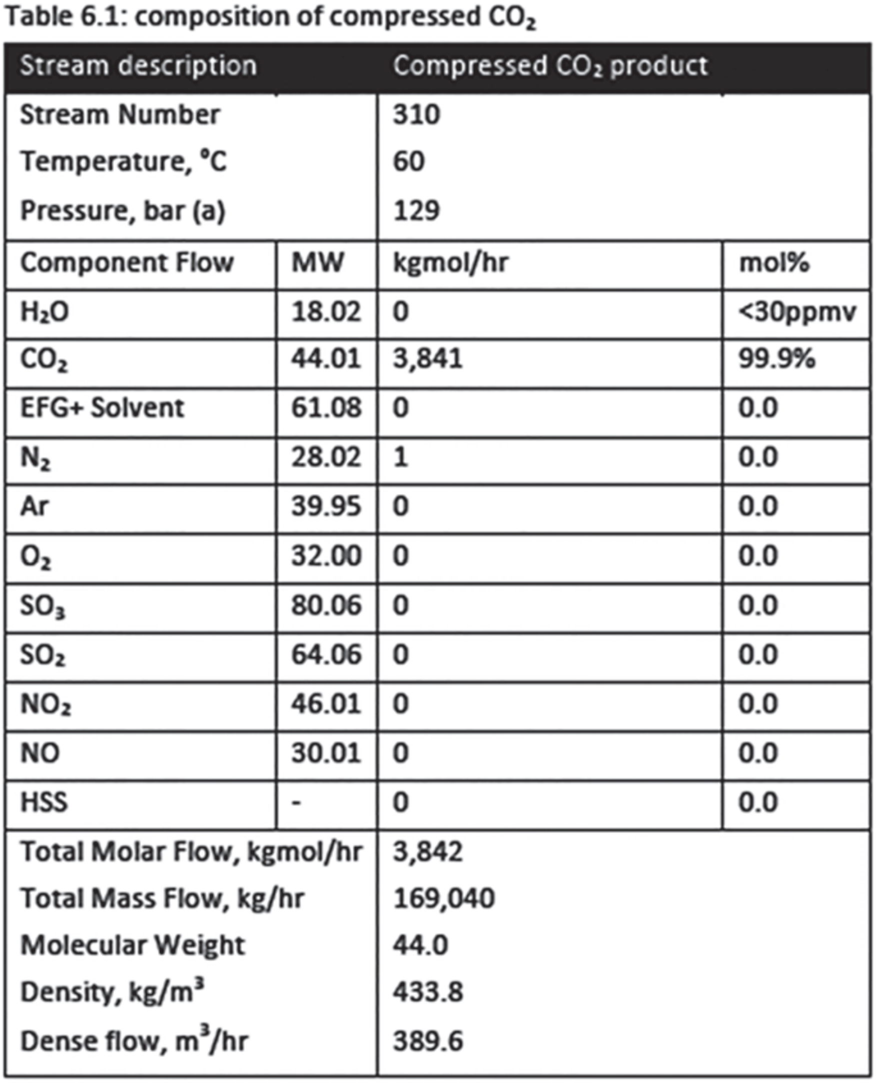


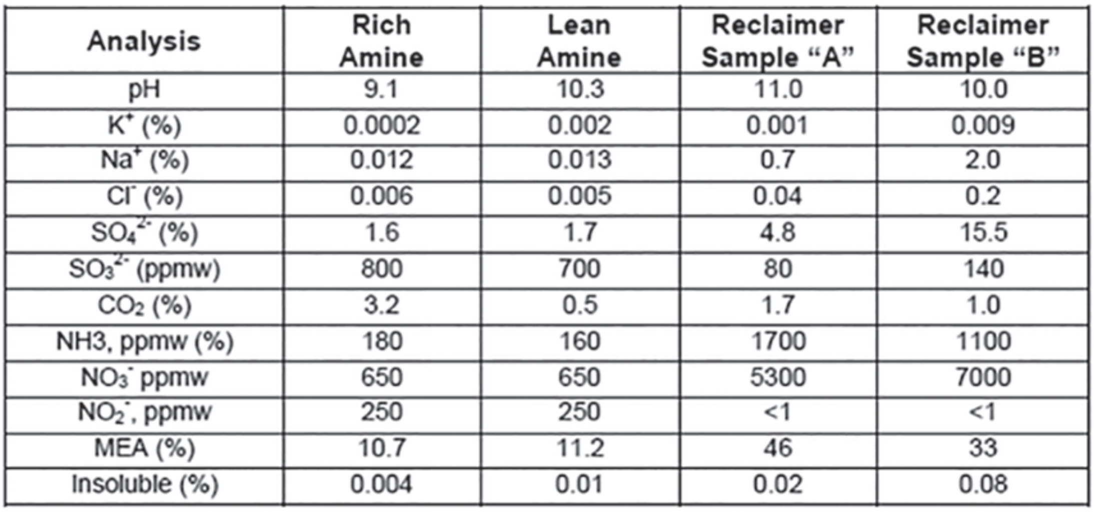
Table 6.1: composition of compressed CO_2

Stream description		Compressed CO_2 product	
Stream Number		310	
Temperature, °C		60	
Pressure, bar (a)		129	
Component Flow	MW	kgmol/hr	mol%
H_2O	18.02	0	<30ppmv
CO_2	44.01	3,841	99.9%
EFG+ Solvent	61.08	0	0.0
N_2	28.02	1	0.0
Ar	39.95	0	0.0
O_2	32.00	0	0.0
SO_3	80.06	0	0.0
SO_2	64.06	0	0.0
NO_2	46.01	0	0.0
NO	30.01	0	0.0
HSS	-	0	0.0
Total Molar Flow, kgmol/hr		3,842	
Total Mass Flow, kg/hr		169,040	
Molecular Weight		44.0	
Density, kg/m^3		433.8	
Dense flow, m^3/hr		389.6	

Cited document: ROAD CCS: “Non-Confidential FEED study report, Special report for the Global Caebon Capture and Storage Institute”, Elvira Huizeling, Gerbert van der Weijde, ROAD Maasvlakte CCS Project C.V. report to GCCSI November 2011 (available from GCCSI.com).

B.5 CSIRO, process modelling for amine-based post combustion capture plant, p.94

Table 53 – Amine solution analysis



Analysis	Rich Amine	Lean Amine	Reclaimer Sample “A”	Reclaimer Sample “B”
pH	9.1	10.3	11.0	10.0
K^+ (%)	0.0002	0.002	0.001	0.009
Na^+ (%)	0.012	0.013	0.7	2.0
Cl^- (%)	0.006	0.005	0.04	0.2
SO_4^{2-} (%)	1.6	1.7	4.8	15.5
SO_3^{2-} (ppmw)	800	700	80	140
CO_2 (%)	3.2	0.5	1.7	1.0
NH3, ppmw (%)	180	160	1700	1100
NO_3^- ppmw	650	650	5300	7000
NO_2^-, ppmw	250	250	<1	<1
MEA (%)	10.7	11.2	46	33
Insoluble (%)	0.004	0.01	0.02	0.08

Cited document: “Environmental Impacts of Amine-based CO_2 Post Combustion Capture (PCC) Process — Activity 3: Process Modelling for Amine-based Post-Combustion Capture Plant, Do Thong, Narendra Dave, Paul Feron, Merched Azzi, CSIRO Report to ANLEC R&D June 2012 (available from ANLECRD.com.au).”

Annex C
(informative)

Physical absorption processes

C.1 Rectisol process

The Rectisol process uses methanol as a solvent to separate and recover various gases such as CO_2, H_2S, COS and organic sulfur compounds. Characterized by its inexpensive absorbent, flexibility, and low capital costs, the Rectisol process is used extensively for the treatment of syngas generated by coal gasification. The process is also effective for removing impurities such as ammonia, mercury, and hydrogen cyanide (HCN). It separates CO_2 in the methanol regeneration process.

In the Rectisol process, low-temperature methanol of approximately −40 °C is used to absorb acid gases from the feed gas at high pressure (2,76 MPa to 6,89 MPa). The rich solvent produced by dissolving the acid gases is reduced in pressure to desorb and recover the acid gases. This process can selectively capture H_2S and CO_2, and the recovered H_2S can be sent to either a Claus unit for the recovery of elemental sulfur or a sulfuric acid production process. At the same time, CO_2 is used for either storage or EOR.

Unlike the solvents used in Selexol and Purisol[39], methanol is relatively inexpensive as a solvent. While the Rectisol process uses more electrical energy for refrigeration to maintain a low temperature, the energy required for regeneration is small. The capital cost of the methanol solvent unit is higher than that of a standard solvent, but methanol can effectively remove acid gases and provide higher purity CO_2.

The Rectisol process is very flexible and is an effective means of removing acid gases to produce various types of syngas-based products.

Compared with other processes, the Rectisol operates at a very low temperature and involves a complex process. It has been reported that the Rectisol process is more suitable for the gasification of coal and heavy fuels than natural gas. Its process conditions and equipment configuration are different from those of other solvent processes. The Rectisol process is a flexible process that can adapt to a range of flow schemes. Product specifications and purposes are the key factors that determine the optimal flow scheme and equipment configuration.

Since methanol operates at a high vapour pressure even under standard process conditions, it requires refrigeration and an effective capture method for solvent recovery. Water washing of the flue gas line should be performed frequently according to the requirements established as well. Since the Rectisol process is normally operated at a low temperature between −40 °C and −62 °C, in some Rectisol plants stainless steel accounts for approximately 5 % of the material used.

One of the advantages of this process is the ability of methanol to selectively capture H_2S and remove COS. In addition, H_2S and COS are more soluble in methanol than in Dimethyl ethers of Plyethylene glycol (DEPG). From the standpoint of capital and operational costs, its disadvantages include the complex flow scheme and the need for refrigeration of the absorbent. The energy requirement for the low-temperature refrigeration, however, is offset by Rectisol's ability to capture CO_2 more efficiently than other physical absorption methods. In physical absorption, the lower the temperature, the higher the solubility of the acid gas. In the Rectisol process, on the other hand, low-temperature operation lowers methanol's vapour pressure, thereby reducing solvent loss.

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39) Purisol is given for the convenience of users of this document and does not constitute an endorsement by ISO of this process.

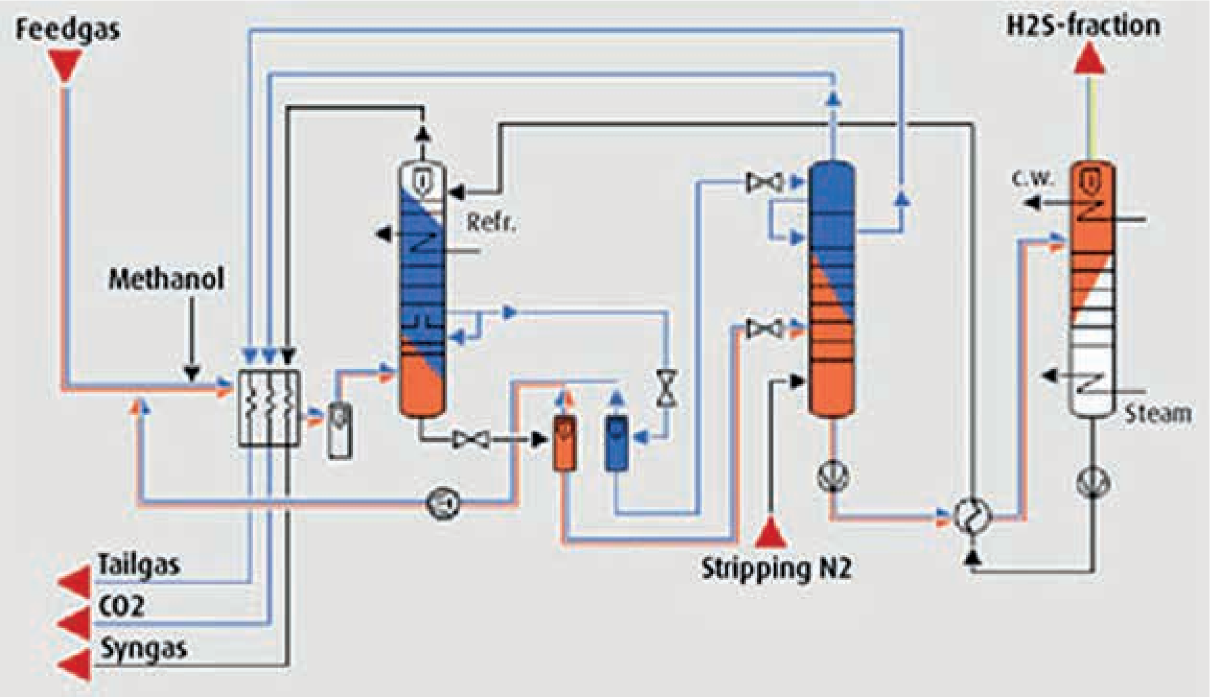

Figure C.1 — Schematic of Rectisol process from NETL homepage

C.2 Selexol process

The Selexol process uses DEPG to remove H_2S, CO_2 and other acid gases from feed gases such as syngas produced by the gasification of coal.

This process absorbs acid gas from syngas using the Selexol solvent at a relatively high pressure (2,07 MPa to 13,8 MPa). The rich solvent used to separate (absorb) the acid gases is reduced in pressure to desorb and recover the acid gases. DEPG can be used for operations within the range of −18 °C to 175 °C.

Since the Selexol process does not rely on chemical reactions as amine-based processes do, it requires less energy. As such, the Selexol solvent capacity is superior to amine-based processes at a pressure of 2,07 MPa or above.

Because the vapour pressure of DEPG used in the Selexol process is very low, water wash is not necessary to recover solvents, making equipment configuration simpler. But DEPG has a higher viscosity which slows down mass transfer, reducing its stage efficiency and increasing packing or tray requirements, especially at low temperatures. From the perspective of solubility and circulation rate, however, reduced temperature is desirable.

This process selectively captures H_2S and CO_2. For highly efficient removal of CO_2 and selective removal of H_2S, a two-stage process is used with two absorbers and a regenerator. The first tower selectively removes H_2S using a lean solution regenerated by steam, and the second tower absorbs CO_2. The solvent in the second absorber solvent is regenerated by oxygen and nitrogen for highly efficient removal of CO_2. Selexol can remove H_2S in CO_2-containing gas and is more favourable than Rectisol in this regard. Selexol is also reportedly lower in cost than Rectisol when deployed for IGCC (with CO_2 capture). The removed H_2S is sent to either a Claus unit to recover elemental sulfur or a sulfuric acid production process. At the same time, CO_2 is used for storage or EOR.

The operating temperature of the Selexol process should be decided based on a trade-off between various parameters such as the type of feed gas, trace components, and equipment configuration.

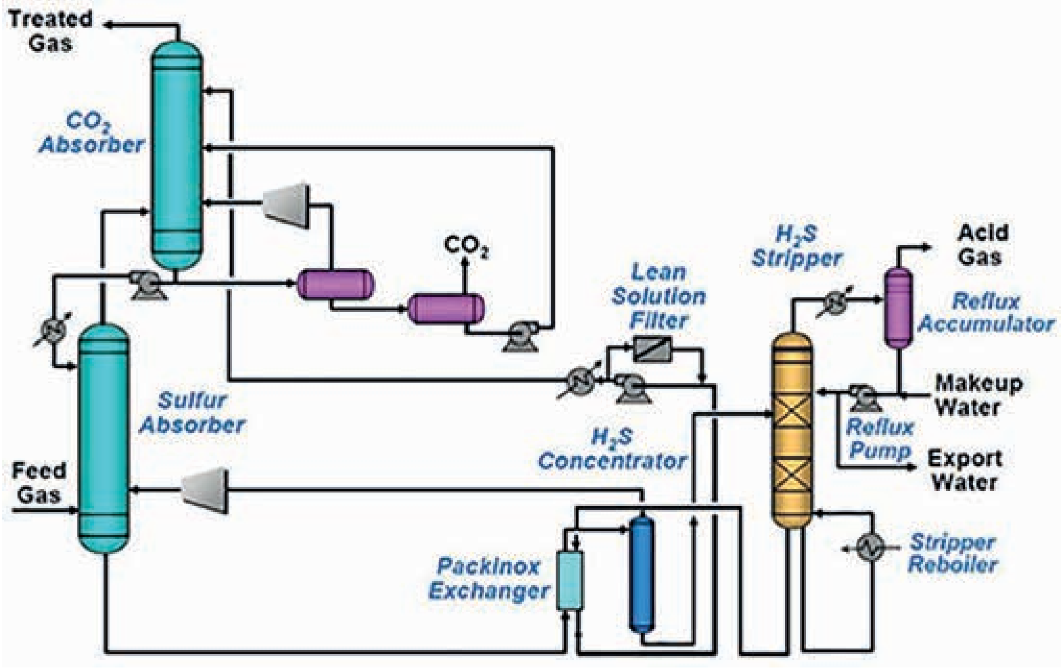

Figure C.2 — Schematic of Selexol process from NETL homepage

C.3 Purisol process

The Purisol process uses N-Methyl-2-Pyrrolidone (NMP) and its flow scheme is similar to that of the Selexol process. The Purisol process is operated at ambient temperature or 15 °C. In comparison to DEPG, NMP has a higher vapour pressure and therefore requires water washing of the treated gas for solvent recovery. When the process is operated below ambient temperature, however, water washing is not required.

Among the physical absorption methods, NMP has the highest selectivity for H_2S. While COS is not as soluble as H_2S, it is hydrolyzed by NMP. Because of its high selectivity for H_2S, the Purisol process is suitable for the capture of high-pressure, high-concentration CO_2 in IGCC.

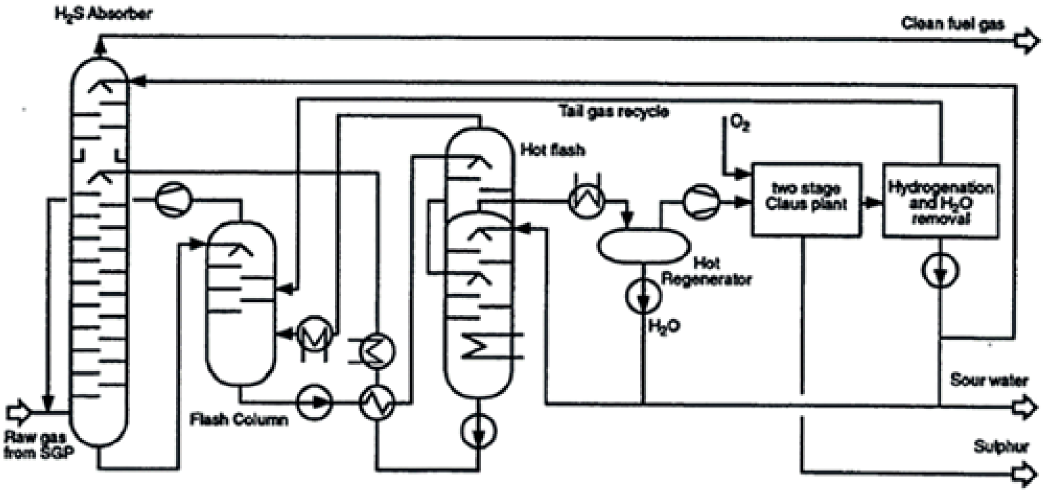

Figure C.3 — Schematic of Purisol process from NETL homepage

Annex D
(informative)

CO_2 capture terms and definitions list

D.1 General

This Annex provides a complete list of specific terms and definitions, abbreviated terms, chemical symbols/names related to CO_2 capture, including those used in this Technical Report.

D.2 Specific terms and definitions relating to CO_2 capture

D.2.1 absorbent
substance able to absorb liquid or gas

D.2.2 acceptance test
test conducted to determine if the contractual requirements on a specification or a performance are fully met which may involve performance tests including utility consumption, availability tests or reliability tests of equipment for the buyer to receive the plant from the contractor, depending on the contents of the contract

D.2.3 affinity
tendency of substances to react with each other

Note 1 to entry: Also defined as the decrease in Gibbs energy on going from the reactants to the products of a chemical reaction.

[SOURCE: IUPAC, Compendium of Chemical Terminology]

D.2.4 air blown gasifier
gasification process in which the oxidizing agent is supplied as air rather than oxygen

[SOURCE: ASME PTC 47-2006]

D.2.5 air integrated air aeparation unit
air separation process that receives all, or a part of, the total air feed requirement by extraction of a portion of the compressed air from the gas turbine

[SOURCE: ASME PTC 47-2006]

D.2.6 air pre-treatment
unit that removes water, carbon dioxide, and some hydrocarbon contaminants from the compressed air stream prior to processing in the cryogenic clauses of the air separation unit (ASU)

Note 1 to entry: Pre-treatment is usually based on a cyclical, adsorption/desorption (molecular sieve) based ambient temperature process using heated, dry nitrogen produced by the ASU for regeneration of the adsorbent.

[SOURCE: ASME PTC 47-2006]

D.2.7 air purification
see *air pre-treatment* (D.2.6)

D.2.8 air separation technology
process used to separate the gases in air, most notably oxygen from nitrogen which typically involves cryogenic distillation, pressure or vacuum swing absorption or membranes

D.2.9 air separation unit
unit separating oxygen, nitrogen and other inert gases from air which delivers the required oxygen for gasification or combustion applications in the context of CCS

D.2.10 alkanolamine
chemical compound that carries hydroxy (-OH) and amino ($-NH_2$, -NHR, and $-NR_2$) functional groups on an alkane backbone

D.2.11 amine
chemical compound consisting nitrogen atoms bound to hydrogen and/or carbon atoms having the general formula R_3N

D.2.12 amino acid
any of a class of organic compounds in which a carbon atom has bonds to an amino group, a carboxyl group, a hydrogen atom and an organic side group

D.2.13 antioxidant
substance that inhibits oxidation or reactions promoted by oxygen, peroxides, or free radicals

D.2.14 availability in capture plant
percentage of the calendar year during which the plant is in an operable state and able to perform a required function at the point in time when it is needed

D.2.15 biomass-based carbon capture system
carbon capture and storage in which the CO_2 source consumes biomass

D.2.16 Brayton cycle
thermodynamic cycle that describes the workings of a constant pressure heat engine such as gas turbine engine

D.2.17 capture ready
state of a CO_2 source facility which could and is intended to be retrofitted with CO_2 capture technology when the necessary regulatory and economic drivers are in place

D.2.18 carbonyl sulfide hydrolysis process
process to convert carbonyl sulphide (COS) to H_2S before nevessary sulfur removal

D.2.19 carcinogen
substance that is an agent directly involved in causing cancer

D.2.20 catalyst
substance that increases the rate of reaction without itself being consumed in the reaction

D.2.21 CCS energy consumption
total energy used for the development and operation of a CCS project

D.2.22 chemical absorption
process in which CO_2 is absorbed by chemical reaction

D.2.23 chemical looping combustion
process in which combustion of a hydrocarbon fuel is split into separate oxidation and reduction reactions by using a solid as an oxygen carrier between the two reactors

D.2.24 chilled ammonia process
process separating CO_2 from a gas stream that is cooled before it is contacted with ammonia that absorbs the CO_2

D.2.25 chilled water
cooling water lowered to the wet-bulb temperature used to cool and dehumidify a flue gas, which is typically between 4 °C and 7 °C depending on the requirement and can be supplied by the chiller

D.2.26 circulating dry scrubber
type of semi-dry FGD using hydrated lime as chemical reagent which is based on a circulating bed reactor set up to desulfurize the flue gas

D.2.27 circulating fluid bed boiler
utility boiler using circulating fluidized bed combustion technology

D.2.28 clinker
mass of incombustible matter fused together

D.2.29 CO_2 capture
separation of CO_2 in the manner as to produce a concentrated stream of CO_2 that can readily be transported for storage

D.2.30 CO_2 capture energy requirement
amount of heat and/or electricity that should be supplied to a CO_2 capture process to remove CO_2 from the gas stream including compression and cooling

D.2.31 CO_2 capture rate
ratio of the captured CO_2 mass flow rate at CO_2 capture system to the inlet CO_2 mass flow rate to CO_2 capture system

D.2.32 CO_2 capture point
point at the inlet valve of the pipeline, provided that the composition, temperature, and pressure of the CO_2-stream is within a certain specified range

D.2.33 CO_2 captured stream
main gas stream overwhelmingly consisting of CO_2 with a limited fraction of other chemical substances to be delivered to the transport boundary

D.2.34 CO_2 dense phase
CO_2 compressed to densities high enough to enable efficient CO_2 transport with pumps

D.2.35 CO_2 emission rate
rate at which CO_2 generated by the system is emitted to the atmosphere

D.2.36 CO_2 generation rate
rate at which CO_2 is generated within the system boundary

D.2.37 CO_2 processing unit
group of processes used in the purification of the CO_2 rich gas to a desired specification

Note 1 to entry: Also known as compression and purification unit (CPU), CO_2 purification unit (CPU), cryogenic purification unit, gas processing unit (GPU).

Note 2 to entry: Use of “cryogenic” term is generally accepted within the oxyfuel combustion community but may conflict with the strict definition of cryogenic as processes involving temperature lower than −150 °C.

D.2.38 CO_2 source point
see *CO_2 capture point* (D.2.32)

D.2.39 coal-fired power plant
power plant where combustion or gasification of coal is the main source of energy in which water is heated and turned to steam for the production of electricity

D.2.40 commissioning stage
testing period to verify if it functions according to its design or specification

D.2.41 cost of CO_2 avoided
average cost of reducing atmospheric CO_2 mass emissions by one unit while providing the same amount of useful product as a reference plant without CCS

Note 1 to entry: Can be defined by Formula (8), which should be applied only to a complete CCS system including transport and storage costs.

[SOURCE: IPCC Special Report on Carbon Dioxide Capture and Storage, 2005]

D.2.42 costs of CO_2 captured
cost measure based on the mass of CO_2 captured (or removed)

Note 1 to entry: Can be defined by Formula (9), which reflects the economic viability of a CO_2 capture system given a market price for CO_2, as an industrial commodity.

[SOURCE: IPCC Special Report on Carbon Dioxide Capture and Storage, 2005]

D.2.43 critical pressure
vapour pressure at the critical temperature

D.2.44 critical temperature
temperature above which liquid cannot be formed simply by increasing the pressure

D.2.45 decarboxylation reaction
chemical breakdown of compounds containing carbonates

D.2.46 degradation
act or process of chemical which makes its functional effectiveness or chemical purity decrease towards the failure to meet the performance of the plant through physical and chemical breakdown or reaction with other substances

D.2.47 dehydration
process of removing water from a stream or material

D.2.48 demineralized water
demin water
water of which the mineral matter or salts have been removed

Note 1 to entry: Sometimes designated as demin water.

D.2.48 demister
device, often fitted with vapour-liquid separator vessels, to enhance the removal of liquid droplets or mist entrained in a vapour stream

D.2.49 DeNOx
equipment normally used in the removal of NO_x in the flue gas by using ammonia or other reducing agent

D.2.50 depleted flue gas
gas exiting a carbon capture device with the CO_2 removed

D.2.51 desorption
release of CO_2 from absorbent or adsorbent

D.2.52 direct quench
process where hot gas is cooled by injection of water, cool gas or water immersion

D.2.53 discount rate
multiplier that converts anticipated return from an investment project to their current market value (present value)

D.2.54 dry ice
solid carbon dioxide

D.2.55 economizer
heat exchange devices in a boiler that heat fluids, usually water, up to but not normally beyond the boiling point of that fluid

D.2.56 efficiency penalty
net power output reduction (total output loss) of the power plant due to the addition of a CO_2 capture plant

D.2.57 effluent
flow of waste material discharged into the environment

D.2.58 electric grid
interconnected network for delivering electricity from suppliers to consumers

D.2.59 electricity output penalty
net power output reduction (total output loss) divided by the absolute mass flow of CO_2 captured

D.2.60 electrostatic precipitator
equipment normally used in the removal of particulate matters by using the force of an induced electrostatic charge

D.2.61 elevated pressure air separation unit
air separation process that operates at air feed pressures above the level required to produce oxygen and nitrogen products at near atmospheric pressures

[SOURCE: ASME PTC 47-2006]

D.2.62 engineering, procurement and construction
form of contracting agreement and also known as the execution phase, normally follows front end engineering and design (FEED)

D.2.63 entrained flow
flow in which a solid or liquid, in the form of fine particles, is transported in diluted form by high velocity gas

D.2.64 entrainment gas
gas employed in entrained flow

D.2.65 equilibrium
state of balance between opposing forces or actions that is either static or dynamic

D.2.66 evaporator
heat exchange device in a boiler that converts fluid, usually water, to saturated gas (i.e. saturated steam)

D.2.67 fabric filter
equipment normally used in the removal of particulate matters by using high temperature resistant fabric as filter media (also known as bag house, bag filter)

D.2.68 fixed bed
gas-solid contactor or reactor formed by a bed of stationary solid particles that allows the passage of gas between the particles

D.2.69 fixation
immobilization of CO_2 by its reaction with another material to produce a stable compound

D.2.70 flash gas
gas separated from a liquid by pressure reduction

D.2.71 flue gas
gases produced by combustion of a fuel that are normally emitted to the atmosphere

D.2.72 flue gas condenser
process of removing water from the flue gas by cooling

D.2.73 flue gas desulfurization
equipment normally used in the removal of SO_x in the flue gas by using chemical reagents

D.2.74 flue gas processing unit
unit of processes used to remove different criteria pollutants (SO_x, NO_x, PM, etc.) from flue gas of boilers or fired heaters

Note 1 to entry: Also known as environmental island, air quality control system (AQCS), gas quality control system (GQCS).

D.2.75 fluidized bed
gas-solid contactor or reactor comprising a bed of fine solid particles suspended by passing a gas through the bed at sufficiently high velocity

D.2.76 forced outage rate
number of hours CO_2 capture plant is unable to treat the flue gas from the hosted power plant due to the (unexpected) inability of CO_2 capture plant operation divided by the total period of hours for CO_2 capture plant with calendar date basis, excluding the periodic maintenance period

D.2.77 forced oxidation wet flue gas desulfurization
type of wet FGD using limestone as chemical reagent

D.2.78 front end engineering design
basic engineering which comes after the conceptual design or feasibility study and generally focuses on the technical requirements as well as rough investment cost for the project

D.2.79 fuel specific emissions
theoretical amount of CO_2 generated by burning a specific fuel completely to obtain the unit of heat output as lower heating value (LHV)

D.2.80 gas turbine
machine in which a fuel is burned with compressed air or oxygen and mechanical work is recovered by the expansion of the hot products

D.2.81 gasification
reaction that coal, biomass, petroleum coke, or natural gas is converted into a syngas composed mainly of carbon monoxide (CO) and hydrogen (H_2)

D.2.82 gasifier
reactor in which coal, biomass, petroleum coke, or natural gas is converted into a syngas composed mainly of carbon monoxide (CO) and hydrogen (H_2)

D.2.83 hazard communication
HazCom
disclosure to all workers the information on the potential hazards, the appropriate handling and the safe use of the chemicals they handle in workplaces for protecting themselves and others against any possible risks

D.2.84 hazardous substances
substances which, upon release into the atmosphere, water, or soil, or which, in direct contact with the skin, eyes, or mucous membranes, or consumed, cause health risks to humans or animals through absorption, inhalation, or ingestion

D.2.85 heats of absorption
heat of absorption is the energy released when the solvent absorbs CO_2

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, February 2013]

D.2.86 heats of reaction
heat of reaction is the energy released when the absorbed CO_2 reacts with a chemical solvent

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, February 2013]

D.2.87 higher heating value
energy released from the combustion of a fuel that includes the latent heat of water

D.2.88 International Agency for Research on Cancer (IARC)
part of the World Health Organization (WHO), which coordinates and conducts both epidemiological and laboratory research into the causes of human cancer

D.2.89 levelized cost of electricity
value calculated by Formula (7), that include only the power plant and capture technologies and not the additional costs of CO_2 transport and storage that are required for a complete system with CCS

[SOURCE: IPCC Special Report on Carbon Dioxide Capture and Storage, 2005]

D.2.90 life cycle assessment
compilation and evaluation of the inputs, outputs and the potential environmental impacts of a CCS project or a component part throughout its life cycle

D.2.91 lignite
sub-bituminous coal
relatively young coal of low rank with a relatively high hydrogen and oxygen content

D.2.92 limit of supply
limit of the scope of supply or battery limit

D.2.93 load following
operation mode of CO_2 Capture Plant that continues operation achieving CO_2 removal efficiency or CO_2 captured amount and properties as required according to the demand, even during the transient period, for the gas amount and the gas properties to be treated which fluctuates throughout the day normally due to the operation load change of the gas sources

D.2.94 mean downtime
time that includes mean time to repair and all other time involved with downtime

Note 1 to entry: Periodical maintenance as preventive inspection and corrective maintenance including logistical delays are some examples.

D.2.95 mean time between failures
MTBF
total operating hours divided by the number of failures

D.2.96 mean time to repair
time that shows how quickly equipment can be made available after failure

D.2.97 membrane
permeable solid material that selectively separates the components of a fluid mixture

D.2.98 methanation
reaction which converts carbon monooxide to methane

D.2.99 mist
stream of liquid in the form of very small drops

D.2.100 natural gas combined cycle
natural-gas-fired power plant with gas and steam turbines

D.2.101 nitrosamine
any of various organic compounds which are characterized by the grouping NNO

D.2.102 nitramine
any of various organic compounds which are characterized by the grouping NNO_2

D.2.103 off-gas
gas that is produced as a by-product of a process

D.2.104 operability
ability to keep a CO_2 capture plant in a safe and reliable functioning condition, according to the operational requirements considered in the plant design

D.2.105 owner's cost
owner's cost include all other costs not expected to be included in the EPC contract

Note 1 to entry: Owner's cost includes legal fees, interconnections cost, land cost, prepaid royalties, start-up costs, working capital, inventory capital, financing cost, owner's engineering and others.

D.2.106 oxy-combustion
or oxyfuel combustion
process involving combustion of a fuel with pure oxygen or a mixture of oxygen and re-circulated flue gas

D.2.107 oxy-CFB boiler
CFB boiler using technology based on oxyfuel combustion with recycled flue gas

D.2.108 oxy-PC boiler
PC boiler using technology based on oxyfuel combustion with recycled flue gas

D.2.109 partial oxidation
oxidation of a carbon-containing fuel under conditions that produce a large fraction of CO and hydrogen

D.2.110 particulate emission
solid and liquid particles that are by-products of combustion entrained in flue gas exiting the stack of a fossil fueled boiler

D.2.111 particulate matter
extremely small particles and liquid droplets suspended in the earth's atmosphere

D.2.112 perfluorocarbon
synthetically produced halocarbons containing only carbon and fluorine atoms, which are characterized by extreme stability, non-flammability, low toxicity and high global warming potential

D.2.113 periodic maintenance
significant maintenance activity carried out regularly after the predetermined period of the continuous operation as the preventive maintenance

D.2.114 permeability rate
quantity of flow of gas (or liquid) through a membrane per unit of time and area

D.2.115 permeance
measure of gas actually flowing through a membrane per unit of pressure differential

Note 1 to entry: In general, it is expressed in gas permeance units (GPU).

Note 2 to entry: 1 GPU = 10^{-6} cm^3(STP)/scm^2(cmHg)

D.2.116 physical absorption
process where a solvent absorbs a gas physically with pressure and without chemical reaction

D.2.117 post-combustion capture
capture of carbon dioxide from flue gas stream produced by fuel air combustion

D.2.118 power output
electricity which is produced or supplied from a power plant

D.2.119 pre-combustion capture
capture of carbon dioxide following the processing of the fuel before combustion

D.2.120 pre-scrubbers
safety equipment that can reduce SO_2 gases to very low levels using alkaline solutions (NaOH) when necessary

D.2.121 pressure ratio
membrane pressure ratio is defined as the ratio of feed pressure to permeate pressure

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, May 2013]

D.2.122 pressure swing adsorption
method of separating gases using the physical adsorption of one gas at high pressure and releasing it at low pressure

D.2.123 pulverized coal
finely ground coal

D.2.124 pulverized coal boiler
utility boilers using pulverized fuel or coal as fuel

D.2.125 pulverized fuel
finely ground solid fuels such as coal or biomass

D.2.126 qualification
process of providing the evidence that the technology will function within specific limits or operating regime with an acceptable level of confidence

D.2.127 quench
<verb> to cool hot gas suddenly

D.2.128 radiant quench design
design of the process where hot gas is cooled by radiant cooler

D.2.129 ramping speed

specified rate at which the load on the boiler system can change from partial load to full load

D.2.130 rank
quality criterion for coal

D.2.131 reaction rate
speed of a chemical reaction

D.2.132 reclaimer
process or unit that regenerates deteriorated absorbent

D.2.133 recycled flue gas
flue gas recycled to moderate the combustion temperature

D.2.134 reforming
method for producing hydrogen, carbon monoxide or other useful products from hydrocarbon such as natural gas

D.2.135 regeneration energy
total amount of regeneration energy required is a combination of sensible heat, heat of absorption (which includes heats of reaction for chemical solvents), and heat of vapourization

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, February 2013]

D.2.136 regenerator
see *stripper* (D.2.161)

D.2.137 reheater
heat exchange devices in a boiler that reheat saturated gas, usually steam from IP steam turbine, to a superheat condition (i.e. temperature above fluid saturated conditions)

D.2.138 reliability
ability of an item to perform a required function, under given environmental and operational conditions and for a stated period of time

[SOURCE: ISO 8402]

D.2.139 retrofit
modification of the existing equipment to upgrade and incorporate changes after installation

[SOURCE: IPCC Special Report on Carbon Dioxide Capture and Storage, 2005 and IEA Technology Roadmap Carbon Capture and Storage, 2013].

D.2.140 saturation
point of a solution condition at which a solution of a substance can dissolve no more of that substance and additional amounts of it will appear as a separate phase at the stable condition

D.2.141 scale-up
to design or construct the larger commercial size plant based on the experience of the mid-size or small pilot plant

D.2.142 scrubber
gas liquid contactor device, normally used to remove gaseous and solid emissions from flue gas streams

D.2.143 secondary thermal energy inputs
additional heat inputs to the test boundary which should be accounted, such as cycle makeup and process condensate return

[SOURCE: ASME PTC 50-2014]

D.2.144 selectivity
degree that one substance is absorbed in comparison to others

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, February 2013]

D.2.145 shift conversion
see *shift reaction* (D.2.147)

D.2.146 shift converter
reactor in which the water-gas shift reaction, $CO + H_2O = CO_2 + H_2$, takes place

D.2.147 shift reaction
chemical formation of carbon dioxide and hydrogen from carbon monoxide and water

D.2.148 sludge
semi-liquid (or semi-solid) residue or solids separated from suspension in a liquid in industrial processes and treatment of sewage and waste water

D.2.149 slurry
thick, flowable mixture of solids and a liquid, usually water

D.2.150 solid oxide fuel cell
fuel cell in which the electrolyte is a solid ceramic composed of calcium- or yttrium-stabilized zirconium oxides

D.2.151 solute
dissolved substance in a solution

D.2.152 solvent
liquid substance capable of dissolving CO_2

D.2.153 sorbent
substance that absorbs CO_2 or to which CO_2 is adsorbed

D.2.154 sour shift (reaction)
shift reaction without removing H_2S or COS

D.2.155 specific energy consumption
energy consumption per unit of CO_2 captured

D.2.156 specific power consumption
power consumed by the capture system including compression and related utility facilities to the amount of CO_2 captured

D.2.157 spray dry adsorption
type of semi-dry FGD using lime slurry as chemical reagent which is based on a slurry atomizer spray reactor set up to desulfurize the flue gas

D.2.158 standard atmospheric conditions
101,325 kPa (14,696 psia), 288,5 K (59°F), and relative humidity of 60 %

[SOURCE: ASME PTC 47-2006]

D.2.159 steam methane reforming
catalytic process in which methane reacts with steam to produce a mixture of H_2, CO and CO_2

D.2.160 steam reforming
catalytic process in which a hydrocarbon is reacted with steam to produce a mixture of H2, CO and CO_2

D.2.161 stripper
gas-liquid contacting device, in which a component is transferred from liquid phase to the gas phase

Note 1 to entry: Can also be referred to as “regenerator” or “desorber”.

D.2.162 super-critical thermal power plant
modern thermal power plant that operates at higher-pressure steam than the supercritical condition to improve the plant efficiency

D.2.163 superheater
heat exchange device in a boiler that heat a wet or saturated gas, usually steam, to a superheat condition (i.e. temperature above fluid’s saturated conditions)

D.2.164 surface area
total area of surface of a sorbent

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, May 2013]

D.2.165 sweet shift (reaction)
shift reaction after removing H_2S or COS

D.2.166 SWIFT
structure of a “What If” analysis

D.2.167 syngas
synthetic gas produced through gasification process

D.2.168 synthetic natural gas
fuel gas with a high concentration of methane produced from coal or heavy hydrocarbons

D.2.169 tail gas
off-gas from the regeneration process of the sorbent that is regenerated

[SOURCE: ASME PTC 47-2006]

D.2.170 test boundary
thermodynamic control volume defined by the scope of the test, and for which the mass and energy flows will be determined

Note 1 to entry: This is an important visual tool that aids in understanding the scope of test and the required measurements.

[SOURCE: ASME PTC 22-2005]

D.2.171 total mass of CO_2 captured
total mass of CO_2 separated from the gas stream going into capture plant

D.2.172 treated gas
gas finally discharged from the CO_2 capture process in the emission side after being processed to have a lower CO_2 concentration than the feed gas

D.2.173 waste water
water for which there is no use in the process anymore

D.2.174 water gas shift
see *shift reaction* (D.2.147)

D.2.175 working capacity
difference between the concentration of CO_2 in the rich solvent exiting the absorber (entering the stripper) and the lean solvent entering the absorber (exiting the stripper)

[SOURCE: US DOE/National Energy Technology Laboratory, Advanced Carbon Dioxide Capture R&D Program: Technology Update, February 2013]

D.2.176 zero-carbon energy carrier
carbon-free energy carrier, typically electricity or hydrogen

D.3 Abbreviated terms

%RH	% relative humidity
AAS	Amino acid salt
ACI	Activated carbon injection
AEP	American Electric Power
AGR	Acid gas removal
AIGA	Asian Industrial Gas Association
AOD	Argon-oxygen decarbonization
AQCS	Air quality control systems
ASME	American Society of Mechanical Engineers
ASU	Air separation unit
A-USC	Advanced ultra-supercritical
BAC	Booster air compressor
BAHX	Brazed aluminium heat exchanger
BAT	Best available technology
BF	Blast furnace
BFG	Blast furnace gas
BFW	Boiler feed water
BOF	Basic oxygen furnace (also known as LD or converter)
BOFG	Basic oxygen furnace gas (also known as LDG or CG)
BOP	Balance of plant
BOS	Basic oxygen steelmaking
BREF	Best available technology reference document
BSF	Boiler simulator furnace
BTG	Steam and power generation unit

BTX	Benzene, toluene and xylene (also known as Benzole)
CalEPA	California Environmental Protection Agency
CAP	Chilled ammonia process
CAPEX	Capital expenditure
CAS	Chemical abstract service
CCF	Cyclone converter furnace
CCS	Carbon capture and storage
CCUS	Carbon capture, utilization and storage
CDA	Circulating dry absorber
CDQ	Coke dry quenching
CDS	Circulating dry scrubber
CEMS	Continuous emission monitoring system
CERC	Cambridge Environmental Research Center
CFB	Circulating fluidized bed
CFR	US Code of Federal Regulations
CG	Converter gas (also known as BOFG or LDG)
CGA	Compressed Gas Association
CIS	Commonwealth of Independent States
CISWI	Commercial and industrial solid waste incinerators
COG	Coke oven gas
COSHHHSE	Control of substances hazardous to health under health and safety executive
CPU	CO_2 processing unit, compression and purification unit, CO_2 purification unit or cryogenic purification unit
CSIRO	Commonwealth Scientific and Industrial Research Organization
CTL	Coal to liquids
CW	Cooling water
DAF	Dry ash free
DCAC	Direct contact and after cooler
DCC	Direct contact cooler
DCCPS	Direct contact cooler polishing scrubber
DP	Dew point
DRI	Direct reduction ironmaking
DSI	Direct sorbent injection
EAF	Electric arc furnace
EHS	Environmental, health and safety
EHSM	Environmental, health and safety management system
EIA	Environmental impact assessment
EIGA	European Industrial Gas Association
EOP	Electricity output penalty
EOR	Enhanced oil recovery
EPA (USEPA)	US Environmental Protection Agency
EPC	Engineering, procurement and construction
ESP	Electrostatic precipitator
ETP	Energy technology perspectives
EU	European Union
FBC	Fluidized bed combustion

FCV	Flow control valve
FD fan	Forced draft fan
FEED	Front end engineering design
FEGT	Furnace exit gas temperature
FF	Fabric filter or bag filter
FGC	Flue gas condenser
FGD	Flue gas desulfurization
FMECA	Failure mode and effects critical analysis
FOH	Forced outage hours
FOR	Forced outage rate
FTA	Fault tree analysis
GBFS	Granulated blast furnace slag
GCCSI	Global Carbon Capture and Storage Institute
GGBFS	Granulated ground blast furnace slag
GGH	Gas-gas heat exchanger
GHG	Greenhouse gas
GHGT	Greenhouse gas control technologies conference
GOX	Gaseous oxygen
GPU	Gas processing unit
GQCS	Gas quality control system
GTCC	Gas-fired combined cycle
GTL	Gas to liquids
HAZOP	Hazard and operability
HBI	Hot briquetted iron
HC	Hydrocarbons
HGI	Hard grove index
HHV	Higher heating value
HM	Hot metal (also known as pig iron)
HP	High pressure
HRC	Hot rolled coil
HRM	Hot rolling mill (also known as HSM)
HRSG	Heat recovery steam generator
HS	Hot stove
HSE	Health, safety and environment
HSM	Hot strip mill
HSS	Heat stable salts
IARC	International Agency for Research on Cancer
ID fan	Induced draft fan
IEA	International Energy Agency
IFA	International Fertilizer Industry Association
IFC	International Finance Corporation
IGCC	Integrated coal gasification combined cycle
IP	Intermediate pressure
IPCC	Intergovernmental panel on climate change
ISO	International Organization for Standardization
JCR	Jumbo coke reactor (also known as SCS)

JT	Joule-Thomson
LCOE	Levelized cost of electricity
LDG	Linz-Donawitz gas (also known BOFG or CG)
LFO	Light fuel oil
LHV	Lower heating value
LIN	Liquid nitrogen
LM	Ladle metallurgy
LNG	Liquefied natural gas
LOI	Loss on ignition
LOX	Liquid oxygen
LP	Low pressure
LTEL	Long-term exposure limit
MAC	Main air compressor
MCM	Mixed conductive membrane
MCR	Maximum continuous rating
MDT	Mean downtime
MHX	Main heat exchanger
MP	Medium pressure (also referred to as IP)
MTBF	Mean time between failures
MTPY	Million tonnes per year
MTTR	Mean time to repair
NAFTA	North American Free Trade Agreement (include USA, Mexico and Canada)
NEDO	New Energy and Industrial Technology Development Organization
NFBF	Nitrogen free blast furnace
NG	Natural gas
NGCC	Natural gas combined cycle
NIPH	Norwegian Institute of Public Health
OBF	Oxy-blast furnace (oxygen blown blast furnace)
OBF-PG	OBF processed gas
OBF-TG	OBF raw top gas
OEM	Original equipment manufacturer
OFA	Overfire air
OFO	Overfire oxygen
OHF	Open hearth furnace
OHSAS	Occupational health and safety assessment series
OPERA	Operational problem analysis
OPEX	Operating expenditure
OREDA	Offshore reliability data
OSHA	US Occupational Safety and Health Administration
Oxy-CFB	Oxyfuel combustion — circulating fluidized bed
Oxy-PC	Oxyfuel combustion — pulverized coal
PC	Pulverized coal (also known as powdered coal)
PCC	Post combustion capture
PCI	Pulverized coal injection
PF	Pulverized fuel
PFD	Process flow diagram

PGAN	Pressurized gaseous nitrogen
PHA	Process hazard analysis
PM	Particulate matter
POH	Period of hours
POX	Partial oxidation
PSA	Pressure swing adsorption
PSM	Process safety management
RAM	Reliability and maintenance
R&D	Research and development
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RFG	Recycled flue gas
RIST	Research Institute of industrial science and technology
SC	Supercritical
SCGH	Steam coil gas heater
SCR	Selective catalytic reduction
SCS	Single chamber system (also known as JCR)
SDA	Spray dry absorber
SDI	Sorbent direct injection
SDS	Safety data sheet
SEC	Specific energy consumption
SECARB	Southeast regional carbon sequestration partnership
SM	Secondary metallurgy
SMR	Steam methane reformer
SNCR	Selective non-catalytic reactor
SNG	Synthetic natural gas
SOFC	Solid oxide fuel cell
SPC	Specific power consumption
SR	Smelting reduction
STEL	Short-term exposure limit
STP	Standard temperature and pressure
SWIFT	Structured what-if checklist
TC 265	Technical committee 265
TCM	Technology Center Mongstad
tcs	Tonne of crude steel
TDL	Target detection limit
TGR	Top gas recycle
thm	Tonne of hot metal
tls	Tonne of liquid steel
TPD	Tonnes per day
TR	Technical Report
TRT	Top gas recycle turbine
TSA	Temperature swing adsorber
TWA	Time–weighted average
ULCOS	Ultra-low CO_2 steelmaking
USC	Ultra-supercritical
UV	Ultraviolet

VLE	Vapour-liquid equilibrium
VOC	Volatile organic compounds
VPSA	Vacuum pressure swing adsorber
WESP	Wet ESP
WGS	Water gas shift (reaction)
WHO	World Health Organization
WID	Waste Incineration Directive
WSA	World Steel Association
ZR	Zero reformer

D.4 Chemical symbols/names

AAS	Amino acid salt
Ar	Argon
Ca	Calcium
$CaSO_4$	Calcium sulfate
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
COS	Carbonyl sulfade
H_2	Hydrogen
HBr	Hydrogen bromide or Bromic acid
HCl	Hydrogen chloride or Hydrochloric acid
HCN	Hydrogen cyanide
HF	Hydrogen fluoride or Hydrofluoric acid
Hg	Mercury
HNO_3	Nitric acid
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
K_2CO_3	Potassium carbonate
K_2SO_4	Potassium sulfate
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
N_2	Nitrogen
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide, Caustic soda

Na_2SO_4	Sodium sulfate
NDMA	*N*-nitrosodimethylamine
NH_3	Ammonia
$(NH_4)_2SO_4$	Ammonium sulfate
NO_x	Nitrous oxide compounds (i.e. NO, NO_2, N_2O, N_2O_4)
O_2	Oxygen
S	Sulfur
SO_x	Sulfur oxide compounds (i.e.., SO_2, SO_3)

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Table 5

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