

Flue gas treatment for CO₂ capture

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Abstract

This report is in two sections: the first describes the flue gas and its treatment in post-combustion capture and the second covers the flue gas in oxyfuel combustion capture. The main components of the flue gas in pulverised coal combustion for post-combustion capture are CO₂, N₂, O₂ and H₂O, and air pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury as well as other contaminants. The most widespread method of post-combustion capture of CO₂ is by solvent absorption. Coal-fired power plants already have units to remove air pollutants prior to CO₂ capture, such as FGD, SCR, and ESP. However, some pollutants will be absorbed in the solvent with the CO₂ and can lead to the formation of heat stable salts. The FGD process may need to be improved to reduce SO_x emissions to an acceptable level for post-combustion capture. The flue gas stream from oxyfuel combustion is composed mainly of CO₂ and H₂O. It will also contain O₂, SO_x, NO_x, HCl, Hg, any diluents from the O₂ stream, and various inerts such as N₂ and Ar. Condensing, compression and cooling of the flue gas are required to obtain CO₂ of an acceptable purity for transport and storage. Various processes are being developed to raise the purity of CO₂ produced from oxyfuel combustion. Air Products have developed a membrane to separate CO₂ from a feed gas; Air Liquide have developed a compression and purification unit; Linde are developing a fast catalytic deNO_x process and an alkali based wash unit for removal of NO_x and SO_x; and Praxair are developing oxygen enhanced coal combustion to reduce NO_x emissions without resorting to complete oxyfuel combustion. Finally, the ThermoEnergy Integrated Power System enables the condensing heat exchanger to collect particulates, acid gases and mercury into a condensed phase. Despite this ongoing research, at present the issue of CO₂ optimum product purity is a question that does not have a satisfactory answer.

Acronyms and abbreviations

ASU	air separation unit
B&W	Babcock and Wilcox
CAPEX	capital expenditure
CCR	carbonation calcination reaction
CCS	carbon capture and storage
CPU	compression and purification unit
daf	dry ash free
DEA	diethanolamine
DECC	Department of Energy and Climate Change (UK)
DOE	Department of Energy (US)
EDTA	ethylenedinitrilo-tetra-acetic-acid
EOR	enhanced oil recovery
ESP	electrostatic precipitator
FGD	flue gas desulphurisation
HHV	higher heating value
IEA GHG	IEA Greenhouse Gas R&D Programme
LCPD	Large Combustion Plant Directive
LHV	lower heating value
MEA	monoethanolamine
mg/m ³	milligramme per cubic metre
MHI	Mitsubishi Heavy Industries
MMBtu	million British thermal units
NETL	National Energy Technology Laboratory (US)
ng/J	nanogramme/Joule
NO _x	nitrogen oxides (NO and NO ₂)
O&M	operation and maintenance
OPEX	operating expenditure
PC	pulverised coal
PM	particulate matter
ppmv	parts per million by volume
RFG	recycled flue gas
SCR	selective catalytic reduction
SDA	spray dryer absorber
TIPS	ThermoEnergy Integrated Power System

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I Introduction

The first main application of carbon dioxide (CO₂) capture is likely to be at large point sources such as coal-fired power plants. CO₂ from the use of fossil fuels can be isolated by:

- post-combustion capture;
- oxyfuel combustion capture;
- pre-combustion capture.

The prime questions considered in this report are: what are the impurities in the flue gas that may affect the transport and storage of CO₂, and how can they be removed? Thus, the focus of this report is on flue gas treatment for CO₂ capture at coal-fired plants, so it includes post-combustion capture and oxyfuel combustion capture. It does not include pre-combustion capture, as in this case the coal is gasified first and the CO₂ removed at this stage.

The capture of CO₂ requires an increased energy input per kWh of output. This raises the resource requirements for the pulverised coal (PC) plant including proportionally greater amounts of coal, as well as limestone (consumed by the flue gas desulphurisation (FGD) system for SO₂ control) and ammonia (consumed by the selective catalytic reduction unit (SCR) for NO_x control). There are also resulting increases in solid residues. In contrast, atmospheric emissions of CO₂ decrease sharply as a result of carbon capture and storage (CCS) systems, which also remove residual amounts of other acid gases, especially SO₂, in flue gas streams. Thus the coal combustion system shows a net reduction in SO₂ emissions rate as a result of CO₂ capture. However, because of the reduction in plant efficiency, other air emission rates per kWh increase relative to the reference plants without capture (IPCC, 2005).

In oxyfuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that is mainly CO₂ and water vapour (H₂O). If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO₂ and/or H₂O-rich flue gas can be recycled to the combustor to moderate this. The oxygen for combustion is usually produced by low temperature (cryogenic) air separation although various novel techniques, such as membranes and chemical looping cycles are being developed (IPCC, 2005).

The CO₂ stream that is captured after oxyfuel combustion may contain impurities which would have practical impacts on CO₂ transport and storage systems and also potential health, safety and environmental impacts. The types and concentrations of impurities depend on the type of capture process and detailed plant design. The major impurities in CO₂ are well known but there is little published information on the fate of any trace impurities in the flue gas such as heavy metals. If substances are captured along with the CO₂ then their net emissions to the atmosphere will be reduced, but impurities in the CO₂ may result in environmental impacts during transport and storage (IPCC, 2005). In addition, the capture process may be harmed by the impurities present in the flue gas. These factors mean that some form of flue gas treatment may be required.

The major impurities in the CO₂ flue gas stream are water vapour, nitrogen, oxygen and argon. SO₂, NO₂, HCl and HF are minor impurities. Mercury is present in trace amounts. Moisture has to be removed to avoid corrosion and hydrate formation during transport.

As the IPCC noted in 2005, 'the impact of fuel impurities and temperature on the functional materials should be an area of future work' (IPCC, 2005). This report looks at the current status of this work.

The composition of the flue gas from post-combustion capture using amines and from oxyfuel combustion are covered in this report. Treatments to reduce the concentration of the impurities are identified and described. It is a new subject area, so much of the research is in the early stages of development. The report is in two sections – the first includes post-combustion capture of CO₂ from the flue gas, and the second features oxyfuel combustion flue gas.

2 Post-combustion capture of CO₂

Post-combustion capture is the term given to the capture of CO₂ from flue gases produced by the combustion of coal. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates out most of the CO₂. The CO₂ is fed to a storage reservoir and the remaining flue gas is discharged directly to the atmosphere (IPCC, 2005).

Flue gases or stack gases in coal combustion systems are usually at atmospheric pressure. The low pressure means that huge flows of gases are generated due to the abundance of nitrogen from air and the large scale of the units. A coal-fired combustion plant can contain less than 15% by volume CO₂. In principle, post-combustion capture systems can be applied to flue gases produced from the combustion of any type of fuel. However, the impurities in the fuel are important for the design and costing of the complete plant. Flue gases from coal combustion contain not only CO₂, N₂, O₂ and H₂O, but also air pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants. Coal-fired power plants will have additional units to remove air pollutants prior to CO₂ capture in an absorption-based process. These additional units can include SCR, electrostatic precipitators (ESP) and FGD. Although capture of CO₂ in these flue gases is, in principle, more problematic and energy intensive than from other gas streams, commercial experience is available at a sufficiently large scale to provide the basis for cost estimates for post-combustion CO₂ capture systems (IPCC, 2005).

According to Puxty and others (2009), post-combustion capture has a number of practical advantages over oxyfuel combustion, and has a similar cost. In particular, post-combustion capture can be retrofitted to existing power plants and integrated into new ones. In addition, the parasitic energy demand of a post-combustion capture plant on a power station can be reduced (at the cost of CO₂ removal efficiency) according to electricity demand, if additional electricity output is required from a power plant during time of peak load or optimal electricity pricing.

There are several commercially available process technologies which could be used for CO₂ capture from flue gases. However, absorption processes based on chemical solvents are currently the preferred option for post-combustion CO₂ capture. They offer high capture efficiency and selectivity, and the lowest energy use and costs when compared with other existing post-combustion capture processes (IPCC, 2005). Robert Davidson has written two reports for the IEA Clean Coal Centre on post-combustion carbon capture, one on solid sorbents and membranes (2009) and one on solvent scrubbing (2007). Absorption processes are discussed in more detail later in this chapter.

The flue gas components are described briefly in the next section. Then the main methods of capturing CO₂ are described. The removal of impurities from the flue gas is the final part of the chapter, which includes descriptions of some research projects.

2.1 Components of the flue gas

In addition to CO₂, N₂, O₂, H₂O, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants, flue gas from coal combustion contains other acid gas components such as NO_x and SO_x. These acidic gas components have a chemical interaction with the alkaline solvent, similar to that of CO₂. This is not desirable as the irreversible nature of this interaction leads to the formation of heat stable salts and hence a loss in absorption capacity of the solvent and the risk of solids forming in the solution. In addition, it results in an extra consumption of chemicals to regenerate the solvent and the production of a waste stream such as sodium sulphate or sodium nitrate. Therefore, the removal of NO_x and SO_x to low levels before CO₂ recovery becomes essential. For NO_x, it is the NO₂ which leads to the formation of heat stable salts. Fortunately, the level of NO₂ is generally a small fraction of the overall NO_x content in a flue gas (IPCC, 2005).

2.1.1 Nitrogen oxides

NO_x produced from coal or lignite firing is mainly NO, with up to about 5% NO₂, but normally less. NO does not react with amines in CO₂ capture plant, but NO₂ does. NO is not absorbed in FGD plant but about 30% of the NO₂ is. This suggests a maximum NO₂ concentration downstream of the FGD absorber of about 7 mg/m³, at 6% O₂ dry (3.4 ppmv at 6% O₂ dry). Two of the main organisations producing amine scrubbers are Fluor and MHI. Fluor requests a limit of 20 ppmv NO₂ for its amine solvents to operate and MHI requires a lower limit. Thus the concentration that results is acceptable for Fluor and is perhaps also low enough for MHI, although they have not stated a limit. It is therefore apparent that no additional NO_x abatement is required to protect a Fluor amine scrubber, and probably an MHI one as well. Thus, NO_x control technologies are not considered further.

2.1.2 Sulphur oxides

The allowable SO_x content in the flue gas is determined primarily by the cost of the solvent – as this is consumed by reaction with SO_x. SO₂ concentrations in the flue gas are typically around 300–5000 ppm. Commercially available removal plants remove up to 98–99% of the SO₂. Amines are relatively cheap chemicals, but even cheap solvents such as monoethanolamine (MEA) may require SO_x concentrations of around 10 ppm to keep solvent consumption (around 1.6 kg of MEA/tCO₂ separated) and make up costs at reasonable values, which often means that additional FGD is needed. The optimal SO₂ content, before the CO₂ absorption process, is a cost trade-off between CO₂-solvent consumption and SO₂-removal costs.

2.2 Separation of CO₂ with sorbents/solvents

Solvents are the most widely used method to separate CO₂ from flue gas, and so are discussed in detail in this section. In post-combustion capture, absorption processes make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine, with an acid or sour gas. The flue gas is cooled and then brought into contact with the solvent in the absorber. A blower is required to overcome the pressure drop through the absorber. At absorber temperatures, typically 40–60°C, CO₂ is bound by the chemical solvent in the absorber. The flue gas then undergoes a water wash section to balance water in the system and to remove any solvent droplets or solvent vapour carried over, and then it leaves the absorber. It is possible to reduce CO₂ concentration in the exit gas down to low values (as a result of the chemical reaction in the solvent) but lower exit concentrations tend to increase the height of the absorption vessel. The ‘rich’ solvent, which contains the chemically bound CO₂, is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100–140°C) and pressures not very much higher than atmospheric pressure, at around 0.18 MPa. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO₂ and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO₂ product gas leaves the stripper. The ‘lean’ solvent, containing far less CO₂ is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level (IPCC, 2005). For more detail, see Davidson (2007).

The purity and pressure of CO₂ typically recovered from an amine based chemical absorption process are as follows (IPCC, 2005):

- CO₂ purity: 99.9% by volume or more (water saturated conditions);
- CO₂ pressure: 50 kPa (gauge).

A key feature of post-combustion CO₂ capture processes based on absorption is the high energy requirement and the resulting efficiency penalty on power cycles. This is primarily due to the heat necessary to regenerate the solvent, steam use for stripping and to a lesser extent the electricity required for liquid pumping, the flue gas fan and finally compression of the CO₂ product (IPCC, 2005). Cooling duty for the condenser, pre-cooler and intercooling is an additional energy requirement of the process (Faber, 2010).

Impurities in the flue gas, particularly SO_x, NO_x, HCl and HF will lead to the formation of heat stable salts in any amine system. Heat stable salts are the product of acid-base reactions between amines and different acidic species in the flue gas. The heat stable salts must be converted back into amine through a reclaiming process. In order to avoid excessive build-up rates of heat stable salts, the flue gas

impurities must be reduced to a low level upstream of the absorber (Reddy and others, 2008).

Currently, three absorption processes are commercially available for CO₂ capture in post-combustion systems (IPCC, 2005):

- The Kerr-McGee/ABB Lummus Crest Process which uses a 15–20% by weight aqueous MEA solution.
- The Fluor Daniel ECONAMINE Process which is an MEA-based process (30% by weight aqueous solution) with an inhibitor to resist carbon steel corrosion and is tailored specifically for oxygen-containing gas streams.
- The Kansai Electric Power Co, Mitsubishi Heavy Industries Ltd, (KEPCO/MHI) Process is based upon sterically-hindered amines and three solvents have been developed (KS-1, KS-2 and KS-3).

These are discussed in more detail in the following sections.

2.2.1 MEA

The widely used chemical solvents are aqueous solutions of alkanolamines, of which the most recognised are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). These alkanolamines are commonly referred to as primary, secondary and tertiary amines according to the number of carbon-containing groups attached to the nitrogen atom. MEA, with only one carbon-containing group is classified as the primary amine, while DEA falls into the secondary amine category. MDEA is one of the tertiary amines having three carbon-containing groups (Veawab and others, 2003).

MEA has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, low molecular weight and thus high absorbing capacity on a mass basis. It has a reasonable thermal stability and thermal degradation rate. Studies have been directed at finding new amines that are able to capture greater amounts of CO₂ than MEA and also to avoid its disadvantages. These include high enthalpy of reaction with CO₂ leading to higher desorber energy consumption, the formation of stable carbamate, and also the formation of degradation products with carbonyl sulphide or oxygen-bearing gases, inability to remove mercaptans, vaporisation losses due to high vapour pressure, and more corrosive effects than many other alkanolamines, thus needing corrosion inhibitors when used in higher concentration (Davidson, 2007). Another major limitation of MEA is that its maximum CO₂ loading capacity based on stoichiometry is about 0.5 mol CO₂/mol amine whereas tertiary amines, such as MDEA, have an equilibrium CO₂ loading capacity that approaches 1 mol CO₂/mol amine (Supap and others, 2009).

A comprehensive study has been conducted to evaluate the contributions of SO₂ and O₂ to the degradation of MEA during CO₂ capture from power plant flue gas (Uyanga and Idem, 2007). The authors noted that information on the effects of SO₂, NO_x and fly ash on MEA degradation is scant. The aqueous MEA was contacted with gas mixtures that had SO₂ concentrations in the range 6–196 ppm. It was found that an

increase in the concentrations of SO₂ and O₂ in the gas phase and MEA in the liquid phase resulted in an increase in MEA degradation, whereas an increase in CO₂ loading in the liquid phase inhibited degradation. It was pointed out that, if CO₂ capture is carried out in the 'rich mode', whereby the lean MEA is still considerably loaded with CO₂ (for example, 0.25 mol CO₂/mol MEA) rather than the 'lean mode' but maintaining the cyclic capacity, CO₂ could actually act as a degradation inhibitor, because this reduces the amount of SO₂ and O₂ that could enter into the aqueous MEA solution to induce degradation. However, the detrimental corrosive effect of excess CO₂ in the system must be taken into account.

If the loaded amine solutions contact gas containing oxygen, the amine is subject to oxidative degradation. The degradation of MEA depends on temperature, initial MEA concentration, and oxygen concentration. However, MEA degradation does not follow a simple rate equation; the reaction order changes from a low to a high value as the concentration of MEA increases. Even though the experimental conditions allowed the reaction to be modelled as a homogeneous liquid-phase reaction, it has been concluded that MEA oxidative degradation itself is not an elementary reaction (Davidson, 2007). Studies have shown that the degradation products are oxidised fragments of the amine including NH₃, formate, acetate, and peroxides. Other studies have shown that the oxidative degradation is catalysed by the presence of various multivalent cations such as iron, copper, nickel and chromium (Goff and Rochelle, 2003). Dissolved iron will always be present in the absorber as a corrosion product and copper (II) salts are often added as corrosion inhibitors. The degradation rate of solutions with high CO₂ loadings increases with a rise in the concentration of dissolved iron. The addition of copper further catalyses the degradation rates. At a lower CO₂ loading, it was found that the degradation was faster (Davidson, 2007).

MEA undergoes degradation when exposed to coal-fired power plant flue gas composed of CO₂, fly ash, O₂, N₂, SO₂ and NO₂. Fly ash is the fine particulates in flue gas consisting of inorganic oxides, such as SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O and P₂O₅. The breakdown of the amine makes the performance of the amine in the absorption process deteriorate. Not only does it reduce the CO₂ removal capacity, but corrosion and foaming are induced due to the presence of degradation products. The prediction of the extent and rate of amine degradation is vital in the estimation of the exact amine make-up rate needed to maintain the CO₂ absorption capacity of the capture process. It is also essential to evaluate the kinetics of the degradation process since this provides the elements for a better understanding of the degradation mechanism during the CO₂ absorption operation. A kinetic evaluation helps in the formulation of a degradation prevention strategy (Supap and others, 2009).

Since O₂ is known to be deleterious to most amines, considerable efforts have been focused on the O₂-induced degradation of MEA. Although the kinetic studies based only on the presence of O₂ in the flue gas could provide useful rate information, their application could be limited. If these kinetic models were applied to a coal-based application in which an aqueous amine was used to remove CO₂, a less than accurate

degradation rate would result. This would be because of the presence of additional impurities such as SO₂ in the flue gas, that also induce degradation. Other variables such as dissolved iron, NO_x, corrosion inhibitors and fly ash could also be present in the CO₂ capture system. Supap and others (2009) adopted a step-wise procedure of adding one variable at a time to determine their effects on amine degradation. They incorporated the effects of SO₂ with the well-studied effects of O₂. When the effects of all the parameters that affect amine degradation have been elucidated separately, it will be possible to determine whether there are interactions between these parameters. The negative effects of SO₂ in amine degradation have been reported in terms of its capability of forming heat stable salts such as thiosulphates and sulphates which reduce the CO₂ absorption capacity (Supap and others, 2009). Rao and Rubin (2002) recommended that SO₂ concentration in the flue gas prior to being treated in a CO₂ capture unit should not exceed 10 ppm in order to avoid excessive loss as amine solvent. Supap and others (2009) used concentrations of SO₂ between 6 and 196 ppm, that can be observed in a typical flue gas stream after the power plant FGD process.

Even though present in small amounts, SO₂ can dissolve and be carried in the amine solution to the regeneration section of the capture process at which point a high temperature can trigger serious degradation reactions with the amine solvent. The objective of the study was to determine the potential for amine degradation as a function of degradation parameters such as temperature, and the concentrations of MEA, O₂, SO₂ and CO₂ based on the initial MEA degradation rate (Supap and others, 2009)

In the study, an initial rate of MEA degradation was used throughout, to evaluate the effect of all the degradation parameters (such as temperature and concentration of MEA, O₂, SO₂ and CO₂) as well as to determine the degradation kinetics. The intention was to show the tendency to degrade caused by different parameters. The concentration profile of each run was constructed by plotting MEA concentration and time to obtain the rate (Supap and others, 2009).

The effect of temperature was evaluated by using 5 kmol/m³ MEA and 100% O₂. The results are shown in Figure 1. The initial degradation rate of the run conducted at 393 K was higher than those carried out at the lower temperatures of 373 and 328 K. The initial rate of MEA degradation was also found to increase if temperature increased for the MEA-O₂-SO₂-H₂O degradation system (Supap and others, 2009).

An increase in initial O₂ concentration in the gas stream results in an increase in the initial MEA degradation rate. Supap and others (2009) showed the initial tendency of MEA to degrade if SO₂ is present in the flue gas stream, as seen in Figures 2 and 3. In an actual CO₂ removal unit, this SO₂-induced degradation effect is cumulative which eventually becomes troublesome after long exposure and repeated use of the amine (Supap and others, 2009).

The effect of CO₂ was also evaluated in the absence of SO₂ by using higher CO₂ loading values. CO₂ was found to be the only degradation component in which an increase in its

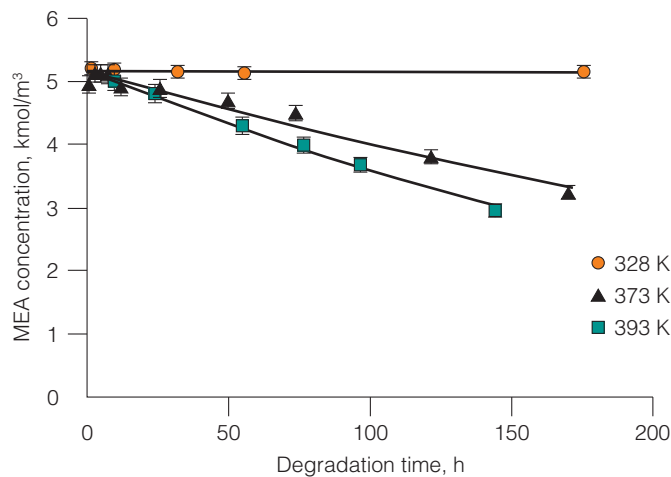


Figure 1 Effect of temperature using MEA concentration-time plot (5 kmol/m³ and 100% O₂) (Supap and others, 2009)

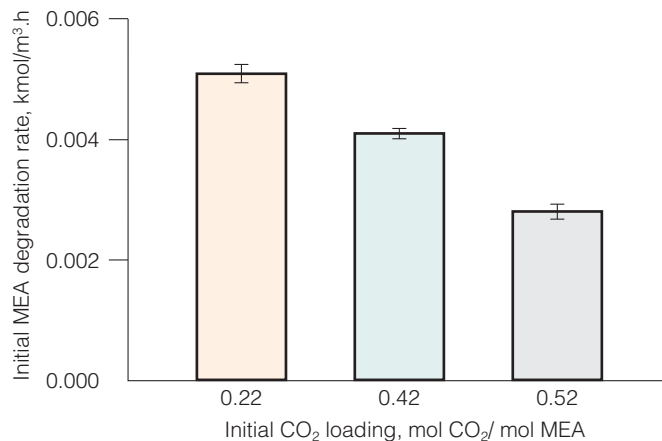


Figure 4 Evaluation of initial CO₂ concentration effect using initial rate of MEA degradation (3 kmol/m³ MEA, 100% O₂ and 373 K) (Supap and others, 2009)

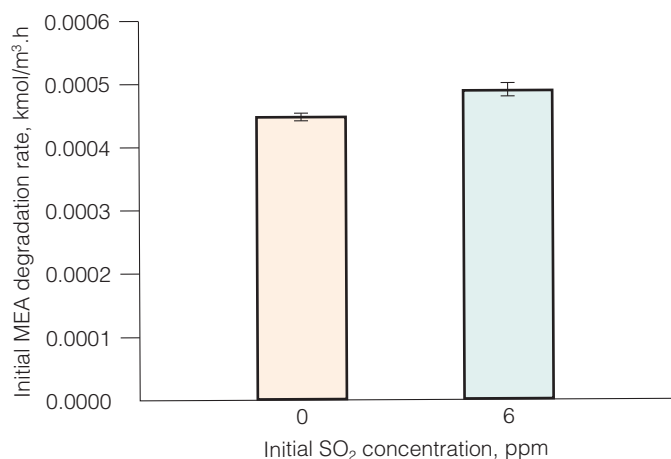


Figure 2 Effect of initial gas phase SO₂ concentration at 5 kmol/m³ using initial rate of MEA degradation (6% O₂ and 393 K) (Supap and others, 2009)

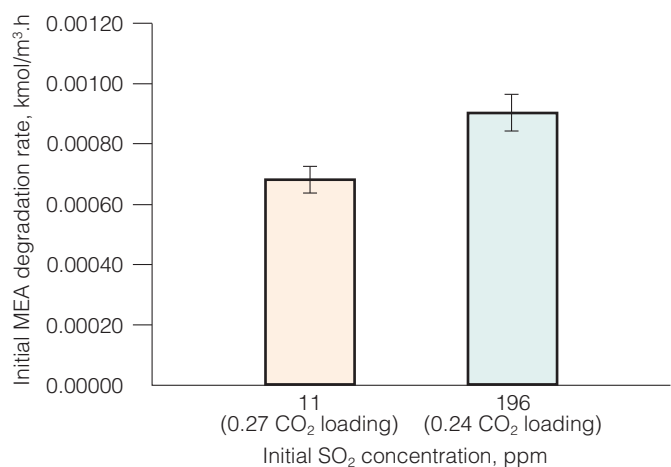


Figure 3 Effect of initial gas phase SO₂ concentration at 7 kmol/m³ with CO₂ using initial rate of MEA degradation (6% O₂ and 393 K) (Supap and others, 2009)

concentration resulted in a decrease in the initial MEA degradation rate. This is confirmed in Figure 4. The results imply that MEA has a tendency to degrade if the conditions used for CO₂ removal from fossil fuel derived flue gas streams in terms of temperature and the concentrations of MEA, O₂ and SO₂ are increased. However, the MEA degradation intensity could be reduced if the MEA contained some CO₂ in the solution prior to being used to treat the flue gas streams (Supap and others, 2009).

The experimental results showed that an increase in the initial concentrations of MEA, O₂ and SO₂ all lead to an increase in the initial MEA degradation rate. The inhibition effect of CO₂ could be simply explained on the basis of the salting out effect, whereby CO₂ goes into the MEA solution in preference to O₂ and SO₂. The degradation of MEA in the presence of O₂, SO₂ and CO₂ proceeds stoichiometrically. For SO₂, although it is present in a smaller concentration compared to MEA, its degradation is not considered catalytic since SO₂ was consumed during the degradation process, forming sulphur-containing products with MEA. These include heat stable salts (Supap and others, 2009).

Goff and Rochelle (2003) tested various degradation inhibitors and found that (ethylenedinitrilo)-tetra-acetic acid (EDTA) was the only compound found to be effective at inhibiting oxidative degradation. EDTA added at a ratio of as low as 1:1 with the dissolved metals decreases the degradation rates by half. EDTA was also shown to be more effective at inhibiting the degradation catalysed by copper than iron (Goff and Rochelle, 2003).

For the Kerr-McGee/ABB Lummus Crest Technology, SO₂-removal is typically not justified for SO₂ levels below 50 ppm (IPCC, 2005).

2.2.2 Econamine

Econamine FGSM (EFG) is a Fluor proprietary amine-based

technology for large-scale post-combustion CO₂ capture. MEA is the basic ingredient of the solvent. However, the solvent formulation is designed to recover CO₂ from low pressure, oxygen-containing streams. The EFG process has been enhanced and is now offered as Econamine FG PlusSM (EFG+). The advanced features of the EFG+ technology include:

- improved solvent formulation;
- absorber intercooling;
- lean vapour compression configuration;
- advanced reclaiming technologies;
- heat integration with the power plant.

Fluor has assessed that it is more cost-effective to remove heat stable salt precursors before the flue gas encounters the solvent for their EFG amine-based technology. The pre-treatment step to remove heat stable salt forming precursors is part of Fluor's process design strategy for coal-fired power plants (Reddy and others, 2008).

A maximum of 10 ppm SO₂ content is generally set as the feed gas specification for the Fluor Daniel Econamine FG process. This can be met by using alkaline salt solutions in a spray scrubber. An SO₂ scrubber might also double as a direct contact cooler to cool down the flue gas (IPCC, 2005).

2.2.3 KS-1

KS-1 is a sterically hindered amine solvent developed by KEPCO/MHI (Mitsubishi Heavy Industries). It is considered by Yagi and others (2005) to be a superior solvent to MEA as it absorbs more CO₂ than MEA on a molar ratio basis, due to its hindered amine structure that allows for higher loading. Thus, the KS-1 solvent circulation rate is about 60% of that of the MEA process. The exothermic reaction during absorption is 20% lower than that of MEA, hence its reverse reaction during regeneration has a lower heat requirement. A combination of lower solvent circulation and reaction heat requirement results in a significant reduction of energy consumption compared to MEA (Yagi and others, 2005).

It is well known that degradation products in amine solvents cause severe corrosion. However KS-1 solvent is resistant to degradation by oxygen. Hence, the oxygen tolerant property of KS-1 solvent means that corrosion inhibitors do not have to be used. Corrosion inhibitors often obstruct the absorption reaction and so their absence is another advantage over the MEA process (Yagi and others, 2005).

A 1 tCO₂/d pilot plant has been constructed in the MHI Hiroshima R&D centre to demonstrate CO₂ capture from coal fired flue gas and to carry out various tests for the treatment of impurities. The plant uses KS-1 solvent and special proprietary equipment (Iijima and others, 2005; Yagi and others, 2005). The plant incorporates countermeasures that can remove SO_x, particulates and other impurities, prior to CO₂ capture. Demonstration began in July 2006 (Iijima and others, 2007). The specifics of the plant are listed in Table 1.

The influence of impurities in the flue gas are summarised in Table 2.

SO_x promotes the degradation of the solvent. An FGD section using caustic soda is installed to reduce the concentration of the SO_x introduced into the absorber. So it is necessary to confirm the removal ratio of SO_x, to verify the desulphurisation efficiency in the FGD section. The gas that passes through the FGD section may contain trace amounts of SO_x. The trace level SO_x may then accumulate in the solvent to produce heat stable salts (Iijima and others, 2007). The optimum concentration of SO_x should be determined by evaluating both FGD and the cost of reclamation of removing sufficient SO₂. The concentration of SO₂ in the FGD outlet would have an influence on the cost of the FGD. If a high rate of SO₂ removal is required, the limestone gypsum process is used, rather than the caustic soda process (Ohishi and others, 2006). Recent references to the twin tower type MHI double contact flow scrubber show that it achieves a 99.9% desulphurisation efficiency. The use of this limestone gypsum process FGD, rather than the deep FGD provided by the caustic soda process, achieves the high SO₂ removal required for CO₂ recovery. In addition, the economics are improved by eliminating a process (Ohishi and others, 2006).

The CO₂ recovery system incorporates a rinse tower for a high level of SO₂ removal using caustic soda, a cooling tower for cooling the cleaned flue gas, an absorbing tower for capturing CO₂ with the KS-1 solvent, and a regenerating tower for stripping CO₂ by heating the solvent absorbing the CO₂ with steam (Davidson, 2007). The regeneration of the KS-1 solvent can be carried out at low pressures and temperatures of 110–120°C. In the pilot test, Australian coal was used and two tests were run, one with <1 ppm (dry) SO₂ at the inlet of the CO₂ absorber and the other with 30 ppm SO₂, other conditions remained the same.

The higher level of SO₂ had no apparent effect on the CO₂ recovery performance. On the other hand, although the concentration of heat stable salts, particularly sulphates, in the solvent increased with the higher concentration of SO₂, it was as low as 1 wt% of the KS-1 or less. The purity of the CO₂ captured from the flue gas was about 99.8% (dry). The major impurities were nitrogen (0.14%) and oxygen (0.04%). SO₂ was not detected in the captured CO₂ even in the high SO₂ case. No heavy metals were detected.

Among the components of NO_x, only NO₂ is absorbed. It reacts with the absorbent to form the heat stable salt (NO₂⁻ and NO₃⁻) which is also regenerated by the caustic soda during the reclamation. Other effects of NO_x on CO₂ recovery are to be examined. The influence of NO_x on the CO₂ recovery plant becomes negligible if SCR is installed (Ohishi and others, 2006).

The accumulation of particulates may lead to scaling of equipment, plugging of strainers, and other undesirable impacts. Equipment design needs to accommodate the potential effects of particulates. Particulate accumulation in the solvent may increase the foaming tendency of the solvent. If this happens, flooding occurs more readily in the regenerator and absorber, which hinders the stable operation of the CO₂ recovery plant (Iijima and others, 2007). Thus, it is necessary to confirm the interaction between the amount of

Table 1 Specifications of CO₂ recovery demonstration plant (Iijima and others, 2007)

Items	Parameters
Installation location	Within Matsushima Thermal Power Station, owned and operated by J-POWER
Flue gas source	Flue gas coal-fired boiler
Amount of flue gas to be treated	1750 m ³ /h
CO ₂ recovery efficiency	90%
CO ₂ recovery capacity	Planned value: 9.5 t/d (maximum 10 t/d)
CO ₂ concentration	14.1 vol%
Other impurities	Particulates, SO _x , NO _x and others
Solvent	KS-1 solvent

Table 2 Influence of impurities in the coal-fired flue gas on CO₂ recovery plant (Ohishi and others, 2006)

Flue gas impurities	Influence	Countermeasures
SO _x	Frequent reclaiming*	FGD
NO _x	Frequent reclaiming*	DeNO _x (SCR)
Particulates	Disturbs the stable operation	Particulate removal in the solvent system
Halogens (HC, HF)	Corrosion and scaling	FGD and pretreatment
Trace elements	Not clear	Particulate removal system FGD

* This is the operation to remove the heat stable salt accumulated in the CO₂ absorber. Part of the lean solvent is sent to the reclaiming, and chemicals and the steam are added to minimise the residue discharges. Reclaiming waste is one product and recovered vapour is returned to the solvent regeneration unit

particulates in the solvent, the foaming tendency and the flooding phenomenon.

The usual concentration of particulates at the FGD outlet for a coal-fired flue gas is about 10 mg/m³. About half of it can be expected to be removed by the CO₂ recovery plant, which means that particulates accumulate gradually in the absorbent. Thus, a filter system to remove the particulates directly from the absorbent is included in the CO₂ recovery plant. The influence of particulates and the potential hindrance of blocking the cooling tower was monitored and reported. No adverse experience was reported during the test (Ohishi and others, 2006).

At the outlet of the FGD facility, halogen concentration is normally 1 ppm or less, which is removed subsequently by the caustic soda FGD and the cooler. This results in a halogen concentration of less than 0.1 ppm at the inlet of the CO₂ absorber. During the 3000 h of operation in the 1 tCO₂/d pilot test, the halogen concentration at the inlet of the CO₂ absorber was less than 0.1 ppm and the accumulation rate in the system could not be detected due to insufficient operating time. While carbon steel is the primary construction material for a CO₂ recovery pilot plant, the accumulation rate of halogens inside the plant should be checked to determine if a reclaiming operation is required to remove the halogens. The entrained mist also brings halogens to the CO₂ absorber, so the mist eliminator of the

pretreatment facility should be designed to minimise entrainment. The performance of halogen removal in the cooling tower during long-term continuous operation should be monitored, as should the rate of accumulation in the CO₂ absorber. The influence of trace elements on the CO₂ recovery process is not clear. After completion of 3000 h of continuous operation, the concentration of trace elements is expected to be in the order of 10–100 ppm. The influence of the trace elements will then be checked (Ohishi and others, 2006).

In the MHI plant, the installation of pretreatment equipment enabled stable operation over a long period (4000 h) with no unexpected problems. Iijima and others (2007) demonstrated that impurities from the coal-fired boilers can be treated by installing a flue gas cooler with caustic soda FGD and flue gas water washing functions as a pretreatment process. They also confirmed that CO₂ can be absorbed stably and regenerated by these pretreatments and filters. The following results were achieved (Iijima and others, 2007):

- Operation for 4000 h and a CO₂ recovery performance equivalent to, or better than the expected performance;
- Data on the capacity of the pretreatment equipment to remove particulates and the behaviour of the particulates in the solvent system;
- Data on the absorption ratios of SO_x and NO_x in the respective sections, and their respective behaviours;
- Quantitative data on the solvent loss.

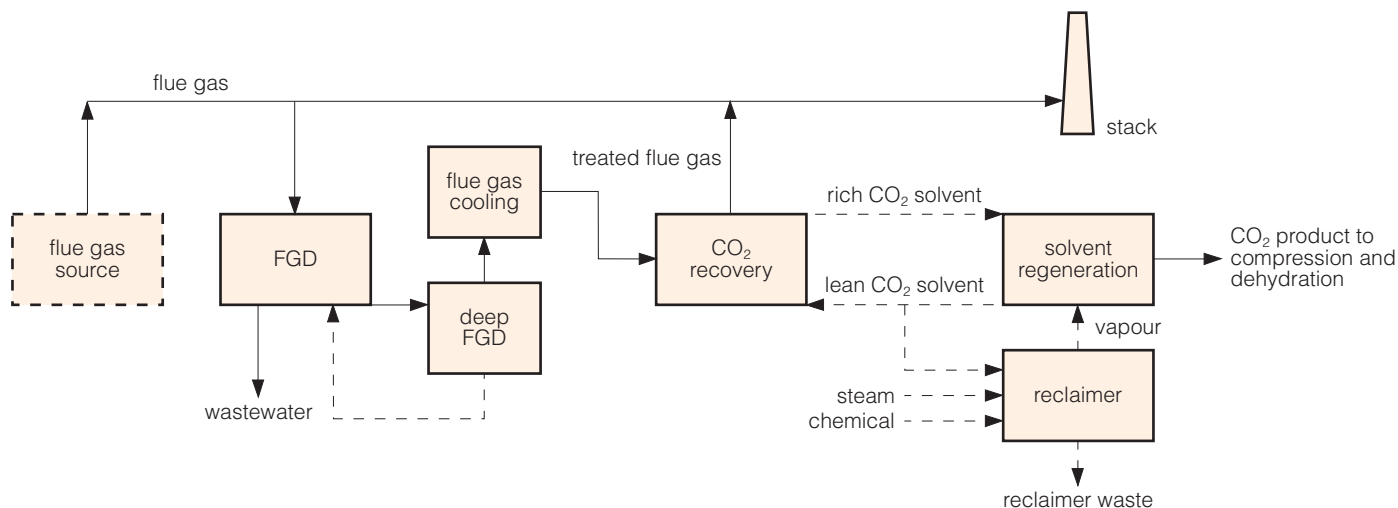


Figure 5 Typical block flow diagram for pre-treatment facility and CO₂ recovery plant (Ohishi and others, 2006)

Table 3 Characteristics to be measured and the items to evaluate for design application (Ohishi and others, 2006)		
Flue gas component	Items to be confirmed	Method of evaluation for application to design
SO _x	The optimum SO ₂ concentration at the outlet of the pretreatment system	<ul style="list-style-type: none"> – Degradation rate of CO₂ absorbent – Removal of heat stable salts including impurities by the reclamation operation – Particulates removal performance of the filter installed inside of the CO₂ recovery plant – Check corrosion of the equipment – Particulate accumulation rate inside the CO₂ recovery plant
NO _x	Confirmation of the effect of NO _x on CO ₂ recovery process during the long period operation	
Particulates	Behaviour of particulates after passing ESP and FGD inside the CO ₂ recovery plant	
Halogens and trace elements	Behaviour inside the CO ₂ recovery plant	

Figure 5 shows a typical block flow diagram for a flue gas treatment facility and CO₂ recovery plant (Ohishi and others, 2006)

Table 3 shows the design items to be confirmed for designing a CO₂ recovery plant.

Clarification of the optimum concentrations of impurities at the CO₂ absorber inlet will make it possible to combine or integrate the MHI’s flue gas treatment technology to improve the efficiency of the CO₂ recovery plant. Optimum configuration of the pretreatment system would improve the reliability of the CO₂ recovery plant.

2.2.4 Improving solvents

Currently available solvents for the removal of CO₂ from flue gases do not fulfil all the demands of post-combustion capture technology. At present, the state-of-the-art is the use of MEA to capture CO₂ from the flue gas. However, this process was developed originally for the production of CO₂ and not for the capture of CO₂ for CCS purposes (Moser and others, 2009).

There are several ways in which an ideal post-combustion capture process could improve upon a generic MEA capture process. Improvements are possible for the solvent itself, and also for the process configuration. Starting with the characteristics of the solvent, the following aspects are of most interest (Moser and others, 2009):

- low regeneration duty;
- high stability against oxygen and thermal stress;
- low vapour pressure to reduce solvent losses;
- high cyclic capacity to reduce the solvent circulation rate;
- high reactivity to CO₂/fast reaction kinetics;
- uncritical safety data (such as non-toxic, high flash and ignition point);
- good availability and low cost.

Puxty and others (2009) screened 76 different amines for their ability to absorb CO₂. They included primary, secondary and tertiary amines; alkanolamines; polyamines of a mixed or single type; cyclic and aromatic amines; amino acids; and sterically free and hindered amines. Of the 76 amines tested, seven were found to have an outstanding CO₂ absorption capacity compared to modelling predictions. Of the four primary and secondary amines showing outstanding

absorption capacity, all showed initial absorption rates similar to MEA. More testing is required to evaluate further these amines as candidate molecules for large-scale CO₂ capture. Detailed information is required on CO₂ absorption rate as a function of temperature, amine concentration and CO₂ loading; the energy requirement of, and their capacity to, capture cyclically and release CO₂; their resistance to oxidative and thermal degradation; their corrosiveness; their resistance to degradation by flue gas impurities (SO_x, NO_x and trace elements); and their toxicity and the toxicity of degradation products.

Puxty and others (2009) conclude from their work that there is still significant scope for improvement in the use of aqueous amine solutions for CO₂ capture by chemical absorption. However, it is also clear that there is a lack of understanding about the chemistry involved. Understanding how the amines that show outstanding CO₂ absorption capacities do so is fundamental to achieving an optimal formulation that maximises efficiency and minimises cost and sustainability for post-combustion capture on an industrial scale. Existing understanding of the reaction pathways is unable to account for these characteristics.

A study to improve post-combustion capture technology has been reported by Moser and others (2009). Two factors characterising the performance of the process were defined as necessary conditions for a future application of post-combustion technology: the loss of efficiency caused by the integration of the post-combustion capture technology should be less than 10 percentage points (including CO₂ compression for pipeline transport to the storage site) and the CO₂ avoidance costs should be less than 30 €/tCO₂. At present neither criteria are fulfilled by the post-combustion capture technology, particularly because of the large, unpressurised flue gas stream of a coal-fired power station that has to be treated and due to its special composition that differs from CO₂-rich gas streams. However, the feasibility study showed that both general goals could be achieved by an optimised post-combustion capture process based on a new scrubbing solvent. Thus new solvents were pre-selected and pre-tested.

Based on these needs, a solvent screening programme has been started by BASF to evaluate different amines in the BASF portfolio for their potential use as a solvent for a post-combustion process (Moser and others, 2009). About 400 substances were screened and about 70 potential candidates were identified and tested in the next step. Based on these investigations, it has become clear that some of the demands for such a solvent are mutually exclusive. Often high reactivity and fast reaction kinetics can be found in combination with a high regeneration duty. Stable solvents are less reactive than more unstable solvents. Thus, it is expected that a potential solvent will consist of more than one active component. The combining of solvents will maximise the advantages and minimise the disadvantages of the component mixture (Moser and others, 2009).

2.2.5 Cansolv process

The Cansolv process was originally designed for SO₂

scrubbing using a proprietary amine scrubber. The solvent, called Absorbent DC101™ is based on tertiary amines, and probably includes a promoter to yield sufficient absorption rates to be used for low pressure flue gas streams. This process can be applied to oxidising environments with the use of oxidation inhibitors, and where limited concentrations of oxidised sulphur exist. It is claimed that this process can also remove simultaneously other acidic components and particulate materials, such as SO_x and NO_x. Although it has not been used on coal-fired plant flue gas, it has been proposed that the process is capable of integrating SO₂ regeneration with CO₂ regeneration since the same solvent can be used for both gases (Hakka, 2007; Davidson, 2007). The solvent is stable to SO₂ and the process eliminates the need for caustic polishing prior to CO₂ capture. Two demonstration plants have been built for the Cansolv CO₂ capture system. One is in Virginia, USA, for the capture of CO₂ from the flue gas of a coal-fired boiler. No commercial plants have yet been built (Herzog and others, 2009).

2.2.6 CO2CRC H3 capture project

The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) is a joint venture linking participants from Australian and global industry, universities and other research bodies from Australia and New Zealand, as well as Australian Commonwealth, state and international government agencies. One of the main activities of CO2CRC in 2009 was the H3 Postcombustion Capture Project (Hooper, 2009).

The launch of the H3 Capture Project coincided with that of Australia's largest post-combustion capture solvent plant at the International Power, Hazelwood power station. The International Power CO₂ capture plant operates at the design capture rate of 25 tCO₂/d. The purpose of the CO2CRC H3 capture project is to understand better the performance of various CO₂ capture technologies with Australian brown coal flue gases and to evaluate the performance of three technologies for larger scale capture. The technologies that are being evaluated are (Hooper, 2009):

- solvent absorption, which is used on the International Power CO₂ capture plant;
- membrane separation, which can be integrated with solvent systems;
- vacuum swing adsorption which captures CO₂ using fixed beds of solid material and releases it through pressure changes.

One of the aims of the project is to determine the effects of the operating parameters of CO₂ concentration, moisture content, SO_x and NO_x concentration and fly ash properties on the behaviour of solvent systems and other novel separation technologies (Hooper, 2009). The H3 Capture Project at the Hazelwood power station is studying solvents for CO₂ capture. Part of the project is to examine the interaction between the solvent system and impurities present in the flue gas, including SO_x and NO_x (Hooper, 2009).

Evaluation of initial test results is under way. CO2CRC plans to run all three capture rigs under continuous industrial

conditions using post-combustion flue gas from the International Power Hazelwood station, collecting data and evaluating it. As well as the plant based tests, there will be ongoing laboratory work feeding into the programme with evaluation of test work and reformulation of tests as the programme progresses. Engineering studies, including heat/process integration and techno-economic evaluations, will continue throughout the programme and will contribute to the final decision on the technology that will be scaled up in the future (Hooper, 2009).

2.3 Removal of impurities

Technologies are available for the capture of most pollutants released from coal-fired power plants. Proven processes are routinely used to remove SO₂, NO_x, HCl, HF, particulates and mercury. Dry lime scrubbing (known as dry scrubbing) and wet lime or limestone scrubbing (wet FGD) are commonly used for the removal of SO₂, HCl and HF from flue gas. The use of various additives can enhance the removal process for limestone, although wet FGD systems can remove around 99% of the SO₂ without the use of additives (Reddy and others, 2008).

Even with the deployment of high efficiency pollutant removal technologies, there are still residual quantities of SO₂ and H₂SO₄, ammonia, particulates, and other trace constituents that remain in the flue gas entering the carbon capture system. However, if the CO₂ is removed by absorption solvent, this will also remove the majority of these pollutants. Thus, although there will be a significant reduction in power plant emissions, the pollutants in the flue gas increase the complexity and operating cost of the CO₂ capture process regardless of the technology (Reddy and others, 2008).

Careful attention must be paid to fly ash and soot present in the flue gas, as they might plug the absorber if the levels of these contaminants are too high. Often the requirements of other flue gas treatments are such that precautions have already been taken. In the case of CO₂ recovery from a coal-fired boiler flue gas, the plant typically has to be equipped with a deNO_x unit, an electrostatic precipitator or a bag house filter and a deSO_x or FGD unit as part of the environmental protection requirement of the power plant facilities. In some cases, these environmental protection facilities are not enough to carry out deep SO_x removal down to the 1–2 ppm level sometimes needed to minimise solvent consumption and its reclamation from sticking of solvent wastes on reclaimer tube surfaces (IPCC, 2005).

In the EU, a new coal-fired power plant (one without CO₂ capture) would be designed to meet the requirements of the revised Large Combustion Plant Directive (LCPD) 2001/80/EC which requires the emissions to air of SO₂, NO_x and particulates to be limited. These are normally enforced in terms of Emission Limit Values (ELV) which are:

- SO₂ of 200 mg/m³ at 6% oxygen dry;
- NO_x of 200 mg/m³ at 6% oxygen dry;
- Particulates of 30 mg/m³ at 6% oxygen dry.

Plants designed to these standards would be fitted with SCR

plant for NO_x control, electrostatic precipitators for particulates control and FGD plant. These were adopted as the starting points by Féraud and others (2006) for assessing the improved performance requirements and increased costs when designing for CO₂ capture.

In the USA there are national emission standards for SO₂, NO_x and particulate matter set in the New Source Performance Standards. There are various standards, for fossil fuel fired steam generators, for electric utility steam generating units and for industrial-commercial-institutional steam generating units, for example. For more detail, see the IEA Clean Coal Centre report by Zhu (2010). The standard for fossil fuel fired steam generators for SO₂ states that affected facilities should not emit any gases that contain SO₂ in excess of 520 ng/J heat input (1.2 pounds per million British thermal units (lb/MMBtu)) derived from solid fossil fuel. The limits for NO_x range between 260 and 340 ng/J heat input (0.60–0.80 lb/MMBtu). The limit is 43 ng/J heat input (0.10 lb/MMBtu) for particulates.

In Japan, regulatory measures for air pollutants emitted from industry are set in the form of emission/discharge standard K value control that limits the amount of flue gas emissions, total amount control that limits the total amount of an air pollutant emitted into the atmosphere, and ambient air quality standard that limits the concentration of air pollutants in ambient atmosphere. The allowable discharge amount of SO₂ is limited on the basis of the value estimated from the constant K that is determined at every designated area, and the effective stack height (Zhu, 2010).

In addition to the base case for SO₂ emissions of 200 mg/m³ at 6% O₂ dry (70 ppmv at 6% O₂ dry), Féraud and others (2006) set two lower SO₂ concentration limits for the purposes of their study:

- 50 mg/m³ (18 ppm);
- 10 mg/m³ (3.5 ppm).

This value of 10 mg/m³ (3.5 ppmv) is lower than the 10 ppmv suggested by Fluor, but slightly higher than the 1–2 ppmv discussed by MHI. If an emission level lower than 3.5 ppm were required, this could probably be achieved by boosting the FGD performance with an organic acid additive (Féraud and others, 2006).

2.3.1 Heat stable salts

For post-combustion capture using amines, it is generally recognised that the flue gas must contain very low levels of SO₂ and NO_x. The preferred SO₂ concentration is usually set at between 1 ppmv and 10 ppmv. This means that post-combustion CO₂ capture on coal-fired power plants requires upstream FGD and deNO_x (Davidson, 2007).

The problem with amines is that they react with more acidic contaminants in the flue gas such as SO₂, SO₃ and NO₂, to form heat stable salts that cannot be broken down in the stripper. Despite a degree of amine recovery with sodium hydroxide in the reclaimer, there is still a net loss of amine through the entry of these acid gases into the amine scrubber.

As a result of this, two of the major suppliers of CO₂ capture plant recommend limits for the concentrations of these contaminants in the flue gas entering the amine scrubber. For example, Fluor have suggested a SO_x limit of 10 ppmv and a NO₂ limit of 20 ppmv. Mitsubishi Heavy Industries (MHI) have discussed a SO_x limit of 1–2 ppmv and a low but undefined NO₂ limit. Féraud and others (2006) investigated the feasibility and costs of reducing the concentrations of SO₂ and NO₂ in flue gases down to, or approaching, the levels required by the amine scrubbing process suppliers.

The decomposition of amines creates effluents, particularly ammonia and heat-stable salts. Rao and Rubin (2002) have estimated these emissions for an MEA-based process based on limited data. In such processes, heat stable salts are removed from the solution in a reclaimer and are disposed of using normal health and safety practices. Heat stable salts are solvent decomposition products, and include corrosion products for example. In some cases, these reclaimer bottoms may be classified as a hazardous waste, requiring special handling. Also, a particle filter and carbon filter is normally installed in the solvent circuit to remove byproducts. Finally, some solvent material is lost to the environment through evaporation and carry over in the absorber, which is accounted for in the solvent consumption. The amount of spent sorbent has been estimated by Rubin and others (2005) at 4.05 kg/MWh for a 492 MWe PC plant with a net plant efficiency of 29.9% (HHV). It is expected that acid gases other than CO₂, which are still present in the flue gas (SO_x and NO₂) will also be absorbed in the solution. This will lower the concentration of these components further and even the net emissions in some cases, depending on the amount of additional energy use for CO₂ capture. As SO₂ removal prior to CO₂ removal is likely in coal-fired plants, this will lead to the production of a waste or byproduct stream containing gypsum and water from the FGD unit (IPCC, 2005).

2.4 FGD

Work has been undertaken to determine whether an FGD plant could be designed to achieve SO_x emissions close to or lower than the concentration limits required by the amine scrubber suppliers; and if so, to assess the increases in capital and operating costs associated with raising their performances beyond those required by current environmental legislation as defined by the revised Large Combustion Plants Directive (LCPD) 2001/80/EC (Féraud and others, 2006).

The limestone gypsum wet scrubbing process is the most widely used FGD process. In this process, the flue gas is treated with ground limestone (calcium carbonate) slurry in order to remove and neutralise SO₂ (Nalbandian, 2004). The final product is calcium sulphate dihydrate (Féraud and others, 2006). It is capable of high SO₂ removal efficiencies, even with fairly high sulphur fuels, consumes a cheap and widely available sorbent and produces a by-product that is normally saleable.

Figure 6 shows a modern power plant that is retrofitted with a CO₂ capture unit. The new equipment added in the flue gas path for carbon capture includes a polishing FGD or direct contact cooler with a scrubbing capability, a blower and a CO₂ absorber (Reddy and others, 2008). There are three polishing FGD concepts:

- Adding a polishing section within an existing FGD. For this option, some of the FGD internals can be removed and replaced with the new internals required to implement a polishing reagent circuit. These modifications would probably be less expensive than adding a new polishing scrubber. However, the FGD modifications would normally require a longer outage than is required for routine maintenance for an FGD

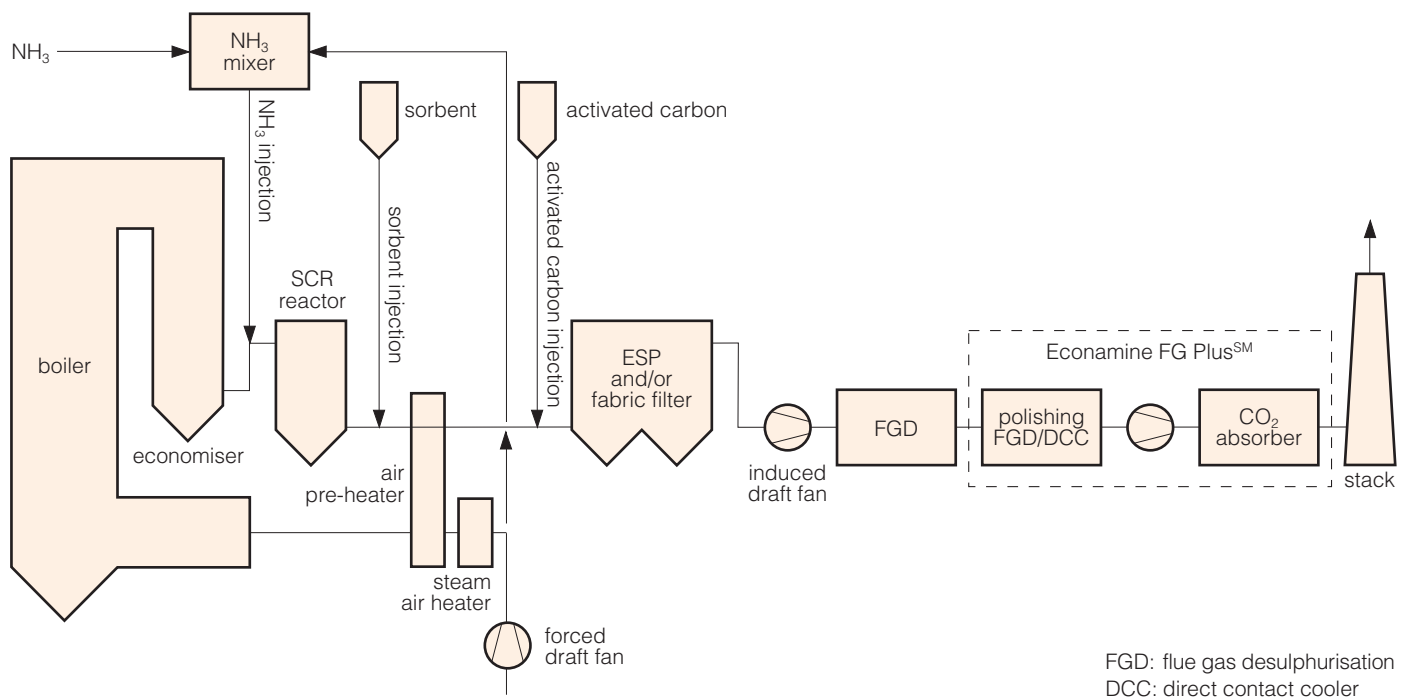


Figure 6 Power plant with CO₂ capture (Reddy and others, 2008)

system. Any work of this nature would require careful construction planning and co-ordination. In many cases, there might not be enough room to install the new internals that are required for polishing scrubbing.

- Adding a new (secondary) polishing scrubber. This option could have a higher capital cost but does not require a lengthy shutdown of the power plant.
- Adding scrubbing capability into the direct contact cooler. As the temperature of the flue gas entering the absorber is decreased, the efficiency of the Econamine FG+ (EFG+) process increases. The EFG+ process is a Fluor proprietary amine-based technology. The direct contact cooler is included in the EFG+ flowsheet to sub-cool the flue gas to a temperature below the adiabatic saturation temperature. The direct contact cooler can be designed to achieve SO_x removal in addition to flue gas cooling. A polishing scrubber can be added to the direct contact cooler to reduce SO_x levels further.

2.4.1 CASTOR project

The Integrated Project CASTOR (from CO₂ Capture to Storage) funded by the European Commission in FP6 is targeted to achieve the following (Feron and others, 2007):

- a major reduction in post-combustion capture costs, from 50–60 €/tCO₂ down to 20–30 €/tCO₂;
- to advance general acceptance of the overall concept;
- to start the development of an integrated strategy connecting capture, transport and storage options for Europe.

Two thirds of the overall project effort is directed to developing novel solvent technologies for post-combustion capture of CO₂ and to validate these on a credible scale using real flue gases (Feron and others, 2007).

A CASTOR pilot plant has been built to fulfil two purposes:

- to demonstrate long-term continuous steady operation of solvent processes on a bituminous coal-based flue gas at a European power plant on a pilot plant industrial scale;
- to make available a test facility for standard and novel solvents.

The CO₂ absorption pilot plant is at the Esbjerg power plant,

on the west coast of Denmark. It is owned and operated by Dong Energy. It is a 400 MW pulverised coal-fired power plant equipped with FGD (wet limestone scrubber) and deNO_x (high dust SCR). The pilot plant operates on a slip stream of the flue gas, taken after the FGD and deNO_x plants.

The test facility, which launched in March 2006, has a capacity of 1 tCO₂/h. It uses a 30% aqueous MEA solution, but other solvents will be tested. The key design and performance figures for the pilot plant are shown in Table 4. The flue gas purity criteria were defined in order to avoid excessive solvent degradation or other adverse impacts on the pilot plant operation, such as foaming and fouling. In daily practice, the NO_x level is allowed to rise significantly above 65 ppm, whereas high SO₂ concentrations will cause plant shutdown.

The flue gas enters the absorber tower at the bottom in a counter-current flow with the solvent. The CO₂ content of the absorber inlet and outlet is continuously monitored by CO₂ analysers. The rich solvent from the absorber is pumped through two mechanical filters in series and a plate heat exchanger before being fed to the stripper. A steam driven reboiler supplies the heat input to the stripper. The steam is supplied by the power plant and the reboiler temperature controls the steam flow. The CO₂ gas and vapours from the stripper pass through a water-cooled condenser and gas/liquid separator. The condensate from the separator is returned to the stripper wash section and the resultant gas, which is essentially pure CO₂ saturated with water, is returned to the power plant flue gas duct. The CO₂ product is monitored online. The regenerated solvent from the stripper is cooled to its final set point temperature by a water-cooler after it has been heat exchanged with the rich solvent. A slip stream of about 10% of the solvent flow is passed through a carbon filter. Part of the pilot plant is a reclaiming vessel where the heat stable salts can be concentrated and removed (Feron and others, 2007).

The first series of 1000 hours operation with a 30% MEA solution was aimed at gathering information on the effect of SO₂ on the overall process performance, determining the pressure drop over the packing materials and determining the CO₂ product quality.

Table 4 Design specifications for CASTOR pilot plant in Esbjerg (Feron and others, 2007)

Parameter	Design value
Flue gas capacity	5000 m ³ /h ≈0.5% of Esbjerg flue gas flow
CO ₂ production (at 12 vol% CO ₂)	1000 kg/h
Absorption degree	90%
Maximum solvent flow	40 m ³ /h
Maximum reboiler steam flow	2500 kg/h (0.35 MPa)
Maximum stripper pressure	0.2 MPa
Flue gas conditions	47°C (saturated), <10 ppm SO ₂ , <65 ppm NO _x , <10 mg/m ³ dust

Table 5 CASTOR base case coal-fired plants and fuels (Féraud and others, 2006)

Power plant case	600 MWe	1000 MWe	380 MWe
Flue gas discharge (temperature, C)	Stack (85)	Cooling tower	Cooling tower
Reheat device	Gas/gas reheater	No reheat	No reheat
Coal	Bituminous	Pre-dried lignite	Lignite
S, %	0.52	1.1	0.94
Moisture, %	8	12	36.8
Net calorific value, MJ/kg	25.174	19.7	7.9

Three boiler/fuel base cases have been established in the CASTOR project and are summarised in Table 5 (Féraud and others, 2006).

The limestone gypsum FGD process was adopted for study. Two designs of limestone gypsum plant were considered by Féraud and others (2006) for the FGD plant design for CASTOR: the conventional open spray tower and Alstom's pumpless scrubber, Flowpac, which is capable of high SO₂ removal efficiency.

SO₃ is produced from the oxidation of SO₂ in bituminous coal and lignite-fired boilers. For all three fuel cases evaluated, as a worst case Féraud and others (2006) assumed 1% conversion of SO₂ to SO₃ in the boiler and 1% conversion in the SCR plant, giving 2% at the FGD inlet. Wet FGD plants are poor at the removal of SO₃, which converts to sulphuric acid mist in the absorber. A conservative estimate could be as low as 30% in an open spray tower (Féraud and others, 2006).

Ultimately there may be a balance to be struck between the costs incurred through allowing a certain amount of SO₂ and NO₂ to enter the amine scrubber, and the increased equipment costs incurred through reducing the flow of these compounds into the amine scrubber.

The path of the flue gas is described in this paragraph. The SO₂ absorption system receives flue gas from the induced draft fans. In the 600 MW bituminous coal fired case, the gas is directed via the booster fan to the gas-to-gas heat exchanger where the gas is cooled down before entering the absorber. The treated flue gas from the FGD absorber then passes through the amine scrubber and is fed back through the gas-to-gas heat exchanger to raise the gas temperature before emission from the stack. In the 1000 MW and 380 MW lignite fired cases, the gas is still drawn through the booster fan but there is no gas-to-gas heat exchanger, because the flue gas from the FGD absorber and amine scrubber is discharged through the station cooling tower.

The open spray tower absorber is a vertical, countercurrent spray tower. The flue gas enters the tower through the inlet duct and is immediately quenched as it travels upward countercurrent to a continuous spray of process slurry produced by several spray banks. The recycled slurry falls from the spray zone into the reaction tank where the liquid phase chemical reactions occur (Féraud and others, 2006).

In the Flowpac turbulent bed absorber (or pumpless scrubber) the flue gas is forced through holes in a tray and a turbulent bed of slurry above it. The absorption of SO₂ takes place while the gas is bubbling through the slurry. The slurry is then moved from the sump to the turbulent bed. The Flowpac at Karlshamn in Sweden has shown that low emissions of SO₂ can be achieved and that the collection efficiency of SO₃ and particulate matter is high. However, with low sulphur fuels it can consume more electrical power than an open spray tower, giving it higher operating costs (Féraud and others, 2006).

Féraud and others (2006) evaluated nine abatement cases, and for each they selected the absorber type that would offer the lowest through life cost. They are presented in Table 6. SO₃ emissions are based on 30% removal in an open spray tower and 60% in a pumpless scrubber. The results indicate that the lowest required target of 10 mg/m³ of SO₂ abatement can be achieved, so those cases are of the most interest in terms of flue contaminant levels (Féraud and others, 2006).

In the 600 MW and 1000 MW cases, the total SO_x levels of 6.0 ppmv and 10.3 ppmv are below or roughly equal to the 10 ppmv target suggested by Fluor but are above the 1–2 ppmv discussed by MHI. In the 380 MW case the total SO_x level of 14.3 ppmv wet at the FGD absorber outlet exceeds by almost 50% the 10 ppmv target suggested by Fluor and is well above the 1–2 ppmv set by MHI. The Fluor target has been exceeded because of the high SO₃ level leaving the FGD plant. This level of SO_x emissions may also prove to be economically acceptable to suppliers and plant operators, if, for example, polishing in the direct contact cooler is a possibility, or if the cost of further SO₃ reduction is higher than the cost of accepting this SO_x into the amine scrubber (Féraud and others, 2006).

When SO₂ is present in the flue gas at levels between 55 and 185 ppm, approximately 99% of it is removed from the flue gas by the CO₂-absorber and the water wash. It accumulates predominantly in the solvent as sulphate and other sulphur compounds (Feron and others, 2007).

Further abatement of SO₂ might be possible with a performance enhancing additive in the FGD plant. SO₃ emissions could be further reduced, for example with a wet ESP or the injection of an alkaline powder into the existing dry ESP. However, at these extremely low emission levels, the issue of measurement accuracy should be discussed before

Table 6 FGD plant designs and performances (Féraud and others, 2006)

Power plant case	600 MW bituminous	1000 MW lignite	380 MW lignite			
Raw gas SO ₂ concentration*	1122	3109	6003			
Emissions 'target'	% SO ₂ removal required					
200	82.2	96.3	96.7			
50	95.5	98.4	99.2			
10	99.1	99.7	99.8			
Absorber type proposed						
200	Open spray tower	Pumpless scrubber	Pumpless scrubber			
50	Open spray tower	Pumpless scrubber	Pumpless scrubber			
10	Pumpless scrubber	Pumpless scrubber	Pumpless scrubber			
	SO ₂ †	SO ₃ †	SO ₂ †	SO ₃ †	SO ₂ †	SO ₃ †
200	69.4	4.4	69.7	6.9	59.3	11.3
50	17.4	4.4	17.5	6.9	14.9	11.3
10	3.5	2.5	3.4	6.9	3	11.3
Gas temperature, °C	49		51		66	

* emissions target, mg/m³ @ 6% O₂ (dry)
† actual gas conditions, ppmv wet

further abatement is seriously considered (Féraud and others, 2006).

Amine scrubbers perform better with flue gas inlet temperatures below about 40°C. All of the FGD outlet temperatures for the CASTOR cases are above 40°C; one is as high as 66°C. If the flue gas fan is located immediately before the main scrubber, it could raise the temperature by another 4°C or so. This suggests that, in some cases, the introduction of a direct contact cooler between the FGD absorber and amine scrubber could be economically beneficial for CO₂ capture performance. If a direct contact cooler is included in the design, it might offer the opportunity for additional flue gas polishing, for example with added sodium hydroxide (Féraud and others, 2006).

In summary, Féraud and others (2006) have studied the situation in Europe that pertains to NO_x and SO₂ removal for three boiler/fuel cases being considered by the CASTOR project. They reported that additional NO_x abatement beyond that required to meet environmental legislation is not likely to be required for amine scrubbing. Limestone gypsum FGD plants can be designed to reduce SO₂ emissions down to 10 mg/m³. However, in some cases of lignite firing, the SO₃ levels entering the amine scrubber could slightly exceed the suppliers' suggested targets unless additional economically acceptable measures can be taken to reduce them. Raising the performance of FGD plants to these levels would increase capital costs by about 7% and operating costs by up to 27%. Through life costs would be increased by up to 17%. However, these cost increases represent only a few euro cents per tonne of CO₂ captured, over a 25 y plant life (Davidson, 2007).

2.5 SCR

Selective catalytic reduction is used to control NO_x in the Fluor example, as shown in Figure 7. First, ammonia is vaporised, mixed with air, and injected upstream of the SCR where NO_x, mainly in the form of NO is converted to nitrogen gas. The next step might be sorbent injection for control of SO₃ gas. The sorbent can be injected in any of a number of locations, such as just before the air preheater, but almost always upstream of the particulate control device. Activated carbon injection is one method of removing mercury from gas streams. This will also occur upstream of the particulate control device which will usually consist of a dry ESP and/or a fabric filter (Reddy and others, 2008).

Figure 7 also shows the path to a wet FGD unit. However, many plants have dry FGD, especially those using low sulphur coal. The dry FGD would be located upstream of the particulate control device. Regardless of whether SO₂ is removed by wet or dry FGD, the CO₂ capture plant will be located downstream of the air quality control system. Ammonia based SO₂ capture processes will also require a wet ESP to remove aerosols produced by ammonia (Reddy and others, 2008).

2.6 Developments and discussion

Innovations in CCS technologies are being pursued worldwide under a variety of R&D programmes. Much of this R&D is directed at novel concepts and potential breakthrough

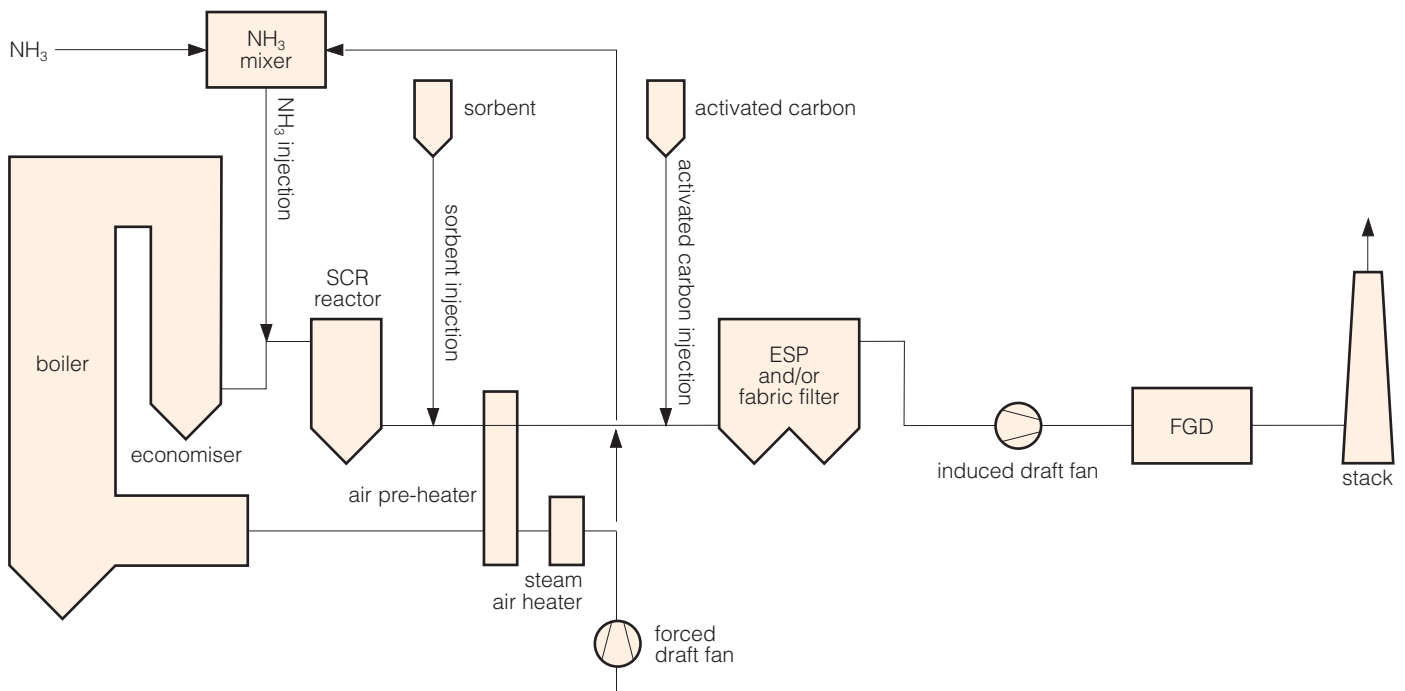


Figure 7 Power plant without CO₂ capture (Reddy and others, 2008)

technologies, but there are also substantial efforts to improve CO₂ capture technologies already in use. Rao and others (2006) examined the potential for future cost reductions in amine-based CO₂ capture systems that may result from continued process development. They questioned twelve leading experts and analysed the results. Rao and others (2006) concluded that significant improvements in the performance of amine-based CO₂ capture systems are possible over the next decade, assuming R&D support in the area continues to grow steadily and new large-scale applications are realised. The development of better sorbents with lower regeneration energy requirement was identified as the highest priority R&D objective. Such improvements are needed to reduce the large energy requirement of current amine-based systems, which is the major contributor to the relatively high cost of this technology for CO₂ capture.

There are proven post-combustion CO₂ capture technologies based on absorption processes that are available commercially. They require a massive scale-up for deployment in large-scale power plants in the 500 MWe capacity range. As air-blown energy conversion processes are dominant in the global energy infrastructure, the availability of post-combustion capture systems is important if CCS is to play a major part in a climate change mitigation strategy (IPCC, 2005).

Considerable effort is being spent developing novel solvents to improve the performance and reduce the energy consumption of solvent regeneration. In addition, work is under way on process designs incorporating new contacting devices such as hybrid membrane-absorbent systems, which may lead to the use of more energy efficient post-combustion capture systems (IPCC, 2005).

There have been concerns that the application of CO₂ capture

technologies may increase emissions of NO_x and SO_x. This is a customary concern with trade-off issues between emissions upon the adoption of mitigation options. Tzimas and others (2007) have shown that SO_x emissions would be reduced. They estimated the difference in the quantities of acid gas pollutants and CO₂ emitted by fossil fuel fired power plants with and without CO₂ capture. Post-combustion capture using solvents were considered. As CO₂ capture requires energy, the requirement to keep power generation constant will result in an increase in emissions of acid gas pollutants. If the interaction of these gases with the solvents used for CO₂ capture is ignored, the increase in emissions can be approximated by the efficiency ratio of plants with and without capture.

However, the actual changes in the emissions of acid gas pollutants will be lower than this as some of the NO₂ and SO_x in the flue gases will be captured by the solvents that will be used to remove the CO₂. The magnitude will depend on the acid gas concentration limits that need to be imposed at the inlet of the CO₂ capture unit to avoid significant solvent loss. However, when carbon capture technologies are implemented on a large scale, NO_x emissions from the power generation sector are likely to increase due to the reduced efficiency of power plants that capture CO₂. Tzimas and others (2007) have estimated the increase of NO_x emissions for coal-fired power plants to be 24%, while at least 80% of the CO₂ generated will be captured. Moreover, the SO_x emissions from PC plants will also decrease, driven by the need to reduce solvent losses, possibly by increasing the removal efficiency of the FGD. The reduction will depend on the solvent used and may vary between 96% and 99%. The power plant efficiency penalty is expected to decrease over time by technology improvement and by the development of new technology options.

In the short to medium term, improvements in both power generation (including flue gas cleaning) and CO₂ capture technology are expected. In terms of power generation, supercritical PC plant, material developments, design optimisation, improvement of FGD and SCR units are expected. For example, there is a need to provide advanced FGD units capable of reducing SO_x to the low limits (around 10 ppm) that are required for amine scrubbing. These FGD developments will benefit power plants both with and without carbon capture (Tzimas and others, 2007).

In terms of CO₂ capture technology, it is expected that there will be development of new amine-based solvents, with the aim of increasing the solvent CO₂ loading, reducing corrosion, and reducing the energy requirements for solvent regeneration for example. It is also likely that energy consumption will be optimised, the capital cost of capture plants will be reduced and the selectivity of CO₂ capture solvents will be improved (Tzimas and others, 2007).

An increase of capture plant efficiency will result in a decrease in the ratio of efficiencies of power plants without and with capture, and therefore will lead to a reduction in the emissions of acid gas pollutants. Development of advanced solvents, which will be able to capture only the CO₂, and not NO₂ and SO_x, to avoid solvent losses, will however lead to higher acid gas pollutant emissions. However, there is not enough information available to allow the assessment of the impact of these changes to the overall emissions (Tzimas and others, 2007).

According to Tzimas and others (2007), the issue of solvent loss, the trade-off in emissions and the possible formation of foaming and scaling, highlight the need for a holistic approach to air pollution control, which should be considered for the design of coal-fired power plants with CO₂ capture. This suggests that air pollution abatement should be included in the techno-economic assessment for the introduction of CO₂ capture technologies in power plants.

3 Oxyfuel combustion capture systems

In this chapter the fundamentals of oxyfuel combustion are explained briefly in Section 3.1. The components and properties of the flue gas are described subsequently, with particular attention to SO_x and NO_x. The role of the air separation unit that provides the oxygen for oxyfuel combustion is described as regards the impact it can have on the components of the flue gas. The reasons for removing these contaminants from the flue gas are covered, including their impact on the transport and storage of CO₂.

3.1 Oxyfuel combustion

Oxyfuel combustion is an option for power generation with CO₂ capture. In simple terms, it is a process that eliminates nitrogen from the oxidant or comburent by burning the fuel in either nearly pure oxygen, or a mixture of nearly pure oxygen and a CO₂ rich recycled flue gas. The resulting flue gas from the boiler contains mainly CO₂ and water vapour.

High temperature processes such as reheating furnaces or glass tank furnaces typically burn fuel with pure, or nearly pure, oxygen. However, steam generation applications, such as PC boilers, require a lower combustion temperature. Thus, in oxyfuel combustion the fuel is burned with oxygen and a mixture of CO₂ rich recycled flue gas or steam. These additions to the oxygen replace the nitrogen and act as diluents to lower the combustion temperature. The basic oxyfuel combustion concept is shown in Figure 8. Oxyfuel combustion for power generation is an emerging technology and, to date, no commercial unit has been built. Several large-scale pilot demonstrations for power generation are planned; Schwarze Pumpe in Germany is the most well known pilot plant in operation.

Oxyfuel combustion is described in detail in the IEA Clean Coal Centre report by Davidson (2010).

The components of oxyfuel flue gas are described in the next sections. It is important to understand the constituents of the flue gas, as a prelude to looking at treatment measures that may be required.

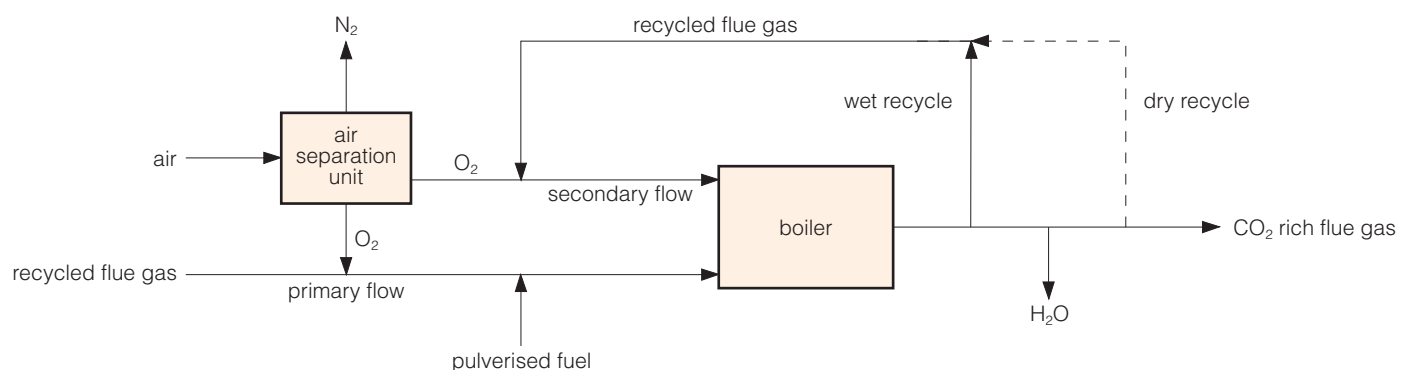


Figure 8 Schematic of a typical oxyfuel combustion unit (Smart and others, 2010)

3.2 Flue gas components and properties

The flue gas from the boiler consists mainly of CO₂ and water vapour, in addition to the excess oxygen necessary to ensure complete combustion of the fuel. Other components of the flue gas include reactive and inert components derived from the fuel, such as NO_x, SO_x, fly ash and trace metals. There are any inert components from the oxygen stream supplied, such as Ar and N₂; any inert components originating from air ingress, such as N₂, Ar and H₂O; and any additional chemicals that are added in any post-combustion treatment of the flue gas, such as ammonia from SCR. Table 7 summarises the typical components that could be present in the CO₂ rich flue gas from an oxy-coal fired boiler.

Table 8 shows the typical range of the composition of the oxidant or comburent gases in the windbox entering the furnace for both air and oxyfuel combustion. The composition is given in percentages (on a wet basis). It also gives the typical range of the composition of the most common major components of the flue gas exiting the boiler, again in percentages (wet basis).

There is a misconception that the recirculation in the oxyfuel process causes a ‘build-up’ of trace contaminants in recirculating boilers. The reasoning behind this conclusion is that most of the combustion products are recirculated back into the boiler and, thus, as most of the contaminants are returned to the boiler, the concentration increases. This is incorrect (Ochs and others, 2008). The overall amount of contaminants is not increased in the oxyfuel process, but there is an accumulation of the contaminants not removed prior to recycle in the flue gas. The flue gas volume flow in the boiler is almost the same as in air firing and the concentrations of contaminants not removed before recycling is about three times higher. Although the flue gas stream is only one third that of air-firing (due to the absence of nitrogen) and therefore the amount of contaminants leaving the plant is the same, but at a higher concentration (Faber, 2010).

Table 7 Major, minor and trace components of the flue gas from an oxy-PC boiler (Santos, 2010)

Major components (present at >0.1%)	Carbon dioxide, CO ₂
	Water vapour, H ₂ O
	Oxygen, O ₂
	Nitrogen, N ₂
	Argon, Ar
Minor components (present at the ppm level)	Carbon monoxide, CO
	Sulphur oxides, SO ₂ SO ₃
	Nitrogen oxides, NO, NO ₂ , N ₂ O, N ₂ O ₄ *
	Other fugitive emissions, such as NH ₃ from SCR
Trace components (any component at ppb level)	Trace metals, Hg and As
	Halogenated compounds, HCl, HF, HBr†
* N ₂ O will predominate only for oxy-CFB, while N ₂ O ₄ may only be present in ppb	
† HCl could be present in ppm, depending on the chlorine content of the coal	

Table 8 Comparison of the gases in the windbox and in the flue gas, concentration on a wet basis (Makino, 2006)

	Item	Combustion with air, composition %	Combustion with oxygen, composition %
Windbox	O ₂	21	21–30
	N ₂	79	0–10
	CO ₂	0	40–50
	H ₂ O	Small	10–20
	Others	–	NO _x , SO ₂ , others
Flue gas	O ₂	3–4	3–4
	N ₂	70–75	0–10
	CO ₂	12–14	60–70
	H ₂ O	10–15	20–25
	Others	NO _x , SO ₂ , others	NO _x , SO ₂

After condensing all the water vapour, typically the net flue gas could contain about 80–95% CO₂ (on a dry basis), for any coal-fired oxyfuel boiler depending on coal type, excess oxygen, air ingress and flue gas processing method used.

Tan and others (2005) have reported that the CO₂ concentration in the flue gas from various industrial scale oxyfuel pilot plant experiments undertaken between 1980 and 2000 have achieved concentrations greater than 90% (dry basis) and have reached up to 95% (dry basis). The balance consists mainly of the nitrogen and argon derived from the air in-leakage, NO_x and SO_x derived from the fuel sulphur and nitrogen during combustion, and excess oxygen supplied.

Buhre and others (2005) have reported that the CO₂ concentration in the flue gas of a pulverised coal boiler could reach concentrations higher than 95%. However, it should be noted that this concentration could only be achieved if operating in lean combustion conditions with minimal air in-leakage.

The concentrated CO₂-rich flue gas from the boiler is purified, dried and compressed further before delivery into a pipeline for storage. In oxyfuel combustion the CO₂ capture efficiency could reach close to 100%. The next sections discuss NO_x, SO_x and other contaminants in more detail.

3.3 Nitrogen oxides

It is widely accepted that less NO_x is formed in oxyfuel combustion than in air-fired combustion. This can be attributed in part to the absence or minimisation of thermal NO_x formation. The absence of N₂ means that the formation of thermal NO_x is suppressed for oxyfuel combustion. However, the fuel NO_x mechanism can be enhanced because of the higher O₂ concentration (Tan and others, 2006). It has also been suggested that the reduction of recycled NO to nitrogen plays a major role in the overall NO reduction through the reburning mechanism. Others have concluded that recycled NO_x reduction depends essentially on the equivalence ratio and on the ratio of flue gas recycled. At an equivalence ratio less than 0.5, only 10% of the recycled NO was reduced, whereas for an equivalence ratio greater than 1.4, more than 60% of the recycled NO was converted to N₂ (Croiset and others, 2005).

Croiset and Thambimuthu (2001) studied combustion in air, combustion in O₂/CO₂ mixtures and actual combustion with recycled flue gas. They used a US eastern bituminous coal (32.2 MJ/kg HHV, 0.96% S) for their experiments. Combustion in air showed the highest NO_x emission rate. This is explained by the higher formation of thermal NO_x when more nitrogen is present in the combustion medium. Combustion with recycled flue gas led to a lower NO_x emission rate than for once-through combustion in O₂/CO₂ mixtures. NO_x emission rates decreased by 40–50% when the flue gas was recycled, compared with experiments that used once-through O₂/CO₂ mixtures. This can be explained by the further reduction of NO into N₂, when NO is recycled back into the combustor. Their results suggested that the higher the concentration of oxygen in the feed stream, the higher the concentration of NO_x. This is due to an increased formation of NO_x at higher oxygen feed (and hence at higher temperature), and also due to lower NO_x dilution. The concentration of NO_x in the reactor is also higher when the flue gas is recycled than when compared to the case of once-through O₂/CO₂ mixtures. This is not to be confused with the lower emission rate found for recycled experiments compared to once-through runs. There is no contradiction here. For recycle experiments the flue gas that is not recycled is more concentrated in NO_x, but its mass flow rate to the stack is

lower than for non-recycle runs. Thus, the emission rate is finally lower for recycle as compared to the non-recycle experiments.

Measurement of NO_x at CANMET has shown that, in order to reach the maximum NO_x reduction in oxyfuel combustion, it is important to have a burner specifically designed for O₂/recycled flue gas combustion that can lead to low emissions of NO_x without sacrificing fuel burnout (Tan and others, 2006).

3.4 Sulphur in oxyfuel combustion

Sulphur is normally present in coal in a range of 0.5–4 wt%. Sulphur in coal is found in the form of sulphides, organic sulphur compounds, sulphates and traces of elemental sulphur. The sulphur content and the way the sulphur is bound vary with coal type and depend on the age and location of the coal source. The main part of the fuel-bound sulphur is released to the gas phase during combustion. A large fraction is usually sulphides in the form of pyrite, and organically bound sulphur is also important. The amount of sulphates in coal is usually low. Sulphur dioxide (SO₂) is the thermodynamically favoured sulphur oxide at high temperature (>1000°C) and oxygen-rich conditions. Under sub-stoichiometric conditions in the flame, hydrogen sulphide is formed in the gas or released from organic sulphur compounds (Fleig and others, 2009). Thus, the outlet concentration of H₂S is negligible if there is excess oxygen. At lower temperatures, the equilibrium shifts towards sulphur trioxide (SO₃), but the reaction rate decreases with temperature and the concentration of SO₃ is several orders of magnitude lower than that of SO₂ in the emitted gas. The main reaction routes of sulphur during combustion of coal are shown in Figure 9 (Fleig and others 2009).

3.4.1 Sulphur dioxide

The conversion of coal-S to SO₂ is lower in oxyfuel combustion, compared to air-fired conditions. In their experiments, Fleig and others (2009) found that the SO₂ concentration in the flue gas is much higher in oxyfuel combustion due to the higher O₂ content in the flue gas

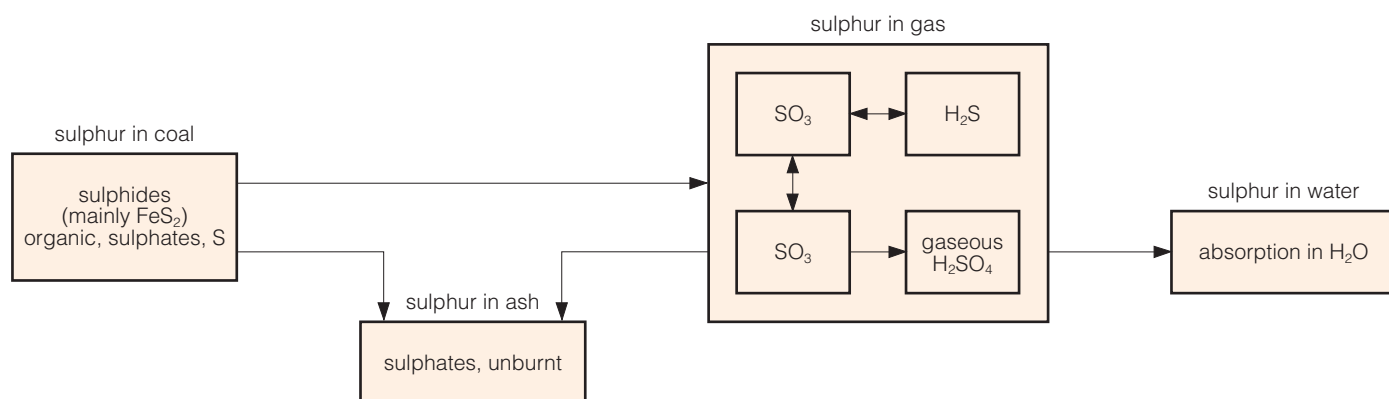


Figure 9 Main reaction routes of sulphur during combustion of coal (Fleig and others, 2009)

resulting from the lower flue gas volume, and the recycling of SO₂.

The reduction in SO₂ concentration in oxyfuel combustion may be attributed to conversion of SO₂ to SO₃ or the reaction of SO₂ with ash. Currently, details about the fate of sulphur are not clear, but it is agreed that the SO₂ concentration (ppmv) in the stack can be considerably greater in oxyfuel combustion than for the same coal combusted in air. The concentration of SO₂ can be 2–3 times higher if SO₂ in the recycle flue gas is not removed prior to combustion (Croiset and others, 2005).

Fleig and others (2009) concluded from laboratory tests on a Lausitz lignite that the release of SO₂ is strongly dependent on the combustion temperature. In oxyfuel combustion, the furnace temperature is closely related to the flue gas recycle rate, which also governs the conversion of fuel-S to SO₂. Previous work has shown that the conversion of fuel-S to SO₂ is lower in oxyfuel than in air-fuel conditions. The SO₂ emission per unit energy supplied is therefore reduced. On the other hand, the SO₂ concentration is higher in oxyfuel combustion due to the recycling of SO₂ and the higher O₂ concentration compared to air-firing. One reason for the interest in sulphur chemistry is the formation of SO₃/H₂SO₄, which may cause operational problems due to low temperature corrosion. Modelling of the gas-phase chemistry shows that the elevated SO₂ molar fraction results in a higher concentration of SO₃ in the flue gas; about four times higher than in air combustion. Also, the reduced flow and the change of the combustion environment from N₂ to CO₂ increase the concentration of SO₃ (Fleig and others, 2009).

Santos (2009) compared SO₂ emissions from oxyfuel and air-fired combustion. He found that the concentration of SO₂ in oxyfuel combustion was 2–5 times higher than that from air-fired combustion, but in terms of the total sulphur mass output, that is specific mass per unit of energy supplied, the SO₂ emissions in oxyfuel cases are about 30–40% lower than in the air-fired cases. The lower specific emissions are attributed primarily to the significant retention of the sulphur in ash.

3.4.2 Sulphur trioxide

Sulphur trioxide (SO₃) promotes particle formation, which is used to improve the performance of electrostatic precipitators (ESP), but it also increases plugging of air-preheater passages and emission of aerosols (Fleig and others, 2009).

The formation of SO₃ depends on the concentration of SO₂, residence time, temperature profile, concentration of O₂, fly ash composition, concentration of NO₂ and the presence of catalysts, such as Fe₂O₃. At temperatures below 500°C, SO₃ reacts with H₂O in the flue gas to form gaseous H₂SO₄, which can cause corrosion if it condenses on metal surfaces or particles.

Tan and others (2006) have shown that with O₂/recycled flue gas combustion, the in-furnace heat transfer and temperature profiles can be made to match those for conventional

combustion by adjusting O₂ concentration and flue gas recycle ratio. Their results showed that if the flue gas were recycled without removal of SO₂, there would be a significant accumulation of SO₂ and consequently, increased SO₃ in the recycle stream, with serious implications for corrosion of boiler systems.

They combusted three different coals in a down-fired, refractory-lined combustor with a rated capacity of 0.3 MWth. Tan and others (2006) observed that as the flue gas was recycled without SO₂ removal, there were significant increases in the concentration of SO₂ in the furnace due to the accumulated effects of flue gas recycle and reduced volume of the flue gas. The concentration of SO₂ in the furnace for O₂/recycled flue gas was 3–4 times higher than the corresponding air cases. However, even though the SO₂ volumetric concentrations were higher, its mass emission rates were usually slightly lower than combustion in air. The reduced mass emission rates were probably due to increased sulphur retention in ash deposits.

Sulphur retention also depends on fuel-specific characteristics, such as coal particle size and the way sulphur, alkali and alkaline earth metals are bound. SO₃ can also be captured by the ash, and adsorption of SO₃/H₂SO₄ by particles is efficient at low temperatures. During combustion of subbituminous coals, which commonly have a low sulphur content, the alkalinity of the fly ash is often high enough to adsorb nearly all the H₂SO₄. After combustion, sulphur compounds in the flue gas can be absorbed in the condensing water (Fleig and others, 2009).

Fleig and others (2009) used a combustion model to investigate the gas-phase reactions and the formation of SO₃ and H₂S. A Lausitz lignite with 10.4% moisture content, a heating value of 21.1 MJ/kg LHV as received, and 0.9 wt % dry ash free (daf) sulphur content was the coal used. Three cases were studied: air-firing, oxyfuel combustion with dry recycle, and oxyfuel combustion with wet recycle. The oxidiser was varied for each study, as shown in Table 9.

The combustion temperature is critical to sulphur release. For example, it is assumed that all sulphur present in the coal is released as SO₂ at 1400°C. At 1200°C, only 76% of the total sulphur is released. Below 600°C, the dominant sources of

Table 9 Composition of the oxidisers used in the calculations (Fleig and others, 2009)

Component	Air	O ₂ /RFG _{dry}	O ₂ /RFG _{wet}
O ₂ , %	21	29	29
N ₂ , %	79	0.5	0.5
CO ₂ , %	0	69.5	48
H ₂ O, %	0	0.9	22.4
SO ₂ , ppm	0	760	760
NO, ppm	0	240	240
RFG = recycled flue gas			

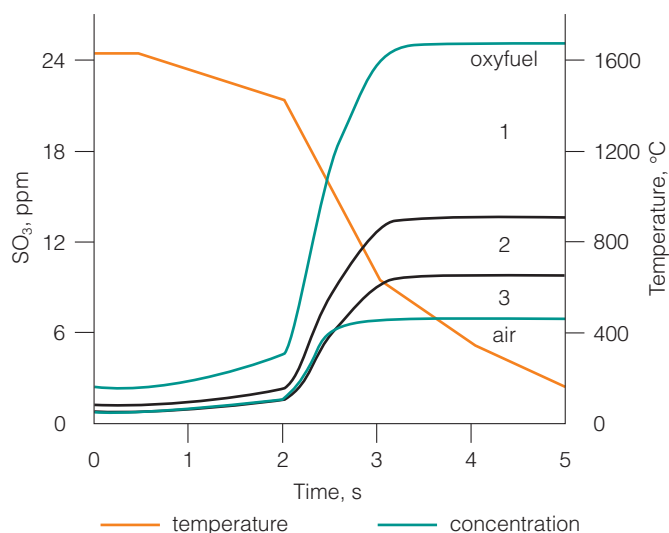


Figure 10 SO₂ concentration during combustion of Lausitz lignite for air and oxyfuel combustion with dry recycle (Fleig and others, 2009)

sulphur release are organically bound sulphur and pyrite (Fleig and others, 2009).

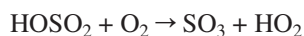
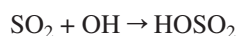
Fleig and others (2009) found that the additional SO₃ formed during wet recycle is negligible, (about 3 ppm), compared to dry recycle. The outlet concentration of SO₃ in oxyfuel combustion is about four times the concentration in air-firing when the gas follows a predefined temperature profile typical for a coal-fired plant. The increase in SO₃ is caused by three properties of the oxyfuel process, whose relative importance is indicated in Figure 10:

- 1 The oxidiser in oxyfuel combustion contains SO₂, which increases the amount of sulphur present during combustion.
- 2 The oxidiser in oxyfuel combustion has a higher concentration of O₂, which decreases the volume flow through the furnace and, thus, increases the concentration of SO₃.
- 3 The change from N₂ to CO₂ increases the SO₃/SO₂ ratio, due to chemical effects, discussed below.

In the temperature region corresponding to a residence time between 2–2.5 s in Figure 10 (Fleig and others, 2009), SO₃ is mainly formed by the reaction:

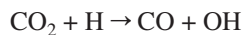


No decisive differences in SO₃ formation are detected in this region between air and oxyfuel combustion. At lower temperatures (between 2.5 and 3 s), the secondary formation of SO₃ via HOSO₂ is more important. This takes place via the reactions:



It is known that the increased concentration of CO₂ during

oxyfuel combustion affects the radical pool, primarily through:



The elevated OH radical concentration enhances the secondary formation of SO₃. Wet recycle with higher concentration of H₂O in the furnace increases this effect slightly, leading to a small increase in SO₃ during wet recycling in the calculations. In practice, the concentration of SO₂ in the oxidiser is probably lower in wet recycle, and consequently, the concentration of SO₃ (Fleig and others, 2009).

Similar to an air-fired furnace, the cooling rate, or residence time in the crucial temperature range, and the stoichiometric ratio during cooling are of great importance to SO₃ formation, while the influence of peak temperature is negligible (Fleig and others, 2009).

As well as the concentration of SO₃, the concentration of H₂O in the flue gas is important for the acid dewpoint. The acid dewpoint temperature increases with the concentration of SO₃ and H₂O in the flue gas. In oxyfuel combustion the dewpoint temperature is higher due to the higher concentration of SO₃. The influence of the H₂O content on the flue gas is considerable in wet flue gas recycle. In this case, an increase in acid dewpoint temperature by 20–30 K is expected due to higher concentrations of SO₃ and H₂O (Fleig and others, 2009).

3.4.3 Hydrogen sulphide

The possibility of H₂S formation during oxyfuel combustion has been examined. Formation of H₂S can be considerable under sub-stoichiometric conditions, combined with temperatures between 1100°C and 1600°C. These are conditions that typically occur in a flame. If there is excess oxygen, the outlet concentration of H₂S is negligible. An increased concentration of H₂S can be anticipated in an oxyfuel flame, due to the SO₂ content in the oxidiser. Furthermore, the recycle rate in oxyfuel operation can directly influence the H₂S concentration as the flame temperature has a considerable influence on its formation under sub-stoichiometric conditions (Fleig and others, 2009).

3.4.4 Calcium

Sulphur can be captured by alkali and alkaline earth metals (Na, K, Mg, Ca) in the ash or it can be bound in the minerals without being released, as well as forming gaseous sulphur products. Calcium has a dominant role in sulphur retention; the Ca/S molar ratio in the coal is one of the main characteristics that governs the retention of sulphur in the ash (Fleig and others, 2009). If calcium is present in the coal or added as calcite (CaCO₃) or dolomite (CaMg(CO₃)₂), and the temperature is suitable, lime (CaO) is formed rapidly. The lime can then react with SO₂ to form CaSO₄. Calcination is favoured. This is when calcite forms lime and CO₂ is inhibited in oxyfuel combustion at atmospheric pressure and

temperatures below 890°C (about 100 K lower in air combustion), due to the high CO₂ partial pressure and direct sulphation of CaCO₃. Chen and others (2007) measured a larger pore diameter of CaO calcined in an oxyfuel atmosphere than that calcined in an air atmosphere. The larger pore diameter yields a better sulphation of CaO due to reduced pore filling and plugging. CaSO₄ may dissociate at temperatures higher than 850°C, depending on the carbonate fraction and the composition of the surrounding atmosphere. However, the higher concentration of SO₂ in oxyfuel combustion stabilises the formed CaSO₄. Hence, the desulphurisation efficiency of oxyfuel combustion is significantly increased compared to air firing.

Part of the SO_x formed is captured and bound to inorganic compounds in the ashes downstream of the combustor. Another part of the fuel-S is still bound in the minerals without being released. For a Lausitz lignite with a sulphur content of 9% in the ash, the sulphur retention would be 60% and nearly 2000 ppm SO₂ would be measured in the flue gas. In principle, Lausitz lignite contains enough calcium to capture all the sulphur as CaSO₄. However, all the calcium is not available to capture sulphur, since calcium is also bound in inactive constellations, such as silicate minerals (Fleig and others, 2009).

Liu and others (2005) have shown that in-furnace desulphurisation can be achieved at high temperatures (>1000°C). In laboratory experiments they observed that in-furnace desulphurisation could be achieved in oxyfuel conditions and that its effectiveness is about 4–5 times greater than in the air-fired case. Liu and others (2005) conclude that these results are due to: (a) the longer residence time as a result of recycling the flue gas; and (b) the inhibition of the decomposition of CaSO₄ at higher temperatures. Thus, these results suggest that the in-furnace addition of calcium such as hydrated lime or limestone could possibly reduce the sulphur content of the combustion gases at high temperature regimes (>1200°C) in oxyfuel conditions, but not air-fired.

At lower temperatures there may be a second mechanism to explain the reduction of SO₂. This could be the retention of sulphur in the ash, aided by the higher conversion of SO₂ to SO₃, and consequently the condensation of SO₃ and its deposition under lower temperature conditions (Santos, 2009).

3.5 Mercury

As mentioned, it is thought that SO₃ formation is increased in oxyfuel combustion. In addition, SO₃ competes with Cl₂ regarding the surface reaction with mercury. Thus, an increased level of SO₃ would inhibit mercury capture in oxyfuel firing, and so emissions of mercury would increase. Little practical work has yet been done, but modelling results at the University of Leeds, UK, indicate that at a level of 5 ppm for SO₃, mercury capture is reduced by 80% (Gharebaghi and others, 2009).

In coal combustion products mercury occurs as elemental Hg (0), oxidised Hg (II) and particulate Hg (P). The latter two

are water-soluble and so can be separated at the back-end of the process and in the flue gas treatment line. However, the transformation of mercury from elemental mercury to the oxidised form is highly temperature dependent and occurs in the range 400–700 K.

It is assumed that all the coal mercury is released as Hg (0) during the devolatilisation process with a reasonable accuracy. However, in the convection duct and flue gas treatment line, where temperature decreases significantly, Hg (0) oxidises to HgO/HgCl₂ and also remains on the particle as Hg (P). Gharebaghi and others (2009) used a British bituminous coal (Thoresby) for their study and modelled the devolatilisation process using the FG-DVC programme. In the study 10% of excess air/oxidant was used, which might be a typical operating condition of burning coal in oxyfuel boilers. They found that HgCl₂ was the dominant form of mercury in the flue gas at temperatures lower than 700 K. When the coal-S is increasing, there is a higher fraction of SO₂/SO₃ in the flue gas, and mercury oxidation decreases. Chlorine acts as the dominant species for mercury oxidation. This may be a result of the interaction of sulphur and chlorine, the different rate of radical release and the operating conditions. Gharebaghi and others (2009) concluded that the elevated concentration of oxygen resulting from oxyfuel combustion affects mercury speciation. A longer residence time influences the extent of mercury oxidation in the flue gas treatment line.

3.6 Air separation unit and oxygen purity

The purity of the oxygen used in oxyfuel combustion is important for several reasons. Higher purity of oxygen requires more energy to produce, but a lower purity will affect adversely the purity of the CO₂ stream to be captured, which can be of critical importance in the case of enhanced oil recovery (EOR). The composition of flue gases can be influenced by the amount of air infiltration in the boiler and associated equipment such as fans, filters, piping and the desulphurisation unit. Boilers are large and complicated and it is virtually impossible to imagine a fully sealed boiler. The amount of leakage is expected to vary widely between power plants, with older plants having more leakage (Ochs and others, 2008). In oxyfuel systems, air ingress causes two problems not seen in air-fired systems. First, the incoming air brings nitrogen into an environment that has low nitrogen levels, providing the raw material for thermal NO_x production. Second, the air being introduced is a contaminant for the CO₂ product. Gases such as nitrogen, oxygen and argon dissolve in CO₂ and depress its critical point, preventing it from becoming a liquid, if pure liquid is the desired product. If the storage mode requires separation of N₂, O₂ and Ar from CO₂, increases in these gases will mean an increased energy demand for separation, and more CO₂ lost during the process. Even if the storage processes can tolerate limited tramp gases in the mixture, limiting impurities is best done by limiting contaminant intake rather than increasing contaminant removal (Ochs and others, 2008).

New oxyfuel combustion plants can be designed to have

minimal air infiltration (Darde and others, 2009). Even with an oxygen purity of 99% and air infiltration at 1%, the purity of the final CO₂ stream will not be suitable for EOR and further purification, likely through refrigeration, would be required. Wilkinson and others (2003) found that it was more economic to design the air separation units for only 95% O₂ purity to comply with practical levels of air leakage into boilers and to separate the associated argon and nitrogen in the CO₂ inert gas removal system to produce a purity of CO₂ suitable for geological storage.

3.7 Transport of CO₂ with impurities

The following sections introduce the impact of impurities on the transport, injection process and storage of CO₂. The physical properties of CO₂ dictate the choice of transport system. Table 10 lists the physical properties of CO₂ and Figure 11 is the phase diagram for CO₂ (Zhang and others, 2006). At the triple point CO₂ coexists in the solid, liquid and gaseous form. The triple point for CO₂ is 216.6 K (-56.4°C) and the vapour pressure is 0.518 MPa. The critical temperature of CO₂ is 31.1°C and the critical pressure is 7.38 MPa. At the critical point, the density is 467 kg/m³; and at the triple point solid CO₂ has a density of 1512 kg/m³. However, at normal temperatures of 10–25°C, liquid CO₂ has a vapour pressure of 4–6 MPa. Thus, pipes, storage tanks and vessels for liquid and supercritical CO₂ need to be constructed with thick walls in order to withstand these pressures (Golomb, 1997).

The low critical temperature of CO₂ (31.1°C) distinguishes it from other substances typically bulk transported in pipelines. Technically, CO₂ can be transported through pipelines as a gas, as a supercritical fluid or as a compressed liquid, depending on the pressure and temperature conditions in the pipeline system. Supercritical CO₂ generally has more liquid like density and more gas like properties such as viscosity and diffusivity. Controlling the system temperature and pressure at a particular condition directly determines significant aspects of the system process design, pressure losses, mechanical construction and, ultimately, the energy and cost efficiency (Zhang and others, 2006).

As the critical point for CO₂ is 31.1°C and 7.38 MPa, a system pressure of more than 7.5 MPa will result in supercritical transportation, as long as the temperature stays above 31.1°C. If the pressure drops below the critical pressure, the phase may be liquid or gas (or both) depending

on the local temperature. It is a disadvantage to have gas in the pipeline (Zhang and others, 2006).

According to Zhang and others (2006), generally, transport of CO₂ in the compressed liquid state has some advantages over supercritical state transport, mostly because of the lower compressibility and higher density of the liquid within the pressure range they considered, which permits smaller pipe sizes or lower pressure losses. However, Golomb (1997) recommends that CO₂ ought to be in the liquid or supercritical phase for maximum throughput and ease of loading and unloading during transport. According to Aspelund and Jordal (2007), CO₂ must be transformed into a form with high density, meaning that transport in liquid, solid or supercritical phase may be considered, in order to transport large amounts of it efficiently. Generally, in pipelines CO₂ will be transported at supercritical pressure, most likely in the range of 8–15 MPa. The CO₂ must be compressed to a pressure high enough to overcome the frictional and static pressure drops. Furthermore, the CO₂ should be delivered at a pressure higher than the critical pressure to avoid two-phase flow to avoid liquid slugs in the pipeline and avoid liquids in the injection compressor.

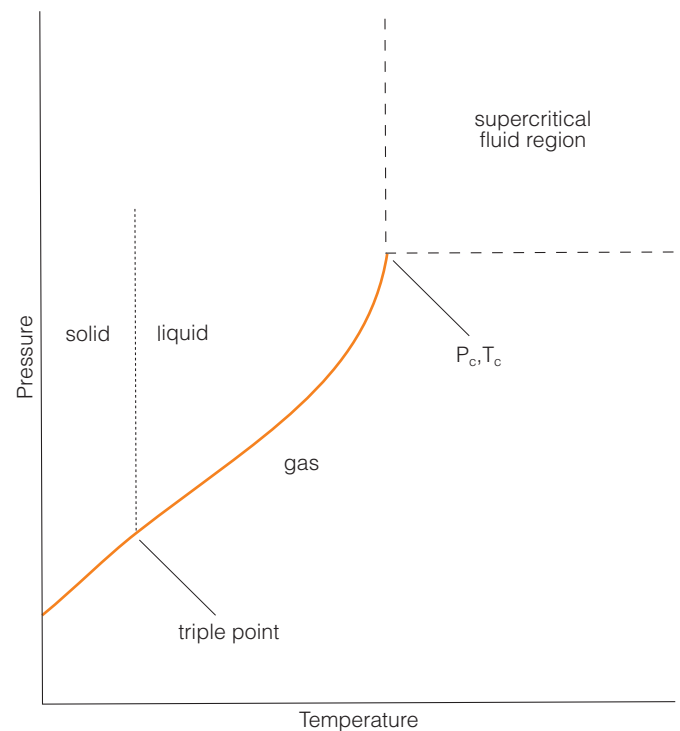


Figure 11 CO₂ phase diagram (Zhang and others, 2006)

Table 10 Properties of gaseous, supercritical and liquid CO₂ (Zhang and others, 2006)

Properties	Gas	Supercritical	Liquid
Density, g/cm ³	~0.001	0.2–1.0	0.6–1.6
Diffusivity, cm ² /s	0.1	0.001	0.00001
Viscosity, g/cm s	0.0001	0.001	0.01
CO ₂ critical parameters: T _c = 31.1°C; P _c = 7.38 MPa; ρ _c = 0.47 g/cm ³			

Pipelines have been widely used for transport in the energy sector. There are about 2400 km of pipelines worldwide transporting CO₂, mainly for EOR purposes. The mechanical requirements for CO₂ pipeline design are subject to standards, the major one being the USA Code of Federal Regulations, parts 190-195. The regulations classify CO₂ pipelines as high volatile/low hazard/low risk facilities over distances from 90 to 808 km (Zhang and others, 2006). These specifications are usually a result of considerations of both pipeline transport as well as the requirements of the end application, and so are not always directly applicable to CO₂ storage in saline aquifers. In addition, these specifications do not include components such as SO_x and NO_x that are present in the flue gas (Darde and others, 2009). The fluid specification will depend largely upon an assessment performed during the design phase including flow assurance, pipeline integrity and safety, and the requirements put upon the CO₂ purity by the end user or destination (Oosterkamp and Ramsen, 2008). Today however, there is no commonly agreed CO₂ product specification for CO₂ storage.

There are currently no recognised specifications for gas quality for CO₂ transport, and it is possible that when specifications eventually are established, the required gas quality may vary depending on the end target (EOR, storage) and it might turn out to vary also depending on legislation in different areas. The main technical constraint will be the maximum allowable impurity content in CO₂ to be injected or the impurities that can be allowed for pipeline or ship transport. It may well be that the requirements for CO₂ transport turn out to be more stringent than those for EOR or storage. The composition of the CO₂ will not change during the transport of CO₂, provided that the CO₂ chains are designed without leakage. Hence, the CO₂ specifications have to be met by the CO₂ capture and conditioning process and will be determined by safety and operation in the transport chain, reservoir requirements, technical/economic evaluation and rules and regulations (Aspelund and Jordal, 2007).

Many preliminary studies have been undertaken regarding CO₂ transport using pipelines. However, there is still a lack of quantitative conclusions about economical CO₂ transmission under variable climatic conditions. In addition, it is difficult to apply the methods or results from existing studies directly to optimising CO₂ transport with CO₂ storage, due to the dissimilar assumptions used in different CO₂ transport studies (Zhang and others, 2006).

Most of the experience in CO₂ pipelines is with a nearly pure product. These pipelines have a good operating history with a safety record that is on a par with natural gas pipeline systems. For pipelines with significant amounts of constituents other than CO₂, the composition has a significant impact on pipeline design, compressor power, pressure drop, and pipeline capacity. These factors influence both the technical and economic feasibility of developing a CO₂ transport infrastructure (Sass and others, 2009).

A pipeline will be designed for a long life time (about 50 y). Thus, it can be expected that the fluid composition in the pipeline will change when different capture sources are connected to the pipeline infrastructure. New CO₂ capture

methods can result in new compounds such as Ar, H₂, SO_x and NO_x in the captured stream, for which there is little or no experience within CO₂ transport. Oxygen and H₂S are transported today to some extent, but at much lower concentrations. The impact of all these impurities on the pipeline transport system should be evaluated. Currently, no CO₂ quality requirements have been decided that take these new compounds into account (Oosterkamp and Ramsen, 2008).

Methods for analysis of CO₂ pipelines with significant levels of inert constituents, such as nitrogen and argon, have become available in the literature only recently. Selecting an appropriate equation of state is an important part of understanding the transport properties of CO₂ with significant amounts of other constituents. Unfortunately, there is no consensus in the literature about the level of applicability of various approaches to pipeline modelling. Additional work is required to understand the implications of impurities (Sass and others, 2009).

The flow of the mixture through the pipelines is relatively straightforward and predictive design equations are well established. However, if the fluid is a mixture and not pure CO₂ there are two challenges. First, it is important to determine the mixture transport parameters for a given fluid state. The major component of the fluid is CO₂, which is quite compressible and undergoes significant changes in properties. Hence, constant properties cannot be assumed for the mixture even if the lesser constituents' transport properties were constant in behaviour, which they are not. Second, the phase behaviour of the components must be compatible also, since a phase change during pipeline transport is typically avoided for reasons of safety and pipeline integrity (Sass and others, 2009). Additionally, the equilibrium composition needs to be studied to ascertain if any significant reactions are present as the fluid undergoes transport. The transport properties of fluid mixtures can be difficult to predict over a wide range of conditions. Many pure fluids have been tested experimentally and validated predictive equations of state exist, but this is not often the case for arbitrary mixtures (Sass and others, 2009).

The oxycombustion flue gas contains nitrogen, oxygen, argon and several other minor constituents in addition to CO₂. This has a bearing on many of the fundamental parameters that affect fluid flow. For example, N₂ mixed with CO₂ reduces the density of the gas mixture compared with pure CO₂, which decreases the hydrostatic pressure inside the well column. Consequently, wellhead pressure must be increased to compensate for the reduced bottom hole pressure which determines the rate of fluid ingress, thus demanding higher compression pressures. Frictional factors also increase with mixing of CO₂ with N₂ and other non-condensable gases. This causes a greater pressure drop, which increases with pipeline distance, and again must be compensated with higher compression or more frequent recompression stations (Sass and others, 2009). When liquid water is present, CO₂ will partially dissolve and form carbonic acid. This will give rise to corrosion problems with the steel alloys commonly used in pipelines. Carbon steel can be used in the absence of free water. No corrosion problems have been reported where the CO₂ is suitably dry or when stainless steel alloys are used (Oosterkamp and Ramsen, 2008).

Impurities in the CO₂ have an affect on (Oosterkamp and Ramsen, 2008):

- design of equipment such as pumps and compressors: specifically setting of suction pressure and compression strategy to avoid the two phase region;
- impurity concentrations may determine the safe exposure limits for the fluid instead of CO₂ concentration;
- impurities reduce the transport capacity of the pipeline;
- raising the vapour pressure means that the higher minimum entrance pressure or shorter recompression/booster station intervals are needed to keep the fluid in the dense phase;
- pipeline integrity: the vapour pressure sets the decompression pressure at a pipeline break. Thus a high decompression pressure can facilitate further propagation of a fracture;
- corrosion;
- the water solubility and hydrate formation conditions.

Critical properties of gas mixtures are important in understanding their behaviour in transport and injection. However, these properties are not well known for multi-component systems near the critical point of CO₂, and they are not easily estimated because such systems do not obey simple mixing rules.

The pressure is kept over the critical point and the fluid is transported in the dense phase for the efficient transport of CO₂ by pipeline. The important properties of CO₂ at typical operating conditions (dense phase) are (Oosterkamp and Ramsen, 2008):

- density is relatively high and sensitive to temperature;
- low viscosity;
- non-linearly varying compressibility factor;
- acts as a solvent.

Many of the studies of CO₂ capture include compression to 10–20 MPa as a requirement for CO₂ transport. In these studies, gas processing usually includes condensation of water at the CO₂ compressor intercoolers, but not necessarily removal of any other components that may be contained in the CO₂ rich stream. Until now general studies of CO₂ gas conditioning and compression/liquefaction for transport have been scarce in the open literature. However, there is an increasing awareness that the removal of liquids other than water and volatile gases must be considered in the CCS chain.

3.7.1 Water in CO₂ pipelines

The composition of the product flow in the pipe has a significant impact on the integrity and selection of materials. Water is the important factor. Most current CO₂ pipelines operate with low levels of water, which is under-saturated with respect to the liquid state, so that it exists only as a vapour. The presence of liquid water in a mixture of CO₂, SO₂ and O₂ can cause severe internal corrosion in steel pipelines, which reduces their safety and operability. Corrosion in pipelines that contain CO₂ in solution (that is, the dissolved phase) is influenced by temperature, CO₂ partial pressure, water chemistry, flow velocity, water wetting and composition and the surface condition of the steel. The flow conditions are

often turbulent, which has the effect of increasing corrosion rates above that which would occur under a static level. Another complicating factor is that some capture systems may introduce small amounts of solvent vapour due to breakthrough, which could accelerate corrosion or initiate stress corrosion cracking in the pipeline steel (Sass and others, 2009).

Carbon steel used for most energy pipeline applications is the most cost-effective material for transporting CO₂. However, steels are susceptible to corrosion in the flue gas environment due to water, O₂, CO₂ and other constituents that can cause corrosive products. Corrosion shortens the service life of pipes. While the oxygen and sulphur components define the corrosion rates, the water content defines the potential corrosion sites with the corrosion rates calculated according to the operation conditions (Sass and others, 2009).

3.8 CO₂ injection process

The process of injecting CO₂ relies on moving the injection stream from the wellhead, through the injection tubing, and into the storage formation. Impurities in the injection stream are unlikely to be detrimental to the concept of CO₂ storage by deep well injection, despite the complexity that they add. The main issues with the injection process are listed below, and are less direct (Sass and others, 2009):

- the overall injection volume with impurities will be greater than a pure CO₂ stream;
- the impurities will lower the density of the injection stream to some extent, mainly due to N₂ and Ar. A lighter injection stream will require additional injection pressure and associated compression;
- impurities may limit the potential to use the gas stream for EOR projects. For example, NO_x can decrease oil recovery.

3.9 CO₂ storage

Density is an important factor in effective storage. A less dense fluid will take up more volume per given mass and will reduce the storage capacity of a formation. The lower compressibility of some flue gas components means that the density of the flue gas is much lower than that of pure CO₂. Preliminary calculations show that the density of the flue gas will be between one quarter and one half that of compressed CO₂ (Sass and others, 2009).

The solubility of CO₂ in brine is less than that in pure water due to the ‘salting out’ effect. Nevertheless, at pressures typical of deep saline formations, CO₂ is sufficiently soluble to lower the pH by forming carbonic acid. In addition to CO₂, any other acid gases in the injectate will tend to hydrolyse, making the brine acidic. The possibility of co-injecting SO₂ has been considered as SO₂ may be a suitable candidate for downhole disposal with a number of provisions (Sass and others, 2009):

- 1 The moisture content of the flue gas is sufficiently low that liquid water will not condense, thus raising the possibility of pipeline corrosion;

- 2 The SO₂ will not interact with the mineralogy of the reservoir formation to precipitate solids that could cause clogging within the pore spaces;
- 3 Immiscibility between CO₂ and SO₂ will not lead to two-phase conditions, which could harm transport equipment.

Co-storage of CO₂ and SO₂ appears to be technically feasible in many deep saline reservoirs, but the injection lifetime of these reservoirs could be reduced if precipitation reactions take place. Sulphates could be a problem in carbonate-rich formations, but not in pure sandstone or feldspar-rich formations. Precipitation of a solid phase, such as calcium sulphate (anhydrite), is influenced to a much greater extent by dissolution of carbonate minerals in the storage formation, than by the addition of sulphate in the form of SO₂ in the injection gas. Therefore, even if anhydrite precipitation is likely to occur in a formation where certain mitigating conditions exist that would minimise the impact on injectivity, it may still be unnecessary to scrub SO₂ from the flue gas because of the minor effect of SO₂ on precipitation (Sass and others, 2009).

3.10 Discussion

Oxyfuel combustion for power generation is an emerging technology and, to date, no commercial unit has been built. Schwarze Pumpe in Germany is the most well known pilot demonstration plant.

The flue gas from oxyfuel combustion consists mainly of CO₂ and water vapour, together with excess oxygen required to ensure complete combustion of the fuel. It will also contain other components from the fuel such as SO_x, NO_x, HCl and Hg, any diluents in the oxygen stream supplied, any inerts in the fuel and from air leakage into the system such as nitrogen, argon and oxygen. The net flue gas, after cooling to condense water vapour, contains about 80–95% CO₂. Thus, flue gas cleaning used for CO₂ capture from oxyfuel combustion must handle high concentrations of impurities, compared with air-firing cases, although the total amount of impurities is not larger.

Currently, details about the fate of sulphur are not clear, but it seems that the SO₂ concentration (ppmv) in the stack can be considerably greater in oxyfuel combustion than for the same coal combusted in air. One reason for the interest in sulphur chemistry is the formation of SO₃/H₂SO₄, which may cause operational problems due to low temperature corrosion. Work by Tan and others (2006) has shown that if the flue gas were recycled without removal of SO₂, there would be increased SO₃ in the recycle stream, with serious implications for corrosion of boiler systems. Another concern with SO₃ is that it competes with Cl₂ regarding the surface reaction with mercury. Thus, an increased level of SO₃ would inhibit mercury capture in oxyfuel firing, and so emissions of mercury would increase. Understanding of the speciation of mercury is developing.

It is widely accepted that less NO_x is formed in oxyfuel combustion than in air-fired combustion. This can be attributed in part to the absence or minimisation of thermal

NO_x formation.

The purity of the oxygen used in oxyfuel combustion is important for several reasons. Higher purity of oxygen requires more energy to produce, but a lower purity will affect adversely the purity of the CO₂ stream to be captured, which can be of critical importance in the case of enhanced oil recovery (EOR). The composition of flue gases can be influenced by the amount of air infiltration in the boiler and associated equipment. Boilers are large and complicated and it is virtually impossible to envisage a fully sealed boiler. In oxyfuel systems, air ingress causes two problems not seen in air-fired systems. First, the incoming air brings nitrogen into an environment that has low nitrogen levels, providing the raw material for thermal NO_x production. Second, the air being introduced is a contaminant for the CO₂ product. If the storage mode requires separation of N₂, O₂ and Ar from CO₂, increases in these gases will mean an increased energy demand for separation, and more CO₂ lost during the process. Limiting impurities is best achieved by restricting contaminant intake rather than increasing contaminant removal.

CO₂ is transported by pipeline as a dense supercritical phase. Inert gases must be reduced to a low concentration to avoid two phase flow conditions developing in the pipeline systems. The acid gas components may need to be removed to comply with legislation covering co-disposal of toxic or hazardous waste or to avoid operations or environmental problems with disposal. Water is the important factor. Most current CO₂ pipelines operate with low levels of water, which exists as a vapour. The presence of liquid water in a mixture of CO₂, SO₂ and O₂ can cause severe internal corrosion in steel pipelines, which reduces their safety and operability. Thus, if SO₂ and O₂ are present, it is important to attain a dry product.

4 Removal of impurities from oxyfuel flue gas

Flue gas cleaning is used in CO₂ capture from oxyfuel combustion to remove undesirable impurities. Until recently, little attention had been given to the removal of these impurities from the flue gas of oxyfuel combustion systems. In some earlier work, the assumption has been made that most of the NO present in the CO₂ feed would leave with the inert gas while NO₂ would leave with the liquid CO₂. It was also generally accepted that the SO₂ present in the raw CO₂ stream would leave with the CO₂ (IEA GHG, 2005). This solution would allow the co-disposal of SO₂ with CO₂, which may or may not be acceptable or allowable under future CO₂ capture regulations. However, more recent work on the chemistry of NO_x and SO_x has led to changes in these ideas, which are discussed later.

From the point of view of CO₂ capture, flue gas cleaning for oxyfuel combustion is completely different from the approaches used in post-combustion CO₂ capture. In post-combustion capture, as described in Chapter 2, selective separation processes such as amine absorption are normally used to extract the CO₂ from the flue gas stream. Yan and others (2006) consider that there is relatively more room for the reduction of CO₂ capture costs in oxyfuel combustion compared with amine absorption approaches depending on the purity of the CO₂ required for transport and storage. Although the flue gas cleaning for CO₂ capture from oxyfuel combustion could rely principally on conventional flue gas cleaning techniques, significant adaptations and modifications are needed because of the differences in the main purpose and requirements of flue gas cleaning (Yan and others, 2006).

Flue gas cleaning has three main functions (Yan and others, 2006):

- as a service for CO₂ capture to meet its CO₂ quality requirements;
- as a service for the oxyfuel boiler systems to meet the necessary operating conditions, by which two major flue gas recycle streams are normally required in addition to the downstream flue gas used for CO₂ capture;
- to meet the air emission requirements for the relatively small vent gas stream.

The concentrations of flue gas components are not defined simply by the fuel properties and combustion. The concentrations of impurities may be affected significantly by flue gas recirculation. In addition, for a given impurity, its interactions within various downstream processes such as CO₂ compression, transport and storage must be considered when choosing the appropriate flue gas cleaning process (Yan and others, 2006).

In an ideal situation the flue gas could be injected into deep geological formations with little or no prior conditioning. At the other extreme, the flue gas could require such extensive purification that the presumed benefits of an oxygen blown system are soon negated (Sass and others, 2009).

Optimisation of the boiler and flue gas purification train

enable cost savings. The key is to view the whole process of oxygen separation, coal combustion, steam generation, flue gas purification (if required), transport and storage together. Cost savings can be realised by optimising the flue gas handling through two fundamental options: one is to compress the flue gas with minimal conditioning and inject it directly into a suitable geologic formation; another is to selectively separate gas components that may not be advantageous to long-term injection. The former case could require less environmental control equipment than is commonly used in air blown PC combustion units to remove SO_x and NO_x. However, the feasibility of this option will require a thorough understanding of reservoir mechanics and geochemistry. For example, non-condensable gases, such as nitrogen, oxygen and argon, may affect the transport processes of the flue gas in the subsurface by creating multiphase flow, which could reduce the injectivity and/or the capacity of the aquifer for CO₂ storage over the lifetime of the power plant (Sass and others, 2009).

One issue that has attracted particular attention is the treatment of the recycle stream, especially with regard to SO₂. The question is whether to remove SO₂ prior to recirculation and also whether the recycle stream should be dried or not. Some have proposed to co-capture CO₂ with SO₂ (and eventually NO_x). In this situation there would be no need for deSO_x or deNO_x treatment, which represents a significant cost benefit. Dillon and others (2004) investigated different options for the recycle stream and selected the option where the secondary recycle stream is cooled to a warm temperature, the particulates removed, and then it is reheated. In this situation the recycle stream was not dried and the ESP operated with warm flue gas. Dillon and others (2004) disregarded the options of maintaining a hot recycle flue gas and drying the recycled stream via cooling. According to Croiset and others (2005), if SO₂ cannot be co-captured, the cost of desulphurisation will still be much lower than in conventional combustion systems as the volume of flue gas in the O₂/CO₂ recycle option is only about 20% of that in air-fired combustion.

Various design issues for flue gas cleaning systems are explored in the next section. A number of flue gas purification techniques for oxyfuel combustion are discussed subsequently.

4.1 Design issues for flue gas cleaning systems

Flue gas cleaning is an integration of various processes that reduce impurities to the level required by CO₂ capture, oxyfuel combustion, and air emission regulations. The acceptable levels for each impurity, together with its original concentration in the flue gas, define the required performance for the cleaning process units. A flue gas cleaning system should be designed based on the cleaning criteria for given impurities and the boundary conditions for

Table 11 Important issues associated with flue gas cleaning for CO₂ capture and oxyfuel combustion
(Yan and others, 2006)

Issues	Major concerns	Comments
Recycled flue gas	Quality and quantity requirement	Directly relates to how many unit processes should be involved, the flue gas volume to be treated and the overall costs of flue gas cleaning (both investment and operation costs)
Fine fly ash recirculation through flue gas recycle	Low removal efficiency of conventional equipment for very fine ash particles; Safety requirement for mixing with high purity of O ₂	It may result in fine PM accumulation in the flue gas recycle pass; Depending on the way of mixing, very clean flue gas may be required
Conversion of SO _x and NO _x	Conversion of SO ₂ to SO ₃ ; Conversion of NO _x ; Conversion of NO to NO ₂ ; Formation of acidic aerosols	High SO ₃ concentration combined with high moisture content results in a high acid dew point of the flue gas; High NO _x conversion may result in problems of emission and corrosion; Acidic aerosols are difficult to remove
Energy saving	Heat recovery from flue gas cleaning (condensation); Hot/cold cleaning processes	Involve both energy saving and reducing of cooling duty; Involve both energy saving and investment costs
Water demand and treatment	Cooling water demand and loss; Water recovery and reuse	High cooling duty required for flue gas condensation; Condensate reuse may be necessary to reduce water demand
Distribution of contaminants in plant	Minimise negative influence on environment, especially for toxic heavy metals and major solid and liquid waste streams	More contaminants will go to solid and liquid waste streams compared to conventional flue gas cleaning. It is necessary to optimise the contaminant distribution in a suitable way, and to improve by-product utilisation
Relations with downstream processes	Avoid or reduce negative impacts on CO ₂ compression/purification; Technical-economic balance on impurity removal between up- and down-streams	Non-condensable gases should be avoided, particulates, acid gases and moisture should be reduced It is necessary to optimise the options of impurity removal between up-and down-streams based on overall technical-economic balance

each process unit. The issues are summarised in Table 11.

Currently there are some uncertainties about the design criteria for flue gas cleaning systems as their development is taking place in parallel with the development of oxyfuel combustion and downstream CO₂ compression/liquefaction/purification, transport and storage. Table 12 shows the evaluation of the design criteria for the flue gas cleaning system, corresponding unit cleaning processes and challenges. It is clear that the design of flue gas cleaning processes must be closely co-ordinated with the development of the up-stream oxyfuel combustion and the downstream CO₂ capture train including CO₂ transport and storage (Yan and others, 2006).

The integration of the unit processes for a flue gas cleaning system should consider the configuration of the flue gas recycle and the performances of the unit processes, and the interactions among the unit processes for given impurities. In practice only a few of the potential configurations for

cleaning options might apply. The major influences on the configurations for flue gas cleaning are the quality requirement for the secondary flue gas recycle, and the quantity requirement for the primary flue gas recycle. In general, there are two options to control the flue gas quality for the secondary flue gas recycle:

- 1 Low-cost flue gas cleaning which only removes particulates;
- 2 A clean recycle with low acid gas content in the recycle flue gas, which means that a larger capacity is required for the corresponding flue gas cleaning units (Yan and others, 2006).

The best available technologies for flue gas cleaning have been investigated based on the characteristics of the flue gas and the features of flue gas cleaning, and the reasonable integration of unit cleaning processes. In general, there are no serious technical obstacles to achieving a clean flue gas.

Table 12 Current evaluation of the design criteria for the flue gas cleaning system (Yan and others, 2006)

Unit process	Components controlled	Status of design criteria	Comments
General PM removal	Most of fly ash and water droplets	Clear on CO ₂ capture stream; somewhat unclear on its influences on boiler system such as accumulation, slagging and fouling	Require higher removal efficiency and rely on conventional PM removal technologies such as ESP and bag house filter in case of ash unsuitable for ESP. Need to investigate if ash properties are affected by oxyfuel combustion
Moisture removal	Water vapour	Clear on CO ₂ compression stream; somewhat unclear on recycled flue gas	The maximum removal is defined by flue gas cooling system; the allowed moisture content in recycled flue gas is mainly defined by the fuel handling requirements. Challenge: large cooling duty, heat recovery integrated with the flue gas condensation, and condensate reuse
Removal of water soluble strong acid gases	Mainly HCl and HF	Somewhat unclear on allowable limits for CO ₂ compression stream	Mainly defined by whether a deSO _x unit is used or not
DeSO _x	SO ₂ , some of SO ₃ and NO ₂	Unclear	Challenges: 1 Major issue if co-capture with CO ₂ is acceptable and to what level. 2 Strongly affected by the requirements of oxyfuel combustion system, CO ₂ compression, transport, storage and environmental regulation, which are under development. 3 The unit process affects removal of other impurities such as strong acid gases, HCl and HF
DeNO _x	NO and NO ₂	Unclear	Challenges: 1 Large uncertainty on the NO _x conversion rate of fuel-N during the coal-fired oxyfuel combustion. 2 NO _x behaviour downstream CO ₂ compression train, which may define the final NO _x emissions
Fine PM and acid aerosol removal	Fine fly ash and SO ₂ aerosol	Somewhat unclear on low limitation for CO ₂ compression train	Challenge: a cost-effective unit process needs to be developed

4.2 Flue gas purification

The approach of Sass and others (2009) to evaluating whether physical or chemical treatment is needed prior to storing oxyfuel flue gas is summarised thus:

- determine the flue gas composition from an oxyfired boiler;
- review the pipeline gas requirement;
- determine the steps that are required for the flue gas purification;
- perform reservoir and geochemical modelling to ensure the feasibility of storing the flue gas.

Table 13 shows the potential impacts of major impurities and available technical options for flue gas cleaning.

A typical flue gas cleaning procedure used for CO₂ capture from coal-fired oxyfuel PC boiler is shown in Figure 12 (Yan and others, 2006).

4.3 Compression and purification

The CO₂-rich gas from oxyfuel processes contains oxygen, nitrogen, argon, SO_x, NO_x and various other trace impurities as have been described in Chapter 3. This gas will normally be compressed and fed to a cryogenic purification process to reduce the impurities concentrations to the levels required to avoid two-phase flow conditions in the transport pipelines. A 99.99% purity could be produced by including distillation in the cryogenic separation unit (IPCC, 2005).

Due to the fact that high gas temperatures are intrinsically associated with gas compression and are also based on materials safe operating limits, the compression of inlet gas generally occurs in a number of stages. Three or more compression stages are usually required to achieve near optimal separation pressures. Strict control of the water content in the CO₂ product stream is also essential to avoid ice formation and corrosion for safe and efficient operation of

Table 13 Impacts of impurities and available technical options of flue gas cleaning for oxyfuel combustion and CO₂ capture (Yan and others, 2006)

Component	Major impacts			Cleaning options
	On boiler systems	On CO ₂ capture (including downstream processes)	On air emissions*	
H ₂ O	Fuel handling, acid dew-point (corrosion)	Corrosion, erosion (water droplet)	No	Condensation, dehydration
O ₂	No significant change is expected compared to air-firing	Corrosion, non-condensable gas, oxidising hydrocarbon in EOR applications, change in redox conditions leading to dissolution/precipitation of minerals in storage sites	No	Physical separation, catalytic oxidation, minimise air in-leakage
Ar	No	(Non-condensable gas) increased transport and storage volume and two-phase behaviour	No	Physical separation in ASU or in CO ₂ compression train, minimise air in-leakage
N ₂	NO _x formation	(Non-condensable gas) increased transport and storage volume and the risk of two-phase behaviour during transport/storage	No	Physical separation, minimise air in-leakage
SO ₂	Corrosion, convert to SO ₃	Corrosion, changing redox or pH conditions, precipitation of sulphur compounds in storage sites	Little	Wet/dry scrubbing, co-capture with CO ₂
SO ₃	Corrosion, fouling concerns	Corrosion	Little	Wet scrubbing
NO	Convert to NO ₂	(Non-condensable gas) somewhat on gas purification	Reduced in mass, but maybe with higher concentration	Combustion control, oxidation then wet scrubbing. Treatment in venting stream. SCR as final option.
NO ₂	Corrosion	Corrosion	No, or very little	Wet scrubbing
CO	Efficiency, maybe corrosion	(Non-condensable gas) somewhat on gas purification	No or very little	Physical separation
Cl	Low temperature corrosion	Corrosion	No	Wet scrubbing
F	Low temperature corrosion	Corrosion	No	Wet scrubbing
PM (ash)	Erosion, fouling	Erosion, fouling	No	ESP, fabric filters, wet scrubbing

* after the flue gas cleaning and downstream processes

the compressors and heat exchangers. A dehydration unit is often installed, especially if a low temperature, or cryogenic, separation process is used. For smaller scale operation, the dehydration unit may be eliminated if the temperature of the gas stream at the intercooler stages can be controlled to cause

the water to drop out. This technique is widely practised in acid gas compression in Western Canada. When dehydration is included, the metallurgy of the piping and pressure vessels can be relaxed, from a corrosion point of view (Zanganeh and others, 2009a).

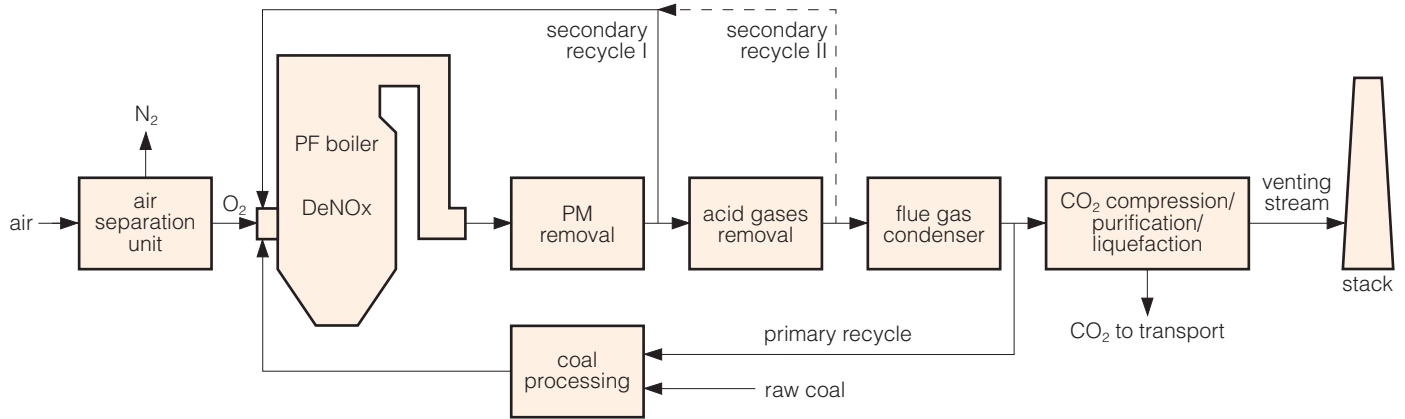


Figure 12 Flue gas cleaning system serviced for various purposes for coal-fired oxyfuel PC boiler (Yan and others, 2006)

4.4 Integrated pollutant removal

Integrated Pollutant Removal (IPR) is a post-combustion exhaust treatment that will use compression, scrubbing and cooling to prepare a dry, supercritical CO₂ fluid suitable for transport and storage. It is being developed by Oryshchyn and others (2006) at the National Energy Technology Laboratory (NETL, USA) and the Jupiter Oxygen Corporation. It is thought that in the process, pollutants such as SO_x, NO_x and particulates will be removed with condensate streams. The energy of compression will be recovered via sensible heat exchange, capture of some of the heat of condensation of vapours and by expansion of pressurised non-condensable flue gases. The recovered energy will be integrated back into the energy cycle of the power plant. According to Oryshchyn and others (2006), bench-scale proof-of-concept experiments in 2004 showed that this combustion and capture process is feasible with current technology and ‘off-the-shelf’ components. Laboratory examination of process operations and planned systems tests continue to define the engineering and operational parameters of the system as it is developed.

Experiments are under way to examine the effectiveness of common desulphurisation processes when treating oxyfuel flue gas. A test section allowing full composition control of a N₂, O₂, CO₂, SO₂ and water mixture is used to create various synthetic flue gas compositions, each of which is treated using the same SO₂ removal process. Sensitivities of the desulphurisation process to partial pressures of CO₂, SO₂, H₂O and N₂, as well as to the temperature of the solvent, are examined while the partial pressure of O₂ is kept constant. Preliminary results show competitive dissolution of CO₂ and SO₂ in a sodium-carbonate solution (Oryshchyn and others, 2006).

4.5 Product recovery train

The product recovery train is a process whereby the concentration of CO₂ in the flue gas is increased from a typical 75–90% (on a dry volumetric basis) to a liquid product stream with a CO₂ purity of 95% or higher. This is then

suitable for EOR or coalbed methane applications (Zheng and others, 2005).

In general, the product recovery train is a multi-staged compression process with intercooling and separation, together with the options of expansion and recycle of flue gas. The product recovery train is capable of handling a wide range of flue gas from oxyfuel combustion units and can produce a liquid CO₂ product stream with a purity of 95% or more, and a recovery rate of up to 90%. The product recovery train does not use any chemical or physical absorption, distillation or membrane technologies (Zheng and others, 2005).

The energy requirement for the product recovery train is significant, but not as great as the ASU. In general, it is believed that about 7–10% of the total output of the power plant is consumed by the product recovery train. This is mainly due to compression shaft power and refrigeration duty, as it was found that in order to have a high recovery rate and high purity, a refrigeration system is necessary (Zheng and others, 2005).

In 2005, Zheng and others observed that the performance of the product recovery train and its energy requirements are closely associated with the ASU and the combustion unit. Since the presence of nitrogen and oxygen makes the thermodynamic behaviour of the flue gas complicated, a high purity of oxygen from the ASU, and little air infiltration are desired. In general, boilers are operated with a small negative pressure, yet such practice has to be revisited under oxyfuel operation since this could introduce too much unwanted air leakage into the flue gas and make it difficult for the product recovery train to produce high purity CO₂ with high recovery rates. As a result, most pilot testing facilities operate with a small positive pressure (Zheng and others, 2005). There will be some safety issues when it comes to building a full-scale plant that operates with a CO₂ atmosphere and over-pressure (Faber, 2010).

The question of optimum product CO₂ purity has a substantial impact on the product recovery train. It is known that the relationship between the product recovery rate and product purity is reciprocal. Therefore, a high purity and a high

recovery rate are associated with high energy consumption (Zheng and others, 2005).

4.6 Integrated emissions control

Although the abatement of CO₂ is usually perceived as an added burden to the power industry, oxyfuel technology provides a platform for integrated emission control and opportunities for emission cost reduction (Zheng and others, 2006). The concept of integrated emissions control is discussed in this section.

In order to protect the recycle fan and burners, an ESP or baghouse has to be used before the recycle. Hence, the ESP or baghouse is not part of the oxyfuel integrated emission control system. In addition, as the volumetric flow of the flue gas before the recycle stream is similar to that of the air case, there are no savings on this piece of equipment (Zheng and others, 2006).

On the other hand, since a small amount of sulphur compounds helps in improving oil miscibility and there is little concern about corrosion if the CO₂ stream is dry, capital and operation and maintenance (O&M) savings can be achieved if an FGD system is not employed. As oxyfuel combustion results in low emission of NO_x, SCR for NO_x control in oxyfuel systems may not be absolutely necessary, or possible for hard coal fired power plants (Zheng and others, 2006; Faber, 2010).

The majority of atmospheric mercury emissions are the direct

result of combustion, and particularly from coal-fired systems. Mercury emissions from coal combustion are mainly in the forms of elemental and oxidised mercury. Typically, a coal with high chlorine content will emit mercury mostly in the oxidised form, which is soluble in water and can be removed effectively in a wet scrubber. A low chlorine coal will emit mercury, mostly in the elemental form, which usually escapes all existing pollution control equipment. As a result, the emission of elemental mercury is a more serious concern than oxidised mercury discharges. Analysis by Zheng and others (2006) shows that in the product recovery train, with all moisture removed and high pressure used, both elemental and oxidised mercury could be captured in the product condensed stream.

This suggests that integrated emissions control is feasible if CO₂ is separated and captured by using a product recovery train. According to Zheng and others (2006), the cost savings from emissions control can be an economic advantage for oxyfuel technologies, especially when compared to amine scrubbing. Comparison of air-based and integrated emissions control oxyfuel systems is given in Table 14.

The total savings of the integrated emission control systems (without FGD, SCR and mercury control) represent 12–15% of the capital and 29–35% of the O&M costs per kW_{net} of oxyfuel plants. Thus, it is estimated that about one-third of the costs associated with the traditional approach with incremental, dedicated and isolated equipment can be saved through integration. The capital costs of CO₂ capture, whether amine scrubbing or with an ASU and product recovery train are similar per kW_{net} (Zheng and others, 2006).

Table 14 Comparison of air-based and integrated emissions control oxyfuel systems (Zheng and others, 2006)

Technology	Capital cost*, \$/kW				Annual O&M cost*, \$/kW			
	Gross	Net			Gross	Net		
		Air without CO	Air with CO ₂	O ₂		Air without CO ₂	Air with CO ₂	O ₂
Baseline plant	790–988	850–1062	1186–1483	1272–1591	28	30.1	42	48.5
ESP	52	56	78	84	2.44	2.63	3.7	3.93
FGD	157	169	236	–	6.69	7.19	10	–
Combustion modifications	21	23	32	34	3.09	3.32	4.6	4.98
SCR	74	80	111	–	2.16	2.32	3.2	–
Mercury control	2.7	2.9	4.1	–	2.53	2.72	3.8	–
Amine scrubbing	388–592	–	582–889	–	14–31	–	21–46	–
ASU and product recovery train	449–658	–	–	723–1059	22–30	–	–	36–49
Total	–	1181–1393	2228–2832	2113–2768	–	48	88–113	93–106

* costs in US\$ 2005

4.7 Economics of flue gas cleaning

In general, the costs of flue gas cleaning are important to a cleaning system. A rough techno-economic evaluation of flue gas cleaning systems has been carried out based on three typical cases under four options of flue gas recycle as defined in Table 15. The three cases represent three general flue gas cleaning levels going from relatively low to high qualities of treated flue gas for both flue gas recycle and CO₂ capture stream, with corresponding cleaning costs from low to high as well. For each case, there are four options for flue gas recycle. The recycle options A and B represent the same secondary flue gas recycle, with a low or large primary flue gas recycle respectively. The recycle options B and C have another secondary flue gas recycle, with similar primary flue gas recycle options like the options A and C (Yan and others, 2006).

The costs of the deepest cleaning (case 3 with a flue gas recycle option D) may be two times higher than that of a simple flue gas cleaning (case 1 with a flue gas recycle option A). For the same recycle option, the investment costs may be increased by 70–140% from the cleaning level of case 1 to the cleaning level of case 3. In addition, flue gas recycle, especially the required quantity of primary recycle flue gas, plays an important role in the costs of flue gas cleaning. In general, a low flow rate of primary flue gas recycle is preferable because of its high costs. For similar investment costs (recycle options B and C), the recycle option C provides much cleaner conditions for the boiler systems because a deeper cleaning is performed for the secondary recycle compared to the recycle option B. This means that, with the same amount of investment, reducing the flow rate of the primary flue gas recycle could provide some benefits for the oxyfuel boiler system (Yan and others, 2006).

Cost issues play an important role in the conceptual development of the flue gas cleaning system. The costs of flue gas cleaning strongly depend on the required cleaning level and flue gas recycle. The costs of flue gas cleaning can be reduced by the use of reasonable cleaning levels in order to achieve the original purpose of the CO₂ capture from coal-fired oxyfuel combustion. Suitable design criteria should be optimised by the overall costs of flue gas cleaning, oxyfuel combustion, and downstream CO₂ capture, transport and storage. More effort should be placed on optimising CO₂ quality requirements through an overall cost-effective target instead of separated CO₂ quality requirements from individual processes. There will not be one optimal flue gas cleaning solution for each type of fuel. A number of unit operations may have different corresponding requirements depending on the types of CO₂ transport and storage. In addition, technical developments are needed for the low-cost removal of fine particulate and aerosol impurities. The enhancement of interactions among unit cleaning processes is also necessary to develop the system further (Yan and others, 2006).

In more recent work, Yan and others (2009b) have considered the impacts of non-condensable components (N₂, O₂ and Ar) on the techno-economic performance of CCS. They looked at three levels of CO₂ processing for transport and storage as shown in Table 16.

Three different transport distances were studied, of 30 km, 90 km and 300 km. Storage of CO₂ at three depths was considered, 1000 m, 2000 m and 3500 m. Table 17 shows a comparison of the cost impacts from non-condensables on capture, transport and storage.

Yan and others (2009b) concluded that the costs of purification play a more significant role for the total costs of CCS compared with those for transport and storage. The

Table 15 Defined case and the options of flue gas recycle for economic-technical evaluations (Yan and others, 2006)

	Case 1	Case 2	Case 3
System in general	Low-cost cleaning system, co-capture of sulphur with CO ₂ , requiring additional concern about boiler and downstream CO ₂ transport and storage	Medium-cost cleaning system, based on conventional flue gas cleaning technologies and leaning levels for impurities, requiring less concern about boiler and downstream CO ₂ transport and storage	High-cost cleaning systems, based on high quality requirements of CO ₂ compression/liquefaction/purification system. Generally used for food and chemical grade CO ₂ products
Recycle option A	Secondary recycle I, small primary recycle (about 3%)	Secondary recycle I, small primary recycle (about 3%)	Secondary recycle I, small primary recycle (about 3%)
Recycle option B	Secondary recycle I, large primary recycle (about 34%)	Secondary recycle I, large primary recycle (about 34%)	Secondary recycle I, large primary recycle (about 34%)
Recycle option C		Secondary recycle II, small primary recycle (about 3%)	Secondary recycle II, small primary recycle (about 3%)
Recycle option D		Secondary recycle II, large primary recycle (about 34%)	Secondary recycle II, large primary recycle (about 34%)

Table 16 Three levels of CO₂ assessed for costs of processing and transport (Yan and others, 2009b)

Component, vol%	CO ₂ -87	CO ₂ -96	CO ₂ -99
CO ₂	87.19	96.00	98.86
N ₂	6.76	3.03	1.10
Ar	3.34	0.51	0.03
O ₂	2.17	0.46	0.01
CO ₂ purification level	1, low	2, medium	3, high

Table 17 Comparison of impacts on cost of non-condensable gases on CCS (Yan and others, 2009b)

Differences in CO ₂ purity	Cost differences (Δ€/pure CO ₂)		
	Capture	Transport	Storage
(CO ₂ -96)–(CO ₂ -87)	4.41	0 to (–2.9)	(–0.23) to (–0.58)
(CO ₂ -99)–(CO ₂ -96)	2.58	0 to (–0.26)	(–0.06) to (–0.17)
(CO ₂ -99)–(CO ₂ -87)	6.99	0 to (–4?)	(–0.29) to (–0.75)

technical impacts of the non-condensable components will have a notable effect on the cost of transport through the properties of the CO₂ mixtures. They found that the absolute cost increase for transport due to the increase in non-condensable gases has a more noticeable influence at longer transport distances. However, the total cost is more dependent on transport distance compared with non-condensable gas contents. The non-condensable components have significant impacts on the effective storage capacity, but less significant impacts on the costs of storage based on the current cost model. The storage conditions have a greater impact on the total costs than the non-condensable gas components. They concluded that a non-condensable gas component of <4 vol% can be considered as a reasonable CO₂ purification level for general cost balance in the oxy-coal combustion CCS chain. A non-condensable component of around 10 vol% can be considered for some special CCS cases, for example where there is only a short distance to transport and no lack of storage capacity is foreseen. However, such a high level of non-condensable components is generally not recommended.

4.8 Assessment of converting plants to oxyfuel combustion

The IEA GHG commissioned a study to confirm the projected costs for CO₂ capture from a new build PC-fired boiler using a supercritical steam cycle and oxyfuel combustion (Dillon and others, 2004). In the study the overall thermal efficiency was reduced from 44.2% to 35.4% (LHV). The net power output was reduced from 677 MWe to 532 MWe (IPCC, 2005).

Important features of the system include (IPCC, 2005):

- Burner design and gas recycle flow rate were selected to

achieve the same temperatures as in air combustion (compatible temperature with existing materials in the boiler).

- The CO₂-rich flue gas from the boiler is divided into three gas streams: one to be recycled back to the combustor, one to be used as transport and drying gas of the coal feed, and the third as product gas. The first recycle and the product stream are cooled by direct water scrubbing to remove residual particulates, water vapour and soluble acid gases such as SO₃ and HCl. Oxygen and entrained coal particulates flow to the burners, together with the second recycle stream.
- The air leakage into the boiler is sufficient to give a high enough inerts level to require a low temperature inert gas removal unit to be installed, even if pure O₂ were used as the oxidant in the boiler. The cryogenic oxygen plant will, in this case, produce 95% O₂ purity to minimise power consumption and capital cost.
- The low temperature (–55°C) CO₂ purification plant (Wilkinson and others, 2003) integrated with the CO₂ compressor will not only remove excess O₂, N₂, argon, but can also remove all NO_x and SO₂ from the CO₂ stream, if high purity CO₂ is required for storage. Significantly, removal of these components before final CO₂ compression eliminates the need to otherwise incorporate upstream NO_x and SO_x removal equipment in the net flue gas stream leaving the boiler. Elimination of N₂ from the flue gas results in higher SO_x concentrations in the boiler and reduced NO_x levels. Suitable corrosion resistant materials must be chosen for construction.
- The overall heat transfer is improved in oxyfuel firing because of the higher emissivity of the CO₂/H₂O gas mixture in the boiler compared to nitrogen and the improved heat transfer in the convection section. These improvements, together with the recycle of hot flue gas,

increase the boiler efficiency and steam generation by about 5%.

- The overall thermal efficiency is improved by running the O₂ plant air compressor and the first and final stages of the CO₂ compressor without cooling, and recovering the compression heat for boiler feedwater heating prior to deaeration.

Engineering studies have confirmed that the concept of retrofitting oxyfuel combustion with CO₂ capture to existing coal-fired power plants does not have any technical barriers and can make use of existing technology systems (IPCC, 2005).

Tigges and others (2008) have considered the plant modifications and new components required for retrofitting oxyfuel firing to an existing power station. The retrofit measures would enable the power plant to be operated both with oxygen and air firing after the retrofit. The retrofit measures are based on a state-of-the-art 600°C, 820 MWe power station that is under construction. During air firing, the flue gas is cooled in the air preheater, NO_x concentration is decreased by catalysis, particulates are removed in the ESP and SO_x is removed using limestone in a wet scrubber.

In considering the retrofit to oxyfuel firing, it is found that the complexity of flue gas recycling is reduced by the progress made in flue gas treatment. Recycling high-temperature flue gas, before the air preheater is advantageous thermodynamically but requires a total change of the heat balance and a redesign of the plant (boiler and components). A high particulate recirculation upstream of the ESP would increase the erosion of all firing and boiler parts. Without deSO_x treatment, the SO₂/SO₃ concentration would be increased by accumulation (about a factor of 3). In addition, SO₃ formation would increase as a result of contact with catalytic surfaces. Thus, all firing and boiler components, such as flue gas and recycle gas ducts, blowers, mill, burners, heat exchangers, boiler materials, would be at risk from corrosion (Tigges and others, 2008).

For retrofit cases, the original plants are not designed on the air side for such an operation involving high temperature, particulates or SO₂/SO₃ concentrations. Modifications would be quite expensive since all equipment in the boiler house would have to be replaced. For these reasons, the retrofit concept is based on the recirculation of cold, cleaned and partially dried flue gas, (improved) deSO_x and additional flue gas cooling (Tigges and others, 2008).

Most of the necessary retrofit measures will be implemented outside the boiler house. Switching between oxyfuel and air separation mode can be done simply by using the gas tight dampers at the former air inlet where the recycle duct is mounted. Other changes outside the boiler house involve pure oxygen oxidation in the improved deSO_x plant, the addition of a flue gas cooler/condenser upstream of flue gas recycling and subsequent cleaning of the flue gas to reduce the SO₂/SO₃ content still further. The purge gas of the mill is switched to CO₂, the atomising gas for the aqueous ammonia in the deNO_x is replaced by CO₂ and the ash removal at the ESP is replaced by a gas tight system. For oxygen preheating a tubular preheater parallel to the air preheater, now used as

gas/gas preheater for the recycle gas, will be installed (Tigges and others, 2008).

In the oxyfuel process, all reactions within the absorber have to work under a CO₂ atmosphere. As already shown on a laboratory scale, the desulphurisation performance is lowered under oxyfuel conditions when scrubbing is done with limestone. This effect is probably even more marked under real conditions because limestone solubility is hindered by the CO₂ atmosphere in the absorber. Saturation of the slurry with CO₂ will see the solubility of limestone drop significantly. For this reason, the reagent should be changed to calcium oxide (quicklime), which does not need to release CO₂ to the flue gas while dissolving (Tigges and others, 2008).

At least the same performance is expected from running the absorber with CaO under oxyfuel conditions as it is from running the absorber with limestone under normal conditions. Using quicklime under normal conditions, experience shows that a lower amount of recirculation is necessary for the same absorber efficiency. The conclusion is to change the absorbent mixing station from limestone to lime which only needs an additional slaking system. Furthermore, the absorber oxidation air system should be changed to use pure oxygen, necessitating a retrofit of the oxidation blowers and agitator system (Tigges and others, 2008).

In the oxyfuel mode the flue gas contains about 93 %wt of CO₂. The mass flow is reduced to 25% of flue gas flow leaving an air-fired furnace. Purification and compression of this CO₂ rich flue gas is the last step of the oxyfuel process. This plant is divided into 3–4 compression units (Tigges and others, 2008).

Some of the remaining contaminant gases, such as NO_x and SO_x, are separated during compression of the flue gas and leave the process as condensate from the intermediate coolers as sulphuric and nitric acids. Most of the water is also removed from these intermediate coolers. There is no other purification step; the other trace gases such as nitrogen, oxygen and argon remain in the compression stream. Liquefaction of the CO₂ is necessary to make a phase separation possible to remove these gases as well. This process is to be done just below the critical point of the CO₂ to avoid low temperatures for liquefaction. Whether this is necessary or not is decided by the requirements of transport and later storage of the CO₂. For EOR purposes, it is important to have no oxygen in the gas. Oxygen limits have not yet been set for other storage alternatives such as deep aquifers. Research on this aspect has not been concluded – in fact, it has only started in most countries (Tigges and others, 2008). The trace gases of nitrogen and argon do not hinder CO₂ storage or use for EOR as long as their concentration is kept low. Water has to be removed down to very low values to prevent corrosion in pipelines and tanks.

4.9 Discussion

There is a need to establish an appropriate and acceptable level of impurities in the CO₂, based on (Santos, 2009):

- health, safety and environmental considerations;

- quality specifications defined by the transport and delivery of CO₂ to storage sites;
- quality specifications defined by the storage CO₂ for different storage options.

Depending on the O₂ content requirement, processes are now available to produce CO₂ with a purity of 95–99.999%.

Pure CO₂ has been thoroughly characterised for a wide range of conditions. A general behaviour of all gases is that a slight change of pressure or temperature near the critical point has a large effect on the density. According to Sass and others (2009), it is not essential that the fluid be in the supercritical state once it is either in the pipeline undergoing transport, or in the injection well being carried to a storage reservoir, but it is desirable that the phase state be constant. The main considerations for flue gas purity as it leaves the boiler and is processed in downstream unit operations are shown in Figure 13.

In the oxyfuel process, the purity of CO₂ is influenced mainly by (Tigges and others, 2008):

- where the flue gas is recycled in the process, that is, the cleaning that has been done up to this point;
- the sealing of the boiler and other components;
- the purity of the oxygen from the air separation unit;
- the performance of all air quality control systems, such as deNO_x, deSO_x and ESP;
- additional CO₂ purification during and after compression.

The issue of optimum product CO₂ purity is a question that at the moment does not have a satisfactory answer. It depends on the type of application and the geological properties of the site. However, the optimum is uncertain from economic and geological points of view. It is clear, though, that storage of low CO₂ concentration streams is not economic.

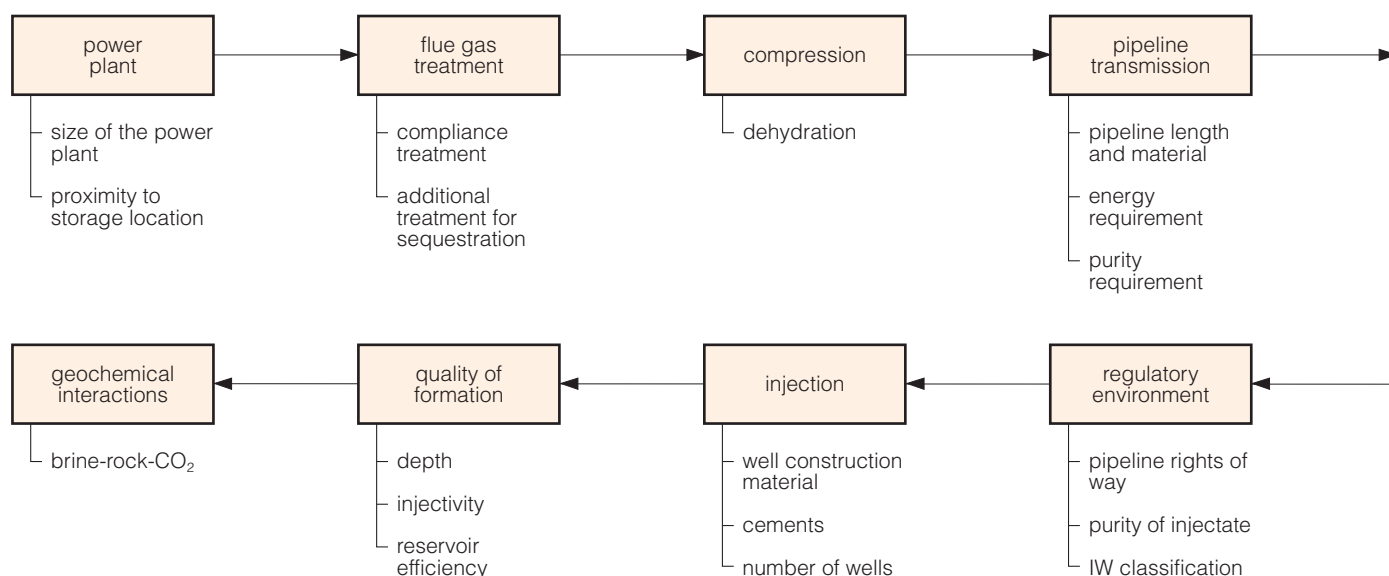


Figure 13 Considerations for flue gas purity (Sass and others, 2009)

5 Current research on oxyfuel flue gas treatment

There are seven main groups who have been active on coal oxyfuel combustion R&D. The groups are Argonne National Laboratories, USA; Alstom in the USA; Babcock and Wilcox/Air Liquide, USA; Electric Power Development/Ishikawajima-Harima Heavy Industry, Japan; Nagoya University, Japan; Vattenfall/Chalmer University, Sweden; CANMET/University of Waterloo, Canada; and Imperial College/Air Products/Doosan Babcock, UK. According to Croiset and others (2005), publications from these groups represent more than 75% of the open literature about coal oxyfuel combustion. The current work by these organisations on oxyfuel combustion flue gas treatment is explored in this chapter.

5.1 Air Products

The focus of work at Air Products in the Oxycoal 1 project has been to determine a new method of producing CO₂ free from NO_x, SO₂, Hg and O₂ to meet possible specifications for CO₂ for geological disposal and enhanced oil recovery (EOR). For EOR, O₂ in the CO₂ stream may need to be removed down to around 10 ppmv (White and Fogash, 2009). Their work is described in this section.

The process for purifying CO₂ takes the impure CO₂ from the boiler and cools it to condense water vapour, remove traces of ash and dissolve soluble gases such as SO₃ and HCl. The cooled, raw CO₂ is then compressed to about 30 bar (3 MPa) and the CO₂ is purified by partial liquefaction and phase separation. White and others (2006) presented reactions that gave a pathway for NO_x to be removed as HNO₃ and SO₂ to be removed as H₂SO₄ during the process of compression of raw CO₂ to 30 bar (3 MPa). Any elemental mercury or mercury compounds present in the flue gas would also be removed as mercuric nitrate, since mercury compounds react readily with nitric acid (White and others, 2009). Typical nitric acid concentrations in the process will be sufficient to remove all mercury from the CO₂ stream, either by reaction or dissolution.

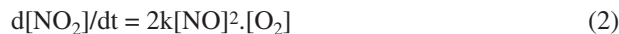
5.1.1 NO_x and SO_x reactions

The NO_x and SO_x reactions are explained in this section. At the high temperatures at which NO_x is formed during combustion the equilibrium dictates that mostly NO will be formed. Subsequent conversion of NO to NO₂ can follow:

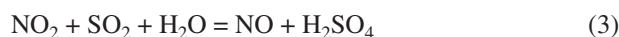


At low temperature, the equilibrium of equation 1 is strongly in favour of NO₂ production rather than NO. However, at low pressure the rate of equation 1 is low and so, in an air-fired boiler without CO₂ capture or NO_x removal, the main NO_x emissions would be as NO. However, although the rate of equation 1 is slow at ambient conditions, it speeds up with *decreasing* temperature and increasing pressure. The reaction

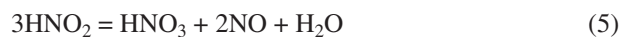
rate is given by equation 2:



where k , in l² mol⁻² s⁻¹, is $1200 \times 10^{230/T}$ where T is in Kelvin. As the rate is therefore proportional to pressure to the third power, this reaction rate is likely to become significant at higher pressures and low temperatures. The second reaction of significance is the reaction of NO₂ with SO₂ to form sulphuric acid, commonly referred to as the lead chamber process for the manufacture of sulphuric acid:



This reaction is known to be fast, and so White and others (2009) assumed it to be equilibrium limited in their modelling work. Whilst SO₂ is removed by equations 1 and 3, NO₂ will be converted to nitric acid by the well understood slower nitric acid process:



with the NO formed in equations 3 and 5 being converted to NO₂ by equation 1.

These reactions give a pathway for SO₂ to be removed as H₂SO₄ and NO and NO₂ to be removed as HNO₃ (White and others, 2009).

The experimental results showed that the main reaction pathways are viable and the rates of reaction sufficient to produce the desired results: SO_x and NO_x removal by compression and contact with water. Some of the modelling results needed minor modifications to match the experimental results. However, in general, the model was a close approximation to the experimental results. H₂SO₄ and HNO₃ are seen together in the condensate, while some SO₂ is left in the gas stream. This means that the assumption of the fast rate of the lead chamber reaction compared to the nitric acid reaction needs to be reassessed. The focus of recent work by White and Fogash (2009) has been to take advantage of this improvement.

5.1.2 NO_x and SO₂ removal from oxyfuel-derived CO₂

Residence time and contact with water must be introduced after compression of the raw CO₂ for the reactions described to proceed so as to remove SO₂, NO and NO₂ from the process. This is shown in Figure 14. After adiabatic compression to 15 bar (1.5 MPa), the CO₂ is cooled and heat integration could be incorporated into the steam system. At this point, holdup is added to the process, by for instance, pumping liquid condensate around a contacting column. In the modelling process, White and others (2009) found that a holdup of only a few seconds was sufficient time for all of the

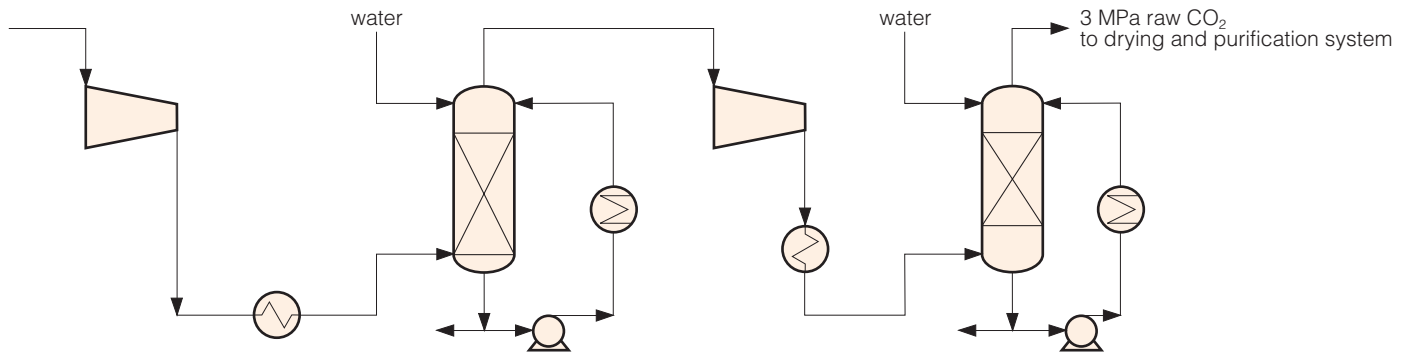


Figure 14 Raw oxyfuel CO₂ comparison with integrated SO_x and NO_x removal (White and others, 2009)

SO₂ to be removed as H₂SO₄. The contactors allow intimate mixing of water with SO₃ and then with NO₂ to remove these components from the gas continuously. This allows reactions to proceed until all the SO₂ and the bulk of the NO is removed. Little HNO₂ or HNO₃ will be formed until all of the SO₂ has been consumed. NO₂ formed by the slow equation 1 is consumed by the fast reaction in equation 3, while the slow reaction in equation 4 produces HNO₂ or HNO₃. The SO₂-lean CO₂ is then compressed to 30 bar (3 MPa) where a similar process as at 15 bar (1.5 MPa) adds another 15 s of holdup to the process. Around 90% of the NO_x and essentially all of the SO₂ can be removed in this way from the CO₂ before being dried and the inerts removed (White and others, 2009).

5.1.3 Removal of inerts

Inerts are removed to avoid increasing the critical pressure of CO₂ in the pipeline and possible two-phase flow developing, leading to CO₂ purities of around 95–98% minimum (White and others, 2006). Low temperature inerts removal from crude CO₂ using phase separation has been researched. Typically, it results in an oxygen content of 1 mol% and a total inerts level of 2–5 mol%.

The impure 30 bar (3 MPa) CO₂ is then dried in a dual-bed thermally regenerated desiccant drier. Oxygen, nitrogen and argon are removed from the CO₂ by low temperature processing, shown in Figure 15. The impure CO₂ is cooled against evaporating lower pressure liquid CO₂ streams to a temperature of –55°C, close to its triple point. This reduces the partial pressure of CO₂ in the uncondensed gas stream to about 5 bar (0.5 MPa), corresponding to a typical concentration of about 20–25 mol% CO₂. The inerts stream leaving the cold equipment at about 30 bar (3 MPa) is heated further and power is recovered from the stream using a power turbine. The purified CO₂ streams leaving the cold equipment are compressed in a second stage of CO₂ compression which is adiabatic with heat recovered to the boiler steam system. Adiabatic compression ensures better aerodynamic characteristics in the CO₂ compression system near the critical points and confines the rapid density change to the aftercooler (White and others, 2006).

Once the net flue gas is cooled by direct contact with water,

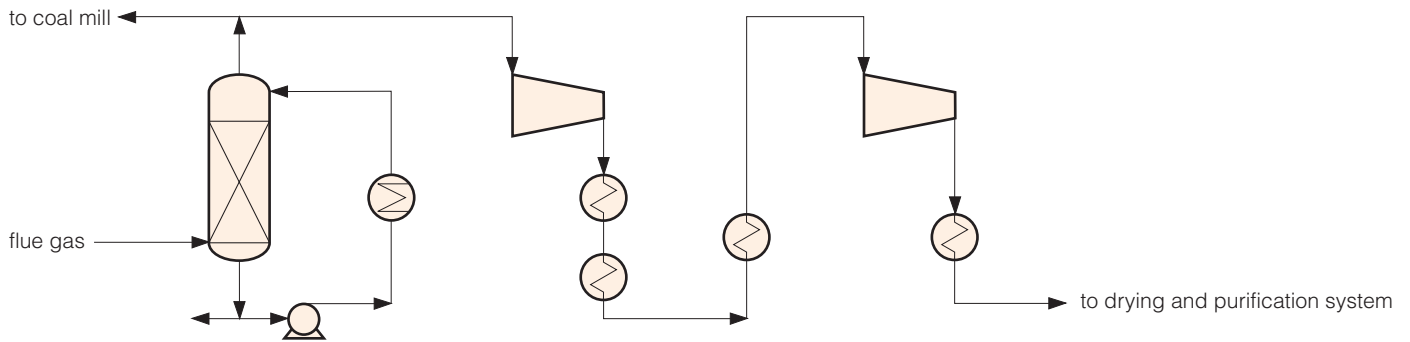
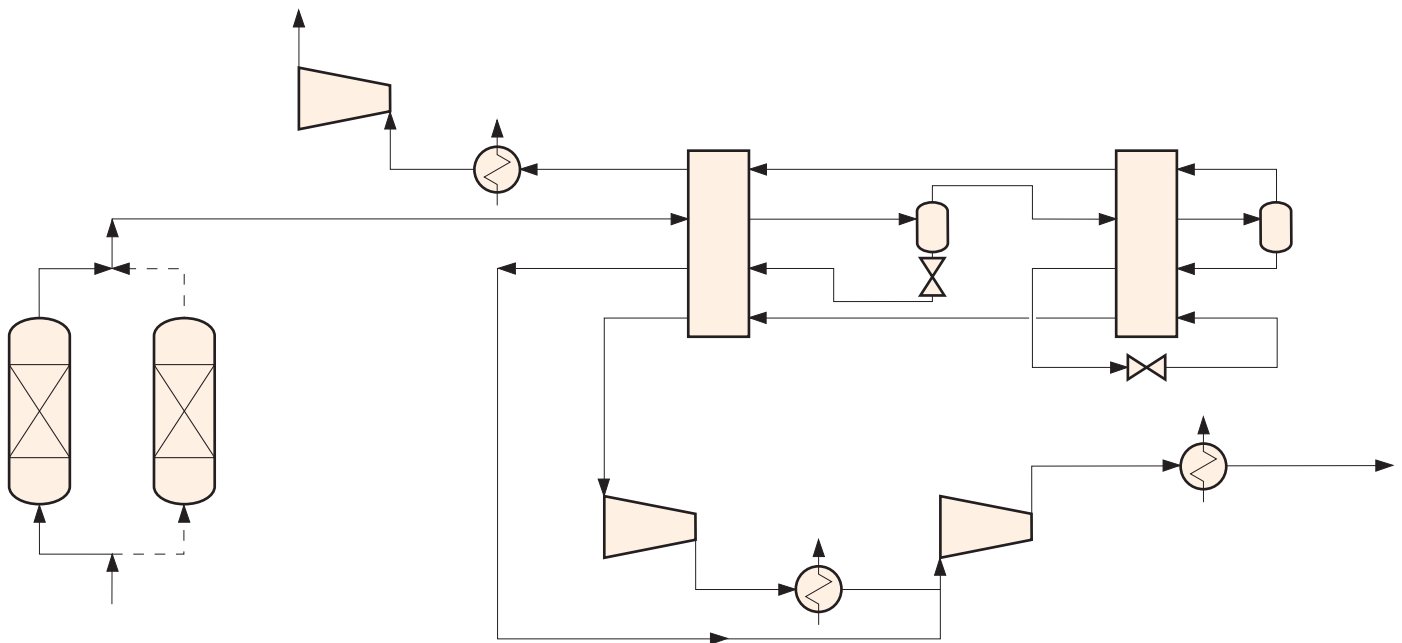
the raw CO₂ composition entering the CO₂ compressor is then typically as shown in the first column of Table 18 (White and others, 2006). After CO₂ purification, as has been described, the CO₂ product has the composition shown in the second column. Although some of the NO_x, N₂, O₂ and Ar are removed, all of the SO₂ was considered to leave with the CO₂. However, White and others (2006) no longer consider this to be the case.

5.1.4 Experimental work

Doosan Babcock has a 160 kWth NO_x reduction test facility with an oxyfuel firing configuration in Renfrew, Scotland. In this setup, primary air is replaced with CO₂ supplied from a liquid storage tank and secondary air is replaced with flue gas recycled from the ESP outlet. Oxygen is injected into the CO₂ and secondary flue gas recycle streams upstream of the coal injection point and windbox respectively. Oxygen is stored as liquid and is vaporised on demand. Tests were carried out over two weeks with the facility operating for ten hours each day to give a steady feed to the sour compression apparatus (White and others, 2009).

The sour compression apparatus at Imperial College, London has been employed. A side stream from the NO_x reduction test facility has been used as the feed, which is taken after the recycle fan. It is then cooled to ambient temperature in a flue gas cooler. The cooler is followed by a condensate trap. Condensate accumulates here during the experimental runs as there is no provision for continuous drainage. Analysis of the liquid condensate collected after the flue gas cooler showed that around 10% of the inlet SO₂ was lost from the gas phase between entering the flue gas cooler and leaving the condensate separator. Then the compressor increases the pressure up to a maximum of 7 bar g (0.7 MPa) and discharges into a receiver. Condensate accumulates in the receiver during runs. The compressed flue gas then goes to a stainless steel cylinder that is externally temperature controlled. The cylinder provides further holdup and can provide liquid/vapour contacting by prefilling with water or acid. Flow control through the system is achieved using the mass flow controlled on the outlet from the reactor (White and others, 2009).

The experiment was run at a pressure of 14 bar g (1.4 MPa)

raw CO₂ cooling and compression to 3 MPa**CO₂ inerts removal and compression****Figure 15 Raw CO₂ cooling, compression and inerts removal** (White and others, 2006)**Table 18 Raw and product CO₂ compositions from basic oxyfuel process** (White and others, 2006)

	Raw flue gas (35°C, 0.102 MPa mol%)	CO ₂ product (35°C, 11 MPa mol%)	CO ₂ product (35°C, 11 MPa mol%) Corrected
CO ₂	71.5	95.8	96.3
N ₂	14.3	2.0	2.0
O ₂	5.9	1.1	1.1
Ar	2.3	0.6	0.6
SO ₂	0.4	0.5	0
NO	0.04	0.01	0
H ₂ O	5.6	0	0

and 7 bar g (0.7 MPa), with the feed composition roughly constant. It showed that the conversion of SO₂ dropped from 98% to 84% as the pressure dropped, and NO_x conversion dropped from 90 to 68%. There is therefore a dependence on

pressure and/or residence time. This tends to confirm one of White and others' (2009) assumptions, that pressure increases reaction rate. However, the effect of increased residence time still has to be separated from the effect of higher pressure.

The effect of flow rate on conversion of SO₂ and NO_x under the same pressure, 5 bar g (0.5 MPa), and inlet feed composition was studied. It was found that conversion decreased as the flow rate increased. This is due to a lower residence time in the compressor receiver, which confirms the importance of residence time for the SO_x/NO_x removal reactions (White and others, 2009).

In further experiments, selective catalytic reduction (SCR) elements were introduced to allow variation of the NO_x concentration in the feed gas to the sour compression apparatus. White and others (2009) found that SO₂ conversion decreased as the SO₂/NO_x ratio increased, which supports the theory that NO_x acts as a catalyst for SO₂ oxidation to SO₃, leading to H₂SO₄ due to the presence of water.

Gas phase mercury analysis was carried out on the NO_x Reduction Facility, but it was not possible to confirm gas phase composition after the sour compression rig. Liquid phase analysis showed that the mercury content of the liquid collected in the receiver and reactor are in the same order of magnitude as the blank runs, which are interpreted as negligible mercury content. However, the liquid collected in the condensate separator has a mercury content one order of magnitude higher, indicating that any mercury present is removed from the gas phase with the first acidic condensate stream (White and others, 2009).

The purity of CO₂ required for EOR is greater than that required for other geological storage sinks due to the requirement to minimise the oxygen content as it reacts with the hydrocarbons in the oil field. This adds a complication to the purification of CO₂ from oxyfuel applications as there may be around 1 mol% oxygen in the captured CO₂ due to the excess oxygen from combustion. This oxygen could be removed by using a fuel rich combustor, or a catalytic combustor, to consume the oxygen present in the CO₂ before removal of inerts. White and others (2006) chose to incorporate distillation of the liquid CO₂ to remove oxygen. This allowed them to reach purities of 10 ppm of O₂ in the CO₂ without adding other impurities that might be created by fuel rich combustion.

5.1.5 Power, recovery and purity trade-off in CO₂ purification

Table 19 shows three different options for CO₂ purification from an oxyfuel-fired coal combustion system. Actual powers

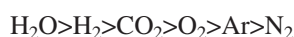
depend upon the type of coal burned and the amount of air in-leakage there is into the boiler, since this dictates the level of inerts that must be removed from the raw CO₂, together with issues such as cooling water temperature. However, the numbers in Table 19 are consistent. It shows that low purity CO₂ requires the lowest power and gives the highest capture of the contained CO₂. Increasing the purity of the CO₂ decreases recovery by 2% with a 1% reduction in power, so overall capture efficiency is reduced. Around a 5% increase in power is necessary to reach the higher purities required for EOR. Therefore, it is possible to say that the extra penalty of achieving EOR-grade CO₂ from oxyfuel-fired coal combustion is both feasible and tolerable.

5.1.6 Membranes

A membrane module has recently been added to the Air Products base process. White and Allam's (2008) invention involves a membrane separation system to separate CO₂ from a feed gas, and use of the CO₂ to improve the performance of the oxyfuel combustion process. It has been added to the vent stream where a CO₂ and O₂ rich stream are recycled to the boiler. This addition may yield a potential CO₂ capture rate as high as 98% overall. It also reduces the size of the air separation unit required by 5%. Table 20 shows the effect that the membrane can have.

In the preferred situation, the total amount of nitrogen and argon that diffuses through the membrane(s) is no more than about 30%, and ideally between 10% and 30% of the total amount of N₂ and Ar in the feed gas. CO₂ is separated from the feed gas by diffusion across at least one hollow fibre polymeric membrane in the membrane separation system. The apparatus of White and Allam's (2008) invention is an oxyfuel combustion unit and a membrane separation system. There is a conduit arrangement for feeding separated CO₂ from the membrane separation system to the oxyfuel combustion unit.

A 'permeable membrane' is a selective barrier that allows different gases, vapours or liquids to diffuse through the membrane at different rates. Different gases have different rates of diffusion through a given permeable membrane. The relative rates of diffusion through a polymeric membrane designed for the preferential diffusion of CO₂ is as follows:



The permeate fraction of a gas is the proportion of that gas

Table 19 Power, recovery and purity in oxyfuel CO₂ purification (White and others, 2006)

CO ₂ purity, mol%	Oxygen content	CO ₂ recovery, %	Power* from 0.1 to 11 MPa, kWh/t CO ₂ captured
95.9	0.9 mol%	89	168.5
98	0.6 mol%	87	166.5
99.7	10 ppmv	87.4	177.1

* Power includes adiabatic compression, without credit for steam system feedwater heating, so numbers may appear high compared to intercooled compression

Table 20 Purity, recovery and power from the Air Products' work (White, 2007)

Description	CO ₂ purity, mol%	Oxygen content	CO ₂ pressure, MPa	CO ₂ recovery, %	Relative specific power
Standard cycle	95.9	0.91 mol%	11	89	1
High purity option 1	99.89	100.00 ppm	11	87.4	1.03
High purity option 2	99.98	100.00 ppm	11	87.7	0.99
3 MPa liquid CO ₂	100	100.00 ppm	3	87.7	1.02
0.7 MPa liquid CO ₂	100	5.01 ppm	0.7	87.7	1.02
Standard with membrane	96.3	0.73 mol%	11	97.7	0.91
High purity option 1 with membrane	99.86	100.00 ppm	11	97.9	0.97

that diffuses through the membrane. The membrane preferably provides a permeate fraction for CO₂ of at least 0.7, ideally more than 0.8, and possibly about 0.9. The permeate fraction for O₂ should be at least 0.3, preferably 0.45, and possibly at least about 0.55. Unfortunately, as the permeate fraction for CO₂ and O₂ increases, the non-permeate fraction of N₂ and Ar decreases. Therefore, the membrane ideally provides a non-permeate fraction for N₂ of no less than 0.8 and for Ar of no less than 0.6 (White and Allam, 2008).

In situations where the feed gas contains O₂ and at least one inert gas (of N₂ and Ar), the membrane separation system is selected to provide an acceptable balance between the permeation factor for O₂ and the non-permeating factor for the inert gases. One advantage is that a significant portion of CO₂ in the feed gas also diffuses across the membrane, thereby increasing the recovery of CO₂ from the process. The preferred membranes are polymeric, that is made from at least one polymer. Air Products have developed the PRISM® membrane separation unit. It contains thousands of polymeric, hollow fibre membranes embedded in a thermoset resin in a pressure resistant vessel. Each unit has the membrane material, seals to isolate the separated gases from the non-separated gases and a pressure vessel housing all the components. The operating pressure is usually 10–50 bar (1–5 MPa) (White and Allam, 2008).

Where nitrogen and argon are present in the feed gas, a small portion of these inert gases also diffuses across the permeable membrane(s) with CO₂ and oxygen, when present. If oxygen is recycled to the oxyfuel combustion process from the membrane separation system, which reduces the load on the oxygen generation system, the total amount of inert gases fed to the oxyfuel combustion process as contaminants in the oxygen feed is also reduced. However, the diffused contaminants recycled to the oxyfuel combustion process increase the level of contaminants within the oxyfuel combustion unit (White and Allam, 2008).

The bulk of the water soluble components (such as acid gases) may be removed from the flue gas by washing the flue gas with water. Washing has the added advantage of cooling the flue gas and causing the water vapour to condense. The

washed gas is then compressed and dried to remove most of the water. The method developed by White and Allam (2008) involves washing a portion of the flue gas with water to remove the water soluble components, then drying it to produce contaminated CO₂ gas. This is then cooled and partially condensed by indirect heat exchange to produce partially condensed crude CO₂ fluid. The fluid is then phase separated to produce impure liquid CO₂ and waste vapour. Part of the waste vapour is then fed to the membrane separation system.

The washing step usually takes place in a counter-current gas-liquid contact vessel such as a wash (or scrub) column. It is preferable for the washed flue gas to be compressed prior to drying. Compression can be incorporated with the membrane system to remove some of the SO₂ and NO_x from the flue gas. In this case, the washed gas is compressed to 10–50 bar (1–5 MPa) and kept at this pressure in the presence of oxygen and water and, when SO₂ is to be removed, NO_x, for a sufficient period of time to convert SO₂ to H₂SO₄ and/or NO_x to HNO₃. The H₂SO₄ and/or HNO₃ is separated from the washed flue gas to produce SO₂-free, NO_x-lean crude CO₂ gas which is usually then fed to the gas drying system after further compression. This has the advantage of removing any mercury present from the flue gas (White and Allam, 2008).

Where the flue gas contains SO₂ and NO_x, the preferred method involves converting SO₂ to H₂SO₄ at a first elevated pressure and converting NO_x to HNO₃ at a second higher elevated pressure. Some of the NO_x may be converted to HNO₃ at the first elevated pressure. For example, if the SO₂ feed concentration is low enough, there could be more HNO₃ than H₂SO₄ produced at the first raised pressure (White and Allam, 2008).

At least 50% and preferably more than 80% of the CO₂ in the feed gas may be separated. Oxygen is usually present in the feed gas. When this is the case, a portion of the O₂ will inevitably be separated with the CO₂ from the feed gas by diffusion across the membrane(s) and then fed to the oxyfuel combustion unit. In this situation, at least about 30 mol%, and preferably about 45 mol% of the oxygen in the feed gas is separated from it. Oxygen for oxyfuel combustion is normally produced from an ASU. One advantage of feeding O₂

separated from the feed gas to the membrane separation system is that the size and power requirement of the O₂ generation plant is reduced (White and Allam, 2008).

The main advantage of the membrane system is that it achieves a recovery of CO₂ of 98 mol%. In addition, recycling excess O₂ reduces the oxyfuel O₂ demand by about 3.5%. In summary, the addition of the membrane system has the following advantages:

- it improves low temperature CO₂ purification;
- CO₂ is produced at a purity of at least 97 mol%, and up to 99.9 mol%;
- CO₂ is produced with a very low level of O₂ or CO, for example no more than 1000 ppm and usually about 10 ppm;
- CO₂ is produced with low levels of N₂ and Ar or other contaminants, typically a combined level of no more than 1000 ppm;
- a reduction in the overall power consumption, defined as kWh/t CO₂ separated;
- an increase in the recovery rate of CO₂.

5.2 Air Liquide

Air Liquide has been working on improving the viability of coal oxy-combustion by developing a CO₂ compression and purification unit (CPU) for CO₂ capture. The role of the CO₂ CPU is to capture CO₂ from combustion flue gases and to purify it to the required specification. Air Liquide has conducted research on the removal of impurities from the flue gas at the laboratory and pilot plant level. When designing a CPU, there are two main considerations to take into account (Court and others, 2009):

- the ability to deal with all the impurities contained in the flue gas to be processed while delivering the required CO₂ stream quality and conditioning required;
- an ability to balance the performances and cost of the processing unit.

The flue gas composition and CO₂ product specifications for transport and storage, (pressure and quality), have a strong influence on the performance and cost of the CO₂ CPU. The overall design of the unit will reflect the trade-off between CAPEX (capital expenditures) and OPEX (operating expenditures) which depend on the valorization of energy and CO₂ stream.

The composition of flue gases can be influenced by the amount of air infiltration in the boiler and associated equipment such as fans, filters, piping and the desulphurisation unit. Existing old plants are likely to have significant air infiltration. In contrast, new oxy-combustion plants can be designed to have minimal air infiltration. Thus, CO₂ capture units designed for retrofitting existing power plants would have to treat a flue gas stream where the CO₂ is more dilute than that in a stream from a new oxy-combustion power plant boiler (Court and others, 2009).

Darde and others (2009) have proposed a basic scheme for processing flue gas to capture CO₂ as follows:

- 1 Compression of the wet flue gas.

- 2 Drying of the flue gas at the outlet of the 'wet compression' step.
- 3 Flue gas purification (if considered).
- 4 Compression of the dry product gas to a pressure at which it condenses at 20°C.
- 5 Pumping of the condensed product to pipeline pressure.

The combination of compression, condensation and pumping minimises the power demand of the process. However, condensation and pumping processes can be used only in cases where the condensation pressure is lower than the final product pressure. The flue gas purification step can contain several unit operations to meet the specifications for different gas components. Darde and others (2009) considered three different flue gas purification schemes:

Case 1, no purification

There was no flue gas purification step in this scheme. Instead the entire flue gas was compressed, dried and compressed again (and pumped if possible) to the final product pressure of 175 bar (17.5 MPa), resulting in 100% CO₂ recovery. However, the CO₂ purity of this product is quite similar to that of the flue gas, on a dry basis. Thus, this scheme is only useful for plants where the flue gas purity is quite close to the desired product purity. In addition, this scheme does not target reduction in any other gas components and so cannot meet any specifications for minor components in the product stream. For example, such a process would typically have O₂ in the single percentage range, which is not acceptable for EOR applications.

Case 2, partial condensation (cold box)

In this scheme, the compressed and dried flue gas is cooled to a low temperature to condense out at least 90% of the CO₂. CO₂ purity in the condensed phase is a function of the pressure and composition of the inlet gas to the partial condenser system, the number of stages of partial condensation in the cold box and the condensation temperature; 95% CO₂ purity is usually achieved quite easily for typical flue gas compositions. This scheme can deliver a product with O₂ in the range of thousands of ppm.

Case 3, cold box including distillation

This is an extension of Case 2, in which a distillation column is used to purify further the condensed CO₂ stream in the cold box. This scheme also targets 90% CO₂ recovery. CO₂ purity in excess of 99% is typically achieved in this scheme. The distillation column also helps to reduce the O₂ content to the low ppm range.

Darde and others (2009) found that the power requirement of the CPU decreases with increasing CO₂ concentration in the inlet flue gas. This is because a lower volume of total gas has to be compressed and treated to capture the same quantity of CO₂. At about 72% inlet CO₂ (dry basis), which is in the range for a retrofit plant, just compression of the gas to the final pressure requires nearly 170 kWh/t of energy. In contrast, compressing the gas to an intermediate pressure and purifying it in a cold box, with or without a distillation column, requires only about 140 kWh/t of energy and produces a much higher purity product (about 95–99%+ CO₂).

As the CO₂ concentration in the inlet flue gas increases, less energy is required for all processes to meet product specifications. If the inlet CO₂ concentration is about 93%, the three processes take nearly the same amount of specific power. However, the CO₂ purity of the product is significantly above 95% for the purification schemes, while it is about 93% in the case of no purification (Darde and others, 2009).

The overall power requirement of the CPU is dependent upon the product pressure, so the relative power requirements of the three schemes were examined with simulations run at different product pressures. For 83% inlet CO₂, it was found that flue gas purification requires significantly less specific energy than simply compressing the entire flue gas to the product pressure, for the range of product pressures studied. In contrast, if the CO₂ is more concentrated in the flue gas, the compression only case is more comparable to the purification cases. For example, at 93% inlet CO₂, the 'no purification' process requires lower specific energy than the cold box with distillation process, up to a product pressure of 185 bar (18.5 MPa). However, the cold box only process can provide a higher CO₂ purity in the product and lower O₂ content while consuming lower specific energy than the 'no purification' process (Darde and others, 2009).

Heat integration aims to improve overall process efficiency by transferring waste heat from various processes to the steam cycle. Considerable heat is generated by the compressors in the CO₂ CPU. If this energy can be used in other parts of the power plants for heating process streams, then the overall energy requirement for the plant can be reduced, and the requirement for cooling water is lessened. Darde and others (2009) found that heat integration can reduce specific energy consumption significantly. For example, at 72% inlet CO₂, the specific energy required by the 'no purification' process is reduced from about 170 kWh/t to about 140 kWh/t by using heat from the wet and dry compressors for heating boiler feedwater.

5.2.1 Babcock and Wilcox

Babcock and Wilcox (B&W) and Air Liquide have been collaborating on the development and demonstration of oxyfuel combustion. Technical and economic studies have been carried out as well as oxyfuel testing in B&W's 30 MWth Clean Environment Development Facility with bituminous, subbituminous and lignite coals. The next development step requires a commercial demonstration at a size sufficient to prove the operability and availability of the process from coal delivery to CO₂ storage. B&W and Air Liquide have developed a design at a net size of 100 MWe for such a demonstration (McDonald and others, 2009).

In 2005 SaskPower approached B&W and Air Liquide to perform an engineering evaluation of oxyfuel for a new plant in Saskatchewan, Canada. As a result B&W and Air Liquide undertook large-scale testing of oxyfuel combustion in 2006. Testing with a bituminous, subbituminous Powder River Basin and lignite coals were completed in the first months of 2008. Although the SaskPower project has yet to proceed, B&W and Air Liquide have continued to develop the process.

In 2008 they completed a study of a variety of options for integrating heat from the ASU, compression and purification unit (CPU), steam turbine and flue gas. The configurations were modelled using Aspen's HYSYS programme to produce performance results. Twenty-seven different cases including cold, warm, hot and reduced recycle configurations as well as wet FGD and a spray dryer absorber (SDA) gas cleaning arrangements were evaluated for Illinois no 6 bituminous coal. In the study, the fuel (heat) input was held constant for all cases to avoid impact on the balance of plant, fuel and ash handling equipment sizing and costs, and to simplify the comparison of options. Air Liquide internally optimised the ASU and CPU reducing auxiliary power and upgrading the heat of compression which was then used in the feedwater cycle, flue gas and oxygen system (McDonald and others, 2009).

Based on the HYSYS analyses and bituminous cost analyses, similar performance and costs were developed for select cases using subbituminous coal. The coal higher heating value, composition and impact on fuel efficiency were considered which had an effect on coal flow, ash flow, oxygen required, CO₂ produced and removed, and plant heat rate for the subbituminous cases (McDonald and others, 2009).

In the planned demonstration plant sulphur compounds are removed from the combined primary recycle and CPU gas flow by a SDA followed by a fabric filter which removes most of the SO₂ and essentially all SO₃, and a polishing sodium based wet scrubber to further reduce SO₂ from the flue gas before it enters the CPU. Most of the mercury is also removed in these devices together with chlorine and fluorine compounds. Moisture is removed from this stream by reducing the flue gas temperature. As the exiting gas is saturated, it must be reheated slightly before entering the primary fan or CPU (McDonald and others, 2009).

The CO₂ CPU designed by Air Liquide (*see previous section*), is purpose built to process the flue gas emissions from a coal-fired plant and to provide a CO₂ product stream at a specification suitable for transport and geologic storage. The direct result of this project has been a reorientation of Air Liquide's efforts toward critical areas such as:

- 1 The need for overall efficiency of the power plant by minimising ASU and CPU auxiliary power.
- 2 Some critical design parameters for the CPU are particulates, drying, and SO_x and NO_x treatment where specific provisions have been made in the CPU design to address these constituents. Air Liquide plans to have two CPUs in operation at pilot plants, Lacq and Callide. Scheduled for start-up in early 2011, the Callide Project, led by CS Energy, consists of a 100 MWth oxycombustion subbituminous coal-fired unit with CO₂ purification, transport and storage. Air Liquide is providing a CO₂ CPU designed to test the key technical features and be technologically representative of a commercial scale CPU. For example, this plant uses a centrifugal CO₂ compressor (instead of a screw compressor, which would typically be used at this size) in order to monitor the behaviour of the remaining particulates, as well as the acid gases (McDonald and others, 2009).

In addition to the significant NO_x reduction produced by oxy-combustion (30–50%), the combustion system design incorporates provisions to reduce NO_x formation in the burner zone. The furnace design and arrangement of burners are co-ordinated to maximise the burner zone cooling surface, reducing the burner zone heat release rate and flame temperature to minimise NO_x formation in the burner zone. The unit is also equipped with burners designed to minimise NO_x production for air- or oxy-firing and have been tested in B&W's Clean Environment Development Facility under both conditions. The combustion system has one level of NO_x ports designed to reduce further the formation of NO_x. NO_x produced in the process passes into the CPU where it is removed during the compression process with a small amount remaining in the non-condensable gaseous vent stream to the atmosphere (McDonald and others, 2009).

The FGD system includes both a SDA and wet FGD polishing scrubber to reduce emissions of SO₂ and particulate matter to low levels entering the CPU. In the warm recycle configuration, the flue gas flowing to the CPU and the primary recycle stream pass through the SDA for SO₂ removal. From the SDA, the flue gas flows to a pulse-jet fabric filter dust collector where the particulates and SO₃ are removed. Ash from the fabric filter is recycled to the SDA to improve sorbent utilisation. From the fabric filter, the flue gas passes through the polishing scrubber where the SO₂ concentration is further reduced and then moisture is removed. The clean, cooled gas then splits between the CPU and the primary recycle stream. SDA auxiliary systems include lime storage, preparation and feed system, recycle ash storage, preparation and feed system, and a fly ash handling system for the fabric filter. The small wet polishing scrubber auxiliary systems include a reagent storage, preparation and feed system and a solids denaturing system. These systems perform and operate in the same manner as in a conventional pulverised coal plant. The small amount of SO₂ that enters the CPU is condensed (McDonald and others, 2009).

Particulate matter is removed from both the secondary and main flue gas streams by high efficiency fabric filters. The small amount remaining is reduced further in the CPU process. Mercury is removed in both the SDA-fabric filter and the polishing scrubber prior to entering the CPU. The remainder is removed within the CPU process. Other heavy metals, as well as chlorine and fluorine are removed completely during the gas cleaning process (McDonald and others, 2009).

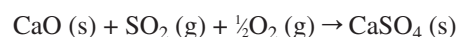
5.2.2 Babcock and Wilcox and other collaborations

Babcock and Wilcox is collaborating with the Ohio State University, the Ohio Coal development office, American Electric Power, Carmeuse Lime & Stone, CONSOL Energy Inc, Duke Energy, FirstEnergy, Clear Skies Consulting and Specialty Minerals Inc, to develop a dry regenerable sorbent based CO₂ capture process for coal-fired power plants. The carbonation calcination reaction (CCR) process uses limestone derived sorbents such as calcium oxide (CaO) to react with CO₂ to reform calcium carbonate (CaCO₃) which is

the main constituent in the original limestone material. The spent sorbent is then regenerated in the calcination process while also releasing concentrated CO₂ which can be compressed and transported to a storage site. A 20 lb/h (9 kg/h) sub pilot scale coal-fired facility has been built at the Ohio State University to test the concept on coal derived flue gas. The test facility consists of a coal-fired stoker furnace, a rotary calciner, sorbent and ash injection systems, a baghouse, fans and particulate control devices as well as a data management system. Over 90% CO₂ capture and near 100% SO₂ capture has been achieved on a once-through basis.

The sorbent has undergone multi-cyclic testing to understand the impact of process variables on its performance. A sorbent reactivation step overcomes the deterioration of performance. The net plant efficiency for the CCR process has been estimated to fall in the 32–34% range using a supercritical steam cycle. Significant heat and process integration is required to accomplish the simulated efficiencies (Sakadjian and others, 2009).

The dry regenerable sorbent process involves the capture of CO₂ using limestone-derived sorbents such as CaO at temperatures of 600–700°C. The process involves the chemical reaction between CaO and CO₂ to form CaCO₃. The carbonation reaction is exothermic and releases extractable heat at temperatures of 600–700°C. Sorbent regeneration takes place in a calciner at temperatures of 900°C or more, which decomposes CaCO₃ to CaO and concentrated CO₂ which can then be sent for compression and transport to final storage. The regenerated sorbent is then used to capture CO₂ in a subsequent carbonation cycle. The calcination reaction is endothermic and requires heat input into the process. In addition to capturing the CO₂, the sorbent can capture SO₂ simultaneously. Under the operating temperatures of the system, the SO₂ remains bound to the sorbent in the form of CaSO₄ and thus the CO₂ evolving in the calcination process can be relatively pure (Sakadjian and others, 2009). The sulphation reaction is shown in the following equation:



The gas that exits the furnace is first cooled to the required carbonation temperature of 600–700°C prior to the sorbent injection point. Sorbent is then injected to scavenge CO₂ from the flue gas. The sorbent is then separated from the flue gas and sent to the kiln for regeneration. The CO₂ depleted flue gas is cooled to around 50°C by aspirating ambient air into the gas. The cooled flue gas is then sent into a baghouse where the remaining sorbent and fly ash are separated. Due to the high calcination temperatures the sorbent activity is reduced. Thus, the regenerated sorbent from the calciner can be treated further in a reactivation step to renew sorbent performance. The sorbent is then conveyed back into the process for a subsequent CO₂ capture cycle. A screw feeder system is available for sorbent delivery and makeup into the calciner (Sakadjian and others, 2009).

Sakadjian and others (2009) found that the technology has the ability to capture more than 90% of the CO₂. The percentage of CO₂ removal increases monotonically with increasing

calcium to carbon mole ratio and 87% CO₂ removal corresponds to a calcium to carbon mole ratio of 1.05:1. The sorbent was able to achieve a range of CO₂ removal with varying sorbent injection rates without modifying the equipment. In addition, the tests yielded near 100% SO₂ capture from flue gas containing about 2000 ppm of SO₂. The carbonator was operated in an entrained flow mode and the effect of residence time was also well characterised (Sakadjian and others, 2009).

The second phase of the test programme involved the integration of the calciner to the facility, followed by shakedown, troubleshooting and testing of the cyclic carbonation-calcination concept. It was found that the sorbent was able to retain full activity over multiple cycles (Sakadjian and others, 2009).

Phase 1 tests showed that the technology has the ability to capture more than 90% CO₂. It was able to achieve a range of 30–100% of CO₂ removal. SO₂ capture was at almost 100%. The carbonator was operated in an entrained flow mode and the effect of residence time was well characterised. The initial tests in Phase 2 showed that sorbent deactivation was significant. Multicycle testing which includes sorbent reactivation showed that the sorbent activity can be fully maintained over the cycles tested (Sakadjian and others, 2009).

Process simulations for the CCR process resulted in net plant efficiencies of 32–34% which is competitive with alternative CO₂ removal processes such as amine or oxycombustion (Sakadjian and others, 2009).

In a report for the IEA Clean Coal Centre, Davidson (2009) discusses the use of limestone derived sorbents for CO₂ capture. The main disadvantage is that the use of these sorbents is limited by the rapid decay of the carbonation conversion with the number of cycles of carbonation/calcination, where calcination is the regeneration reaction. This means that a fresh supply of limestone sorbent is needed in large volumes.

5.3 Linde

Part of the Linde Group's work on oxyfuel combustion has been an involvement with the Schwarze Pumpe 30 MWth

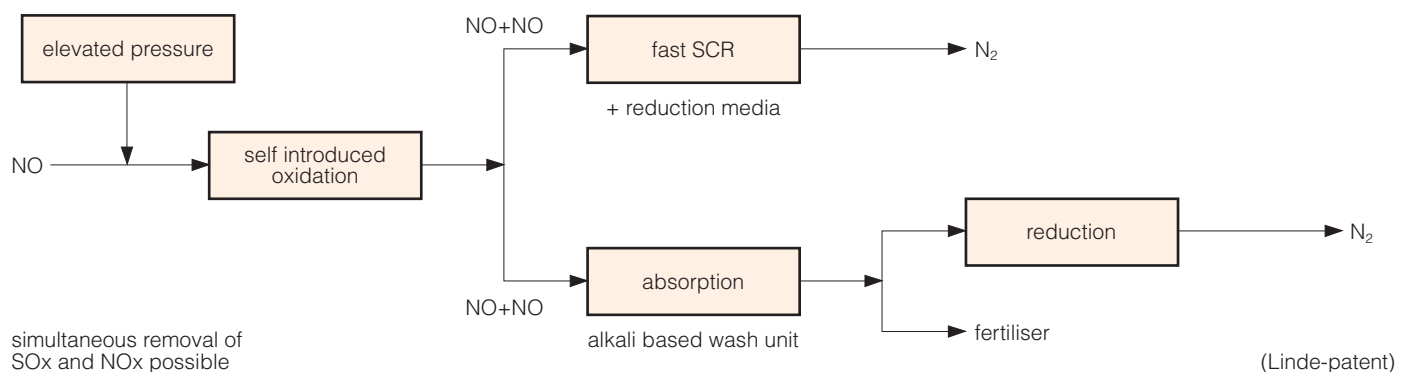


Figure 16 Selected Linde concepts (Ritter and others, 2009)

oxyfuel pilot plant in Germany. Linde built the air separation unit (ASU) and a CO₂ liquefaction plant. Most of the CO₂ produced is separated, liquefied and treated. Linde also provided Vattenfall with support in the areas of cryogenic air separation, CO₂ separation and the process engineering design of the whole plant.

Following on from the pilot plant, the next stage is the demonstration plant, which will be designed to be about 600 MWth and so will require a much larger ASU. Another challenge for CO₂ purification is the compression plant. The CO₂ product will be compressed to a supercritical phase (about 10 MPa) for transport by pipeline. The plant will be designed for a flow rate of about 225 t/hCO₂. The product purity is >96vol% CO₂. However, it is still important to meet the limits for impurities such as O₂, NO_x, SO_x, CO and others (Ritter and others, 2009).

The major sulphur compound in oxyfuel flue gas is SO₂, as discussed previously, which has a low solubility in water. The equilibrium of the solubility can be shifted by including a reaction step, which removes the dissolved SO₂. Due to the slightly acidic character of SO₂, alkaline reagents are suitable for this application. Other possibilities include oxidation or electrochemical processes. An exception is the Solinox process developed by Linde, which allows the SO₂ to be recovered, as a purely physical scrubbing system (Ritter and others, 2009).

Implementation of the purification stage for SO_x and NO_x removal in power plants can be costly and reduces the efficiency of the overall process. Thus, it is important that it is optimised. The high pressure of operation means that oxyfuel applications with a CO₂ plant for carbon capture offer new opportunities for process design. The major change is that at these pressures, up to 5 MPa and more, the oxidation of NO_x and SO_x can be initiated in the presence of oxygen without an additional catalyst or oxidation agent. This leads to a different feed composition and changed sorption and reaction behaviour. Based on this, a selection process for new ideas has been started, considering some criteria, for example (Ritter and others, 2009):

- improvement of energy efficiency;
- reduction of equipment cost;
- reduction of feed cost;
- attractiveness of the product;
- time to market.

A fast catalytic deNOx and an alkali based wash unit are concepts from Linde that are shown in Figure 16. Both concepts are discussed in more detail below.

5.3.1 Catalytic deNOx concept

The state-of-the-art technology for low NOx outlet concentrations is a catalytic deNOx system. In general a vanadium/titanium oxide catalyst with a typical operation temperature of 300–400°C is used. Less often, a zeolite catalyst suitable for higher temperatures (350–600°C) is applied. The reduction agent is ammonia or an ammonium-producing derivative, such as urea. There are three typical positions for the deNOx system in a power plant, which are all located in the ‘close-to-atmospheric pressure range’ (see Figure 17) (Ritter and others, 2009).

In the **high dust** arrangement, the catalytic deNOx unit is the first purification stage for the flue gas in front of the particle filter or the sulphur removal stage. For this application, typically V₂O₅/TiO₂ or zeolite catalysts are used at temperatures of 350–400°C. In this position the lifetime of the catalyst is limited due to the high catalyst poison- and particle load. There is a risk of plugging with dust or salts and for corrosion by SO₃ formation. The consumption of ammonia is

increased due to the effects of adsorption (Ritter and others, 2009).

In the **low dust** arrangement the catalyst is located after the particle filter but still in front of the deSOx (catalyst V₂O₅/TiO₂ or zeolite, temperature 300–400°C). There is still a risk of salt formation and corrosion. Catalyst poisons are still present (Ritter and others, 2009).

In the **tail end** arrangement, the unit is located after the particle filter and the deSOx unit. Typically, a V₂O₅/TiO₂ catalyst is used at relatively low temperatures (300–350°C), due to the pre-purified gas. On the other hand, the temperature has to be increased again after the deSOx. As a result, the other two options are preferred for energetic reasons (Ritter and others, 2009).

Linde has investigated a new arrangement for oxyfuel plants with CCS, where the deNOx unit is located in the compression stage of the CO₂ plant (see Figure 18) and is operated at different conditions, shown in Table 21.

First proof-of-concept tests have been performed in the Linde R&D laboratories in Pullach, Germany. The experiments have confirmed that the conversion is possible under pressure with the reaction systems. Increasing the reaction pressure has a

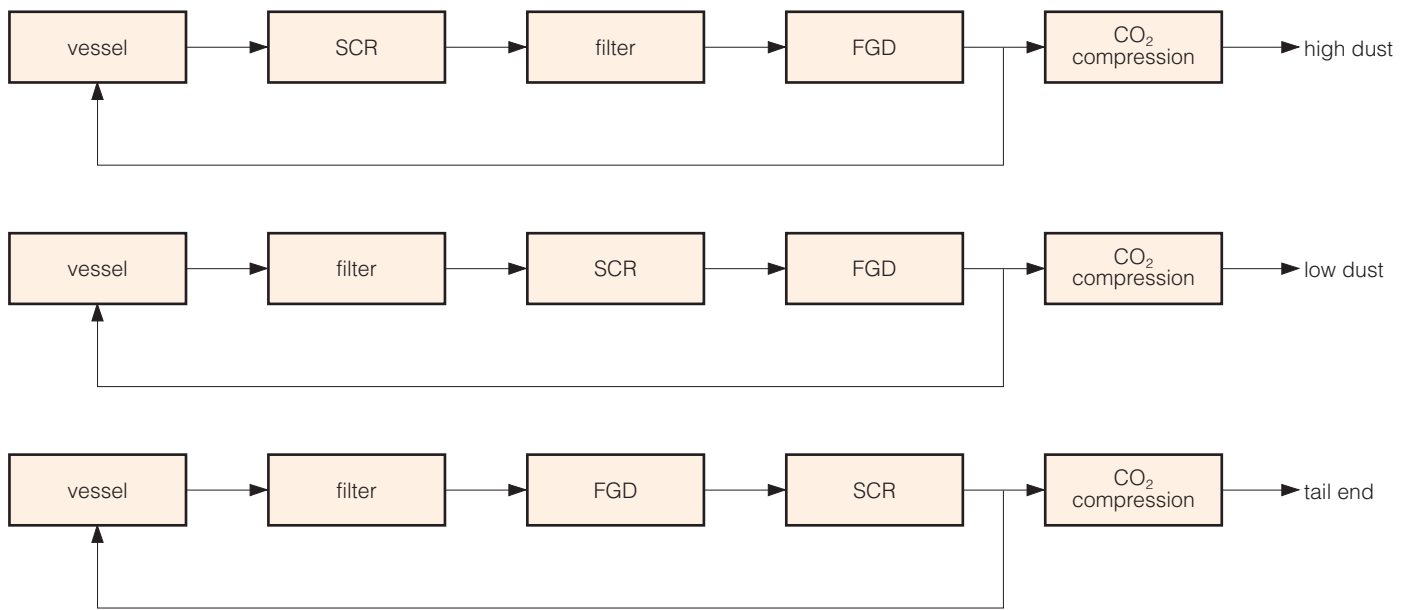


Figure 17 Linde state-of-the-art deNOx technology (Ritter and others, 2009)

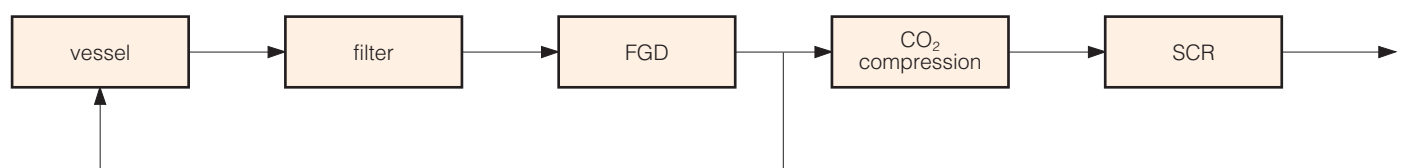


Figure 18 Linde catalytic deNOx concept (Ritter and others, 2009)

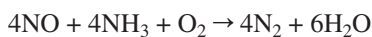
Table 21 Operational conditions in Linde catalytic deNOx concept (Ritter and others, 2009)

Pressure	0.2-10 MPa → preferred: 0.5–5 MPa
Reaction	4NO + 4NH ₃ + O ₂ → 4N ₂ + 6H ₂ O 2NO + 2H ₂ → N ₂ + 2H ₂ O
Catalyst	vanadium-titan-oxide or noble metal
Temperature	100–350°C → 120–250°C

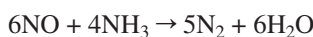
positive effect on the performance. For hydrogen, a steady increase of conversion with increasing pressure was detected in all experiments up to 2.5 MPa (Ritter and others, 2009).

The pressure effect is more complex with ammonia. There is an optimum conversion, depending on the NO/NO₂ ratio, which is affected by the operational conditions. This behaviour can be explained as follows:

The 'standard' SCR reaction is shown as:



The reaction that does not consume oxygen is much slower and so is less relevant:

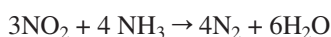


The reaction rate with equimolar amounts of NO and NO₂ is much faster than the standard SCR reaction, and is known as the 'fast SCR reaction':



The increase in reaction rate is well known and it is now proposed as an efficient measure to increase the performance of an automotive deNOx system. In order to increase the fraction of NO₂ in the exhaust, a strong oxidation catalyst is usually placed upstream of the SCR catalyst. Under pressure operation the reaction of NO with oxygen is significantly faster and no longer needs a catalyst, so that with an increase of the pressure and the presence of oxygen, NO is directly shifted to NO₂. Therefore, an increase of the pressure could have a positive effect on the reaction rate (Ritter and others, 2009).

However, any excess of NO₂ will behave according to the following reaction:



The reaction with NO₂ only is slower than the standard SCR reaction. Several studies confirmed that the best deNOx efficiency is achieved with a 1:1 NO-NO₂ feed ratio and that the reaction rate decreases in the order NO-NO₂-NH₃ > NO-NH₃ > NO₂-NH₃.

A 'fast SCR' mechanism for NH₃-SCR was observed due to a

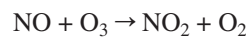
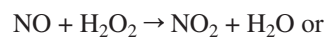
pressure increase, and an increased reaction rate for H₂-deNOx. An energy efficient system is possible for the investigated routes using the low temperature catalysts and heat integration from the compression stage. This makes a small-scale design for a deNOx unit possible (Ritter and others, 2009).

5.3.2 Alkali-based wash concept

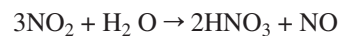
There are several methods for classic, close-to-atmospheric pressure, NOx or simultaneous NOx/SOx removal processes, which are typically used in niche applications, such as with low NOx flue gases or a specific market environment. An example is the Walther Process using O₃ and NH₃ for NOx reduction. In these processes, an oxidation stage is included using strong oxidisers like ClO₂, H₂O₂ or O₃ followed by a scrubbing step with water or alkaline media such as aqueous ammonia solution. The product of these processes is nitric acid or a fertiliser (Ritter and others, 2009).

The involved reaction steps for NOx removal are:

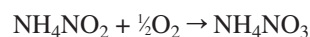
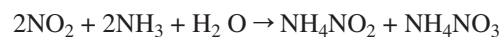
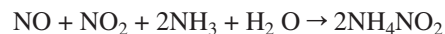
NO oxidation:



Water scrubber for nitric acid production:



Alkaline scrubber for fertiliser production:



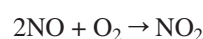
An alkali-based wash unit, operated at higher pressure, was investigated for oxyfuel applications with CCS by Linde. The conventional NO oxidation stage was no longer needed as the NO₂ is formed by oxidation of NO under pressure and oxygen. Based on this, a new concept for NOx or simultaneous NOx/SOx removal was investigated.

In the case of front end SOx removal, the novel NOx removal step can also be realised with a regeneration stage to promote corrosion avoidance. The process concept is shown in Figure 19.

A more detailed description of the deNOx reaction is given below:

NO oxidation

The washing unit will oxidise the NO to NO₂ at elevated pressure in the presence of oxygen.



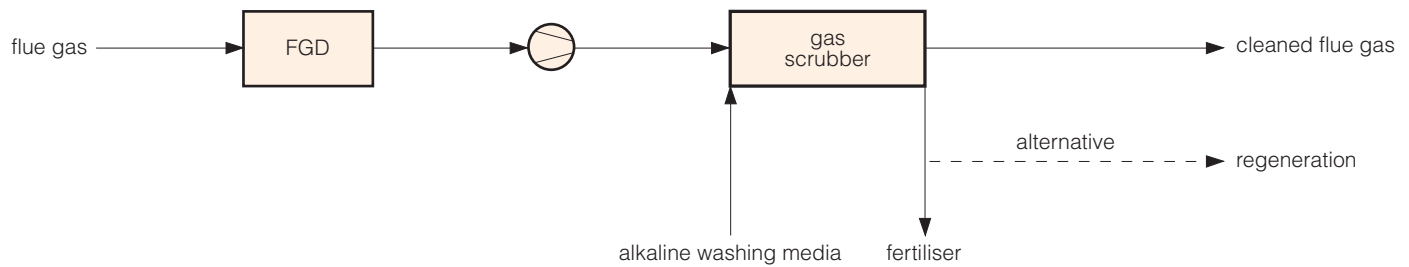
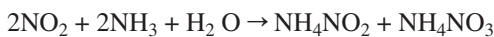
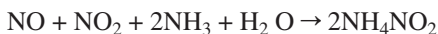


Figure 19 Linde alkali-based wash concept (Ritter and others, 2009)

Chemical absorption

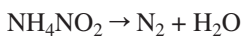
The NO and NO₂ can be absorbed chemically by the following mechanisms:



Preliminary experiments have proved the mechanism. For this purpose, NO and NO₂ were mixed in nitrogen and sent to a gas scrubber at ambient conditions. As long as the NO/NO_x ratio in the feed gas was <0.5, almost all NO_x was converted to nitrites with ammonia (Ritter and others, 2009).

Reduction

The ammonia nitrites can decompose to N₂ and H₂O at moderate temperatures.



First proof of principle tests have been performed in the Linde R&D laboratories in Pullach, Germany. Several influences have been investigated and observed, as follows:

- NO_x removal rate depending on washing media;
- NO_x removal rate depending on pressure, temperature and residence time;
- nitrate and nitrite formation depending on NO/NO₂ ratio;
- nitrite decomposition (regeneration);
- simultaneous removal tests.

Linde researchers conclude from their results that (Ritter and others, 2009):

- An alkali-based solvent has a significantly better capability for the removal of NO_x than water. This is due to the fact that NO can be removed directly up to a NO/NO₂ ratio of 1:1 as well.
- The alkaline washing unit was able to reduce the NO_x content significantly below 100 ppmv in a few seconds. NO_x conversion of up to 97% has been observed.
- Up to 98% of the removed NO_x was converted to nitrites.
- There is a potential for regeneration of the washing media starting from the nitrites: $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$. For selective NO_x removal, about 50–90% regeneration is conceivable.
- It is possible to use relatively cheap construction materials due to the avoidance of acid formation.

- A simultaneous SO_x and NO_x removal is also possible. SO₂ adsorption is independent of the NO kinetics and can be removed directly together with SO₃. Oxidation is not required.
- In principle, the product can be used directly as fertiliser.

The proof of principle tests have been completed successfully at Linde. A feasibility study is ongoing, which will include assessment of:

- technology ownership and the patent situation;
- process economics;
- technical feasibility;
- implementation concept;
- time schedule and time to market.

In addition, potential implementation concepts in the piloting phase are under discussion.

5.4 Praxair

Praxair, in partnership with the US DOE National Energy Technology Laboratory, have developed a way to use oxygen to reduce NO_x emissions without resorting to complete oxyfuel conversion. Oxygen is added to the combustion process to enhance operation of a low NO_x combustion system. Only a small fraction of combustion air is replaced with oxygen in the process. By selectively adding oxygen to a low NO_x combustion system it is possible to reduce NO_x emissions from nitrogen-containing fuels, including pulverised coal, while improving combustion characteristics such as unburnt carbon (Thompson and others, 2004).

A combination of experimental work and modelling was used to define how well oxygen enhanced combustion could reduce NO_x emissions. The results of this work suggest that small amounts of oxygen replacement can reduce the NO_x emissions as compared to an air-fired system. NO_x emissions significantly below 0.15 lbs/MMBtu (60 g/GJ) were measured. The addition of oxygen was also shown to reduce carbon in ash. According to Thompson and others (2004), comparison of the costs of using oxygen for NO_x control with competing technologies such as SCR, showed that this concept can cost less than SCR.

Oxygen enhanced coal combustion can reduce NO_x in several ways. Oxygen enrichment can be used in conventional burners and low NO_x burners operated under globally staged conditions for primary combustion control. Oxygen can also

be used to enhance the effectiveness of coal based reburning. In burners, the careful addition of oxygen leads to rapid ignition and enhanced coal devolatilisation which reduces the flame standoff distance and creates a more fuel rich zone near the burner. The higher temperature achieved by oxygen enriched combustion accelerates NO_x reduction kinetics under fuel rich conditions below certain stoichiometric ratios. The advanced oxygen enhanced combustion process can be incorporated in air-staged combustion systems utilising conventional non-staged burners or low NO_x burners for primary combustion NO_x control with relatively minor burner modifications (Thompson and others, 2004).

Secondary NO_x control by coal reburning can also be enhanced through the use of a novel hot oxygen burner developed by Praxair. In this burner, rapid ignition and enhanced coal devolatilisation can be used to enhance the effectiveness of NO_x reduction in coal-based reburning while reducing char yield and promoting lower carbon content in ash. Work by Praxair showed that burnout of both pulverised and granular coal increased significantly when the coal stream mixed with a hot oxygen jet, even at very short (~5 ms) residence times. Another oxygen based technology, Praxair's CoJet® technology, can be used to deliver the reburn fuel or air into the centre of large boilers (Thompson and others, 2004).

Unlike many current NO_x control techniques, oxygen enrichment improved, rather than degraded, unit operability. For example, flame stability problems and residual carbon in the ash associated with low NO_x burners or ultra low NO burners were virtually eliminated with the judicious use of oxygen. Replacing some small portion of the combustion air with oxygen also slightly improved unit heat rate and regained boiler capacity lost due to boiler balancing problems, such as when a boiler switches from a bituminous to a subbituminous coal.

In 2004, Praxair had seven patents pending for oxygen enhanced combustion testing work.

5.5 ThermoEnergy Integrated Power System (TIPS)

The pressurised oxyfuel approach known as the ThermoEnergy Integrated Power System (TIPS) is a concept designed to produce energy and liquid CO₂ from coal with near zero emissions to air of pollutants. Combustion in the TIPS process takes place at pressures between 4.83 and 8.96 MPa. Increasing the pressure of combustion shifts the temperature at which water, CO₂, mercury and acid gases condense. Elevated pressures and condensation temperatures enable TIPS to utilise heat transfer, mass transfer and liquid vapour equilibrium regimes well suited to the capture of pollutants and CO₂. Increasing the pressure enables TIPS to use the phenomenon of nucleate condensation at temperatures in the range 262–303°C in a heat exchanger that simultaneously recovers heat and condenses and captures pollutants. Two components of pressurised oxyfuel technology central to achieving the goals of efficiency and pollution control are the air separation unit to provide oxygen

under pressure, and the condensing heat exchanger to capture both pollutants and heat from the combustion gases (Fassbender, 2005).

The TIPS configuration enables the condensing heat exchanger to collect particulates, acid gases and mercury into a condensed phase that is roughly 2500–3000 times smaller than the volume of gas treated by conventional flue gas clean-up systems operating at atmospheric pressure. According to Fassbender (2005), the nucleate condensation phenomenon is so rapid and efficient that, once developed, the TIPS process may be less costly than current atmospheric pressure systems requiring particulate collection, desulphurisers, deNO_x and mercury abatement equipment.

Figure 20 shows a flow schematic of a coal-fired TIPS process. The numbers 1 to 4 on the figure correspond to the numbers and the pressure and temperature conditions shown in Figure 21. The curve in Figure 21 corresponds to the pure component liquid vapour equilibrium, lines for mercury, water, SO₂ and CO₂. The curves show the effect of increasing the pressure on condensation temperature of the main exhaust gases. The higher pressure corresponds to a higher liquid-vapour equilibrium temperature for the gaseous compounds of the exhaust. TIPS makes use of this pressure-induced temperature shift to enable the recovery of heat, condensation of pollutants and removal of particulates from the exhaust gas. Position 1 shows the point at which a dirty exhaust gas would exit the radiative section of the pressurised combustion and heat transfer unit. Liquid water sprayed into this gas evaporates rapidly and cools the exhaust gas to position 2. The large surface area of the droplets in the liquid spray provides rapid heat transfer. Although the mass of the gas stream, exhaust gas plus evaporated water, is increased, the volumetric flow decreases due to the cooling of the gas. The water spray cools the exhaust gas and rapidly moves the temperature and pressure of the combined stream to position 2. Position 2 is at the liquid-vapour equilibrium line for water at the system pressure. The heat energy that was in the hot exhaust gas was not lost during the cooling process. It was transformed into the latent heat of vapourisation of the evaporated water. In the example given by Fassbender (2005), this moisture laden exhaust stream then goes into a condensing heat exchanger at a temperature of 302°C and a pressure of 8.8 MPa. The heat exchanger transfers the heat from the moisture-laden exhaust to the boiler feed water. The boiler feed water is about 27°C cooler than the temperature at which the moisture in the exhaust gas will condense. The large temperature difference between the boiler feed water and the moisture in the exhaust gas drives rapid heat transfer to condense the water in the exhaust gas and to heat the boiler feed water. The temperature of the moisture-laden exhaust gas stream (302°C) does not change significantly as it transfers heat to the boiler feedwater until the bulk of the water vapour has been condensed to liquid. This enables the heat exchanger in the current example to maintain a temperature difference suitable for efficient heat transfer. The exhaust gas is cooled below the liquid vapour equilibrium temperature to position 3. At position 3, the bulk of the moisture and energy has been removed from the exhaust gas and the remaining gas, primarily CO₂, is cooled

further to position 4. At position 4, CO₂ in the exhaust gas has condensed into a liquid (Fassbender, 2005).

When steam or CO₂ are cooled and condensed into a liquid, surface forces cause the condensing gas to condense preferentially on solid or liquid surfaces. When the liquid water and CO₂ gas condense, the liquid goes preferentially onto the surfaces of particles to make large droplets. Large droplets with little seed particles are then easily removed. This nucleate condensation or steam hydroscrubbing exhibits a high particle capture efficiency (Fassbender, 2005).

The pressurised oxyfuel system benefits from two key combustion control elements. For a given flow of oxygen and coal, the CO₂ recycle and water concentration of the feed coal-water slurry can be varied to adjust the flame temperature independently of the coal and oxygen flow ratio. Increased pressure and decreased flame temperature favour CO₂ production and inhibit the back reaction of CO to carbon. This gives the possibility of minimising soot formation. In an oxidising environment, the high-pressure and low-temperature condition in the condensing heat exchanger favours SO₃ and NO₂ formation. These oxidised compounds react with water to form sulphuric and nitric acid and are readily scrubbed from the CO₂ gas. The second key element is that robust high temperature oxygen sensors are a proven technology that allows combustion process oxygen concentrations to be monitored and controlled on a real time basis (Fassbender, 2005).

Most of the unit operations required to implement TIPS are proven in existing industrial applications or are under active development. Cryogenic air separation technology is known and research is under way to improve its efficiency as well as develop ion-transport membrane oxygen separation technology (Fassbender, 2005).

According to Fassbender (2005), while CO₂ capture adds complexity to all power plant configurations, it adds the least complexity to the pressurised oxyfuel, or TIPS approach. TIPS has fewer and simpler unit operations, less complexity and greater intrinsic reliability.

5.6 Discussion

The flue gas from an oxyfuel-fired coal power station is wet CO₂, containing SO_x, NO_x and mercury. This CO₂ must be dried, compressed and purified before being sent for sequestration or used for EOR. In the process of compressing the CO₂, conditions are created for the reaction of SO₂ with NO₂ to form sulphuric acid, given enough residence time. Further, once all of the SO₂ has reacted, NO₂ is converted to nitric acid by the addition of water. All of the SO_x is removed and around 90% of the NO_x, before drying, removal of inerts, and compression to 100–200 bar (10–20 MPa). Removing inerts involves cooling the raw CO₂ to a temperature close to its triple point where inerts are removed in the gas phase. This leads to CO₂ purities of around 95–98%. Modifications to this cycle allow purities of CO₂ greater than 99.9 mol% with ppm levels of oxygen, a key impurity in the required purity of CO₂ for EOR (White and others, 2006).

The reactions and process described by White and others (2009) rely on assumptions about the reactions that will occur and the rate at which they will occur. It is clear that the reactions as posed seem to produce the desired results: SO_x and NO_x removal by compression and contact with water. The fact that further reaction happens in the reactor indicates that residence time and vapour/liquid contacting are important to maximise conversion.

Some of the modelling assumptions may need to be addressed. H₂SO₄ and HNO₃ are seen together in the condensate, whilst there is still some SO₂ left in the gas stream, which means that the assumption of the fast rate of the lead chamber reaction compared to the nitric acid reactions needs to be reassessed.

However, SO_x and NO_x components can be removed during compression of raw oxyfuel-derived CO₂, given sufficient pressure, holdup and vapour/liquid contacting time. Therefore, for emissions control and CO₂ product purity, traditional FGD and deNO_x systems should not be required in an oxyfuel-fired coal plant (White and others, 2009).

Flue gas has to be purified before the CO₂ can be stored. Water soluble components such as SO₃, HCl and HF are usually removed from the flue gas by direct contact with water which not only washes out these components, but also cools the flue gas and condenses water vapour. SO₂ and NO_x may be removed during compression of the CO₂ to pipeline pressure. This process also removes any mercury that may be present.

The pipeline pressure of CO₂ is usually 100–250 bar (10–25 MPa), which is above the critical pressure of CO₂. It is preferable to remove the bulk of the contaminant gases to reduce the power required to compress the CO₂ and to ensure that two phase conditions do not arise in the pipeline or in the geological formation for CO₂ storage (White and Allam, 2008).

The presence of O₂ may cause problems if the CO₂ is intended for use in EOR, as oxidation can cause corrosion problems in downhole equipment. Typical specifications for CO₂ purity would be a maximum contaminants level of 3 mol%. In the case of CO₂ for EOR, the maximum O₂ content would be typically 100 ppm, or lower, even down to 1 ppm (White and Allam, 2008).

An important objective for carbon capture in an oxyfuel power system is to provide a method of treating compressed crude CO₂ to remove nitrogen and argon and to reduce the concentration of O₂ to less than 100 ppm, preferably with a low consumption of energy and high recovery of CO₂. Ideally, CO₂ recovery should be better than 97%, based on CO₂ in the total flue gas stream. In addition, if the purified CO₂ product is produced as a low temperature liquid stream at a pressure below its critical pressure, transport as a liquid or as a supercritical fluid to a CO₂ storage site is facilitated (White and Allam, 2008).

6 Conclusions

The capture of CO₂ from the flue gas of coal-fired power plants using post-combustion capture and oxyfuel combustion techniques has been considered. The focus has been on the other components of the flue gas, the effects that they have on the capture process, and ways to remove them if they are likely to cause problems during capture, transport or storage of CO₂. This is a new area of research.

Post-combustion capture using selective separation processes such as amine absorption is the most established method of removing CO₂ from the flue gas. The main components of the flue gas are CO₂, N₂, O₂ and H₂O, followed by air pollutants such as SO_x, NO_x, particulates, HCl, HF, mercury, other metals and other trace organic and inorganic contaminants. Coal-fired power plants will have units to remove air pollutants prior to CO₂ capture in an absorption-based process. These additional units can include SCR, ESP and FGD. However, some of the pollutants will be absorbed in the solvent with the CO₂. This can result in the formation of heat stable salts, and increase the requirement for solvent regeneration and replacement. NO_x is unlikely to be a major problem and is usually removed to an acceptable level by SCR processes. SO_x may need to be present in the flue gas at a level lower than that normally achieved by FGD. Thus the FGD process may need to be improved.

From the point of view of CO₂ capture, flue gas cleaning for oxyfuel combustion is completely different from the approaches used in post-combustion CO₂ capture. Oxyfuel combustion with CO₂ capture is a newer process, only operational at pilot scale in a few locations. The advantage of oxyfuel combustion is that it generates a flue gas stream that is composed mostly of CO₂ and H₂O. However, it also contains excess oxygen required to ensure complete combustion of the fuel, and any other components derived from the fuel such as SO_x, NO_x, HCl and Hg, any diluents in the oxygen stream supplied, any inerts in the fuel and from air leakage into the system from the atmosphere such as nitrogen, argon and oxygen. The net flue gas, after cooling to condense water vapour, contains about 80–95% CO₂ depending on the fuel used and the particular oxyfuel combustion process. This concentrated CO₂ stream can be compressed, dried and further purified before delivery into a pipeline for storage.

In the oxyfuel process, the purity of CO₂ is influenced mainly by:

- where the flue gas is recycled in the process, that is, the cleaning that has been done up to this point;
- the sealing of the boiler and other components;
- the purity of the oxygen from the air separation unit;
- the performance of all air quality control systems, such as deNO_x, deSO_x and ESP;
- additional CO₂ purification during and after compression.

Some contamination via air ingress is inevitable in an oxyfuel plant. Large air separation units are costly to construct and operate, so although new oxyfuel combustion plants can be designed to have minimal air infiltration, it may be more

economic to design the air separation units for only 95% O₂ purity, and then to separate the associated argon and nitrogen in the CO₂ inert gas removal system to produce a purity of CO₂ suitable for geological storage.

The flue gas from an oxyfuel-fired coal power station is wet CO₂, containing SO_x, NO_x and other impurities. This CO₂ must be dried, compressed and purified before being sent for sequestration or used for EOR. In the process of compressing the CO₂, conditions are created for the reaction of SO₂ with NO₂ to form sulphuric acid, given enough residence time. Further, once all of the SO₂ has reacted, NO₂ will be converted to nitric acid by the addition of water. All of the SO_x is removed and around 90% of the NO_x, before drying, removal of inerts, and compression to 10–20 MPa. Removing inerts involves cooling the raw CO₂ to a temperature close to its triple point where inerts are removed in the gas phase. This leads to CO₂ purities of around 95–98%. Modifications to this cycle allow purities of CO₂ greater than 99.9 mol% to be achieved, with ppm levels of oxygen, a key impurity in the required purity of CO₂ for EOR (White and others, 2006).

Air Products have added a polymeric membrane module to their base separation process. It has been added to the vent stream where a CO₂ and O₂ rich stream are recycled to the boiler. It may result in an overall CO₂ capture rate as high as 98%, while reducing the size of the air separation unit required by 5%.

Air Liquide have developed a CO₂ compression and purification unit (CPU) for CO₂ capture. In collaboration with Babcock and Wilcox, they have planned a demonstration plant where sulphur compounds will be removed by a spray dryer absorber followed by a fabric filter and a polishing sodium based wet scrubber. Most of the mercury, chlorine and fluorine compounds are also removed in these processes. Moisture is removed as well before the flue gas enters the CO₂ CPU. Air Liquide has reorientated its research efforts towards minimising the auxiliary power requirement of the ASU and CPU. Other critical design parameters for the CPU are particulates, drying and NO_x and SO_x treatment.

At Linde the focus is on improving the energy efficiency of the process, reducing the cost of equipment, reducing the feed cost, increasing the attractiveness of the product and reducing the time to market. Work at Linde includes development of the a catalytic deNO_x system and an alkali-based wash concept which has a better capability to remove NO_x than water.

Praxair have researched oxygen enhanced coal combustion to reduce NO_x emissions.

An important objective for carbon capture in an oxyfuel power system is to provide a method of treating compressed crude CO₂ to remove nitrogen and argon and to reduce the concentration of O₂ to less than 100 ppm, preferably with a low consumption of energy and high recovery of CO₂. Ideally,

CO₂ recovery should be better than 97%, based on CO₂ in the total flue gas stream. In addition, if the purified CO₂ product is produced as a low temperature liquid stream at a pressure below its critical pressure, transport as a liquid or as a supercritical fluid to a CO₂ storage site is facilitated.

CO₂ is transported by pipeline as a dense supercritical phase. Inert gases must be reduced to a low concentration to avoid two phase flow conditions developing in the pipeline systems. The acid gas components may need to be removed to comply with legislation covering co-disposal of toxic or hazardous waste or to avoid operations or environmental problems with disposal in deep saline reservoirs, hydrocarbon formations or in the ocean. Water is an important factor in pipelines. Most current CO₂ pipelines operate with low levels of water, which is under-saturated with respect to the liquid state, so that it exists only as a vapour. The presence of liquid water in a mixture of CO₂, SO₂ and O₂ can cause severe internal corrosion in steel pipelines, which reduces their safety and operability. Thus the CO₂ must be dried.

The issue of optimum product CO₂ purity is a question that at the moment does not have a satisfactory answer. It depends on the type of application and the geological properties of the site. The optimum is uncertain from economic and geological points of view. It is clear though, that storage of low CO₂ concentration streams is not economic.

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