Non-calcium desulphurisation technologies

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Abstract

Flue gas desulphurisation (FGD) is traditionally based on limestone/lime sorbent. The majority of the installed FGD systems worldwide use limestone or lime as sorbent. However, technologies are rapidly evolving that allow desulphurisation in regions where there are limited resources of lime or limestone. These technologies provide alternatives to limestone/lime scrubbers for efficient and cost effective control of SO_2 emissions from coal combustion. This report reviews the existing and emerging non-calcium based FGD processes as well as FGD technologies currently under development that apply new concepts and different approaches. It looks at the fundamentals and features of these processes, the recent technical advances and their applications in coal-fired power plants. The capital and operating costs of the processes are evaluated where information available.

Acronyms and abbreviations

AC   alternating current
AMP   American Municipal Power
BACT   best available combustions technologies
CCT   clean coal technology
CFB   Circulating fluidised bed
COD   chemical oxygen demand
DBD   dielectric barrier discharge
DC   direct current
DO   dissolved oxygen
DOE   Department of Energy
ESP   electrostatic precipitator
FGD   flue gas desulphurisation
GGH   gas-gas heat exchanger
GWe   gigawatts electricity
IGCC   integrated gasification combined cycle
IPCC   Integrated Pollution Prevention and Control
kWe   kilowatts electricity
MGA   membrane gas absorption
MWe   megawatts electricity
NPV   net present value
PNNL   Pacific Northwest National Laboratory
ppm   parts per million
SCR   selective catalytic reduction
SNCR   selective non-catalytic reduction
VOC   volatile organic compounds

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Contents

1 Introduction

Global energy demand has been growing strongly in the past two or three decades and will continue to increase, particularly in developing countries where energy is needed for economic growth and poverty alleviation. All energy sources such as fossil fuels, nuclear and renewable energy will be needed to satisfy that demand and to provide a diverse and balanced energy supply mix. Coal is an essential part of the energy mix and is vital for global energy security. Coal is the world's most abundant fossil fuel. It is found the globe over, and distributed quite evenly. It is the most economic and most widely available fuel in developing and developed countries. Coal is easy and safe to transport and therefore it provides reliable supplies of affordable energy essential for global continuing development.

The International Energy Agency (IEA, 2009) projects that the world demand for coal will grow at an average annual rate of 1.9% to 2030 – more strongly than the demand for any other fossil fuels. The main driver of demand for coal is the inexorable growth in energy needs for power generation. Most of the coal used is burned to generate electricity. Coal-fired power plants today provide approximately 40% of the world's electricity. However, coal combustion has its impacts in terms of human health and the environment. Despite the fact that the environmental concern of the public media has shifted towards climate change, the environmental problems and detrimental effects to human health caused by SO_2 emissions continues to be an issue in the 21st century.

In response to public concern regarding SO_2 emissions, legislative and regulatory actions have been taken by international bodies and governments of individual countries. The 1979 Geneva Convention on Long-range Transboundary Air Pollution was the first international legally binding instrument to deal with problems of air pollution on a broad regional basis. It laid down the general principles of international co-operation for air pollution abatement, and set up an institutional framework bringing together research and policy. Since entering into force in March 1983, the Convention on Long-range Transboundary Air Pollution has been extended by eight specific protocols concerning the control and reduction of certain air pollutants emissions. The 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone aimed to cut emissions of four pollutants: SO_2, NOx, volatile organic compounds (VOC), and NH_3 by setting country-by-country emission ceilings for the year 2010. The Protocol also set emission limit values for specific emission sources and required best available technologies to be used to keep emissions down.

In the European Union, the Directive on Integrated Pollution Prevention and Control (96/61/EC) (IPPC) was adopted in 1996 and came into effect in 1999. The IPPC Directive provides an integrated approach to establish pollution prevention from a wide range of industrial activities. The Directive lays down a framework requiring Member States to introduce permitting procedures which apply to various industrial processes, including combustion installations greater than 50 MWth. Limits on emissions and concentrations of air pollutants are set in the Directive on National Emission Ceilings for Acidifying and Ozone-Forming Air Pollutants (2001/81/EC), and the Directive on the Limitation of Emissions from Large Combustion Plants (2001/80/EC). Directive 2001/81/EC covers four air pollutants: SO_2, NOx, volatile organic compounds, and ammonia. It sets binding emission ceilings to be attained by each Member State by 2010. Directive 2001/80/EC lays down limit values for emissions of air pollutants from combustion plants with a rated thermal capacity of at least 50 MWth, irrespective of the fuel used. The new directive also includes emission ceilings and reduction targets specifically for SO_2 and NOx emissions from existing plants. The limit values for SO_2 emissions from existing or new coal-fired power plants set by the UN and the EU can be found in IEA CCC's online Emission Standards Database (2010).

Today, most countries have established some type of environmental law or clean air act under which environmental targets are set. More than forty countries have set emission standards/limit values for SO_2 emissions from coal-fired power plants and other industrial processes. The regional and national emission standards/limit values for major air pollutants from coal combustion plants have recently been published by the IEA CCC (2010). The legislation and regulations have become increasingly stringent over the years and they have influenced the nature and pace of innovation of SO_2 emissions control technologies.

There are various measures that can be taken to control SO_2 emissions from coal combustion. Flue gas desulphurisation (FGD) is an effective measure and it is applied widely in coal-fired power plants globally. There are a range of FGD processes commercially available. However, the majority of the FGD systems installed in power plants use a calcium-based sorbent. Technologies are evolving rapidly that allow desulphurisation in regions where there are limited resources of lime or limestone. This report provides information on the non-calcium based on flue gas desulphurisation technologies. It begins with an overview of the currently commercially available FGD technologies in Chapter 2. The environmental performance of these technologies and their applications in coal-fired power plants are discussed. Chapter 3 presents the non-calcium based FGD processes that are already in commercial operation. The features and mechanism of the processes are described in detail. Information on the desulphurisation performance, capital and operating costs of these processes are given, and where possible, comparisons are made with other FGD technologies. The applications of these processes in coal-fired power plants are also discussed in Chapter 3. The non-calcium based FGD processes that have been offered recently to the commercial market are reviewed in Chapter 4. This chapter provides detailed descriptions of the emerging FGD processes. The process features and mechanisms are described. Where information is available, the costs, water

and/or energy consumption of the processes are estimated and/or evaluated. Some of the innovative FGD technologies that are still in the early stage of development but have the potential to become competitive FGD processes applicable to coal-fired power plants are reviewed in Chapter 5. And finally, conclusions are drawn in Chapter 6. In addition, this report also looks at the recent technical advances and improvements in the engineering design of the processes.

The focus of this report is on the non-calcium based FGD technologies applicable to coal-fired power plants. It intends to provide comprehensive information on the FGD processes that are alternative to those conventional FGD systems based on lime or limestone sorbent.

2   FGD technologies

The earliest application of flue gas desulphurisation (FGD) at coal-fired power plants can be traced back to the early 1930s in England. The application of FGD technologies in earnest for the control of SO_2 emissions began in the late 1960s and early 1970s in Japan and the USA, and this was followed by Western Europe in the 1980s. Since then, FGD technologies have undergone considerable developments in terms of improved sulphur removal efficiency, reliability and reduced costs. Today, there are a wide range of FGD processes that are commercially available, differing significantly in terms of sorbent used, by-products produced, SO_2 removal efficiency and costs. Some of the major processes can be divided into the following categories:

Wet process:
- limestone/lime gypsum process;
- seawater scrubbing;
- ammonia scrubbing;
- regenerative process.

Semi-dry process:
- spray dry scrubbing;
- duct spray dry scrubbing.

Dry process:
- circulating fluidised bed scrubbing;
- furnace sorbent injection;
- sodium bicarbonate injection;
- activated carbon/coke injection.

Almost all commercial FGD processes are based on the chemical reactions between acidic SO_2 with a suitable alkaline sorbent. The most commonly used alkaline substance is limestone or lime. According to the IEA CCC's database, by the end of 2008, more than 1400 coal-fired power generating units worldwide with a total capacity of over 502.5 GWe had been fitted with FGD systems; more than 230 FGD units with a capacity of 102 GWe were under construction; and more than 520 coal-fired generating units with a total capacity of over 212.6 GWe were planned to have FGD systems installed (including the power plants proposed to be built) (IEA CCC, 2009). The fundamentals of, and recent advances in, FGD technologies have been reviewed by several authors (DTI, 2003; European Commission, 2006). An overview of some of the FGD processes can be found in the following sections.

2.1   Wet processes

Wet scrubbing is by far the most common FGD process being installed on coal-fired power plants worldwide, with a share of over 84% of the total installed FGD capacity, whilst semi-dry and dry processes account for over 6.1% and 1.6% of the installed FGD systems, respectively (IEA CCC, 2009).
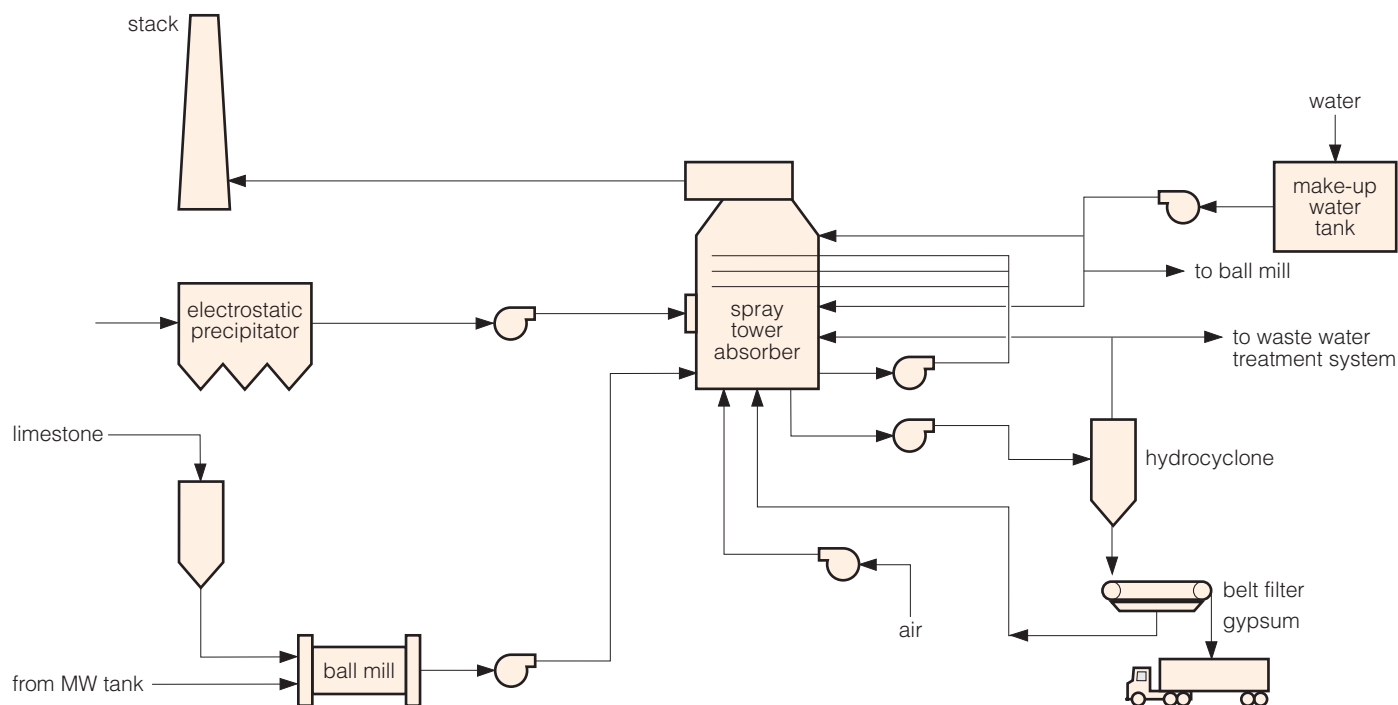
2.1.1   Limestone/lime gypsum process

The limestone/lime gypsum process has evolved over thirty

years and there are a number of process variants and equipment arrangements that can be adopted (DTI, 2000). Some processes (mostly in early installations) use lime instead of limestone. Limestone (calcium carbonate) is an abundant and relatively cheap material. Lime is more reactive than limestone but it has to be produced from limestone by heating and therefore is more expensive than limestone. Nowadays, a limestone gypsum process is normally designed to produce a high quality gypsum by-product that can be sold for plasterboard manufacture. The limestone gypsum process is the most well-developed and most widely deployed FGD process worldwide, especially in large power plants. By the end of 2008 the total installed capacity for coal-fired power plants alone was more than 417 GWe, with over 69 GWe being under construction and 113 GWe having been planned or proposed to be installed (IEA CCC, 2009). The process can offer high sulphur removal efficiency even with high sulphur fuel. It is now capable of routinely achieving SO_2 removal efficiencies of greater than 95%. Some recent plants have achieved 98% of SO_2 removal (IEA CCC, 2009). In addition, the process can also remove trace quantities of fly ash and almost 100% of any hydrogen chloride (HCl) in the flue gas.

In a limestone gypsum process, the flue gas leaving the particulate control system usually passes through a heat-exchanger and then enters an FGD absorber. In the absorber the SO_2 in the flue gas is removed by direct contact of the flue gas with an aqueous suspension of finely ground limestone. The most common type of absorber is the open spray absorber where the limestone slurry is atomised into fine droplets and sprayed into the absorber continuously. The scrubbed flue gas passes through the mist eliminator and is emitted to the atmosphere. The spent sorbent slurry is collected in a recycle tank at the bottom of the absorber where the absorbed SO_2 is converted by in situ oxidation into sulphate. The products are withdrawn from the absorber and are sent for dewatering and further processing. Figure 1 presents the schematic flow diagram of limestone/lime gypsum process.

The core of the wet scrubbing technology is the absorber system. Over the years various limestone gypsum process designs and operation specifics have evolved driven by the differences in fuel characteristics and economic pressures. Detailed descriptions of the processes can be found elsewhere (European Commission, 2006; Schuettenhelm and Dreuscher, 2005).

The limestone gypsum process has a relatively high capital cost and it is more complex than some other types of process. However, for many applications it has a lower operating cost compared with the lime-based and some other processes. This is because limestone is cheaper than lime and a disposal cost can be avoided by producing gypsum, a saleable by-product. In addition, any income from the sale of gypsum may partially offset the operating cost. With widespread applications worldwide and over thirty years operating experience, the technology is well understood and thereby it has a lower commercial risk than any other process.

Figure 1   Limestone/lime gypsum process diagram (Radl and Zhang, 2005)

2.1.2   Seawater scrubbing process

The seawater scrubbing process uses untreated seawater to scrub the flue gas, taking advantage of seawater's natural alkalinity to absorb SO_2. After scrubbing, the seawater used is treated with air to reduce its chemical oxygen demand and its acidity, and is then discharged back to the sea. Although it has been developed and applied on small-scale industrial and power plants since 1968, the seawater scrubbing process was applied for 300–700 MWe power stations since the mid 1990s and is now a technology that is expanding rapidly. By the end of 2009, seawater scrubbers with a total capacity of more than 35 GWe had been built, around 4.4 GWe were under construction or were planned to be installed on coal-fired power generating units (IEA CCC, 2009). The majority of the installed capacity was commissioned since 1998.

Seawater has a large neutralising capacity with respect to SO_2 and the process is capable of achieving up to 98% SO_2 removal efficiency. It can also remove almost all of any HCl in the flue gas. The process has a lower capital cost compared to the limestone gypsum process due to the simplicity of its process design. It also has a low operating cost, but only if the coal sulphur content is below 2.5–3.0% by weight (DTI, 2000). The seawater scrubbing process, the recent advances in the technology and its environmental performance will be discussed in detail in Chapter 3.

2.1.3   Ammonia scrubbing process

The ammonia scrubbing process works in a similar way to the limestone gypsum process except that aqueous ammonia is used as reagent. SO_2 is removed from the flue gas by reacting with ammonia and the final product is ammonium sulphate, a relatively high-value product that can be used in fertilisers.

The high value by-product is the major advantage of this process. Although ammonia scrubbing units have been installed on coal- and oil-fired boilers, there is limited commercial experience of ammonia scrubbing FGD. Several ammonia scrubbers with designed SO_2 removal efficiencies of 95% are planned to be installed on coal-fired power generating units (IEA CCC, 2009). Recently, there has been a renewed interest in the ammonia scrubbing process due to its ability to effectively remove CO_2 from the flue gas. Research is being carried out to develop the ammonia scrubbing process for the simultaneous removal of CO_2 and SO_2, The ammonia scrubbing process will be discussed in detail in Chapter 3.

2.1.4   Regenerative process

In a regenerative process, the reagent used for removing SO_2 from the flue gas is regenerated and returned to the absorber for re-use. As a result, the process does not consume a large quantity of sorbent nor produce a large quantity of waste. The captured SO_2 is released in concentrated form that may be converted into a saleable product such as liquid SO_2, sulphuric acid or elemental sulphur. The two major regenerative FGD processes that have been developed and deployed in power plants and other industrial plants are the Wellman-Lord process and the magnesium oxide (MgO) process. The Wellman-Lord process uses an aqueous sodium sulphite solution whilst the magnesium oxide process uses an aqueous slurry of magnesium hydroxide formed from magnesium oxide as sorbent.

Wellman-Lord process

The Wellman-Lord process is the most widely used regenerative process that is installed on industrial boilers and power plants burning fossil fuels and petroleum coke. This process can be divided into two main stages: absorption

and regeneration. In the absorption stage, the hot flue gas first passes through pre-scrubber where hydrogen chloride (HCl), hydrogen fluoride (HF), SO_3 and some of the particulate remaining in the flue gas are also removed. The flue gas is then cooled and fed into the absorber where it comes into direct contact with a saturated solution of sodium sulphite in a countercurrent flow. The sodium sulphite reacts with the SO_2 forming sodium bisulphite and the reaction is as follows:

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$$

The resulting bisulphite solution is collected and passed to an evaporation system for regeneration. In the regeneration stage, the bisulphite solution is boiled in an evaporator-crystalliser, where it decomposes to SO_2 and water (H_2O) vapour and sodium sulphite is precipitated through the following reaction:

$$2NaHSO_3 \rightarrow Na_2SO_3 + SO_2 + H_2O$$

Sulphite crystals are separated and redissolved for reuse as lean solution in the absorber whereas the released SO_2 is converted to elemental sulphur, sulphuric acid or liquid SO_2.

The Wellman-Lord process has been installed on coal-fired power plants, mainly in 1980s. However, there appears to have been no new plants being built in recent years. The process can remove well over 95% of SO_2 on high-sulphur fuels. The SO_2 removal efficiencies achieved by the regenerative processes are typically in the region of 95–98%. They are expensive to install but relatively cheap to operate and are therefore best suited to high SO_2 removal requirements, high-sulphur fuel and a plant with a long residual life (DTI, 2000).

Magnesium oxide process

The magnesium oxide process is essentially the same as the limestone gypsum process except for the regeneration step of the spent sorbent. It uses magnesium hydroxide slurry as sorbent. The flue gas goes through a pre-scrubber where HCl and HF in the flue gas are removed. The flue gas then enters the absorber where the SO_2 is removed by direct contact with the aqueous slurry of magnesium hydroxide.

In the earlier magnesium oxide process, the spent slurry is continuously bled from the absorber, the magnesium sulphite/sulphate formed are separated by centrifugation and dried in a dryer. The mixture is calcined at around 900ºC in the presence of carbon to regenerate magnesium oxide and to produce concentrated SO_2 as a by-product or for the production of elemental sulphur or sulphuric acid. The magnesium oxide is returned to the absorption system.

In the recently developed magnesium hydroxide-gypsum process, the resulting magnesium sulphite solution is collected and sent to an oxidiser where the magnesium sulphite is converted to magnesium sulphate, which then reacts with lime ($Ca(OH)_2$) in a decomposer to regenerate $Mg(OH)_2$. The regenerated $Mg(OH)_2$ is fed back to the absorber for reuse as absorbent. The gypsum ($CaSO_4\ 2H_2O$) formed during the regeneration process is recovered as a by-product.

Several magnesium oxide processes have been installed on coal-fired power plants and have been operational since the 1980s, mainly in Japan and the USA. The most recent application on coal-fired power plants was the installation of the process on two 225 MWe units in China that went into operation in 2007 (IEA CCC, 2009). The magnesium oxide process can achieve >95% desulphurisation efficiency. The magnesium hydroxide-gypsum process consumes less energy compared with the earlier magnesium process and therefore has a lower operating cost.

2.2   Semi-dry processes

In dry and semi-dry processes, lime is most often used as a sorbent. The sorbent is brought into contact with the flue gas in an aqueous slurry form or as a dry powder, and a mixed solid waste is produced for disposed.

2.2.1   Spray dry process

Globally, the spray dry process is the second most widely applied FGD process among coal-fired power plants after wet scrubbers. The process typically uses lime as sorbent. In the spray dry process, lime slurry is sprayed into the flue gas in a spray dryer vessel to react with and remove acidic compounds such as SO_2, SO_3 and HCl. Rotary atomiser or two-fluid nozzles are used to finely disperse the lime slurry into flue gas. The water in the slurry will humidify the flue gas and so improve both SO_2 and particulate removal. The final product is a dry powdered mixture of calcium compounds. Some of the product is mixed with the lime slurry and returned to the spray dryer vessel to improve the sorbent utilisation.

The spray dry process is one of the most well-developed. It is most often used by small- to medium-sized power plants that burn low- to medium-sulphur coal, and is preferable for retrofit. By the end of 2008, the worldwide coal-fired electricity generating units with a total capacity of around 25 GWe had been fitted with spray dry scrubbers, over 1.5 GWe were being fitted and a further 5.6 GWe were planned to have spray dry scrubbers installed (IEA CCC, 2009). In general, the process can remove 80–90% of SO_2. Several spray dry FGD plants have even achieved SO_2 removal efficiencies of over 95% (IEA CCC, 2009).

The spray dry process is cheaper to install than a wet scrubber but relatively expensive to operate due to its lower sorbent utilisation and the costs of by-product disposal. Several spray dry processes now commercially available are very similar to one another in terms of the process configuration, constituents and the sorbent used. The main difference among these processes is the lime slurry dispersion system used in the spray dry absorber. Full descriptions of the process chemistry, process designs and the cost of spray dry process can be found elsewhere (European Commission, 2006).

2.2.2   Duct spray dry process

The duct spray dry process is essentially the same as a

conventional spray dry process. The main difference is that in a duct spray dry process the lime slurry is sprayed directly into the ductwork upstream of the existing particulate control devices, omitting the spray dryer vessel. The SO_2 in the flue gas reacts with the alkaline slurry droplets as they dry, forming $CaSO_3$ and $CaSO_4$. The final product is a dry powdered mixture of calcium compounds.

This process is developed primarily for retrofitting to existing plants where a moderate degree of SO_2 removal (50–75%) is required and where plant operating hours and remaining lifetime are limited (DTI, 2000). The process does not require a dedicated absorber vessel and the new hardware required is mainly the sorbent delivery equipment. Therefore, it should have a low capital cost. This process is yet to reach the full-scale commercial operation.

2.3   Dry processes

In dry scrubbing processes, either the alkali sorbent is injected into the gas stream or the flue gas passes through a bed of sorbent. The SO_2 reacts directly with the solid alkali to form sulphite or sulphate product. In general, dry processes are less effective than wet processes, cheaper to install but expensive to operate.

2.3.1   Circulating fluidised bed (CFB) process

In the CFB process, the humidified flue gas passes upwards through a circulating fluidised bed of hydrated lime, reaction products and fly ash particles contained within a vertical absorbing vessel. A large quantity of the particulate matter in the CFB is carried downstream by the flue gas and is then collected by the particulate control devices. Some of the solids collected are recirculated into the CFB absorber to maximise the utilisation of the sorbent. In a circulating fluidised bed, a rapid absorption rate of SO_2 by the sorbent can be obtained due to the intimate mixing of the solids with the flue gas, and the bed also provides a long contacting time between the two phases. As a result, up to 99% of SO_2 and all of SO_3 and HCl can be removed from the flue gas.

This process is well established and has been in commercial operation on coal-fired utility boilers for more than 20 years. It is an expanding technology, particularly for retrofitting to small- to medium-sized power plant. Over the last decade, the CFB process has been installed at coal-fired power plants with a total capacity in excess of 5.8 GWe, and over 1.8 GWe are currently being fitted or are planned to be installed on coal-fired power plants (IEA CCC, 2009). The CFB process is capable of high SO_2 removal efficiency, even with very high inlet SO_2 concentrations. A CFB plant in Germany achieved 97% of SO_2 removal with an inlet SO_2 concentration of 13,000 mg/m³. It has also been reported that several CFB plants achieved higher than 99% SO_2 removal (DTI, 2000).

The CFB process does not normally suffer from scaling, plugging or corrosion problems. It has almost unlimited turndown capability and can accommodate rapid changes in inlet SO_2 concentration. It is not complicated to operate and is easy to maintain because it does not require high maintenance mechanical equipments such as grinding mills, abrasion resist slurry pumps, agitators, and rotary atomisers. As a result, the process has a lower capital cost and requires a much smaller footprint compared with the limestone gypsum process. Other advantages include that the increased effective surface area of the circulating bed permits the successful capture of virtually all of the SO_3 in the flue gas, eliminating the possibility of gas pass corrosion from condensate of SO_3 aerosol mist. However, the CFB process is relatively expensive to operate, and generates solid waste that has to be disposed of.

2.3.2   Furnace sorbent injection

In the furnace sorbent injection process, dry sorbent is injected directly into the section of the furnace where temperatures are between 950ºC and 1000ºC. Sorbent particles (hydrated lime or limestone) decompose and become porous solid with a high surface area. The spent sorbent, including any remaining unreacted sorbent, is collected with fly ash and the mixture has to be dumped. This process can remove up to 70% of SO_2 from the flue gas and is one of the cheapest FGD processes to install. However, it has a high operating cost due to the insufficient utilisation of sorbent. Therefore it is most suitable for retrofit situations where only a low SO_2 removal efficiency is required and where there is little space available in the plant (DTI, 2000). In some cases, the reaction product is re-injected into the furnace in order to improve efficiencies of both SO_2 removal and sorbent utilisation. There are now several furnace sorbent injection systems being in commercial operation in coal-fired power plants.
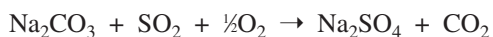
LIFAC process
The LIFAC (limestone injection into furnace and activation of unreacted calcium) process is a variant of the furnace sorbent injection process. In the LIFAC process, finely pulverised limestone is injected into the upper part of the furnace, where a portion of the SO_2 is removed in a similar manner to the furnace sorbent injection process described above. The flue gas, along with the reaction products and fly ash pass through an activation reactor into which water is sprayed to humidify the flue gas and a major portion of SO_2 in the flue gas is removed at this stage.

The LIFAC process has an improved SO_2 removal efficiency and increased sorbent utilisation than the conventional furnace sorbent injection process. Several LIFAC FGD units have been installed on coal-fired power plants worldwide. They have been in operation for around 20 years and the SO_2 removal efficiencies achieved by these LIFAC plants are typically in the region of 75–80% (IEA CCC, 2009). It has a low capital cost but the operating cost is high. The process is considered simple and easy to operate and requires little maintenance.

2.3.3 Sodium bicarbonate injection process

In this process, sodium bicarbonate as dry fine powder is

injected directly into the flue gas duct downstream of the air heater. When sodium bicarbonate is injected into the duct, it thermally decomposes to form carbonate and evolves gaseous H_2O and CO_2. This creates a network of void spaces throughout the particles resulting in a much larger surface area than the original particles. The carbonate then reacts with the SO_2 in the flue gas as shown below:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$$

$$Na_2CO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2$$

This process removes up to 70% of the SO_2, and the SO_3, HCl as well as NOx in the flue gas can also be removed to some extent. The final products are dry powdered sodium compounds mixed with fly ash.

This process has a low capital cost and can achieve a moderate degree of SO_2 removal. The operating cost can be high due to the use of relatively expensive sodium bicarbonate as sorbent and the insufficient sorbent utilisation. The process has only been installed on a handful of coal-fired power plants, all in the USA.

2.4 Integrated multi-pollutant control systems

Extensive research work has been carried out over the last two decades to develop integrated, multi-pollutant control systems that can remove several pollutants such as SO_2, NOx, Hg, and/or fine particulates in one process. Integrated environmental control has many advantages over the traditional, single pollutant removal systems. In particular it may lead to significant cost reductions over separate emission controls. A number of multi-pollutant control processes have been developed and some of them are already in commercial operation. Brief descriptions of some of the processes and their environmental performance are given below.

2.4.1 SNOX/DESONOX process

Both SNOX and DESONOX are catalytic processes capable of controlling SO_2 and NOx emissions. The flue gas is cleaned of fly ash in high-efficiency particulate collectors and then is heated before entering the NOx reduction reactor where the NOx is reduced catalytically to water and nitrogen by NH_3 injection. The flue gas is then heated further and a second catalytic reactor oxidises SO_2 to SO_3. The SO_3 is hydrated to H_2SO_4 vapour that is then to condense into 94–95% concentrated sulphuric acid. It is claimed that 97–99% of SO_2 removal and 90–95% of NOx removal (measured after the acid condenser) can be achieved. A surplus of NH_3 is used in the SCR reactor to achieve a high NOx reduction efficiency without any problems with NH_3 slip, as all the NH_3 in the gas after the SCR reactor is oxidised completely in the oxidation reactor. The processes have been installed on several coal-fired power plants in Europe and the USA (IEA CCC, 2009).

2.4.2 Activated carbon process

This is a regenerative process. The flue gas from the boiler first passes through the particulates collection device and it then enters a moving bed adsorption system that contains activated carbon. SO_2 is oxidised through catalytic reaction with oxygen and water vapour in the flue gas to form sulphuric acid, which is adsorbed onto the activated carbon surface. Prior to entering the second stage absorber, ammonia is injected into the flue gas in a mixing chamber. Nitrogen oxides in the flue gas are removed by reacting catalytically with ammonia in the second stage to form nitrogen gas (N_2) and water. The cleaned flue gas passes to the stack for discharge. The sulphur-laden activated carbon is sent to the desorber and is regenerated thermally. Enriched SO_2 is generated from the desorber and is then converted to elemental sulphur by a Claus reaction, or to sulphuric acid that can be sold as a by-product. The process can achieve higher than 95% SO_2 removal and up to 80% NOx reduction and has been installed on several coal-fired power plants in Germany and Japan (IEA CCC, 2009). This process and its recent advances will be discussed in more detail later in Chapter 4.

2.4.3 Electron beam irradiation process

This is a dry scrubbing process capable of simultaneous removal of SO_2 and NOx. In the process, flue gas is exposed to a high energy flux of electrons with ammonia to generate ammonium sulphate or nitrates for collection by a particulate control system. Flue gas is humidified and cooled, and it then enters a reactor. In the reactor, a beam of high energy electrons is fired into the flue gas in the presence of ammonia which is injected into the flue gas upstream of the reactor. High energy electrons react with molecules in the flue gas to produce radicals that then react with the SOx and NOx in the flue gas to produce sulphuric and nitric acids that in turn react with the added ammonia to form ammonium sulphate and ammonium nitrate. The ammonium salts are carried in the flue gas as aerosols which are collected in a downstream electrostatic precipitator or bag filter, and the salts are recovered and sold as fertiliser.

Processes differ in terms of the method of exposing the flue gas to the energy flux, and the control equipment employed to form and collect the particulates. These processes have been tested or demonstrated on coal-fired power generating units, mainly in China and Poland. One 120 MWe coal-fired unit in Bulgaria is currently being installed with an electron beam irradiation system and it was scheduled to start operation in 2009 (IEA CCC, 2009). Investigations have been carried out in several countries and the results from these works will be discussed Chapter 4.

2.4.4 SOxNOxROxBOx process

The process combines the removal of SO_2, NOx and particulates in high temperature catalytic scrubbing

baghouses. SO_2 removal is accomplished using either calcium- or sodium-based sorbent injection into the flue gas. NOx emissions are reduced by injecting ammonia to reduce NOx selectively in the presence of a zeolite-based catalyst incorporated into the baghouse. Particulate removal is accomplished by high-temperature fabric bag filters. Lower capital costs and space requirements are achieved through the integration of the SO_2, NOx and particulate removal process into a single unit. Operating procedures are also simplified. This process was tested on a 1000 m³/h plant under the US DOE CCT Programme. A 5 MWe pilot plant was operated at a coal-fired power plant in the USA from 1991-93.

2.4.5 Airborne process

The Airborne process integrates wet sodium scrubbing and dry sorbent injection of sodium bicarbonate to achieve estimated emission reductions of 99.5% SO_2, 90% SO_3, 90% NOx and 90% mercury. The process employs a proprietary method of sodium bicarbonate regeneration. The sodium sulphate by-product is regenerated into two end products. The first product is sodium bicarbonate for re-use in the scrubbing process, and the second is an saleable fertiliser and therefore eliminating disposal costs. The process will be discussed in detail later in Chapter 4.

2.4.6 Electro-catalytic oxidation (ECO) process

The ECO system is a patented technology designed for coal-fired power plants to achieve SO_2, NOx, Hg and fine particulate emissions control. The first commercial demonstration is currently being carried out at FirstEnergy's R E Burger coal-fired power plant to treat a slipstream equivalent to 50 MWe. Test results showed that ECO process significantly exceeded the removal goal for NOx, and was capable of removing more than 98% SO_2, over 80% Hg, and better than 95% SO_3, metals and fine particulates. Encouraged by the results, FirstEnergy decided to install ECO systems on units 4 and 5 at R. E. Burger and the 215 MWe unit 4 at its Bay Shore power plant (IEA CCC, 2009). The process mechanisms, desulphurisation performance and technical developments are discussed in Chapter 4.

3 Commercial non-calcium based FGD processes

Selection of an FGD system is based on both technical and financial considerations which are site-specific. Technical considerations include the size and location of a plant, fuel sulphur content, SO_2 removal requirement, reagent availability and cost, water availability, by-product and waste water discharge requirements, and installation type (new or retrofit). Financial considerations include capital cost, operating and maintenance cost, and the remaining life of the plant. Flue gas desulphurisation is traditionally based on limestone/lime sorbent. The majority of the installed FGD systems worldwide use limestone or lime as sorbent. However, technologies are rapidly evolving that allow desulphurisation in regions where there are limited resources of lime or limestone. For power plants located on an ocean coast, seawater is normally used as cooling medium instead of freshwater. Seawater is naturally alkaline and therefore can absorb and neutralise acidic SO_2 in a flue gas. Utilisation of seawater from the cooling system of the plant to scrub SO_2 provides several advantages such as simplicity in process design and operation, and cost effectiveness. As a result, the seawater FGD process has become a promising and attractive alternative to using other alkaline chemicals such as limestone and magnesium hydroxide. However, the application of seawater FGD processes is limited to power plants located in coastal areas. For plants in regions where neither lime/limestone nor seawater is readily available, FGD processes using sorbents such as ammonia or magnesium oxide may be an attractive option.

3.1 Seawater FGD process

Seawater is alkaline by nature with a typical pH value of 7.6 to 8.4. The inherent alkalinity of seawater results mainly from the bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) contained in seawater. The alkalinity is expressed as $CaCO_3$, and is typically in range of 100–110 mg/L. The major constituents of seawater are shown in Table 1. As shown in Table 1 sulphate is a natural ingredient of seawater, which is an essential substance of the marine environment. Every tonne of seawater contains approximately 0.9 kg of sulphur (Oikawa and others, 2003).

Seawater FGD processes utilise seawater's inherent properties to absorb and neutralise SO_2 in a flue gas. The absorbed SO_2 is oxidised to sulphate, which is a natural ingredient of seawater and therefore it can be discharged into the sea without causing environmental damage.

Seawater FGD systems have been in commercial operation since the 1970s. They have found application in coal- and oil-fired power plants, metal smelters, oil refineries, petrochemical industries and chemical processing plants. However, the earlier seawater FGD systems were mainly applied to small scale industrial and power plants. Although it has been developed and has been in commercial operation for over 40 years, the seawater FGD process is a relatively new but now rapidly expanding technology. Since 1998, a number

| Table 1	Major constituents of seawater (Oikawa and others, 2003)
Constituent as dissolved ion (salinity ≈ 3.5%)	Concentration in seawater, g/kg seawater
Chloride	19.35
Sodium	10.76
Sulphate	2.71
Magnesium	1.29
Calcium	0.411
Potassium	0.399
Bicarbonate	0.142
Bromide	0.067
Strontium	0.008
Boron	0.0045
Fluoride	0.0013

of seawater scrubbers have been or are currently being installed on coastal power plants in Asia, Europe and Middle East. Recent developments of the seawater FGD process mainly relate to the reduced place requirements, improved lifetime, and the improved operation and simpler design aimed to maximise its performance and minimise the investment and operating costs.

3.1.1 Process description and mechanism

The seawater FGD process consists of two major systems, the SO_2 absorption system and the seawater treatment plant. The schematic diagram of a seawater FGD process is shown in Figure 2. The flue gas from the particulate collector passes through a gas-gas heat exchanger (GGH) to cool down before entering the SO_2 absorber. In the absorber the flue gas comes into close contact with seawater, most commonly in a countercurrent flow. The absorption section of an absorber contains perforated plates or packings to promote vigorous gas-liquid transfer and large gas-liquid interfacial area depending on the design, resulting in highly efficient SO_2 absorption. The cleaned flue gas passes through a mist eliminator to prevent carryover of droplets and then is heated up to the required temperature in the GGH before being released into the atmosphere through a stack.

Seawater (a portion or all of the cooling water from the steam turbine condenser outlet) is pumped to the top of the absorber, dissolves the SO_2 and any HCl in the flue gas while flowing down through the absorption section. The seawater passes the absorber in once through mode and is not recirculated back to the top of the absorber. The acidified absorber effluent
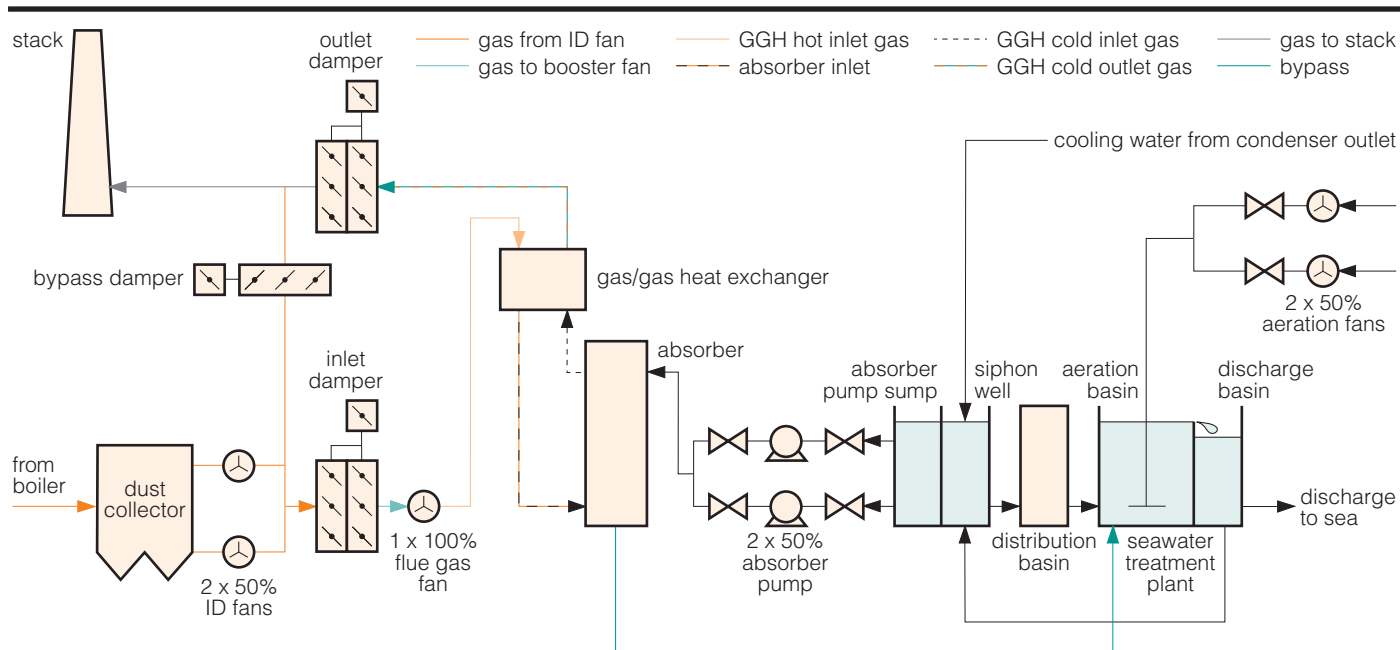
Figure 2   Schematic diagram of a seawater FGD process (Alstom, 2006)

collects in the absorber sump and is then mixed with the remaining spent cooling water in an external mixing basin before aeration. The aeration step involves blowing air through the seawater to reduce the chemical oxygen demand and raise its pH before final discharge to the sea.

When the flue gas comes into contact with seawater in the absorber, the SO_2 in the flue gas dissolves in water to form bisulphite (HSO_3^-). A portion of bisulphite can be converted to sulphite (SO_3^{2-}) which is known to be a source of chemical oxygen demand (COD) in the seawater effluent. The reactions are as follows:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+$$

$$HSO_3^- \rightarrow SO_3^{2-} + H^+$$

Due to the oxygen present in the flue gas and the seawater, the bisulphite and sulphite formed is oxidised to sulphate through the following reactions:

$$HSO_3^- + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-} + H^+$$

$$SO_3^{2-} + \tfrac{1}{2}O_2 \rightarrow SO_4^{2-}$$
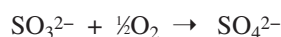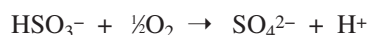
As SO_2 dissolves in the seawater to form bisulphite and sulphite, and the subsequent oxidation of bisulphite and sulphite to sulphate, hydrogen ions (H^+) are produced and acidify the seawater, lowing its pH value. The acidified effluent must be neutralised before discharge back to the sea. This can be achieved by utilising the HCO_3^- and CO_3^{2-} that is available in the seawater through reactions:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
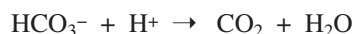
The neutralisation step is performed in the mixing basin by adding more seawater from the cooling system of the power

plant to obtain the excess alkalinity required. Blowing air through the seawater effluent in the aeration step is the key process of a seawater treatment plant. The technical significance and environmental benefits of this process include: 1) ensuring sufficient oxidation of HSO_3^- and SO_3^{2-}; 2) aerating the seawater effluent results in stripping of CO_2 and increasing the efficiency of neutralisation and 3) dissolved oxygen in the seawater is replenished.

3.1.2   Environmental requirements for water quality

The quality of seawater effluent must meet certain environmental requirements before it can be discharged back into the sea. The parameters that are of concern with respect to the local ecology include the pH value, temperature, COD, dissolved oxygen (DO), sulphate levels and the suspended solids concentration of seawater.

The acidified seawater effluent normally has a low pH value of 3 to 4 at the absorber outlet. The effluent is neutralised by mixing it with more seawater and blowing air through it. By controlling the amount of seawater and air added, the pH value of the effluent can be adjusted to somewhere between 6 and 7. The critical pH value for marine and estuarine animals is, in general, 6.5 (Batten and Mamber, 1996).

In the seawater FGD process, the sulphite ions (SO_3^{2-}) are the source of COD in the seawater effluent. COD is a wastewater quality indicator that determines whether or not a specific wastewater will have a significant adverse effect upon fish or aquatic plant life. Limits for COD are often specified without taking into account the magnitude of the effluent flow from a power plant. A maximum limit of 100–150 mg/L COD is sometimes considered to be acceptable for a relatively small industrial effluent. However, the cooling water effluent from a 700 MWe power plant is typically 100,000 m³/h, similar to the size of a small river. Such a large flow with a high COD

value could result in oxygen depletion in a large area around the point of discharge, harming the marine life seriously. Studies and surveys carried out by Alstom concluded that the COD for a seawater FGD process discharge should be limited to a maximum value of 5 mg/L (Nodland, 2009).

Sulphite can be oxidised by the oxygen dissolved in the seawater to form sulphate. The oxidation reaction of sulphite is fast and the pH value of the seawater has an influence on the oxidation rate and ratio. Some researchers predicted that the highest oxidation ratio and rate would be achieved at a pH value in the range of 4.1 to 4.5 whilst others reported that the optimum pH value for the oxidation reaction was found in the range of 5 to 5.6 (Schuettenhelm and others, 2004). Although the oxidation takes place in the absorber due to the oxygen contained in the flue gas and seawater, the amount of oxygen from these sources is not sufficient for complete oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-}. Therefore, it is important to ensure sufficient oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} by blowing air into the seawater effluent. Before aeration, the acidified absorber effluent is mixed with more seawater from the plant cooling system for the excess alkalinity required to raise the pH of the effluent to an optimum value for an efficient oxidation of sulphite ions to sulphate ions through aeration and without stripping off any SO_2. In general, high sulphite conversion (>99%) can be achieved through aeration and the COD in the discharged seawater effluent is normally in the range of 2.5 to 5.0 mg/L O_2 (Nodland, 2008). The small COD is the result of the oxidation process not being completed within the seawater treatment plant. This oxidation process will continue outside the point of discharge and therefore it is important to ensure a certain oxygen concentration in the effluent leaving the seawater FGD process. EU Directive 79/923/EEC specifies the Dissolved Oxygen (DO) values of 70% and 80% (Nodland, 2009).

Sulphate completely dissolves in seawater, so there is no waste product. Sulphate is a natural ingredient in seawater and the increase of sulphate in the effluent is within the variations occurring naturally in seawater. A calculated excess aeration provides the additional oxygen required to obtain an environmentally acceptable level of dissolved oxygen before the seawater returns to the estuary.

In general, the temperature increase of the seawater due to FGD is less than 2°C. The dissolved oxygen (DO) in the effluent can reach 70–90%, or higher than 6 mg/L after aeration compared to the 50–100% in the inlet seawater (Nodland, 2008; Oikawa and others, 2003). The differences in pH value, temperature and DO between the seawater and seawater discharge are within the natural variations of seawater. Long term bioassay testing and recipient monitoring were carried out at different seawater FGD plant sites. Results from these studies showed that no significant effects of the discharge on the local environmental and ecological conditions were observed (Nodland, 2009; Ringnes, 2008).

3.1.3 Recent developments

Absorption section

The absorption section of a seawater process typically uses either perforated plates or a packed tower design. In the perforated plates design, the perforated plates have openings that are partially covered by target plates. The plates are flooded with the aqueous sorbent and the flue gas is accelerated upwards through the perforations. The flue gas and sorbent liquid make contact around the target plate, creating a turbulent frothing zone to provide the desired reaction contact. The perforated plates design benefits from the extremely vigorous gas-liquid contacting leading to a high mass transfer rate between the gas- and liquid-phase. As a result, a smaller absorber is used to achieve the required SO_2 removal. In the packed tower design, the flue gas flows upwards through a packing material counter-current to the sorbent which is introduced at the top of the packing through a distributor. The packing material provides the required contacting surface area between gas and aqueous absorbent. While a smaller absorber size means a lower capital cost, the perforated plates design requires a larger volume of seawater and a higher gas velocity, and has a higher pressure drop in the absorber leading to higher operating costs. The packed tower design, on the other hand, has a higher capital cost due to the larger absorber size needed to achieve the required SO_2 removal, but it uses a smaller volume of seawater and a lower gas velocity. The pressure drop in the absorber is also smaller and therefore has lower operating costs compared with perforated the plates design.

A recently developed design uses combined packing/perforated plates that overcomes the shortcomings and takes full advantage of both the perforated plates and the packed tower designs. An absorber with the combined packing/perforated plates design can achieve a high SO_2 removal rate, is reliable and more cost effective (Oikawa and others, 2003). A technical comparison of the three designs is given in Table 2.

It can be seen from Table 2 that the absorber with combined packing/perforated plates design can achieve the same SO_2 removal efficiency as the other two designs. It is smaller in size compared to the packed tower design and has a lower seawater consumption and pressure drop compared to the perforated plates design. It was reported that, under the same flue gas conditions, for a 600 MWe power generating unit burning coal that contains 0.6–0.7% sulphur, the operating costs of an absorber with combined packing/perforated plates design would be approximately 35% lower over a 10-year period compared to a perforated plates absorber (Oikawa and others, 2003). The lower operating costs are mainly the result of reduced energy consumption due to, for example, smaller seawater pumps and lower pressure drop in the absorber. When the capital cost is taken into consideration, the total cost of an absorber with combined packing/perforated plates design would be 7% lower than that of a perforated plates absorber (Oikawa and others, 2003). The costs comparison of the perforated plates and combined packing/perforated plates design is shown in Table 3. It should be stressed that, although Oikawa and others indicated that the absorber with packed tower would be likely to suffer clogging or channelling, Alstom, the company that has built around a hundred seawater FGD plants and has over forty years experience, has never experienced such a problem in its packed tower absorbers (Nodland, 2009).

Table 2 **Technical comparison of the different designs of seawater FGD's absorption section** (Oikawa and others, 2003)

	Packed tower	Perforated plates	Combined packing/ perforated plates
Gas velocity (m/s)	1.0–1.5	3.0–3.5	1.6–1.8
Seawater volume	small	large	small
Pressure drop in absorber	small	large	small
Absorber size	large	small	medium
SO_2 removal efficiency %	95–98	90–98	95–98
Clogging/channelling	likely	unlikely	unlikely

Table 3 **Costs comparison of a seawater FGD absorber with different designs (for a 600 MWe power plant burning 0.6–0.7% S coal)** (Oikawa and others, 2003)

	Perforated plates	Combined packing/perforated plates
Flue gas flow rate, m³/h	1,916,000	
SO_2 at inlet/outlet, ppm	700/50	
Temperature at inlet/outlet, °C	130/40	
Capital cost*†, US$	39,000,000	42,000,000
Operating cost‡, US$ (operated 6312 h/y for 10 years)	19,000,000	12,000,000
Total cost	100%	93%

* based on Japanese conditions
†. excluding ESP, GGH, stack and civil work
‡. applied for electricity 65%, maintenance 30% and process water 5%

Construction materials

Both the untreated flue gas, especially the flue gas containing acid mist and the acidified absorber effluent are highly corrosive and therefore corrosion resistant materials are required for the seawater FGD equipment and pipes. The choice of construction material is of paramount importance if the plant is to have a reasonable life without suffering from accelerated corrosion. The choice of material is critical to the procurement and fabrication cost. Alloys such as Hastelloy and Duplex steel are highly corrosion-resistant materials but they are expensive. The more alloyed the material is, the higher the cost. Over the years, new corrosion-resistant materials and technologies for corrosion protection have been developed. Today, this protection may take many forms, for example, selecting corrosion-resistant materials such as FRP (fibre-reinforced polymer), chlorobutyl rubber, silicone rubber, or protecting the base material with 'wall papered' stainless steel or Hastelloy coatings, or a suitable organic lining. These technologies allow the use of relatively cheap construction materials like concrete and carbon steel resulting in a significant reduction in investment costs of a seawater FGD plant. Figure 3 shows the materials used in an Alstom's seawater FGD plant.

Reduced size

Whether designed for new plants or retrofitting existing units, modern seawater FGD systems provide increased redundancy and reliability in much smaller packages than earlier generations. Today, a single absorber can support a 700 MWe unit or even larger. The benefits of the reduction in seawater FGD size include a smaller footprint, lower capital cost and lower maintenance cost.

Comments

The main advantages of the seawater FGD process include: 1) it does not require the addition of chemical reagents; 2) there is no by-product to handle or dispose of; 3) the plant design and operation are relatively simple. The process is capable of high SO_2 removal (up to 99%). However, it is obvious that the application of seawater FGD process is limited to the plants located at coastal sites. Theoretically, the seawater FGD process can be applied to combustion plants burning high-sulphur fuels and meet stringent emission standards. However, high SO_2 removal efficiencies at higher SO_2 loadings would require additional sea water, above that used by the plant for cooling, and therefore significantly increase capital and operating costs. The coal sulphur content range for
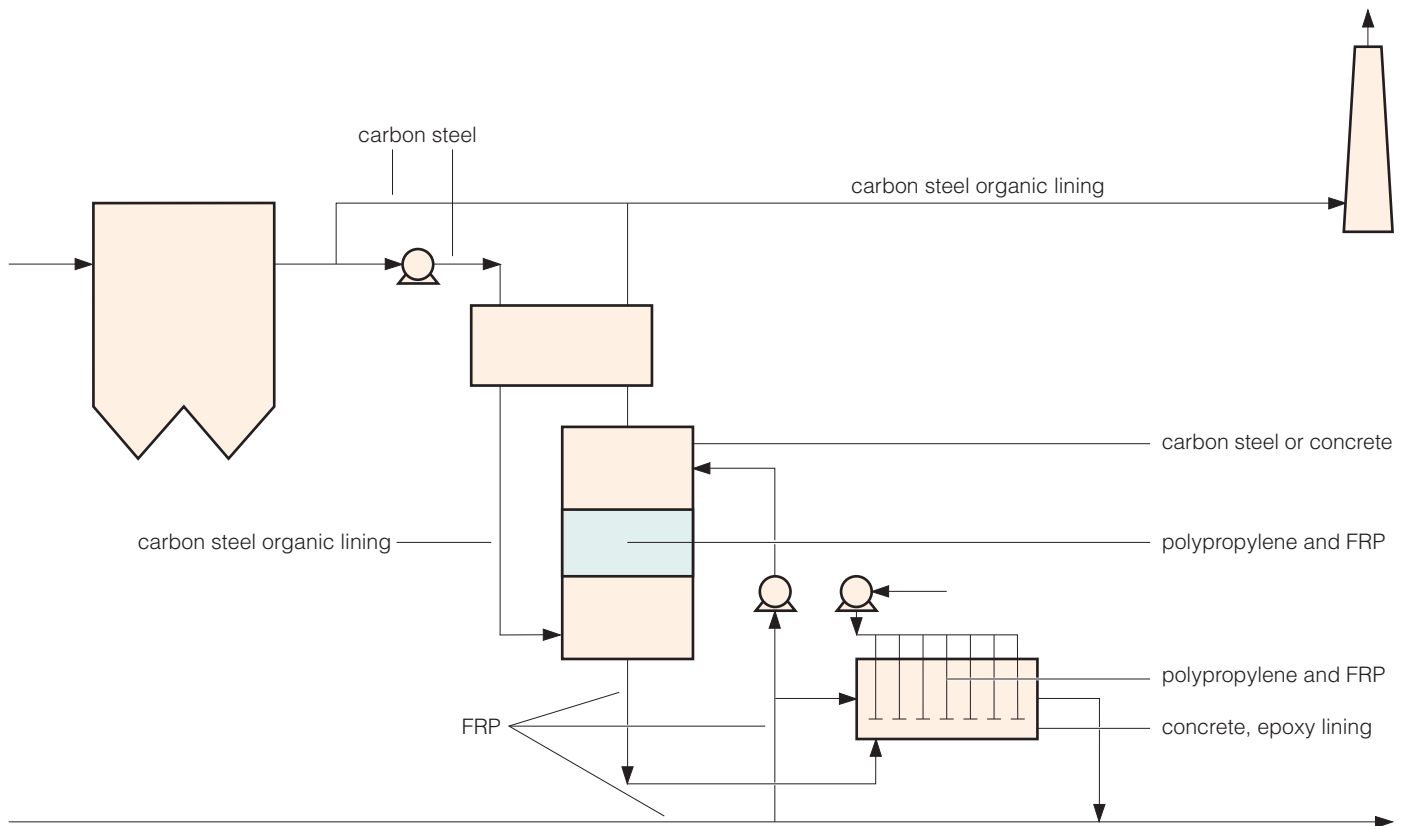
Figure 3   Materials used in an Alstom's seawater FGD plant (Nodland, 2008)

the economic application of a seawater FGD process is less than 1.5% (Nodland, 2008). When high sulphur coal is burned, additional additives to the seawater absorbent is required. Generally, sodium hydroxide, magnesium oxide or lime are used as additives to boost the seawater FGD process. The additional alkalinity is required not to remove the SO_2 from the flue gas, but to neutralise the absorber effluent before its discharge to the sea. This becomes more attractive if there are peaks when high sulphur coal is used or seasonal variations of seawater alkalinity. However, Nodland argued that if extra seawater is available from other sources or can be pumped from the sea, in many cases it is more economic to pump seawater to the seawater FGD process (Nodland, 2009).

3.2   Ammonia scrubbing process

The ammonia scrubbing process works in a similar way to the limestone gypsum process. In an ammonia scrubbing process, anhydrous or aqueous ammonia is used as a scrubbing agent to remove SO_2 from the flue gas and the final product is ammonium sulphate that can be used as agricultural fertiliser. Ammonia based desulphurisation technology was developed in the early 1970s in Japan and Italy for applications in fertiliser manufacture. Continuous developments and advances in the technology and process improvements means that since the 1990s, the ammonia scrubbing process has found applications in other industries including power generation. Several ammonia scrubbing processes applicable to power plants have been developed and are now commercially available. Brief descriptions of some of the processes are given in the following section,

3.2.1   Ammonia based FGD systems

Walther process
The Walther process was developed between 1970s and 1980s by Krupp Koppers GmbH. The flue gas from particulate collector first passes through a gas-gas heat exchanger (GGH) to cool down. The cooled flue gas enters the top of the pre-scrubber, and flows down co-currently with aqueous ammonia (25%). The ammonia solution is collected from the bottom of the scrubber and recycled back to the top of the pre-scrubber. The flue gas leaving the bottom of the pre-scrubber then enters the second stage scrubber. In the second scrubber the flue gas is brought into contact with aqueous ammonia in a countercurrent flow. On exiting the second scrubber, the cleaned flue gas passes through a washing tower to remove ammonium salt particles in the flue gas. The flue gas is then heated up to the required temperature by passing through the GGH before being released into the atmosphere. The spent scrubbing liquid containing ammonium sulphite flows to an oxidiser where forced oxidation takes place by blowing air into it to convert ammonium sulphite to ammonium sulphate. The ammonium sulphate is crystallised by the evaporation of water in a spray dryer. The heat of evaporation is supplied by untreated flue gas.

A 40,000 m³/h demonstration unit was built in Italy and two commercial Walther FGD systems were installed on a power plant and a municipal heating and power plant in Germany (Kohl and Nielsen, 1997).

AMASOX process

The AMASOX process is an improved ammonia scrubbing process based on the Walther process. The major advance of the AMASOX process is that it combines the multi-tower into a single tower in the absorption section. As a result, the process design and operation are much simpler and the total costs are reduced compared with the Walther process. A schematic diagram of the AMASOX process is shown in Figure 4. The flue gas from the particulate collector is saturated and cooled after passing through a GGH. It is then quenched in a quencher, and enters at the bottom of a two-stage packed bed absorber. The flue gas flows upwards through the packing while ammonia solution is sprayed onto it from the top of the packed bed. The scrubbing solution is withdrawn from the bottom sump, recycled back to the top of the packed bed and sprayed up. The pH value of the circulating scrubbing solution is controlled to within a range of 5.0–6.5. A part of the spent scrubbing solution is withdrawn and sent to an oxidiser. Air is blown into the spent scrubbing solution to convert ammonium bisulphite and ammonium sulphite into ammonium sulphate. At the same time, the required pH value is controlled and kept by ammonia water solution (25%). The ammonium sulphate solution is processed in a separate evaporation/crystallisation unit to produce marketable fertiliser. A wet ESP is installed inside the absorber to remove the ammonium salt aerosol that causes visible plume stack emissions, a problem suffered by earlier ammonia scrubbing systems (Ferrao, 1998).

MET AS process

The MET AS process was originally developed by General Electric Environmental Services Inc (GEESI) in the early 1990s, and later acquired by Marsulex Environmental Technologies (MET). The first field pilot of this technology was carried out at Dakota Gasification Company's (DGC) Synfuels Plant. The successful tests led to a subsequent full scale commercial installation of a MET AS plant with a capacity of 350 MWe at the site and the system has been in operation for over ten years now.

In the MET AS system operated at DGC's plant, flue gas leaving the boilers enters the pre-scrubber just above liquid level and the hot flue gas comes into contact countercurrently with a recirculating spray of scrubbing solution. In the pre-scrubber, the flue gas becomes saturated by the evaporation of water from the circulating solution. On leaving the pre-scrubber, the saturated flue gas passes through a mist eliminator before entering an absorber where it flows countercurrently with recirculating solution of subsaturated ammonium sulphite liquor. The cleaned flue gas then passes through two stages of high efficiency mist eliminators to remove any entrained droplets.

Ammonia is fed into the absorber recycle tank with oxidation air to maintain the recycle liquor at the desired pH (5.2–5.9) to ensure that required SO_2 removal rate is achieved. Primary reaction products ($(NH_4)_2SO_3$ and $(NH_4)HSO_3$) are converted to $(NH_4)_2SO_4$ through forced oxidation in the absorber recycle tank. Using the thermal energy of the flue gas, a portion of by-product ammonium sulphate is continuously crystallised from the saturated absorber liquor forming a suspension of ammonium sulphate. By maintaining a high recirculation ratio of absorbing liquor and relatively low pH, ammonia slip in the outlet flue gas is kept at low levels avoiding the plume visibility problem suffered by earlier ammonia scrubbing systems (Walsh, 2005).

The primary purpose of the pre-scrubber is to separate the process function of SO_2 absorption and oxidation from product crystallisation. Thermal energy from the flue gas is used to evaporate water causing crystallisation of ammonium sulphate in the pre-scrubber vessel. In later installations of the MET AS process, the process design has been simplified by eliminating the pre-scrubber and the SO_2 removal, evaporation and crystallisation all take place in the absorber (Walsh, 2005).
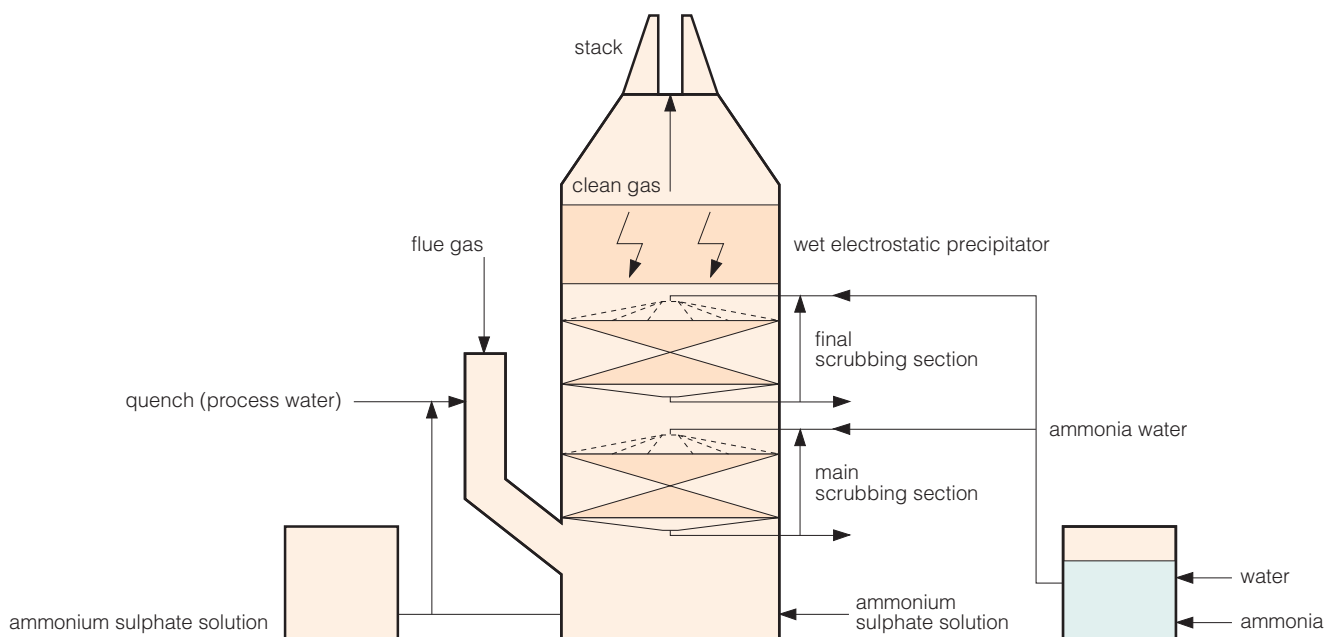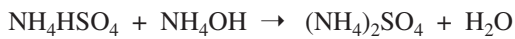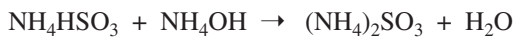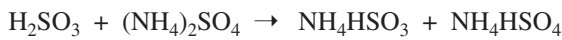

Figure 4   Schematic diagram of the AMASOX process (Ferrao, 1998)

3.2.2 Process chemistry

When ammonia dissolves in water, it reacts with water to form ammonium hydroxide (NH_4OH). Since the scrubbing solution is continuously recycled back and is circulating in the absorber, the solution also contains ammonium sulphite and ammonium sulphate. When the flue gas comes into contact with the scrubbing solution, SO_2 dissolves into the water forming sulphurous acid, which then reacts with ammonium sulphite/sulphate and ammonium hydroxide.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 + 2NH_4OH \rightarrow (NH_4)_2SO_3 + 2H_2O$$

$$H_2SO_3 + NH_4OH \rightarrow NH_4HSO_3 + H_2O$$

$$H_2SO_3 + (NH_4)_2SO_3 \rightarrow 2NH_4HSO_3$$

$$H_2SO_3 + (NH_4)_2SO_4 \rightarrow NH_4HSO_3 + NH_4HSO_4$$

$$NH_4HSO_3 + NH_4OH \rightarrow (NH_4)_2SO_3 + H_2O$$

$$NH_4HSO_4 + NH_4OH \rightarrow (NH_4)_2SO_4 + H_2O$$

The formation of sulphurous acid and the acidic intermediate species lowers the pH of the scrubbing solution so ammonia is added into the solution to neutralise the acidic species and restore the pH to its desired value.

Due to the presence of oxygen in the flue gas, part of the ammonium sulphite is oxidised into ammonium sulphate. Air is injected into the solution to oxidise the remaining sulphite to sulphate.

$$2(NH_4)_2SO_3 + O_2 \rightarrow 2(NH_4)_2SO_4$$
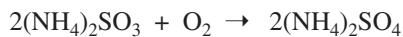
The resulting ammonium sulphate solution is then saturated and ammonium sulphate precipitates from the solution in a crystalline form that can be dried to produce saleable fertiliser.
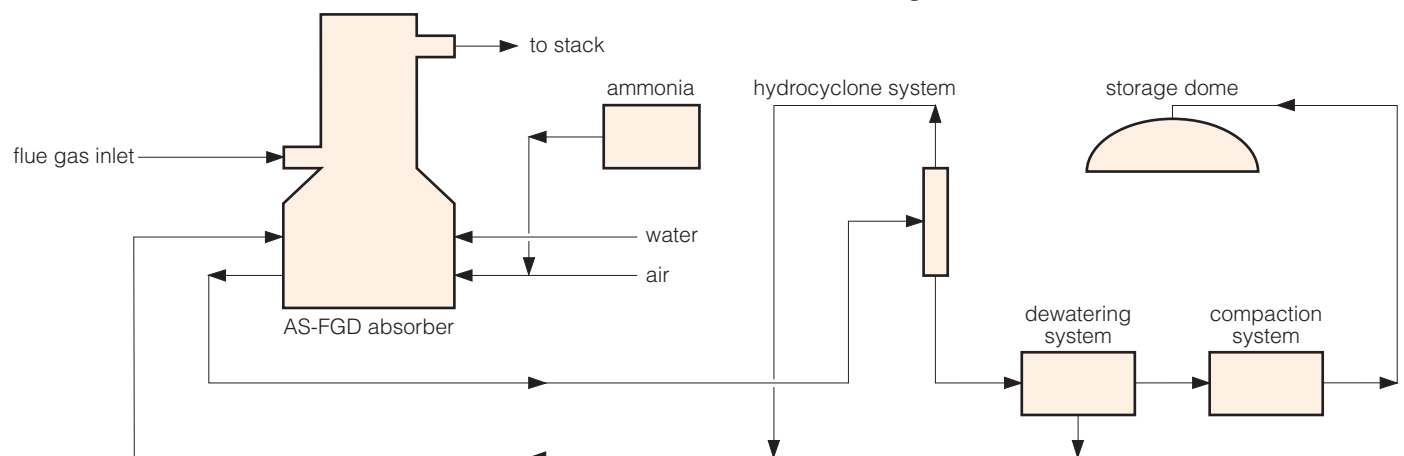
3.2.3 Advances in ammonia scrubbing technologies

The earlier ammonia FGD systems suffered from visible stack emissions of blue or white plumes. The white plumes are the result of the formation of submicron ammonia salts aerosols in the absorber that pass through the mist eliminator. This was later corrected by modifying and improving the efficiency of the mist elimination system. In modern ammonia scrubbing process installations, wet ESPs are generally used to remove submicron ammonium salt particles effectively from the exiting flue gas.

It is a well-known fact that ammonia is volatile and its vapour pressure increases with increasing absorbent pH value and temperature. This causes the formation of ammonia/sulphur aerosols that result in a blue haze or plume exiting the stack. On the other hand, ammonia is an expensive reagent. Ammonia slip to the stack means higher ammonia consumption and therefore higher operating costs. Earlier attempts to solve the problem mainly involved adding washing tower or washing sections inside the absorber, and/or installing a high efficiency mist eliminator. These measures resulted in significant increases in capital and operating costs. In recent ammonia scrubbing processes, the pH value of the scrubbing solution and reaction temperature are controlled at values under which conditions the formation of ammonia aerosols is avoided. As a result, ammonia slip to the stack can now be maintained at less than 10 ppm, and ammonia loss is lower than 0.19% (Wei, 2008).

The effective oxidation of ammonium sulphite into the final by-product of ammonium sulphate is an important part and it affects the economics of ammonia scrubbing systems. In earlier ammonia FGD systems, the oxidation was carried out in a separate oxidiser. However, the process design inside the absorber has been modified to promote the natural oxidation of sulphite during the absorption process by the oxygen present in the flue gas. Forced oxidation takes place at the bottom of the absorber where air is blown into the spent solution to ensure the oxidation is complete. The conversion of sulphite to sulphate in the spent scrubbing solution leaving the absorber can reach as high as 99%, eliminating the need for a separate oxidiser and reducing the investment cost of an ammonia scrubbing process. Figure 5 shows a diagram of a recent MET AS process.

Figure 5   The MET AS-FGD Process diagram (MET, 2009)

3.2.4 Economics of the ammonia scrubbing process

Ammonia is considerably more expensive than lime or limestone. However, the process produces a high-value fertiliser by-product. The income from the sale of ammonia sulphate can offset the high cost of ammonia. Table 4 compares the reagent costs and revenues generated by sales of the by-products from the ammonia scrubbing process and the limestone gypsum process.

The economics of the ammonia scrubbing process depend on many factors such as the availability and price of ammonia, the sulphur content of the fuel, the size of the unit. Using the ammonia process allows a power plant to fire potentially lower cost, higher sulphur coals while producing more high-value fertiliser, making the technology more attractive economically.

For one mass unit of ammonia consumed, approximately four mass units of ammonium sulphate are produced. The market prices for ammonia and ammonium sulphate followed a similar trend over the years and are shown in Figure 6. Evans and others (2009) compared the costs of ammonia reagent with the possible income from the sale of ammonium sulphate while burning fuel with varying sulphur content. They assumed that 100 tonnes of ammonium sulphate were produced annually for per megawatt of electricity generated firing a fuel containing 1% sulphur. For a 600 MWe power plant at 85% load, approximately 50,000 tonnes of ammonium sulphate would be produced in a year. Given the market prices of 450 $/t for ammonia and 200 $/t for

ammonium sulphate, and considering that one tonne of ammonia can produce four tonnes of ammonium sulphate, a net income of 87.5 $/t of ammonium sulphate is generated. It is equivalent an annual income of $4.38 million. For the same plant, the net income will be $8.9 million a year if firing a 2% sulphur fuel, or $17.8 million a year for a 4% sulphur fuel (Evans and others, 2009). This income will offset a significant portion of the FGD operating costs. For plants at certain sites, particularly those burning high-sulphur fuels, or with the potential to do so, the ammonia scrubbing process could be a very attractive option.

3.2.5 Application of ammonia scrubbing process

The viability of applying the technology to any particular plant is site-specific, depending on the availability and delivered price of ammonia, the utility's ability or willingness to handle and store the ammonia reagent, the ability to fire high sulphur fuels, the regional market demand and the price for ammonium sulphate, for example. The ammonia scrubbing process can remove more than 98% of SO_2 even if fuels with an extremely high sulphur content are burned. Other advantages of the process include: there is no waste water to discharge or waste solid to dispose of; it produces a high-value by-product; and it is unlikely to suffer scaling or blockage problems. The MET AS process uses designs with a standard conventional critical equipment redundancy similar to that of limestone gypsum processes, allowing flexibility to operate the FGD system with either limestone or ammonia as a reagent (MET, 2007). However, the process has a high

Table 4	Comparison of reagent costs and by-product revenues of ammonia scrubbing process and limestone gypsum process (Staehle and Zhang, 2005)		
	Ammonia scrubbing, $ million	Limestone gypsum, $ million
Reagent cost	8.0*	1.8†
By-product revenue	19.0*	-1.3†
Net income	11.0	-3.1
* ammonia 145 $/t, consumption 56,000 t/y; ammonium sulphate 85 $/t, production 224,000 t/y		
† limestone 10 $/t, consumption 180,000 t/y; gypsum –4 $/t to dispose, production 330,000 t/y		
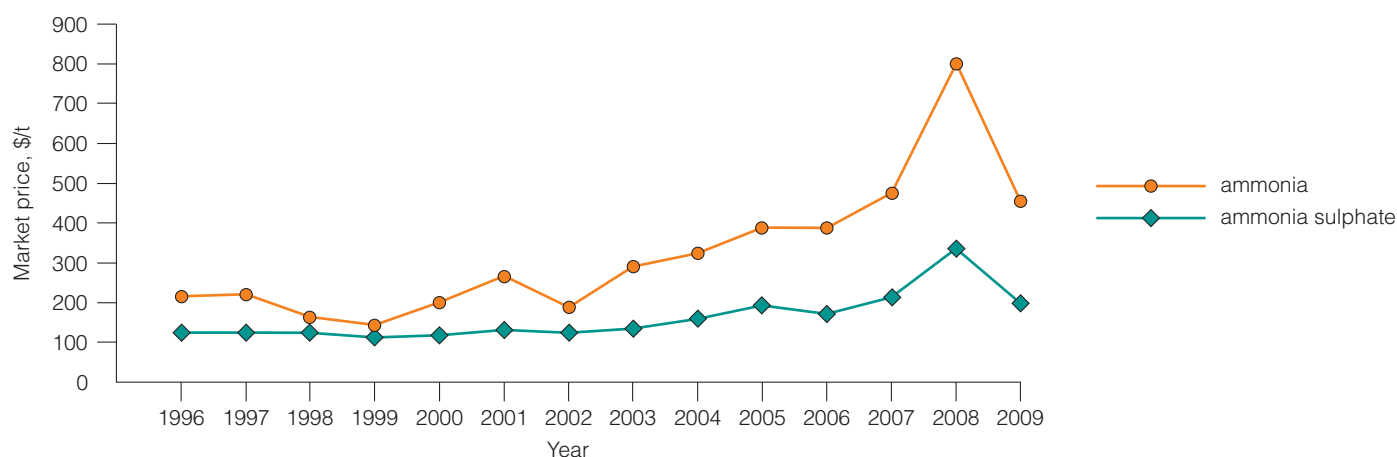
Figure 6   Market prices of ammonia and ammonium sulphate (Evans and others, 2009)

capital cost (30–40% higher than that of a limestone gypsum process) and requires a large footprint. Another major drawback of the process is that ammonia is both caustic and hazardous, and exposure to ammonia can cause harm to human health. As a result, the transport and storage of ammonia are regulated, which may cause difficulties in the planning stage at certain sites. Many utility companies, wary of getting into the fertiliser business, are reluctant to own and operate a fertiliser plant on site. In addition, there is a limited market for ammonium sulphate fertiliser in industrialised countries and therefore this process is seldom utilised in power plants.

Ammonia is alkaline and it can effectively remove acid gases like SO_2, CO_2, NOx, HCl and HF from flue gas. Ammonia is also the reagent used in selective catalytic (SCR) and non-catalytic reduction (SNCR) of NOx for NOx emissions control. There is an increasing interest in the ammonia based scrubbing processes. Works are ongoing to develop ammonia scrubbing processes for CO_2 sequestration (Resnik and others, 2004; Yeh and others, 2004; Powerspan, 2009a). It is envisioned that an integrated ammonia scrubbing process could be developed to capture the three major acid gases (SO_2, NOx and CO_2), reducing significantly the total costs and complexity of emission control systems. The final products from the simultaneous removal of SO_2, NOx, and CO_2 using the ammonia process are $(NH_4)_2SO_4$, NH_4NO_3 and NH_4HCO_3, which can all be sold as fertilisers. In regions such as China where there is a high demand for fertilisers, the ammonia scrubbing process is an attractive alternative to limestone-based FGD processes and may be advantageous economically.
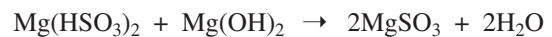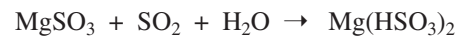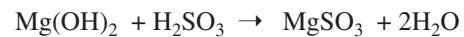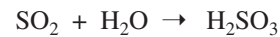
3.3   Magnesium hydroxide process

The magnesium hydroxide process is a wet FGD process that uses magnesium hydroxide as a scrubbing reagent. Magnesium hydroxide processes have been applied in oil refineries, in the iron and steel, chemical, cement, waste disposal industries and other industries as well as power plants. They have operated successfully for years. Most of the
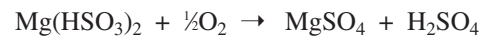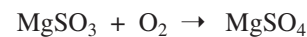
applications of the magnesium hydroxide process for SO_2 emissions reduction are found in Japan, whereas its use elsewhere is fairly uncommon.

3.3.1   Process chemistry

The magnesium hydroxide process consists mainly of two steps: absorption and waste water treatment. In the absorption tower, SO_2 dissolves into the water to form sulphurous acid. Sulphurous acid then reacts with magnesium hydroxide to form magnesium sulphite, which can further react with SO_2 to form magnesium bisulphite. The basic reactions are as follows:

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$Mg(OH)_2 + H_2SO_3 \rightarrow MgSO_3 + 2H_2O$$

$$MgSO_3 + SO_2 + H_2O \rightarrow Mg(HSO_3)_2$$

$$Mg(HSO_3)_2 + Mg(OH)_2 \rightarrow 2MgSO_3 + 2H_2O$$

In the water treatment step, forced oxidation takes place by blowing air into the spent solution to convert sulphite and bisulphite into magnesium sulphate through the following reactions:

$$MgSO_3 + O_2 \rightarrow MgSO_4$$

$$Mg(HSO_3)_2 + \tfrac{1}{2}O_2 \rightarrow MgSO_4 + H_2SO_4$$

The resulting magnesium sulphate solution is harmless and can be discharged without risk of secondary pollution.

3.3.2   Process description

Figure 7 shows a diagram of the MORETANA magnesium hydrate process. The MORETANA FGD process was originally developed in 1972. It uses a specially designed internal tray – MORETANA perforated plate, and it can use
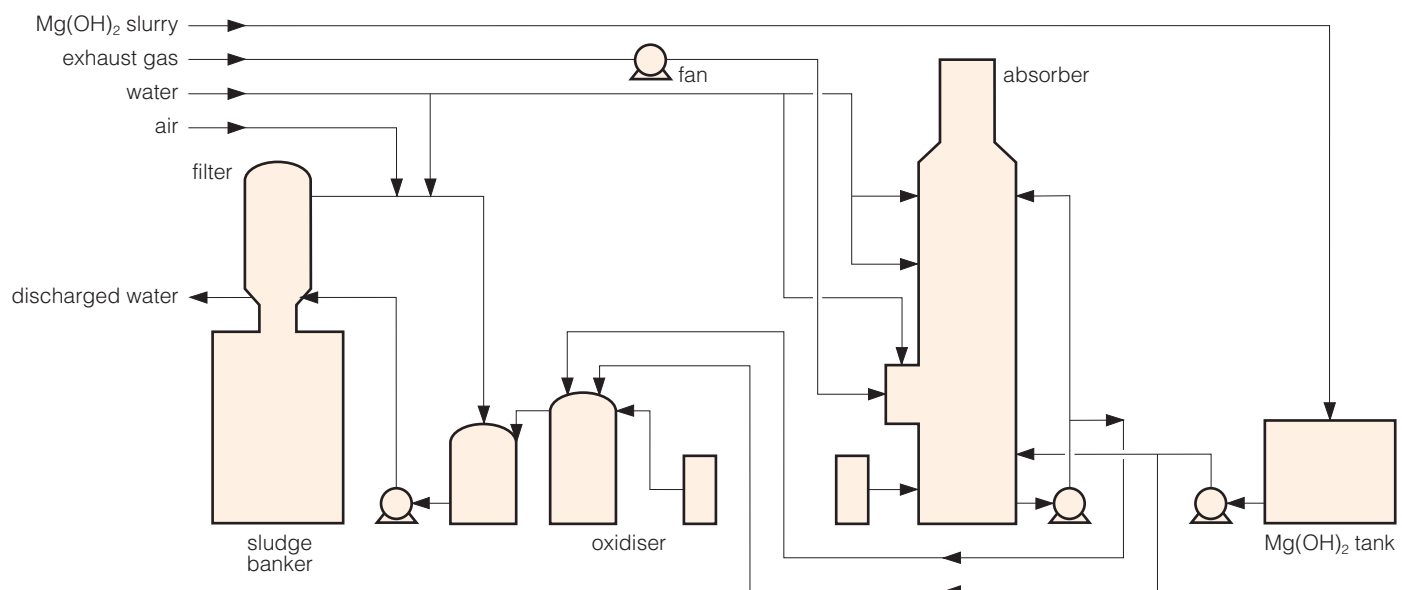

Figure 7   Diagram of the MORETANA magnesium hydroxide process (GEC, 2002a)

either calcium carbonate (limestone gypsum process) or magnesium hydroxide (magnesium hydrate process) as scrubbing agent (GEC, 2002a). Entering the absorber, the flue gas is cooled by process water to saturation temperature in the cooling zone. The flue gas flows upwards and comes into turbulent contact with scrubbing slurry through MORETANA trays. SO_2 and dust are removed simultaneously in the absorber and the cleaned gas passes through a mist eliminator before being released into the atmosphere through the stack.

Normally, a 30% slurry of magnesium hydroxide is used as absorbent. The slurry enters at the top of the absorber and is sprayed onto the MORETANA tray. The scrubbing slurry flows down countercurrently to the flue gas removing SO_2 and particulates contained in the gas. The spent solution is collected at the bottom of the absorber and is recycled back into the absorber. A portion of the spent solution is withdrawn from the sump at the bottom of the absorber as waste water. Magnesium hydroxide solution and process water are added to the slurry to control the pH value of and the $MgSO_3$ concentration in the scrubbing solution. $MgSO_3$ in the waste water is oxidised to highly soluble $MgSO_4$ in an oxidiser by aeration. Particulates suspended in the solution are filtered and dehydrated into filter cake and the filtrate can then be disposed of freely as long as no hazardous material such as fluorine is contained. The waste water contains magnesium sulphate which is harmless and can be discharged.

3.3.3 Process features

Magnesium hydroxide process can achieve higher than 98% SO_2 removal efficiency. It can remove SO_2 and particulates simultaneously in a single tower with high efficiency (outlet particulate concentration <50 mg/m³) eliminating the need for a separate dust collection system. The process is compact and simple, requiring less equipment. Consequently, the magnesium hydroxide process has a low capital cost. Some designs combine the absorption tower and oxidiser into one unit and/or incorporate a stack into this unit, further simplifying the process and reducing the capital cost. The process has a low energy consumption and is unlikely to suffer scaling problems. The operation and maintenance of the process are easy. The existing limestone gypsum process and sodium hydroxide scrubbing process can be converted to use magnesium hydroxide as the scrubbing reagent without major changes to the system or loss of SO_2 removal efficiency. Magnesium hydroxide is more expensive than limestone but cheaper than caustic soda (NaOH). The process is suitable for small- and medium-sized plants, especially those with a short remaining lifetime. This technology is particularly attractive to plants located in coastal areas where the waste effluent can be discharged into the sea without any environmental impacts. Elsewhere, discharging a large $MgSO_4$ effluent can still be a problem although it is harmless. The magnesium hydroxide-gypsum process regenerates

Table 5	Comparison of FGD processes and their costs (Nodland, 2009)				
	Ammonia scrubbing	Seawater scrubbing	Sodium scrubbing	Limestone gypsum	Dry FGD
Features	high-value by-product economics improved at high sulphur levels low operating cost	low capital cost operational simplicity	low capital cost operational simplicity	high efficiency spray zone low cost reagent by-product flexibility	low capital cost dry by-product small footprint no liquid waste
Reagent	ammonia	seawater	caustic, soda ash	limestone	lime
By-product	fertiliser	treated seawater	sodium sulphate	marketable gypsum or landfill	landfill
SO_2 inlet	high	low/medium	high	high	low/medium
SO_2 removal, %	>98	>95	>98	>98	90–95%
Capital cost, $/acfm	35–60	15–25	10–20	25–45	15–25
Power consumption, kW/acfm	3–6	2	2–3	3–6	2
Rreagent cost, $/ton SO_2 removed	80–105	0	100–130	15–25	60–75
By-product cost, $/ton SO_2 removed	150–250 - sale	0	n/a	12–20 - disposal 15 - sale	12–20

Table 6 Comparison of costs of various FGD technologies for a 2×500 MWe system (Nguyen, 2004)			
Technology	Capital cost (2003 $* million)	NPV of 20-year cost (¢*/kWh)	Average 20-year cost of control and coal (¢*/kWh)
Limestone gypsum process	409	0.37	3.49
Ammonia process	371	0.35	3.45
Lime spray dry process	268	0.33	4.08
Multi-pollutant control system – low S coal	366	0.43	4.26
Multi-pollutant control system – high S coal	545	0.62	4.09
* Canadian dollars and cents			
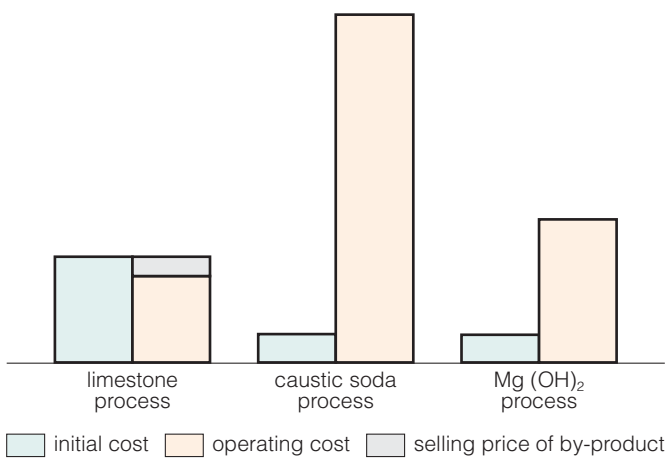
Figure 8   Costs comparison of three FGD processes (GEC, 2002b)

Mg(OH)$_2$ by reacting MgSO$_4$ with lime in a double decomposer. This process produces gypsum as the final by-product and disposal of waste water is avoided.

Magnesium hydroxide process has been installed on several coal-fired power plants both in Japan and the USA and they have operated successfully for a number of years (IEA CCC, 2009; Shand, 2009).

3.4   FGD costs

The capital, operating and maintenance costs of an FGD plant are determined by many factors including the technology chosen, the plant size, the SO$_2$ removal requirement, the fuel used, the costs of reagent and waste disposal. For most of the FGD processes commercially available, with operating experience accumulated and advances in the technologies over the years, the process designs have been improved significantly leading to an overall reduction of the total costs. There are several publications on studies of the costs of different FGD processes. Sharp (2007, 2009) carried out surveys to investigate the recent trend of installation costs of new wet limestone FGD systems. The economics of retrofit FGD technologies has recently been analysed in detail by Nalbandian (2006). The features and various costs of several FGD processes are compared in Table 5.

It can be seen from Table 5 that the seawater FGD process has lower capital and operating costs compared to most other FGD processes listed. It can achieve higher than 98% SO$_2$ removal efficiency and it is simple to operate, making this technology a most attractive choice, both technically and economically, for power plants located at costal sites that burn low or medium sulphur fuel.

The ammonia scrubbing process requires the highest capital investment compared to the other FGD processes in Table 5. The ammonia reagent cost is also high. However, the income from the sale of the high-value by-product fertiliser can offset to a certain extent the high capital and reagent costs. The economics improves when high sulphur fuel is burned. Nguyen (2004) assessed the life cycle economics of several FGD processes if applied to Lambton and Nanticoke power stations. The total capital cost, the net present value (NPV) of cost over a 20-year plant life when the system is operated at 70% capacity factor, and the total cost of emission control and coal used are shown in Table 6. Somehow, Nguyen's estimates show that the capital and NPV costs of ammonia scrubbing process is 5–10% lower than those of the limestone gypsum process. When considering the average 20-year cost of emission control and fuel, the ammonia system is comparable to the limestone system, and there is not much difference between the two technologies.

The magnesium hydroxide process has a low capital cost, 40–60% lower than a corresponding limestone gypsum process. Magnesium hydroxide absorbent is more expensive than limestone but much cheaper than caustic soda (NaOH). Figure 8 compares the capital and operating costs of the limestone gypsum, caustic soda and magnesium hydroxide processes. It can be seen from Figure 8 that the magnesium hydroxide process has a similar investment cost but much lower operating cost compared to the caustic soda process. The recent steep price increases for caustic soda have resulted in several paper mills converting their caustic soda FGD system to the magnesium hydroxide process (Shand, 2009). In many cases, Mg(OH)$_2$ can substitute NaOH directly with little modification to the existing FGD system.

The magnesium hydroxide process can achieve a very high SO$_2$ removal efficiency, similar to that of the limestone gypsum process. Its capital cost is significantly lower than a

limestone gypsum process but it has higher operating costs due to the higher price for $Mg(OH)_2$ absorbent. Therefore, this technology should be an attractive alternative to lime/limestone based FGD systems for small- and medium-sized plants in areas where the emission requirements are stringent, especially those with limited remaining life.

4 Emerging FGD technologies

Work has been ongoing in many fields to either improve the existing FGD processes or to develop new, better and/or cheaper FGD technologies. Extensive research work has been carried out over the last two decades to develop integrated, multi-pollutant control systems that can remove several pollutants such as SO_2, NOx, Hg, and/or fine particulates in one process. Integrated environmental control has many advantages over the traditional, single pollutant removal systems. In particular it may lead to significant cost reductions over separate emission controls. A number of multi-pollutant control processes have been developed and some of them are already in commercial operation. Recently, there have been several projects investigating and developing processes that can simultaneously remove CO_2, SO_2 and possibly NOx and other pollutants. Some of the processes applicable to SO_2 emissions reduction that have been offered to the market recently are discussed in the following sections.

4.1 Electro-catalytic oxidation (ECO) process

The ECO process, developed by Powerspan, is an integrated air pollution control system that can simultaneously remove SO_2, NOx, mercury and fine particulates ($PM_{2.5}$) from the flue gas of coal-fired power plants. The process can also remove acid gases such as HF, HCl, SO_3 and other metals from the flue gas.

4.1.1 Process description and fundamentals

The ECO technology incorporates an advanced ammonia scrubber in a multi-pollutant control system. The core of the technology is a dielectric barrier discharge (DBD) reactor composed of cylindrical quartz electrodes residing in metal tubes. Electrical discharge through the flue gas, passing between the electrodes and the tube, produces reactive O and OH radicals. The radicals react with flue gas components to oxidise pollutants which are subsequently removed in a downstream ammonia scrubber and wet ESP. The ECO process flow is shown in Figure 9. The flue gas from the dust collector passes through a DBD reactor in which nitric oxide (NO) is oxidised to nitrogen dioxide (NO_2) and nitric acid (HNO_3), a small portion of the sulphur dioxide (SO_2) is converted to SO_3 leading to the formation of sulphuric acid (H_2SO_4) mist, and some mercury is oxidised to mercuric oxide. The flue gas then enters the bottom and the lower loop of the absorber. Spray nozzles distribute droplets of scrubbing liquid comprising ammonia, ammonium sulphite, ammonium sulphate (AS), and water into the flue gas. Water evaporates from the solution due to the heat of the flue gas, saturating and cooling the flue gas, as well as concentrating the by-products. The recycle pump circulates the liquid back to the spray headers of the lower loop, with a bleed stream to the by-products processing system. In the upper loop, SO_2 and NO_2 are absorbed into the ammonia solution. Ammonia reacts with SO_2 to form ammonium sulphite ((NH_4)$_2SO_3$) and ammonia bisulphite (NH_4HSO_3). The likely chemical reactions in this step are as follows:

$$NH_3 + H_2O \rightarrow NH_4OH$$

$$2NH_4OH + SO_2 \rightarrow (NH_4)_2SO_3 + H_2O$$

$$NH_3 + H_2O + SO_2 \rightarrow NH_4HSO_3$$

$$NH_4HSO_3 + NH_3 \rightarrow (NH_4)_2SO_3$$

Interaction between the sulphite and NO_2 oxidises the sulphite to sulphate and reduces the NO_2 to nitrogen. The likely reactions that take place in this step are as follows:
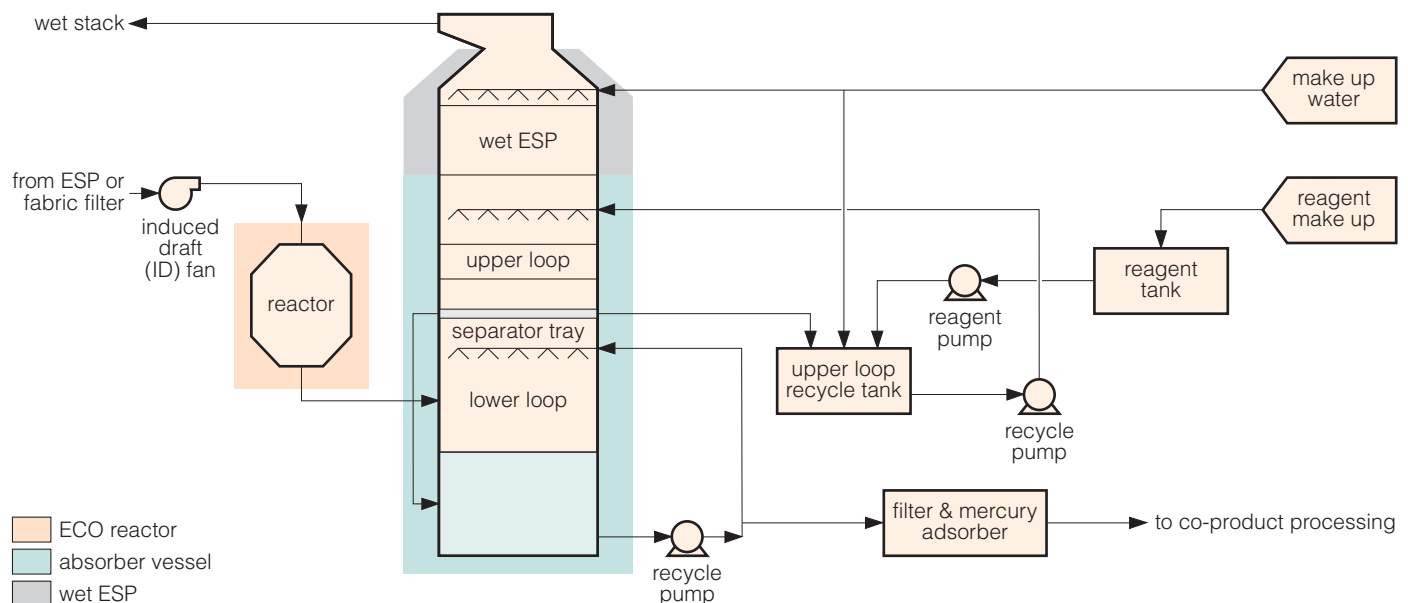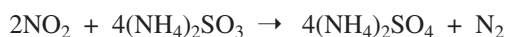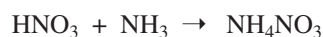

Figure 9   Diagram of the ECO process flow (Powerspan, 2009b)

$$2NO_2 + 4(NH_4)_2SO_3 \rightarrow 4(NH_4)_2SO_4 + N_2$$

$$NO + NO_2 + 3(NH_4)_2SO_3 \rightarrow 3(NH_4)_2SO_4 + N_2$$

Most of the HNO_3 that is created by the DBD reactor, and/or that may have been formed by further oxidation of NO and NO_2, will react with ammonia forming ammonium nitrate according to the following reaction:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

In a similar way, most of the sulphuric acid formed in the reactor will react with ammonia to form ammonium sulphate. On exiting the upper loop, the flue gas enters a wet ESP. Aerosols generated in the reactor and the ammonia scrubbing process, along with air toxics and fine particulate matter, are captured here and returned to the lower loop. The flue gas is then released through the wet stack (Duncan and others, 2005).

Another circulation loop is provided wherein the scrubbing liquid is recycled back to the upper spray heads. The liquid then falls to a dual flow tray allowing some of the liquid to flow into the sump at the bottom of the lower loop. The remainder is piped to the upper loop recycle tank in which additional makeup ammonia is added to maintain the optimal process chemistry conditions.

As one can see from the above reaction formulae, the process removes SO_2 and NOx from the flue gas and produces ammonium sulphate, ammonium nitrate and nitrogen. Over time, the ammonium sulphate and ammonium nitrate concentrate in the solution and precipitate out of solution. The solid precipitates can then be removed from the scrubber and processed for use as agricultural fertiliser.

4.1.2   Process features and application

The ECO process integrates proven technologies into one system to simultaneously remove SO_2, NOx and other emissions in a single absorber vessel. Commercial demonstration of the ECO process on a 50 MWe coal-fired power generating unit showed that the ECO process can achieve high removal efficiencies of the four major pollutants: >99% of SO_2, up to 82% of NOx, 80% of Hg and >95% of $PM_{2.5}$. Several financial models have been developed which show that capital costs for commercial application will be less than the costs of implementing existing control technologies to achieve the same performance objectives (OCDO, 2005). The ECO process produces a fertiliser by-product which can be sold in the agricultural market, and the income from the sale can offset its operating costs. Captured mercury is isolated from the fertiliser by-product for separate disposal. The process uses less water because it requires no water treatment or disposal.

In applications where additional NOx removal is not required, the ECO technology can be installed without the NOx control component. The resultant scrubber installation, called the ECO-SO_2 process, achieves major reductions in emissions of sulphur dioxide (SO_2), fine particulate matter ($PM_{2.5}$) and oxidised mercury. The ECO process can also be integrated

with Powerspan's ammonia-based CO_2 capture technology the ECO_2 process. It requires no enhancement in emissions reductions performance (that is SO_2 control) to accommodate a CO_2 capture process, saving capital and operating costs when adding CO_2 capture capability.

The first commercial demonstration of the ECO process was carried out from February 2004 to August 2005 at FirstEnergy's R E Burger coal-fired power plant to treat a slipstream equivalent to 50 MWe. Test results showed that the ECO process substantially met or exceeded target removal efficiencies for NOx, SO_2, Hg and $PM_{2.5}$. The process operated reliably with high availability. Encouraged by the results, FirstEnergy decided to install an ECO system on the 215 MWe unit 4 at its coal-fired Bay Shore power plant. In June 2007, American Municipal Power-Ohio (AMP) announced it had chosen to use the ECO-SO_2 technology on its proposed 1000 MWe American Municipal Power Generating Station (AMPGS) in southern Meigs County, Ohio, USA.

## 4.2   Electron beam (EB) irradiation process

This is a dry scrubbing process capable of simultaneous removal of SO_2 and NOx. The technology was first developed in Japan in the early 1970s. The intent at the time was to treat off-gases from iron ore sintering plant. Since then, more than a dozen facilities, mainly pilot- and commercial-scale demonstration plants, have been built in Japan, Germany, USA, Poland, China, and Bulgaria on coal-fired power plants, steel mills and other industrial sectors.

4.2.1   Process description and mechanism

Research shows that irradiation of flue gas with an electron beam can bring about chemical changes that make the removal of SOx and NOx easier. In the EB process, radiation energy is absorbed by gas molecules in proportion to their mass fractions. After irradiation, fast electrons interact with gas molecules and the energy is consumed by the ionisation, excitation and dissociation of the molecules generating various ions and radicals. These species then take part in a series of radio-thermal and chemical reactions. The SO_2 and NO in the flue gas are first oxidised to form SO_3 and NO_2 by reacting with the radicals. The SO_3 and NO_2 formed are then converted to H_2SO_4 and HNO_3 in the presence of water vapour and oxygen via several pathways. H_2SO_4 and HNO_3 are neutralised by ammonia that is injected upstream of the irradiation chamber, forming $(NH_4)_2SO_4$ and NH_4NO_3 (Chmielewski, 2005; Edinger, 2008).

The electron beam process is simple compared with wet FGD systems. It consists of four main components:

1   A flue gas conditioning system that cools and humidifies the flue gas to the desired temperature and humidity by injecting water into the flue gas. Ammonia is also added to the flue gas in the conditioning step with additional.

2   An ammonia supply system that delivers and distributes
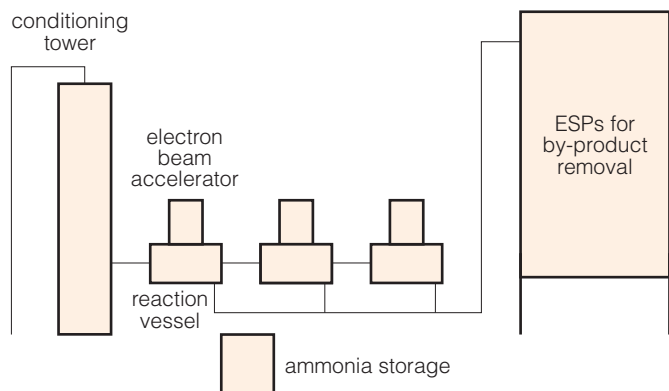
Figure 10 Simplified diagram of an EB process
(Edinger, 2008)

doses of the exact amount of ammonia to the flue gas.

3 A reaction unit in which the flue gas is irradiated with a beam of high energy electrons triggering various reactions for SOx and NOx removal.

4 A by-product collection and storage system that removes and collects the by-product from the flue gas.

The concept of an electron beam process is shown in Figure 10.

The flue gas from particulate control devices is humidified and cooled, and it then enters a reactor. In the reactor, a beam of high energy electrons are fired into the flue gas in the presence of ammonia which is injected into the flue gas upstream of the reactor. High energy electrons react with molecules in the flue gas to produce radicals that then react with the SOx and NOx in the flue gas to produce sulphuric and nitric acids. The acids formed in turn react with the added ammonia to form ammonium sulphate and ammonium nitrate, which are high-value fertilisers. The ammonium salts are carried in the flue gas as aerosols which are collected in a downstream electrostatic precipitator or bag filter, and the salts are recovered and can be sold for agricultural use.

4.2.2 Features and status of the technology

Two similar electron beam processes have been developed,

one by Japan's Ebara Corporation and the other by the Polish Institute of Nuclear Chemistry and Technology. Commercial-scale demonstrations of the two EB processes installed on coal-fired power plants were carried out in countries like China and Poland in the 1990s and these plants have been in operation since. Pilot tests of the processes have also been performed on other coal-fired power plants (Doutskinov, 2005). China started to develop the electron beam irradiation process in the late 1980s and in 2005, the first commercial demonstration plant was installed on Jingfeng Thermal Power Plant, a coal-fired plant in Beijing (Mao, 2005). The main technical parameters of these installations are shown in Table 7. The results from pilot plants tests and demonstration operations show that the EB process can achieve higher than 95% SO_2 removal and up to 75% NOx removal. It should be noted that the EB processes installed on Chinese coal plants were designed mainly for SO_2 removal. Results also show that the EB process can remove chlorine and VOC from the flue gas.

The reaction unit, which is the key part of an EB process, consists of a reaction chamber, electron beam accelerators with power supplies and cooling systems. The reaction chamber is separated from the accelerators by two layers of titanium foil, through which the high-energy electrons pass. The accelerators are the most important and technically most advanced apparatus of this technology, and there is still room for improvement. The price of an accelerator depends on its power. The power required is proportional to the mass flow of the flue gas and the dose necessary for effective removal of SO_2 and NOx. For this technology, accelerator with energy of electrons up to 800 kV and beam current up to 500 mA are applied. These values are limited by the power supply. The accelerators are very sensitive and have to be serviced frequently together with replacement of the titanium foil and accelerator cathodes, limiting the annual operating hours of the process to around just 6500 hours. All the maintenance work has to be carried out by the accelerator manufacturer (Tyminski and Pawelec, 2005).

The by-product of this process is a mixture of ammonium sulphate and ammonium nitrate, which can be sold as fertiliser. In the by-product collection and removal system, various types of devices have been tested in different

Table 7	Main technical parameters of EB demonstration installations on coal-fired power plants				
		(Chmielewski and Licki, 2008; Mao, 2005)			
Parameter	Unit	Chengdu P/S, China	Hangzhou P/S, China	Jingfeng P/S, China	Pomorzany P/S, Poland
Flue gas flow rate	m³/h	300,000	305,400	630,000	270,000
Inlet flue gas temperature	°C	150	145	146	140
Inlet SO_2 concentration	mg/m³	5150	2770	4200	2000
Inlet NOx concentration	mg/m³	820	410	1200	600
SO_2 removal efficiency	%	80	85	90	90
NOx removal efficiency	%	18	55	20	70
Electron accelerators	kV	800 kV/400 mAx2	800 kV/400 mAx2	100 kV/500 mAx2 100 kV/300 mA kWe	700 kV
Total power consumption	kWe	≤1900	≤1896	≤2850	

installations. Due to the size (approximately 1 µm) and sticky nature of the by-product precipitate it has been found that filter bags cannot be efficiently cleaned of filter cake when using bag filters. Consequently electrostatic precipitators are used in industrial scale plants. The by-product precipitate may be corrosive when wet. For protection from the condensation of water, ESP with heated bottoms and scrapers are used in recent designs (Tyminski and Pawelec, 2005).

4.2.3 Cost evaluations

Based on the technical data of the commercial demonstration EB installation at Pomorzany coal-fired power plant in Poland, Tyminski and Pawelec (2005) calculated the capital and operating costs for retrofitting an EB process on an 130 MWe power generating unit. They estimated that the total capital cost of retrofitting an electron beam FGD plant similar to the one installed in Pomorzany would be US$21 million, which is equivalent to 160 $/kWe. This value varies with plant size. For EB installations with a plant size of 35, 200 or 300 MWe or larger, the capital cost would be around 300 $/kWe, 150 $/kWe, and 140 $/kWe, respectively. Apparently, larger installations are more competitive economically.

The annual costs of operating an electron beam FGD plant similar to the one at Pomorzany, according to Tyminski and Pawelec, would be US$1.125 million. The energy consumption as well as maintenance and spare parts for the accelerators are estimated to cost 620,000 $/y and 200,000 $/y, respectively, accounting for a major part of the operating costs. Assuming that the sale of by-product could generate an income of 35,000 $/y, and the saved penalties for emissions exceeding the national standards being 135,000 $/y, Tyminski and Pawelec calculated that the total operating cost of such an EB process would be 955,000 $/y, equivalent to 806 $/t of SO_2/NOx removed or 7346 $/MWe of installed capacity (Tyminski and Pawelec, 2005).

The commercial demonstration electron beam FGD plant at Jingfeng Thermal Power Plant in China is installed on a 50 MWe and a 100 MWe coal-fired unit. This process was designed mainly for SO_2 removal. Based on the technical data of the Jingfeng plant and Beijing local prices, and assuming that the by-product of the EB plant could be sold for 60 $/t, Mao (2005) compared the costs of the Jingfeng EB plant burning coal with varying sulphur contents with other local installations with a conventional FGD process (*see* Table 8). It can be seen from Table 8 that an EB process has a considerably higher capital cost but lower operating cost

Table 9	The costs of various emission control methods for retrofitting a 120 MWe unit (Tyminski and Pawelec, 2005)	
	Capital cost, $/kWe	Annual operating cost, $/MWe
Wet FGD	120	3000
SCR	110	4600
Wet FGD + SCR	230	7600
EB process	160	7350

compared with conventional wet scrubbers. The competitiveness of the EB process improves with increasing coal sulphur content.

The EB process is capable of removing SO_2 and NOx simultaneously. Most often, a power plant uses a wet FGD system and a separate DeNOx system for SO_2 and NOx emissions reduction. Tyminski and Pawelec (2005) evaluated the costs for retrofit of a wet FGD process and a selective catalytic reduction (SCR) system on a 120 MWe coal-fired unit, and compared the figures with those of an EB process. Their results showed that when compared with the combined costs of a wet FGD and a SCR system, this technology became economically competitive. The comparisons of the costs are shown in Table 9.

Comments
Although development started in the 1970s, the electron beam technology is still not mature. More tests are needed to improve current understanding of the process. The availability of the process cannot meet the requirement of power plant operators who normally require a FGD system to be available for 95% or more of a power plant's operating hours. Also, the costs are relatively high. However, there is much room for improvements in process design and further developments of the EB technology. With a better understanding of the process, accumulation of operating experiences and advances in technologies, it can be expected that the process and engineering design will be improved and optimised, leading to a more reliable, more efficient EB process with significantly reduced costs.

4.3   Airborne process

Developed by Airborne Clean Energy Ltd., the Airborne

| Table 8	Economic evaluation and comparison of the Beijing Jingfeng EB demonstration plant (Mao, 2005)			
	Jingfeng electron beam FGD plant (150 MWe)			Wet FGD plant (300 MWe)
Sulphur content in coal	2%	1.5%	1.1%	
Operating cost, $/y	518600	569900	591300	
DeSO$_2$ cost, $/ton	38.11	55.84	78.99	100–120
Capital cost, $/kWe	74.5			40

process is a multi-pollutant emissions reduction system that combines dry sodium bicarbonate injection with wet sodium scrubbing technology.

4.3.1 Dry sodium bicarbonate injection

A dry sorbent injection process using sodium bicarbonate as a sorbent for SO_2 emission control was developed in the 1970s and this technology has been demonstrated on full-scale, coal-fired boilers both in the USA and the UK (DTI, 2000). Sodium bicarbonate is known to be highly reactive and efficient at removing pollutants such as SO_2, SO_3 and HCl over a wide temperature range. When sodium bicarbonate ($NaHCO_3$) is injected into a flue gas, it undergoes thermal decomposition due to the heat of the flue gas. This decomposition results in porous sodium carbonate (Na_2CO_3) particles that have a large surface area and are highly reactive to acid gas species. Sodium carbonate formed by activating sodium bicarbonate in this manner has been found to be a better absorbent than ordinary, commercially available sodium carbonate. Although the reactions taking place are complex and not fully understood, it is generally accepted that the following represents the reactions occurring in the sodium bicarbonate injection process:

$$2NaHCO_3 \xrightarrow{\text{heat}} Na_2CO_3 + H_2O + CO_2$$

$$Na_2CO_3 + SO_2 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4 + CO_2$$
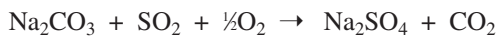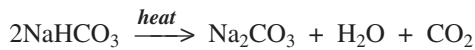
Sodium carbonate also reacts with NO. Although this chemistry is not well understood, it is known that in the presence of sodium sorbent and SO_2, a small portion of the NO is converted to NO_2. Part of this NO_2 is removed as $NaNO_3$, thus resulting in reduced emissions of NOx, but that part not removed increases the concentration of NO_2, a brownish-orange gas that can cause a visible stack plume. The overall reactions involved in the process may be presented as follows (Johnson and others, 2005):
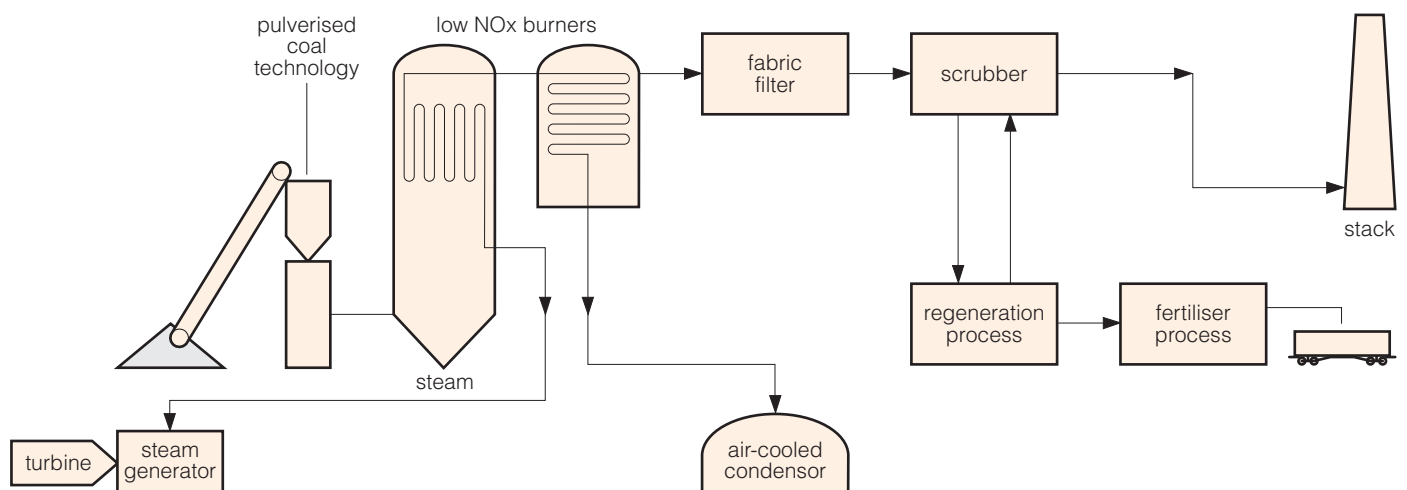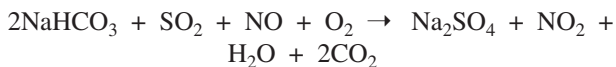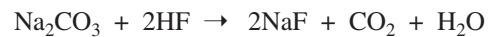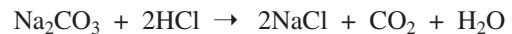
$$2NaHCO_3 + SO_2 + NO + O_2 \rightarrow Na_2SO_4 + NO_2 + H_2O + 2CO_2$$

$$2NaHCO_3 + 2NO_2 + \tfrac{1}{2}O_2 \rightarrow 2NaNO_3 + H_2O + 2CO_2$$

There are measures that can help to avoid the brown stack plume, for example, injecting the sorbent at higher temperature, using low NOx burners to reduce the concentration of NOx, or adding urea to the sodium bicarbonate sorbent.

In addition to reacting with SO_2 and NOx, sodium sorbent can also effectively remove SO_3, HCl and HF from the flue gas through the following reactions (Johnson and others, 2005; Kong and Vysoky, 2009):

$$2NaHCO_3 + SO_3 \rightarrow Na_2SO_4 + H_2O + 2CO_2$$

$$Na_2CO_3 + SO_3 \rightarrow Na_2SO_4 + CO_2$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

$$Na_2CO_3 + 2HF \rightarrow 2NaF + CO_2 + H_2O$$

Sodium bicarbonate has long been recognised as a better absorbent than lime and limestone for sorbent injection FGD processes. However, sodium bicarbonate reagent is very expensive. The by-product, sodium sulphate produced from the process has little economic value. Sodium sulphate is water soluble and therefore its disposal is expensive and poses significant environmental challenges. As a consequence, sodium sorbent has had very limited commercial application.

4.3.2 Airborne technology development

The Airborne process has been developed based on sodium scrubbing and sodium bicarbonate regeneration technologies. A simplified flow diagram of the Airborne process is shown in Figure 11. Sodium bicarbonate sorbent is injected into a flue gas downstream of the particulate collection device. On contact with the hot flue gas, sodium bicarbonate undergoes thermal decomposition to form sodium carbonate which reacts with SO_2, NOx and other acid gases present in the flue gas. The mixture of flue gas and sorbent then enters the

Figure 11 A flow diagram of the Airborne process (Johnson and others, 2005)

bottom of a wet scrubber where the flue gas flows upwards and comes into contact with sodium scrubbing solution. The sodium sulphate and sodium nitrate formed are dissolved into the solution which enters from the top of the scrubber. Unreacted SOx and NOx are also removed by the scrubbing solution. The spent solution is collected and withdrawn from the bottom of the scrubber. The spent solution flows into an oxidiser where aeration is carried out to convert sulphite to sulphate. Sodium carbonate is then added into the solution to adjust its pH value so that the heavy metal compounds in the solution precipitate and are filtered out to ensure the purity of the final products. The resulting spent solution is then mixed with ammonium bicarbonate that reacts with sodium sulphate and sodium nitrate as follows:

$$2NH_4HCO_3 + Na_2SO_4 \rightarrow (NH_4)_2SO_4 + 2NaHCO_4$$

$$NH_4HCO_3 + NaNO_3 \rightarrow NH_4NO_3 + NaHCO_3$$

The sodium bicarbonate crystals formed precipitate out and are separated from the ammonium solution.They are then dried and recycled back to the scrubber. The ammonium sulphate/nitrate in the solution is crystallised in an evaporator and then granulated to produce commercial grade fertiliser by-products. The regeneration system, which regenerates sodium bicarbonate and produces a high quality fertiliser by-product, is the key part of the Airborne process. Airborne's patented pan granulation technology provides an efficient means of producing high quality, commercial grade granular fertiliser product that can blend with other fertilisers (Mortson and Telesz, 2001).

As an option, potassium chloride (KCl) and calcium oxide (CaO) can be added into ammonium solution to produce potassium sulphate (K$_2$SO$_4$) fertiliser and to recycle ammonia. This eliminates the need for ammonia feed stock, which is costly to produce and difficult to store.

The NOx and Hg removal efficiencies of Airborne process are much improved by adding an oxidant into the scrubbing solution. Results from pilot tests showed that for the selected oxidant, under optimal conditions, the Airborne process can achieve higher than 99% NOx and Hg removal (Johnson and others, 2005). The mercury captured is later filtered out from the spent scrubbing solution with other heavy metal compounds for disposal.

4.3.3 Features and current status of the Airborne process

The Airborne process is a regenerative process that integrates dry and wet sodium bicarbonate scrubbing, sodium bicarbonate regeneration and fertiliser formulation technologies into one system. The process is capable of removing SOx, NOx, Hg as well as HCl, HF and heavy metals simultaneously. The process is suitable for new installations and for retrofitting to existing power plants. The developer claims that the process can achieve greater than 99% removal efficiencies for SO$_2$, NOx and Hg. The developer also claims that the capital and operating costs of the Airborne process are very competitive when compared

with the combined costs of separate systems for SO$_2$ and NOx emission reductions (Mortson and Telesz, 2001; Mortson and Xia, 2007). Pilot tests of the Airborne process on a 5 MWe facility have been completed and the results are very encouraging. Airborne Clean Energy is keen to demonstrate this technology on a commercial scale. Peabody Energy chose to install the Airborne process on its proposed coal-fired power plant – Mustang Energy Project in New Mexico. In October 2004, the project was given a $19.7 million Clean Coal Power Initiative grant by the US Department of Energy for demonstrating technology to achieve ultra-low emissions at the proposed power plant. The State of New Mexico required Peabody Energy to consider advanced combustion technologies in its best available combustion technology (BACT) analysis. Peabody concluded that neither integrated gasification combined cycle (IGCC) nor circulating fluidised bed (CFB) technology was a feasible option, for economic and technical reasons. In September 2006, Peabody announced it would withdraw the Mustang plant applications and instead build a syngas plant. Airborne Clean Energy is yet to find another host to demonstrate its Airborne process.
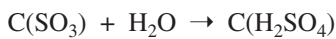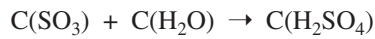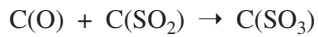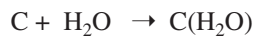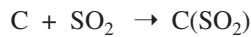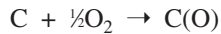
4.4 Activated carbon/coke dry scrubbing process

Research and development of a dry desulphurisation process using activated carbon/coke started in the 1960s in Germany and later in Japan. In 1978, a 10,000 m^3/h pilot plant was installed on Takehara coal-fired power plant in Japan to test a regenerative, activated coke scrubbing process (Miyagawa and Miya, 2008). The earlier work was focused on SO$_2$ emissions reduction. However, test results revealed that the process was also capable of removing air pollutants such as NOx, Hg and other acid gases in the flue gas. Subsequently, investigation and development of technologies for multi-pollutant emissions control using activated carbon/coke were carried out in the laboratory and on pilot scale. In 1995, the first commercial application of ReACT process, an activated coke dry scrubbing process developed by Mitsui Mining and acquired by Japan's J-Power in 2005, commenced operation at Takahara power plant. The ReACT process was installed on Takehara unit 2, a coal-fired, 350 MWe fluidised bed power generating unit and it has since been in operation. Today, there are more than a dozen ReACT processes being in commercial operation at large power stations and industrial plants in Japan and Germany.
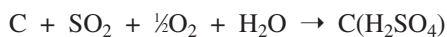
4.4.1 Process mechanisms and features

Porous activated carbon/coke particles provide a large surface area for the adsorption and reactions of SO$_2$ and/or NOx, Hg. For NOx emissions reduction, ammonia (NH$_3$) is injected into the flue gas to promote NOx removal. The process chemistry takes place primarily on the surface of the sorbent. SO$_2$, O$_2$ and H$_2$O present in flue gas can all be adsorbed onto the carbon surface. The adsorbed species are mobile and migrate on the surface. The carbon acts as a catalyst for the oxidation of SO$_2$ to SO$_3$ on the carbon surface. In the presence of H$_2$O, the SO$_3$ formed then combines with adsorbed H$_2$O forming

H_2SO_4. The process of SO_2 removal by activated carbon/coke can be presented as:

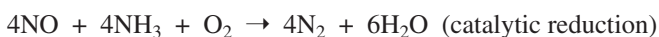$$C + \frac{1}{2}O_2 \rightarrow C(O)$$

$$C + SO_2 \rightarrow C(SO_2)$$

$$C + H_2O \rightarrow C(H_2O)$$

$$C(O) + C(SO_2) \rightarrow C(SO_3)$$

$$C(SO_3) + C(H_2O) \rightarrow C(H_2SO_4)$$

$$C(SO_3) + H_2O \rightarrow C(H_2SO_4)$$

The overall reaction is:

$$C + SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow C(H_2SO_4)$$

When ammonia is injected into the flue gas, the $C(H_2SO_4)$ may react with NH_3 to form NH_4HSO_4 and $(NH_4)_2SO_4$.

For NOx removal, it is reported that NOx is reduced to nitrogen (N_2) through catalytic reaction with NH_3 in the gaseous phase and reduction on the carbon surface as follows (Miyagawa and Miya, 2008):
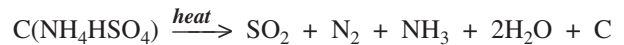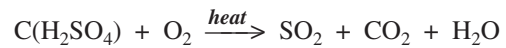
$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \text{ (catalytic reduction)}$$

$$NO + C(NH_xO) \rightarrow N_2 + H_2O + C(OH) \text{ (surface reduction)}$$

Where $C(NH_xO)$ represents the reducing agents on the carbon surface.

Heavy metals such as mercury in gaseous form can also be adsorbed and removed efficiently by activated carbon.

The activated carbon/coke saturated with pollutants can be regenerated by heating it to a desired temperature at which the adsorbed pollutants on the carbon surface are desorbed. The

desorption of sulphurous compounds can be presented as follows (Miyagawa and Miya, 2008):

$$C(H_2SO_4) + O_2 \xrightarrow{\textit{heat}} SO_2 + CO_2 + H_2O$$

$$C(NH_4HSO_4) \xrightarrow{\textit{heat}} SO_2 + N_2 + NH_3 + 2H_2O + C$$

By controlling the desorption temperature, the adsorbed sulphur dioxide and mercury may be desorbed and subsequently recovered separately.

The activated carbon/coke saturated with pollutants can be regenerated by heating it to a desired temperature at which the adsorbed pollutants on the carbon surface are desorbed. The desorption of sulphurous compounds can be presented as follows (Miyagawa and Miya, 2008):

Activated carbon/coke dry scrubbing process is capable of removing SOx (SO_2 and SO_3), NOx, mercury and other heavy metals simultaneously. The sorbent can also remove acid gases such as HCl as well as particulates from the flue gas. The process is suitable for application in power plants and industrial boilers burning low- to medium-sulphur fuels. It can achieve removal efficiencies of >98% for SOx, >90% for Hg and up to 80% for NOx. The process has a small footprint, very little water consumption (for example, the water consumption of ReACT process is around 1% of that of a wet FGD) and low power consumption compared with limestone gypsum process. It can produce a saleable by-product, and it is possible to design a regenerative activated carbon dry scrubbing process that has no solid or liquid waste for disposal. It has the potential to become a competitive technology in certain applications.

4.4.2 ReACT process

The ReACT process consists of three stages: adsorption, regeneration and by-product recovery. The flow diagram of the ReACT process in operation at Isogo unit 1, a 600 MWe
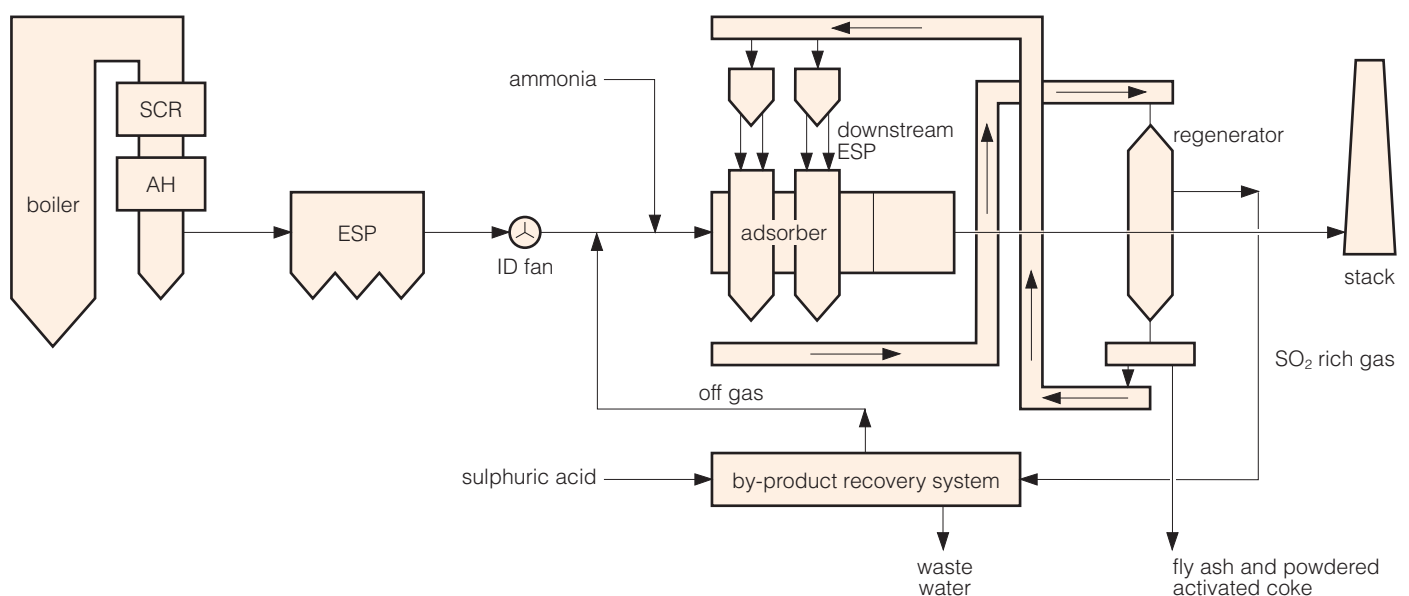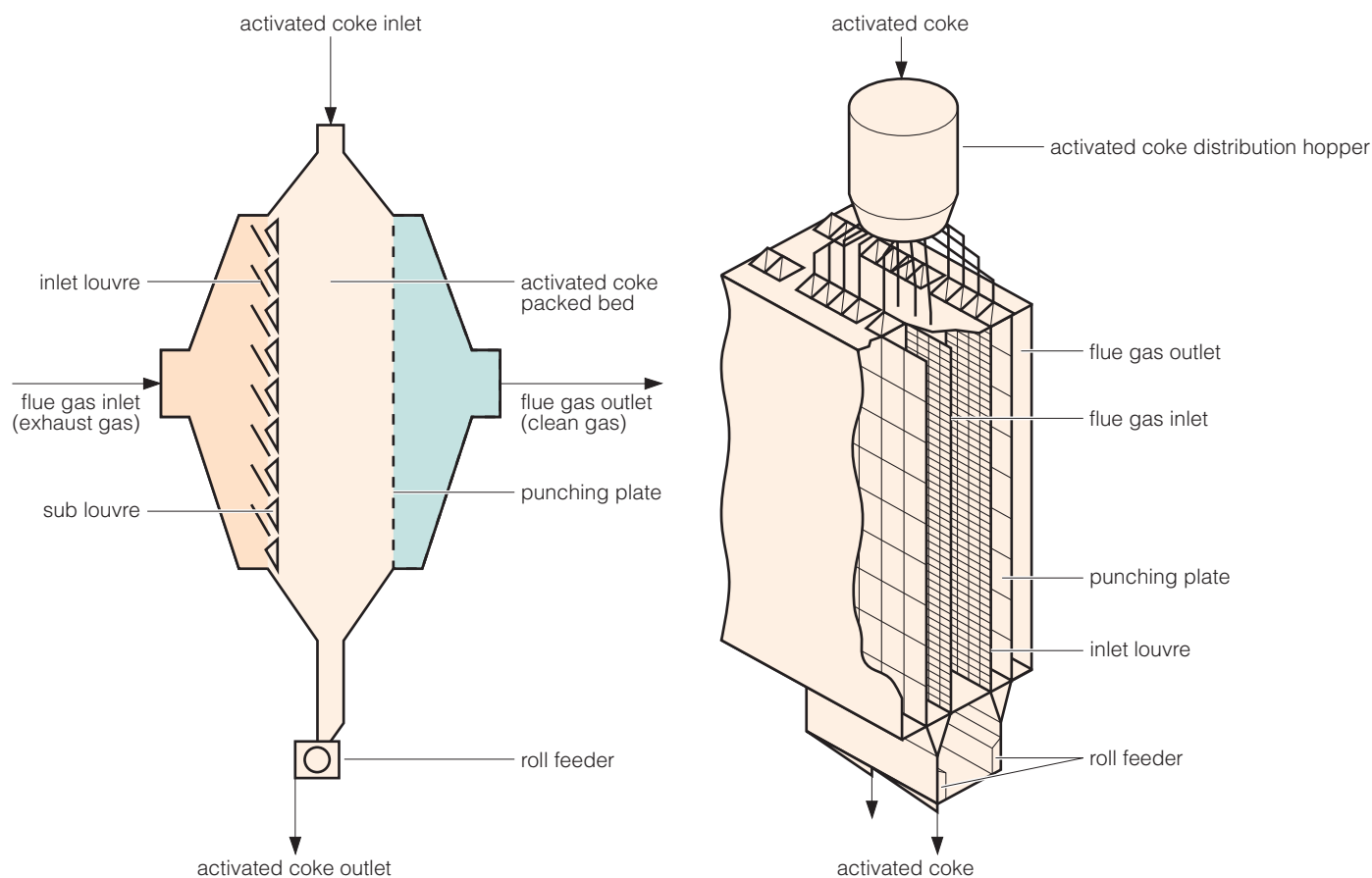

Figure 12 Flow diagram of the ReACT process installed on Isogo unit 1 (Miyagawa and Miya, 2008)

Non-calcium desulphurisation technologies

Figure 13 Basic structure of the ReACT adsorber (Miyagawa and Miya, 2008)

coal-fired ultra-supercritical power generating unit in Japan, is shown in Figure 12.

In the adsorption stage, the flue gas from the particulate collection device enters an adsorber in which it passes through a bed of activated coke that moves slowly downwards. The flow of activated coke through the adsorber is controlled by a roller feeder at the bottom of the adsorber. The adsorber is divided into several cartridges (sections). Each cartridge consists of an inlet louver, sub-louver, activated coke-packed bed and outlet punching plate (Miyagawa and Miya, 2008). The basic design of the adsorber is shown schematically in Figure 13. As the flue gas passes through the activated coke, SO_2, SO_3, NOx, and mercury are adsorbed by the sorbent and removed from the flue gas. The cleaned flue gas exits the adsorber and is released through a stack. NOx removal is promoted by staged injection of NH_3 into the duct upstream of the adsorber and into the regenerator.

In the regeneration stage, the spent sorbent leaving the adsorber is conveyed through a bucket elevator to the regenerator. The regenerator is a shell and tube type heat exchanger composed of three zones: pre-heating, heating and a cooling zone. The spent absorbent moves downwards and is heated to up to 200ºC in the pre- heating zone. The adsorbent then moves down to the heating zone where it is heated to 400–500ºC. At this temperature, sulphuric acid or ammonium salts on the surface of the activated coke are decomposed and desorbed along with other adsorbed pollutants. The desorbed gas flows upwards countercurrently with the adsorbent. The desorbed ammonia

and mercury are recaptured by the activated coke in the section between pre-heating and heating zones. The SO_2-rich gas exits from the top of the regenerator. In the cooling zone, the absorbent is cooled down to 150°C or lower and is then removed from the bottom of the regenerator. After cooling, the regenerated activated coke passes through a separator (vibrating screen) that separates particulates and small particles from large activated coke particles, which are returned to the adsorber (Miyahawa and Miya, 2008; Dene and others, 2008).

In the ReACT process, Hg is retained in the activated coke and, depending on the Hg concentration at the adsorber inlet, the used activated coke is replaced every few years.

In the by-product recovery stage, the SO_2 in the SO_2-rich gas from the regenerator is converted to a saleable product such as sulphuric acid or gypsum.

ReACT process is a multi-pollutant emissions control technology. It has been commercially applied on coal-fired power plants in Japan and achieved impressive results. In 2007, a demonstration test of the ReACT process was carried out at Valmy coal-fired power plant in the USA on a slip stream equivalent to 2.5 MWe power generating capacity. The purpose of the demonstration was to verify ReACT's performance with US coals, and to optimise the process design and reduce its costs. The results from the demonstration testing showed that the ReACT process achieved emissions reduction efficiencies of >98% for SOx, 40% for NOx and >90% for Hg (Dene and others, 2008). Results from previous tests on other sites and commercial

operations showed that the process could reduce SOx by more than 95%, NOx by 20–80% (depending on the design conditions), Hg emissions by more than 90%, and particulates emissions could be kept under 15 mg/m^3 at stack.

4.4.3 Technical developments

Activated carbon with a large surface area and pore volume that can be used as desulphurisation sorbent is commercially available. Activated carbon/coke can be produced from various precursor materials. The characteristics that affect the performance and suitability of an activated carbon material as desulphurisation sorbent include the surface area, pore size distribution, pore volume, and abrasion resistance. Work has been carried out to investigate the performance of activated carbon/coke made of different precursors. Advanced Fuel Research Inc developed a regenerative dry scrubbing process for Hg, SO_2 and NOx emissions control using activated carbon made from scrap tyres (Wójtowicz and Serio, 2000). The activated carbon produced from scrap tyres is significantly cheaper than those available on the commercial market. Yoshikawa and others (2005) investigated the characteristics and desulphurisation efficiencies of coal tar pitch-based activated carbon fibres produced under different conditions. They found that the coal tar pitch-based carbon fibres activated under optimal conditions could achieve nearly 100% desulphurisation efficiency in laboratory tests. Studies carried out by Li and his colleagues (2007, 2008, 2009) showed that the surface area, pore size/volume and therefore the SO_2 adsorption capacity of an activated coke are largely influenced by the type of coal from which it is made, the activation agents, and activation temperature and time. Their work also showed that mixing coal with coal tar when preparing the activated coke, or adding metal compounds such as $CaCO_3$, $CoCl_2$ or V_2O_5 to the activated coke resulted in a sorbent with enhanced desulphurisation performance. Other researchers reported that treating the activated carbon fibres with ammonia or ammonia/steam markedly enhanced its desulphurisation performance (Boudou and others, 2003). More work is currently ongoing and the findings from this research may one day lead to a cheaper, more efficient sorbent that can meet different emissions control requirements.

5 Technologies under development

Research and development on numerous innovative FGD technologies applying new concepts and different approaches have been carried out by scientists and engineers in many countries over the years. Pilot tests and demonstrations of some of the technologies have been or are currently being carried out, whilst the others are under laboratory scale investigation. Some of the technologies have already been applied successfully in some industrial processes. With advances in technology and some innovations in engineering design they may one day become a competitive technology alternative to the limestone/lime based FGD processes applicable to coal-fired power plants. Encouraging results have been achieved from some of the technologies that could lead to eventual commercial applications. An overview of a few such technologies is given in the following sections.

5.1 Corona discharge technology

Corona discharge technology has been investigated since the 1980s as a means for controlling air pollutants such as SOx, NOx, Hg, and HCl. Corona discharge technology for SOx and NOx emissions reduction works in a similar way to electron beam irradiation technology. When an electric field (DC, AC or pulsed) is applied to a flue gas, energetic electrons are discharged. These electrons transfer energy to gas molecules through collisions, resulting in excitation, attachment, dissociation, or ionisation producing radicals and ions. The SO_2 and NO in the flue gas are oxidised to SO_3 and NO_2 by reacting with the radicals. The SO_3 and NO_2 formed are then converted to H_2SO_4 and HNO_3 in the presence of water vapour. When ammonia is injected into the flue gas, the H_2SO_4 and HNO_3 are neutralised by NH_3 to form $(NH_4)_2SO_4$ and NH_4NO_3, which can be recovered and sold as agricultural fertilisers. Studies revealed that a pulsed corona exhibits a higher removal efficiency than a DC corona for simultaneous removal of SOx and NOx.

Both pulsed corona discharge and electron beam irradiation technologies apply cold plasma. The main difference between the two is, with corona discharge technology, the energetic electrons are generated within the flue gas whereas electron beam technology generates high energy electrons externally and then injects the electrons into the flue gas. The pulsed corona discharge process has a lower capital cost but a higher operating cost compared with the electron beam process. A comparison of the two technologies can be seen in Table 10.

Corona discharge technology has been studied intensively at the laboratory and pilot scale by scientists and engineers in many countries. Wu and others (2003) carried out pilot tests of flue gas desulphurisation using a pulsed corona discharge process. A pilot pulsed corona discharge desulphurisation unit with a capacity of 12,000–20,000 m³/h was installed on a 300 MWe coal-fired power generating boiler. The concentrations of the major air pollutants presented in the inlet flue gas were in the range of 1000–2000 ppm for SO_2, 200–800 ppm for NO, and 300 mg/m³ for particulates. Ammonia was injected into the flue gas and the by-product ammonium sulphate was collected using an ESP. Under the conditions used by Wu and co-workers, SO_2 removal efficiencies of more than 80% were achieved. The system also achieved over 50% NOx removal efficiency. They estimated that the capital cost of a pulsed corona discharge FGD system would be approximately 10% of the investment of the power plant, and the operating cost of the system would be around 60 $/t SO_2 removed (Wu and others, 2003). A concept flowchart of the pulsed corona discharge FGD process is shown in Figure 14.

DOOSAN of Korea also built a pilot plant using pulsed corona discharge technology for simultaneous removal of SO_2 and NOx from flue gas. The pilot plant could treat a flue gas of 1800 m³/h. The system achieved removal efficiencies of 95% for SO_2 and 70% for NOx. Encouraged by the results, DOOSAN built a 35,000 m³/h demonstration unit on a coal-fired power plant to demonstrate and further test the process (Kim and others, 2003).

Yan and colleagues (2006) tested a semi-wet FGD system using corona discharge technology. The pilot plant had a capacity of 12,000 m³/h. The plasma reactor was partitioned

Table 10	A comparison of corona discharge and electron beam technologies (Tseng, 2000)	
	Corona discharge	Electron beam
Operational pressure	atmosphere	vacuum
Electron generation	internal	external
Electron energy*	~10 eV	105–106 eV
Capital cost	lower	higher
Operating cost	higher	lower
Disadvantages	electrode corrosion	dirty electron injection window; X-ray hazard
*1 eV = 1.6x10⁻¹⁹ J		
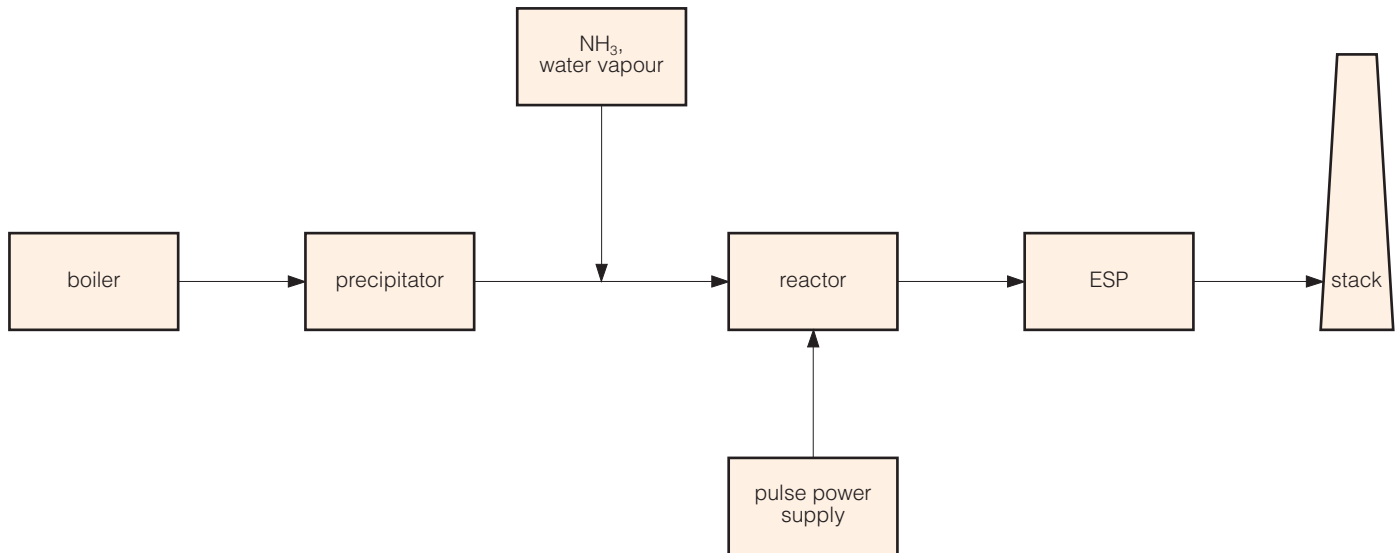
Figure 14 A concept flowchart of the FGD process with pulsed corona discharge (Wu and others, 2003)

into a thermal chemical section and a plasma section. The thermal chemical section worked in a similar way to an ammonia scrubber. There was no electric discharge in this section. Flue gas from the particulate collection device first passed through the thermal chemical section of the reactor. Ammonia water was sprayed into the thermal chemical section to absorb SO_2 from the flue gas. The spent solution was recycled back to the reactor in a circulating manner. The flue gas and scrubbing solution then entered the plasma section of the reactor where a DC voltage superimposed with an AC voltage was applied to generate streamer plasmas. In the plasma section, SO_2 absorbed by the liquid was enhanced by the electric wind, and the sulphite in the solution experienced plasma oxidation to form sulphate. The flue gas had an inlet SO_2 concentration of 500 ppm. The test results showed that this system could achieve >95% SO_2 removal efficiency. The energy consumption in the reactor was 1.8 Wh/m^3. Ammonia slip was less than 5 ppm, and commercial grade fertiliser was obtained as a by-product (Yan and others, 2006).

## 5.2   Reversible absorption processes

In August 2009, the US DOE's Pacific Northwest National Laboratory (PNNL) announced that it had developed a reusable organic liquid that can scrub acid gases such CO_2 and SO_2 out of industrial emissions from power plants (PNNL, 2009). The process is called Reversible Acid Gas Capture. It uses acid-gas binding organic liquids that contain no water and appear similar to oily compounds. These liquids capture the acid gases near room temperature. The liquids are then recovered by heating the liquids to the required temperature to release the captured gases. PNNL's previous work with the organic liquids was focused on CO_2 capture from power plant emissions. PNNL is now working on variants targeting SO_2 and other acid gases. PNNL claims that the regeneration of the liquids requires much less energy but has a large absorption capacity. As a result, the process has a low energy consumption and therefore lower operating cost. PNNL also claims that power plants can easily retrofit to use this process as a direct replacement for existing technology.

Other liquids that can be used for reversible absorption of SO_2 are also being investigated by scientists in different countries. Huang and colleagues (2006) found several imidazolium-based ionic liquids that are excellent solvents for SO_2 and can physically absorb SO_2 from flue gas. The results from their laboratory experiments showed that the examined ionic liquids had large SO_2 absorption capacities at room temperature. The absorbed SO_2 remained in the molecular state without any chemical reactions during absorption process, and could be effectively desorbed by applying a vacuum or by heating. The results also showed that the liquids could be reused several times for consecutive absorption/desorption cycles without loss of capacity. More investigation into the selective capture of SO_2 using ionic liquids is being carried out by the same researchers and scientists elsewhere.

5.3   Membrane gas absorption

The membrane gas absorption (MGA) process has emerged as a potential technology for the absorption of air pollutants such as CO_2, SO_2, H_2S, Hg and NH_3 from gas streams. Membrane gas absorption uses porous membranes for the transfer of components between a gas and a liquid. The membrane forms a gas-permeable barrier between a liquid and a gaseous phase. Gaseous components diffuse through the pores and are absorbed by a suitable liquid. In other words, an MGA system contains a microporous membrane that separates the gas and liquid phases. Mass transfer occurs as the gas diffuses through the membrane and absorbs into the absorbent. Figure 15 shows the principle of a MGA process. The essential element in an MGA process is a microporous hydrophobic hollow fibre membrane contactor. A hollow fibre membrane contactor is a device that achieves gas-liquid mass transfer without dispersion of one phase into the other. The advantages of gas absorption membranes over conventional wet scrubbers include:

- high specific surface area and rapid mass transfer resulting in very compact and low weight equipment;
- gas and liquid flow are independent so operation over a wide range of gas and liquid flow rates is possible;
- no entrainment, flooding, channelling or foaming.

Non-calcium desulphurisation technologies
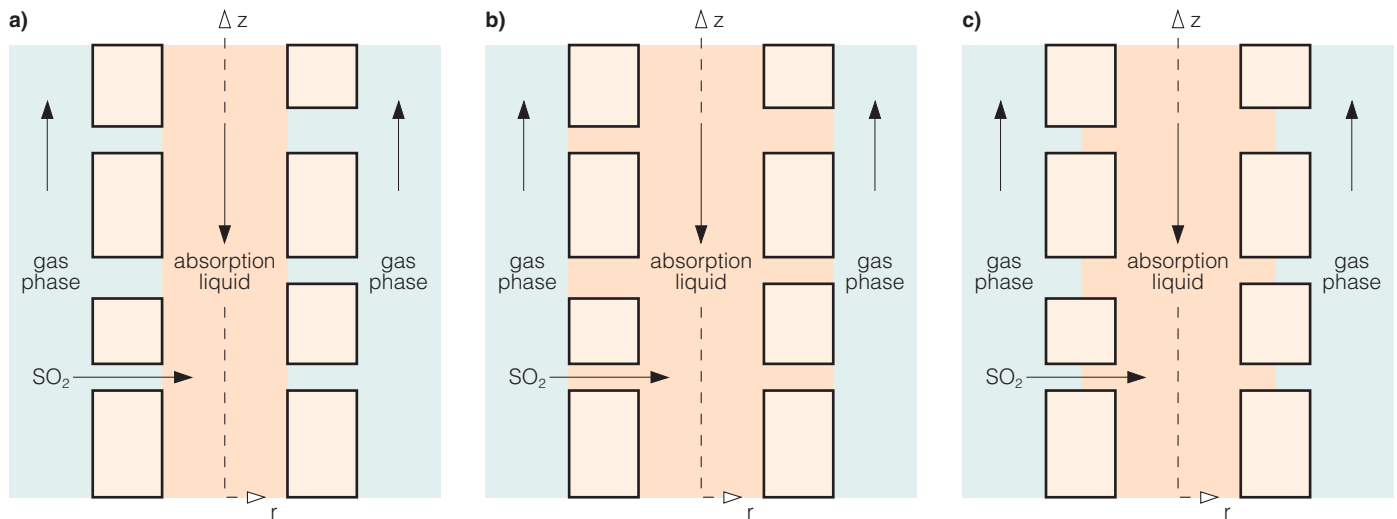
Figure 15 Principle of a MGA process (Luis and others, 2009)

By using hollow fibre membranes it is possible to develop a very efficient gas-liquid contactor that is so compact its size is much smaller than a conventional wet scrubber. The comparison made by Klaassen and Jansen (2003) showed that, for a 645 MWe coal-fired power plant, the size of an FGD absorber (spraying tower) would be 9000 m^3 if a conventional wet scrubbing process was used whereas the size of a MGA absorber would be 250 m^3. An MGA desulphurisation process has low capital and operating costs.

MGA can be used in the removal of components from a gas stream where a suitable absorption liquid is available. An MGA pilot plant was installed on a biomass-burning boiler in the Netherlands. In the MGA unit, SO_2 is removed from the flue gas and recovered as bisulphite. The pilot plant was tested successfully for two production seasons, each six months long. An SO_2 recovery of >95% was achieved at a capacity of 120 m^3/h although it was designed for 100 m^3/h (Klaassen and Jansen, 2003). No fouling of the membranes or decline in mass transfer was observed during the tests.

Using an MGA process with various membranes and absorption solutions for SO_2 removal from a flue gas has been under intensive investigation by various scientists. Luis and co-workers (2009) investigated selective absorption of SO_2 from a gas mixture using the MGA and ionic liquids as absorption solutions. Park and colleagues (2008) studied the absorption of SO_2 from a flue gas using MGA process. The microporous hydrophobic PVDF (polyvinylidenefluoride) hollow fibre membranes were used in a gas-liquid contactor. The effectiveness of different absorption solvents namely NaOH, Na_2SO_3, Na_2CO_3 and $NaHCO_3$ as an absorbent for SO_2 removal were investigated. The results from their laboratory experiments showed that the PVDF hollow fibre membrane contactors demonstrated high mass transfer coefficient, and the SO_2 removal efficiency of around 85% was achieved with NaOH (2 mol/l) solution used as absorbent.

Although the MGA process for gas separation has been commercially applied in many industrial processes with success, flue gas desulphurisation using MGA technology is still in the early stage of development. Most of the

experiments that have been carried out to date are on the laboratory scale.

Comments
Investigations on various desulphurisation sorbent and on other FGD technologies have also been being carried out by researchers in many countries. For example, sorbent based on zinc, copper, iron, or other metals have been developed over the last two decades for desulphurisation of synthesised gas from coal gasification. Another example is the microwave reactor for microwave catalytic removal of SOx and NOx simultaneously (Wei and others, 2009). A large number of articles on new FGD technologies or new sorbent have been published over the years and it is beyond the scope of this report to cover them all. For interested readers, an in-depth review is available on the recent research and development of the mid- and high-temperature sorbent for desulphurisation of synthesis gas generated from coal gasification (Cheah and others, 2009).

6   Conclusions

Flue gas desulphurisation is traditionally based on limestone/lime sorbent which is used by the majority of the installed FGD systems worldwide. However, technologies are evolving rapidly that allow desulphurisation in regions where there are limited resources of lime or limestone. Some of the non-calcium based FGD processes have already been successfully applied in coal-fired power plants and have been in operation for years. Some new processes have recently been offered to the FGD market. There are more innovative FGD technologies under investigation.

6.1   Current commercial non-calcium based FGD processes

Seawater FGD process

For power plants located on an ocean coast, seawater is normally used as cooling medium instead of freshwater. Seawater is naturally alkaline with a typical pH value of 7.6–8.4 and therefore can absorb and neutralise acidic SO_2 in a flue gas. The main advantages of a seawater FGD process include: 1) addition of chemical reagent is not required; 2) there is no by-product requiring handling or disposal; 3) the plant design and operation are relatively simple due do the utilisation of seawater from the cooling system of the plant to scrub SO_2. The technology and process design have improved significantly over the years. The process is now capable of high SO_2 removal (up to 99%). It has relatively low capital and operating costs compared with many other FGD processes, making this technology a most attractive choice, both technically and economically, for power plants located at coastal sites that burn low or medium sulphur fuel. As a result, the application of the seawater FGD process in coal-fired power plants has been expanding rapidly recently. However, the application of seawater FGD processes is limited to power plants located in coastal areas.

Ammonia based FGD processes

The ammonia scrubbing process works in a similar way to the limestone gypsum process except that aqueous ammonia is used as reagent. Several ammonia scrubbing FGD processes have been developed. The earlier ammonia scrubbing systems suffered visible plume stack emission problems. This has now been overcome by controlling the pH value of the scrubbing liquid and/or installing a wet ESP to effectively remove ammonium salt aerosols from the exiting flue gas. Over the years, significant technical advances and much improved process engineering designs have been achieved. The process can remove more than 98% of SO_2 even when fuels with an extremely high sulphur content are burned. Other advantages of the process include: there is no waste water to discharge or waste solid for disposal; it produces a high-value by-product; and it is unlikely to suffer scaling or blockage problems. However, the process has a high capital cost and requires a large footprint. Ammonia reagent is more expensive than lime or limestone. Another major drawback of the process is that ammonia is both caustic and hazardous, and therefore its

transport and storage are regulated. This may cause difficulties in the planning stage at certain sites.

In regions where there is high demand for ammonium sulphate fertiliser, the ammonia scrubbing process could be very attractive to the combustion plants, particularly those burning high-sulphur fuels since the income from the sale of the by-product fertiliser can offset a significant portion of the FGD operating costs. Recently, there has been a renewed interest in the ammonia scrubbing process due to its ability to remove CO_2 effectively from the flue gas. Research is being carried out to develop the ammonia scrubbing process for simultaneous removal of CO_2 and SO_2 and the process may receive wider application in coal-fired power plants in the future.

Magnesium hydroxide process

The magnesium hydroxide process is a wet FGD process that uses magnesium hydroxide as a scrubbing reagent. It can remove SO_2 and particulates simultaneously in a single tower with high efficiency eliminating the need for a separate dust collection system. The process can achieve greater than 98% of SO_2 removal efficiency and the outlet particulate concentration can be kept under 50 mg/m³. The process design and operation are relatively simple. The magnesium hydroxide process has a lower capital cost than a corresponding limestone gypsum process. However, magnesium hydroxide absorbent is more expensive than limestone and therefore has higher operating costs than a corresponding limestone gypsum process. The process is suitable for small- and medium-sized plants, especially those with a short remaining life. The waste water discharged from this process contains magnesium sulphate which is a natural ingredient in seawater. Therefore, this technology is particularly attractive to plants located in coastal areas where the waste effluent can be discharged into the sea with minimal environmental impacts.

6.2   Emerging FGD processes

Electro-catalytic oxidation (ECO) process

The ECO process integrates a dielectric barrier discharge (DBD) reactor and an advanced ammonia scrubber into one multi-pollutant emissions control system to simultaneously remove SO_2, NOx, mercury, and fine particulates ($PM_{2.5}$) from the flue gas of coal-fired power plants. The ECO process produces a fertiliser by-product which can be sold, and the income from the sale can offset its operating costs. Commercial demonstration of the ECO process was recently carried out on a 50 MWe coal-fired power generating unit and the results showed that the ECO process could achieve high removal efficiencies of the four major pollutants: >99% of SO_2, up to 82% of NOx, 80% of Hg and >95% of $PM_{2.5}$. The process operated reliably with high availability. The process uses less water because it requires no water treatment or disposal. Cost analysis shows that the capital costs of the ECO process will be less than the costs of implementing

existing control technologies to achieve the same performance objectives for all the major pollutants.

The ECO process can also be integrated with the ammonia-based CO_2 capture technology ECO_2 process. It requires no enhancement in emissions reduction performance (that is SO_2 control) to accommodate a CO_2 capture process, saving capital and operating costs when adding CO_2 capture capability. Two ECO processes are planned to be installed at coal-fired power plants in the USA and more commercial application of ECO process in coal-fired power plants is anticipated.

Electron beam (EB) irradiation process
This is a dry scrubbing process capable of simultaneous removal of SO_2 and NOx. In the process, flue gas is exposed to a high energy flux of electrons with ammonia to generate ammonium sulphate or nitrates for collection by a particulates control system. Commercial demonstrations of the two EB processes installed on coal-fired power plants were carried out in China and Poland in the 1990s and these plants have been operational since. The results from pilot tests and demonstration operations show that the EB process can achieve higher than 95% SO_2 removal and up to 75% NOx removal. The EB process has a high capital cost, low operating cost and a high maintenance cost. This technology is still not mature, and more tests are needed to improve current understanding of the process. The availability of the process is not sufficient. Improvements in process design and further developments of the EB technology are required before it can compete with other FGD processes in the commercial market.

Airborne process
The Airborne process is a regenerative process that integrates dry and wet sodium bicarbonate scrubbing, sodium bicarbonate regeneration and fertiliser formulation technologies into one system. The process is capable of removing SOx, NOx, Hg, as well as HCl, HF and heavy metals simultaneously. Pilot tests of the process on a 5 MWe facility have been completed and the results are encouraging. The developer is now keen to demonstrate this technology on a commercial scale. It is claimed that the process can achieve more than 99% removal efficiencies for SO_2, NOx and Hg. The capital and operating costs of the Airborne process are competitive when compared with the combined costs of separate systems for SO_2 and NOx emission reductions.

Activated carbon/coke dry scrubbing process
This is a regenerative dry scrubbing process using activated carbon/coke as sorbent. It is capable of simultaneously removing air pollutants such as NOx, Hg and other acid gases in the flue gas. Commercial demonstration of the process for reduction of SO_2 emissions from coal-fired power plants have been successful and today it has found application in power plants and other industrial processes. Recent work has focused on the development of a multi-pollutant emissions control process using activated carbon/coke sorbent. As such, the ReACT process has been applied commercially on coal-fired power plants in Japan and achieved impressive results. Results from previous tests at various sites and commercial operations showed that the ReACT process could

reduce SOx by up to 98%, NOx by 20–80% (depending on the design conditions), Hg emissions by more than 90%, and particulate emissions can be kept under 15 mg/m^3 at the stack.

6.3 Technologies under development

Corona discharge technology
Corona discharge technology works in a similar way to electron beam irradiation technology and is capable of removing SOx and NOx simultaneously. Corona discharge technology has been studied intensively in the laboratory and at the pilot scale by scientists and engineers in many countries. Studies revealed that a pulsed corona exhibits a higher removal efficiency than a DC corona for simultaneous removal of SOx and NOx. Results from various pilot tests showed that the process could achieve removal efficiencies of up to 95% for SO_2 and 50–70% for NOx. A demonstration unit on a coal-fired power plant was built in South Korea to demonstrate and test the process further.

Reversible absorption processes
Reversible absorption processes is a regenerative wet scrubbing process that uses a liquid for the reversible absorption of SO_2. Various liquids can be used to capture the acid gases at room temperature. The liquids are then recovered by heating them to the required temperature to release the captured gases. The appropriate liquids for reversible absorption processes should have a large SO_2 absorption capacity and require less energy for regeneration. In 2009, the US DoE's Pacific Northwest National Laboratory (PNNL) announced that it had developed a reusable organic liquid that can scrub acid gases such CO_2 and SO_2 out of industrial emissions from power plants. Other liquids such as ionic liquids for the reversible absorption of SO_2 are under intensive investigations by scientists in different countries.

Membrane gas absorption (MGA)
The MGA process has emerged as a potential technology for absorption of air pollutants such as CO_2, SO_2, H_2S, Hg and NH_3 from gas streams. MGA for gas separation has been used in some industrial processes for many years. The main advantage is that an MGA absorber is much smaller compared with a corresponding conventional wet scrubber. The MGA desulphurisation process has low capital and operating costs. An MGA pilot plant was installed on a biomass-burning boiler in the Netherlands. Using an MGA process with various membranes and absorption solutions for SO_2 removal from a flue gas has been under investigation mainly at the laboratory scale.

In short, there are commercially available FGD processes which are alternative to limestone/lime based scrubbers. Some of the technologies have already found application in coal-fired power plants. Recently, several new FGD systems have been developed and offered to the market. Work has been ongoing to increase the efficiency and overall performance, to improve the process design, and to reduce the cost of the existing and the emerging FGD technologies. Intensive investigation is also being carried out to develop innovative FGD technologies that applies new concepts and

different approaches. Today, the power generators are having increasingly more choices over the FGD technologies which are competitive, both technically and economically, for SO_2 emission control from their coal-fired power plants.

7 References

Alstom (2006) *Seawater flue gas desulphurization at the Mawan coal fired power station*. Available from: http://www.power.alstom.com/_eLibrary/presentation/upload_83146.pdf Levallois-Perret, France, Alstom, 1 pp (Feb 2010)

Batten S D, Bamber R N (1996) The effects of acidified seawater on the polychaete *nereis virens sars, 1835*. *Marine Pollut. Bull.*; **32**(3); 283-287 (1996)

Boudou J P, Chehimi M, Siemieniewska T, Bimer J (2003) Adsorption of H_2S or SO_2 on an activated carbon cloth modified by ammonia treatment. *Carbon*; **41** (10); 1999-2007 (Oct 2003)

Cheah S, Carpenter D L, Magrini-Bair K A (2009) Review of mid- to high-temperature sulfur sorbents for desulfurization of biomass- and coal-derived syngas. *Energy and Fuels*; **23** (11); 5291-5307 (Nov 2009)

Chmielewski A G (2005) Application of ionizing radiation in environmental protection. In: *Technical meeting on radiation treatment of gases and liquid effluents for contaminant removal*, Sofia, Bulgaria, 7-10 Sep 2004, Vienna, Austria, International Atomic Energy Agency, pp 11-24 (Dec 2005)

Chmielewski A G, Licki J (2008) Electron beam flue gas treatment process for purification of exhaust gases with high SO_2 concentrations. *Nukleonika* **2008**:53(Supplement 2); S61-S66 (Sep 2008)

Dene C, Gilbert J, Jackson K, Miyagawa S (2008) ReACT Process demonstration at Valmy generating station. In: *Power Plant Air Pollutant Control 'Mega' Symposium*, Baltimore, MD, USA, 25-28 Aug 2008, Air and Waste Management Association, Pittsburgh, PA, USA, CD-ROM, paper 123, 13 pp (2008)

DTI (2000) *Flue gas desulphurisation (FGD) technologies.* Technology Status Report 012, London, UK, DTI, 13 pp (Mar 2000)

DTI (2003) *Flue gas desulphurisation (FGD) technologies for coal-fired combustion plant.* CB013, London, UK, DTI, 7 pp (Mar 2003)

Duncan J L, McLarnon C R, Alix F R (2005) *NOx, Hg and SO_2 removal using ammonia.* United States Patent, Patent No. US 6936231 B2, US Patent and Trademark Office, Alexandria, VA, USA, (Aug 2005)

Doutskinov N (2005) Results of the startup operation of a pilot installation electron beam flue gases treatment in the Maritsa East 2 thermal power plant. In: *Technical meeting on radiation treatment of gases and liquid effluents for contaminant removal*, Sofia, Bulgaria, 7-10 Sep 2004, Vienna, Austria, International Atomic Energy Agency, pp 35-43 (Dec 2005)

Edinger R (2008) *Reduction of SOx and NOx emission by electron beam flue gas treatment.* Available from: http://www.ebfgt.com/file_library/userfiles/file/COM2008_WINNIPEG_20080529.pdf Richmond, British Columbia, Canada, PAVAC Industries Inc, 9 pp, (2008)

European Commission (2006) *Integrated Pollution Prevention and Control: Reference Document on Best Available Techniques for Large Combustion Plants.* European Commission, available from: http://ec.europa.eu/comm/environment/ippc/brefs/lcp_bref_0706.pdf (Jul 2006)

Evans A P, Miller C, Pouliot S (2009) *Operational experience of commercial, full scale ammonia-based wet FGD for over a decade.* Available from: http://www.met-apc.com Firelawn, Ohio, USA, Marsulex Environmental Technologies (MET), 22 pp,(Aug 2009)

Ferrao L (1998) Lentjes Bischoff ammoniawater process for SO_2 absorption from flue gas. *Chemical engineering World*; **33** (11); 75-77 (Nov 1998)

GEC (2002a) *MORETANA Flue Gas Desulfurization Process*. Available from: http://www.gec.jp/JSIM_DATA/AIR/AIR_2/html/Doc_065.html Osaka, Japan, Global Environment Centre Foundation (GEC) (Jul 2002)

GEC (2002b) *$Mg(OH)_2$-based flue-gas desulfurization process*. Available from: http://www.gec.jp/JSIM_DATA/AIR/AIR_2/html/Doc_073.html Osaka, Japan, Global Environment Centre Foundation (GEC) (Jul 2002)

Huang J, Riisager A, Wasserscheid P, Fehrmann R (2006) Reversible physical absorption of SO_2 by ionic liquids. *Chemical Communications;* **2006** (38); 4027-4029, (Oct 2006)

IEA (2009) *World energy outlook 2009*. Paris, France, International Energy Agency, pp 696 (Nov 2009)

IEA CCC (2009) *CoalPower.* World coal-fired power plants database, London, UK, IEA Clean Coal Centre (2009)

IEA CCC (2010) *Emission Standards.* Emission Standards database, London, UK, IEA Clean Coal Centre (2010)

Johnson D W, Ehrnschender M S, Scott L, Walcott J (2005) 'Airborne Process™'- Advancement of multi-pollutant emissions control technology and by-product utilization. In: *Electric Power Conference*, Chicago, Illinois, USA, 5-7 Apr 2005, 15 pp (2005)

Kim Y S, Paek M S, Yoo J S, Kim T H, Choi S H, Moon, K H (2003) Development of demonstration plant using non-thermal plasma process to remove SO_2 and NOx from flue gas. *Journal of Advanced Oxidation Technologies*; **6** (1); 35-40 (Jan 2003)

Klaassen R, Jansen A E (2003) Achieving flue gas desulphurization with membrane gas absorption. *Filtration and Separation*; **40** (10); 26-28 (Dec 2003)

Kohl A L, Nielsen R B (1997) Sulfur dioxide removal. In: *Gas purification - 5th edition*. Houston, Texas, USA, Gulf Publishing Company, pp 466-669 (1997)

Kong Y, Vysoky J (2009) Comparison of sodium bicarbonate and trona for SO_2 mitigation at a coal-fired power plant. Paper presented at: *11th Annual Electric Power Conference & Exhibition*, Rosemont, Illinois, USA, 12-14 May 2009, 23 pp (2009)

Li J, Kobayashi N, Hu Y (2007) A new flue gas activation process for SO_2 removal with activated coke in coal power plants. *Journal of Environment and Engineering*; **2** (4); 740-751 (Dec 2007)

Li J, Kobayashi N, Hu Y (2008) Effect of additive on the SO_2 removal from flue gas by activated coke. *Journal of Environment and Engineering*; **3** (1); 92-99 (Apr 2008)

Li J, Kobayashi N, Hu Y (2009) Performance of V_2O_5/AC activated with the flue gas on SO_2 removal. *Journal of Environment and Engineering*; **4** (1); 176-187 (Apr 2009)

Luis P, Garea A, Irabien A (2009) Zero solvent emission process for sulfur dioxide recovery using a membrane contactor and ionic liquids. *Journal of Membrane Science*; **330** (1-2); 80-89 (Mar 2009)

Mao B J (2005) Process of flue gas desulphuration with electron beam irradiation in China. In: *Technical meeting on radiation treatment of gases and liquid effluents for contaminant removal*, Sofia, Bulgaria, 7-10 Sep 2004, Vienna, Austria, International Atomic Energy Agency, pp 45-51 (Dec 2005)

MET (2007) *Ammonium sulfate WFGD technology - Overview for general industry information*. Available from: http://met-apc.com Firelawn, Ohio, USA, Marsulex Environmental Technologies (MET), 6 pp (Jul 2007)

MET (2009) *Ammonium Sulfate WFGD Technology*. Available from: http://met-apc.com Firelawn, Ohio, USA, Marsulex Environmental Technologies (MET), 3 pp,(2009)

Miyagawa S, Miya M (2008) Regenerative activated coke technology (REACT) – a commercial multi- pollutant control technology. In: *Proceedings. 7th international symposium on gas cleaning at high temperatures*, Newcastle, NSW, Australia, 23-25 Jun 2008. Newcastle, NSW 2308, Australia, Chemical Engineering, University of Newcastle, CD-ROM, Paper 3-1p-2 88 Shyo Miyagawa.pdf, 1-11 (2008)

Mortson M, Telesz R W (2001) Flue gas desulfurization using recycled sodium bicarbonate. In: *The U.S. EPA/DOE/EPRI Combined Power Plant Air Pollutant Control Symposium: 'The Mega Symposium'*, Chicago, Illinois, USA, 20-23 Aug 2001, 6 pp (2001)

Mortson M, Xia Q (2007) *Advanced pollution control – the Airborne Process™ and its benefits to China*. Paper presented at: International Forum on Innovation and Environment, Beijing, China, 23-24 Oct 2006, Available from: http://www.airbornecleanenergy.com/papers/Paper_for_China_Conference.pdf Calgary, Alberta, Canada, Airborne Clean Energy Ltd., 11 pp (Oct 2007)

Nalbandian H (2006) *Economics of retrofit air pollution control technologies*. CCC/111, London, UK, IEA Clean Coal Centre, 68 pp (May 2006)

Nguyen Y V (2004) A life cycle economic assessment of multi-pollutant control technologies in a more restrictive emission control environment. In: *Coal utilisation & fuel systems*, Clearwater, Florida, USA, 18-22 Apr 2004 12 pp (2004)

Nodland K F (2008) Alstom Seawater FGD: operation and development since 1968. *Seminar given on Alstom Power Day*, Santoago, Chile, 18 Nov 2008, 39 pp (2008)

Nodland K F (2009) Oslo, Norway, Environmental Control Systems, ALSTOM Norway AS, *personal communication* (Nov 2009)

OCDO (2005) *Commercial demonstration of Electro-catalytic Oxidation (ECO) Technology*. CDO/D-01-20 Final report, available from: http://www.ohioairquality.org/ocdo/pdf/2005D-01-20.pdf Columbus, Ohio, USA, The Ohio Coal Development Office, Ohio Air Quality Development Authority, 5 pp (Sep 2005)

Oikawa K, Yongsiri C, Takeda Kazuo, Harimoto T (2003) Seawater flue gas desulfurization: its technical implications and performance results. *Environmental Progress*; **22** (1); 67-73 (Apr 2003)

Park H H, Deshwal B R, Kim I W, Lee H K (2008) Absorption of SO_2 from flue gas using PVDF hollow fibre membranes in a gas-liquid contactor. *Journal of Membrane Science*; **319** (2008); 29-37 (Mar 2008)

PNNL (2009) *Scrubbing sulfur*. PNNL news release, Richland, WA, USA, Pacific Northwest National Laboratory, available from: http://www.pnl.gov/news/release.aspx?id=393 (Aug 2009)

Powerspan (2009a) *ECO_2 technology for CO_2 capture from existing and new coal-fired power plants*. Available from: http://www.powerspan.com Portsmouth, HN, USA, Powerspan Corporation, 3 pp (2009)

Powerspan (2009b) *Powerspan ECO process flow*. Available from: http://www.powerspan.com/uploadedFiles/Technology/ECO/Powerspan_ECO_Process_Flow.pdf Portsmouth, HN, USA, Powerspan Corporation, 1 pp (2009)

Radl B J, Zhang D (2005) Wet flue gas desulphurisation (FGD) optimization. *Presentation at 2nd US - China NOx and SO_2 Control Workshop*, Dalain, Liaoning Province, P. R. China, 2-5 Aug 2005, (2005)

Resnik K P, Yeh J T, Pennline H W (2004) Aqua ammonia process for simultaneous removal of CO_2, SO_2 and NOx. *Int. J. Environmental Technology and Management*; **4** (1/2); 89-104 (2004)

Ringnes F (2008) The Alstom Flakt-Hydro process/flue gas desulfurization by use of sea water: process principles and recent power plant. *Paper presented at Power-Gen Europe conference and exhibition*, Milan, Italy, 3-5 Jun 2008, 8 pp (2008)

Schuettenhelm W, Braun W, Dreuscher H (2004) Most recent developments and optimisation aspects for FGD technologies. *Paper presented at Power-Gen Europe 2004*, Barcelona, Spain, 25-27 May 2004, 21 pp (2004)

Schuettenhelm W, Dreuscher H (2005) State-of-the-art FGD technologies. *Paper presented at Russia Power Conference and Exhibition*, Moscow, Russia, 9-11 Mar 2005, 18 pp (2005)

Shand M A (2009) A new look at SO_2 removal. *Pulp & Paper International (PPI)*; digital edition, available from: http://www.ppimagazine.com/ppiissue/200904/?pg=33 31-32 (Apr 2009)

Sharp G W (2007) What's that scrubber going to cost? *Power*; **151** (7); 56-60 (Jul 2007)

Sharp G W (2009) Update: what's that scrubber going to cost? *Power*; **153** (3); 64-66 (Mar 2009)

Staehle R C, Zhang G H (2005) Wet FGD technology advanced ammonium sulfate. *Presentation at 2nd US – China NOx and SO_2 Control Workshop*, Dalian, Liaoning Province, P. R. China, 2-5 Aug 2005, 15 pp (2005)

Tseng C H (2000) *Enhanced pulsed corona method for the removal of SO_2 and NOx from combustion gas in a wet electrostatic precipitator*. Ph.D thesis, Department of Civil and Environmental Engineering of the College of Engineering, University of Cincinnati, Ohio, Cincinnati, USA, available from: http://etd.ohiolink.edu/view.cgi?ucin962380157 University of Cincinnati, 188 pp (2000)

Tyminski B, Pawelec A (2005) Economic evaluation of electron beam flue gas treatment. In: *Technical meeting on radiation treatment of gases and liquid effluents for contaminant removal*, Sofia, Bulgaria, 7-10 Sep 2004, Vienna, Austria, International Atomic Energy Agency, 25-34 (Dec 2005)

Walsh M A (2005) *Marsulex AS technology significantly cuts power generation costs*. Available from: http://www.met-apc.com Firelawn, Ohio, USA, Marsulex Environmental Technologies (MET), 7 pp,(Aug 2005)

Wei W M (2008) *Ammonia scrubbing FGD technology*. Available from: http://info.epjob88.com/html/2008-11-13/2008111385647.htm Shenzhen, Guangdong, China, Power Generation Experts Net (Nov 2008)

Wei Z, Zeng G, Xie Z (2009) Microwave catalytic desulfurization and denitrification simultaneously on Fe/Ca-5A zeolite catalyst. *Energy and Fuels*; **23** (6); 2947-2951 (Jun 2009)

Wójtowicz M A, Serio M (2000) *Simultaneous mercury, SO_2, and NOx control by adsorption on activated carbon*. United States Patent, Patent No. US 6103205, US Patent and Trademark Office, Alexandria, VA, USA, (Aug 2000)

Wu Y, Li J, Wang N, Li G (2003) Industrial experiments on desulfurization of flue gases by pulsed corona induced plasma chemical process. *Journal of Electrostatics*; **57** (3-4); 233-241 (Mar 2003)

Xu C X, Fu G G (2005) Review on ammonia flue gas desulfurization. *Electric Power Environmental Protection*; **21 (2)**; 17-20 (Jun 2005)

Yan K, Li R, Zhu T, Zhang H, Hu X, Jiang X, Liang H, Qiu R, Wang Y (2006) A semi-wet technological process for flue gas desufurization by corona discharge at an industrial scale. *Chemical Engineering Journal*; **116** (2); 139-147 (Feb 2006)

Yeh J T, Resnik K P, Pennline H W (2004) Regenerable aqua ammonia process for CO_2 sequestration. *Am. Chem. Soc., Div. Fuel Chem.*; **49** (1); 247-248 (Spring 2004)

Yoshikawa M, Mochida I, Yasutake A (2005) Advanced flue gas treatment by novel de-SOx technology over activate carbon fibers. In: *Proceedings of the international conference on coal science and technology 2005*, Okinawa, Japan, 9-14 Oct 2005, Ibaraki, Japan, National Institute of Advanced Industrial Science and Technology, CD-ROM, paper-pdf 1A03.pdf, 1-5 (Oct 2005)